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PREFACE

Chemical engineering increasingly faces new opportunities of transferring advances in science to technologies beneficial to mankind. The 1st South-East European Congress of Chemical Engineering (**1st SEECChE**) will assess the impact of rapid changes in science on the practice of chemical engineering in the development of novel and the improvement of existing processes. It will highlight the possibilities and opportunities in South-Eastern Europe as well as the possibilities for future joint projects, scientific research and investments.

Nine invited plenary lecturers, from the USA and Europe will review current topics and, together with 10 key-note lecturers and researches presenting 42 oral and 179 poster presentations, will entirely illustrate the ongoing research in the region, new trends and directions. Several hundreds of authors have prepared these oral and poster contributions, giving an average of less than 3 authors per one presentation. Most of them are from Serbia and Montenegro (about 60%), but there is also a significant number of scientists from Romania, Bulgaria, Greece, FRY Macedonia, as well as from 16 other countries coming from several continents. All the abstracts presented in this Book are reproduced with only minor changes, and the responsibility for possible errors lies solely on the authors.

The oral and poster presentations are separated into six sessions: **General Chemical Engineering** (*Education in Chemical Engineering, Reaction Engineering and Catalysis, Transport Phenomena, Separation Processes and Thermodynamics*), **Process Engineering** (*Food Science and Technology, High Pressure Processes, Management in Chemical and Process Industry, Process and Product Innovation, Process Operation, Automation and Control, Process Synthesis and Design*), **Bio- and Pharmaceutical Engineering** (*Biochemical Engineering, Biomedical Engineering, Biomaterials, Pharmaceutical Engineering*), **Materials Science and Engineering** (*Electrochemical Engineering, Materials Science, Metallurgy, New Materials, Nanotechnology*), **Polymers and Interfacial Phenomena** and finally, **Environmental Engineering**.

Submitted papers selected by the Scientific Committee will be published after the standard reviewing procedure in the journal Chemical Industry or Chemical Industry & Chemical Engineering Quarterly published by the Association of Chemical Engineers, Belgrade (**www.ache.org.yu/hi** and **www.ache.org.yu/ciceq/**).

Many colleagues were involved in the preparation this Congress and the Scientific Committee is very grateful for their important contribution. Unfortunately, one month before the beginning of the Congress, Professor Aleksandar Saša Duduković, who initiated the organization of the 1st SEECChE, linking many colleagues in the South-East Europe and from other countries, died at the age of 55. A special commemoration during the Congress will be organized and the scientific and professional work of Aleksandar Duduković will be summarized.



Dejan Skala
President of Scientific Committee

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Jean Claude Charpentier

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In today's economy, chemical engineering must respond to the changing needs of the chemical process industry in order to meet market demands. The evolution of chemical engineering is necessary to remain competitive in global trade. The ability of chemical engineering to cope with managing complex systems met in scientific and technological problems is addressed in this lecture.
Chemical Engineering is vital for sustainability: to satisfy both the market requirements for specific end-use properties of products and the social and environmental constraints of industrial-scale processes. An integrated system approach of complex multidisciplinary, non-linear, non-equilibrium processes and phenomena occurring on different length and time scales is required. This will be obtained due to breakthroughs in molecular modelling, scientific instrumentation and related signal processing and powerful computational tools. The future of chemical engineering can be summarized by four main objectives: (1) increase productivity and selectivity through intensification of intelligent operations and a multiscale approach to process control: a good illustration is the nanostructural and microstructural tailoring of materials required with controlled structure; (2) Design novel equipment based on scientific principles and new production methods: process intensification using multifunctional reactors and microengineering and microtechnology: examples concern multifunctional reactors, and the use of microtechnology for high throughput material screening experiments; (3) Extend chemical engineering methodology to product design and engineering using the "triplet molecular Processes-Product-Process Engineering (3PE)" approach: synthesize structured products, combining several functions and properties required by the customer, with special emphasis on complex fluids and solids technology. Examples dealt with the quality of microemulsions and emulsions for foodstuff, cosmetic, pharmaceutical and bitumous and asphalt products; (4) Implement multiscale application of computational chemical engineering modelling and simulation to real-life situations from the molecular scale to the production scale in order to understand how phenomena at a smaller length scale. With computer aided process engineering (CAPE) the long term challenge is to combine the thermodynamics and physics of local structure-forming processes like network formation, phase separation, nucleation, … with multiphase computer fluid dynamics (CFD) and with multiphase computer fluid mixing (CFM).

PL 2

Making Friends with Chemical Reactors

Octave Levenspiel

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Why does a true French chef insist on using the specially designed omelette pan to prepare a perfect omelette, and why does the Texas multimillionaire insist on using a mesquite-burning outdoor barbecue to grill his buffalo steaks? Why? Because these are the right types of reactors for these particular purposes.

We chemical engineers face the same kinds of decisions -- to choose the right type of reactor to run this or that particular reaction system. One approach is to apply the general rules and concepts coming from the study of chemical reaction engineering to help lead the engineer to a good design.

An alternative and new approach says that with the enormous computer power available today and with clever and well-developed computer programs, we can leave the decision-making to the machine. Let us see what could be the result.

Advances in Tissue Engineering: Bridging the Gaps between Engineering and Biology

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Tissue engineering is one of the areas of science and technology that may change our life. It combines the principles of biology, engineering and medicine to create biological substitutes of native tissues. The overall objective of tissue engineering is the restoration of normal tissue function. Ideally, a lost or damaged tissue should be replaced by an engineered graft that can re-establish normal structure, composition, cell signaling and biomechanical function across different size scales, and on a long term. Engineered tissues of sufficiently high fidelity can also provide controllable models for basic studies of cell function and tissue development, and responses to genetic alterations, drugs, hypoxia and physical stimuli. The clinical and scientific utility of tissue engineering will likely depend on our ability to predictably direct the cells to express a specific differentiated phenotype. There is an increasing awareness that the same factors (genetic, molecular and physical) that regulate tissue development *in vivo* also direct the assembly of an engineered tissue *in vitro*. In recent years, tissue engineering is becoming an effort of "imitating nature" and to recapitulate the aspects of the native environment during tissue development to stimulate the cells to regenerate functional tissues. Based on these principles, a "biomimetic" approach has been established that involves the in vitro creation of immature but functional tissues by an integrated use of cells (the actual "tissue engineers"), biomaterial scaffolds (a structural and logistic template for tissue development), and bioreactors (providing environmental control and biophysical signaling necessary for tissue development).

Cardiac muscle is an example of a complex tissue structure that can be created *in vitro*. To mimic the capillary network, cells were cultured on a highly porous elastomer scaffold with a parallel array of channels that were perfused with culture medium. To mimic oxygen supply by hemoglobin, the culture medium was supplemented with a perfluorocarbon (PFC) emulsion. A mathematical model was developed to describe oxygen transport and utilization within engineered constructs.To induce synchronous contractions of cultured constructs, electrical signals mimicking those in native heart (continuous trains of rectangular pulses, 2 ms, 5 V/cm, 1 Hz) were applied to cultured constructs. Over only 8 days *in vitro*, electrical stimulation induced cell alignment and coupling, increased the amplitude of synchronous construct contractions by a factor of 7, and resulted in a remarkable level of ultrastructural organization. To identify some of the mechanisms underlying the observed enhancement of tissue development, constructs were cultured in the presence or absence of verapamil (a L-type Ca channel blocker), palmitoleic acid (a blocker of gap junctions), and LY294002 (a blocker of the PI3K pathway). Pharmacological studies confirmed that functional gap junctions, cytoskeletal organization and excitation-contraction coupling were all necessary for the development of contractile function in engineered constructs.

We review here recent advances in tissue engineering, including the use of human stem cells, and the development of a new generation of biomaterials and bioreactors. Together, these advances are necessary for the creation of clinically useful human tissues and for the improvement of our understanding of tissue development.

PL 4

Chemical Reaction Engineering, Environmental Protection and Sustainability

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This presentation illustrates the links between chemistry, the environment, reaction engineering principles, pollution prevention and sustainable development. The choice of the process chemistry impacts the atom efficiency and the degree of environmental damage due to the production of the chosen product. However, the execution of the selected chemistry requires multi-phase reaction engineering, and depending on the contacting scheme used, leads to different degrees of product yield, energy efficiency and formation of unwanted by-products. As a consequence, the number and type of separation units used and the recycling burden created is a function of the chosen reactor type and operating conditions. Clearly, proper understanding and application of the reaction engineering principles are essential for proper execution of truly environmentally benign processes. Examples from production of fuels, chemicals and other applications will be provided. All of this points out to the necessity of selecting the process chemistry, including the catalyst, and reactor type in which it could be executed, simultaneously. While the choice of raw materials from renewable resources is to be favored, the efficiency of the technology implemented for their conversion depends on our ability to design and operate multiphase reactors optimally.

Advances in improved quantitative understanding of multiphase reactors, which lead to more predictive models, rest on our increased ability to "see" the flow structures in these opaque systems and use such data in validation of appropriate computational fluid dynamic (CFD) codes. Two unique techniques used in our CREL for velocity measurement (Computer Aided Radioactive Particle Tracking - CARPT) and phase holdup measurement (Computed Tomography – CT) are introduced. It is shown how the data generated assists in validation of CFD multiphase codes and development of improved reactor models for production of clean fuels and chemicals.

The Prediction and Importance of the Uniformity of Coating of Solid Dosage Forms in the Pharma Industry

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Solid pharmaceutical dosage forms (tablets, capsules, beads, etc) are most often coated to control the release or slow the degradation of the active ingredient. Masking the unpleasant taste of a drug, improving the cosmetic appearance of a tablet, controlling the site of release of a drug through enteric coating, and prolonging the release of an active over a long period of time are common examples of why products are coated. More recently, coating of a second active ingredient onto tablets in a "precision coating" operation has been practiced and several commercial products use this technology.

The uniformity of the coating process becomes increasingly important as the functionality of the applied coating increases. For example, for precision-coated tablets, a very narrow coefficient of variation for the mass of active ingredient deposited on a batch of tablets must be maintained. This presentation will discuss the coating of solid dosage forms with liquid, solvent-based coatings in fluidized beds and rotating drums (perforated coating pans). Models to describe and predict coating variation in this equipment will be covered. These models include lumped analyses as well as CFD, and discrete element model (DEM) approaches. The limitations and applications of these models to coating processes in the Pharmaceutical Industry will be discussed.

PL 6

The Effect of Particles on Wall Friction in Vertical Pneumatic and Hydroulic Transport in a Turbulent Fluid

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This lecture is concerned with the prediction of the effect of particles on wall friction in vertical pneumatic and hydraulic transport in a turbulent fluid.

An equation will be derived for predicting the ratio of the augmentation of wall friction due to the presence of particles (F_p) to that for turbulent flow in a pipe without particles (F_f) in "parallel" flow pneumatic transport. The particle phase friction factor, f_p, is assumed to follow the Konno and Saito (1969) Froude number relationship $\left[(gD)^{1/2}/\nu\right]$.

The derived equation for F_p/F_f is shown to be qualitatively correct as well as consistent with both experimental observations and literature data. Qualitative predictions are good also for low loading values. To improve predictions, data are needed to formulate the variation of f_p with loading. The bounds for this function are addressed.

The interaction of particles with the turbulent fluctuations both in the turbulent core and the near-wall region of the pipe determines whether particles enter or are excluded from the near-wall region. These interactions are fundamental to particle deposition on a wall and thereby to wall friction.

The fundamental parameters governing this interaction involve the ratio of the particle relaxation time and the appropriate eddy lifetime as well as ratio of the superficial fluid velocity to the particle terminal velocity.

An analogous equation is derived for hydraulic transport based on the Froude number $\left(gD/\nu^2\right)$ derived from the data of Grbavčić et al (1992).

References:

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Recent Developments in Residence Time Distribution

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We use to apply the concepts of Danckwerts to describe residence time distribution (RTD) phenomena, although Danckwerts himself in his original paper warned the reader, that his approach would hardly ever describe the RTD problems adequately. Realistic experiments are known that only may be interpreted with the Danckwerts approach, provided we introduce negative dispersion coefficients. Numerous papers have been written to give a possible physical interpretation of the boundary conditions at the inlet and the outlet of the system; but still they keep puzzling experts. In many experiments never a upstreams dispersion in packed beds could be found despite such predictions by the theory of Danckwerts.
We, therefore, derived a new model to interpret RTD phenomena, which still maintains the ease of a one-dimensional approach. We called the model the "wave model ", because of the analogy with the description of wave problems in hydrodynamics. This model only needs boundary conditions at the inlet of the system, adequately describes dispersion in packed beds and asks for realistic dispersion parameters in the case where the Danckwerts model would need negative dispersion coefficients. The wave model will be explained and applied.
Chaotic temperature fields in running packed bed reactors have been observed which could not be interpreted with the usual models to describe the behaviour of packed bed plug flow reactors. This led to the investigation of the influence of free convection on the RTD in packed bed reactors. The results of this investigation will be explained and the correlation of the dispersion data will be shown to be quite accurate. Extrapolation of the correlated data to industrial equipment warns for very serious consequences in such equipment, which will be explained. Urgent large scale experiments are required.

PL 8

Science of Opportunity on the International Space Station

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Science done during Expedition 6, November 23, 2002 through May 3, 2003, to the International Space Station consisted of a mix of programmatic science and science of opportunity. The science of opportunity was done at the discretion of the scientists onboard using simple materials that would not impact the programmatic supplies and was dubbed “Saturday Morning Science”. A number of raw Saturday Morning Science observations will be presented whose value rests not in the rigors of the experiments but in providing observational-based incite into the counter-intuitive nature found in the reduced gravity environment of orbit. Some examples that will be presented are described here. It was discovered that films of de-ionized water could be drawn with no added surfactants. These films were made with a thickness from 60 micrometers to several millimeters. An easily obtained thickness was 300 micrometers that resulted in a robust film that could be used for subsequent experimentation. Diameters ranged from 50 to 160 millimeters. No optical interference patterns were seen until the film thickness approached 60 micrometers. Lifetimes were several hours to several weeks depending on the control of evaporation and the initial film thickness. These water films were used as a vehicle to investigate a number of phenomena where fluid dynamics was limited to two dimensions. Thin film crystallization was demonstrated with sodium chloride where thin flat crystals of 5 to 15 millimeters on edge were grown over a period of about a week. Protein films of gelatin were made and used as substrates to suspend spherical drops of water and subsequently regulate by diffusion of sucrose or sodium chloride into the drop where crystallization took place. Marangonii convection was readily driven in water films from the heat generated when the beam from a mini-Mag flashlight was directed onto the film. Nucleate boiling was demonstrated in 2 millimeter thick films where the 15 millimeter diameter barrel of a soldering iron provided a heated cylindrical wall held perpendicular to the film. Water vapor bubbles formed at the heated wall and were rapidly convected away from the onset of strong convective flow. Video and digital images will be presented to illustrate these and other the raw observations stemming from the unique orbital environment.

Particles Formation Using Supercritical Fluids

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Particle formation and design of solid particles and powdery composites with unique properties is at the moment one of major development of supercritical fluids (synonyms: dense gasses, dense fluids, high pressure) applications.
Conventional well-known processes for particle-size re-distribution of solid materials are crushing and grinding (which for some compounds are carried out at cryogenic temperatures), air micronization, sublimation, and recrystallization from solution. There are several problems associated with the above-mentioned processes. Some substances are unstable under conventional milling conditions, in recrystallization processes the product is contaminated with solvent, and waste solvent streams are produced. Applying supercritical fluids may overcome the drawbacks of conventional processes, and powders and composites with special characteristics can be produced. Several processes for formation and design of solid particles using dense gases are studied intensively.
The unique thermo-dynamic and fluid-dynamic properties of supercritical fluids can be used also for impregnation of solid particles, for formation of solid powderous emulsions, particle coating, e.g. for formation of solids with unique properties for the use in different applications.
This review will focus on fundamentals and on recent advances of particle formation and design processes using supercritical fluids, on their applications and the technological advantages and disadvantages of various processes.

Section

General Chemical Engineering

GCEN

GCEN X-NN yyy

X = KN – Keynote lecture
O – Oral presentation
P – Poster presentation

NN = Number

yyy = Topic:
rec - Reaction Engineering and Catalysis
sep - Separation Process
tph - Transport Phenomena
ece - Education in Chemical Engineering
thd - Thermodynamics

Downscaling Three Phase Hydrotreaters

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Downscaling of process equipment and mainly of chemical and biochemical reactors is attempted with the aim to increase experimental productivity, to reduce experimentation cost and to investigate process characteristics. The reduction of the continuous flow reactors scale results in demand of lower superficial fluid velocities through the reactor space although the other process parameters do not alter significantly. But the change of the fluid velocities may have a major impact on the reactor performance because they directly influence mass transport and reactor hydrodynamics. Therefore, the reduction of the reaction scale must be carefully designed and investigated, especially when the small scale equipment is intended to be used for derivation of meaningful data and to replace expensive pilot units.

Hydrotreatment of petroleum fractions is widely used in refineries for the improvement of fuel product characteristics. It is a catalytic process and at reaction conditions most of the middle and heavy distillate fraction petroleum feeds are in liquid phase while the gas phase consists mainly of hydrogen. The interest on this three phase process is due to the need for ultra deep desulphurization of the gas oils and for upgrading heavy fractions to increase the production of middle distillates.

Effective reduction of the experimental hydrotreaters size will contribute to process development, catalyst development as well as to follow-up of existing units. As the reactor size is reduced, minimization of the inter-particle mass transfer resistances and hydrodynamic effects is necessary. Usually, experiments are conducted in upflow and downflow mode by diluting the catalytic bed in order to decouple fluid dynamics from kinetics. If the fluid dynamic drawbacks are not vanished it is necessary to take them into account in the mathematical simulation of the reactor. To this end it is indispensable to quantitatively estimate their effect on the reactor performance. Moreover, the effect of the change of process conditions on the reactor operation must be carefully studied in small scale hydrotreaters because the process characteristics may change. Then, scale down could be a tool to both investigate these effects as well as overcome the problems associated with them. Scale down is not a simple reduction of the reactor size but it must be designed on the basis of the analysis of the operation of pilot and bench scale units.

Some Theoretical Problems in Chemical Engineering

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Many models of the industrial processes are based on the hypothesis for linearity of the mass transfer. However, there are many cases of a big difference between the experimental data and the prediction of the linear theory of mass transfer kinetics. A composition of **the non-linear models of mass transfer** is one of the mane problems of the modern chemical engineering.

Theoretical analysis of the non-linear effects in the mass transfer processes show that its order is about 10-30%. However in many cases the difference between experimental data and linear theory is bigger. This effects are result of the lost of stability of the systems, when small disturbances increase to the stable periodical structure with constant amplitude. This self – organizing dissipate structures are characterized with very big heat and mass transfer rates. In these cases the dissipation energy value is not very big, because the system is before the flow tubulization. The modelling of these processes with intensive mass transfer is related with the **theoretical analysis of hydrodynamic stability**, which is another main problem in chemical engineering.

Many models in chemical engineering contain parameters, which must be obtained on the bases on the experimental data. Very often the solution of this inverse problem for parameter identification lead to big mathematical difficulties, related with the **inverse problem incorrectness**. These are the cases when problem solution (parameters values) is sensible with respect to experimental data error of the objective function. This is important problem in chemical engineering.

The process simulation leads to the scale-up problems. In the cases of physical modelling they are result of the similarity criteria non-compatibility. In mathematical modelling a column diameter increasing leads to the scale effect, i.e. a decreasing of the process efficiency. The creating of **diffusion type models permit to solve the scale-up problems** of column apparatuses for interphase mass transfer and chemical reactions. This is another important problem in chemical engineering.

Studies on the Iron-Catalyzed Fischer-Tropsch Process in a Laminar Flow Slurry Column Reactor

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The Fischer-Tropsch process was studied in a laminar flow slurry bubble column reactor. Prior to experiments, hydrodynamic studies were done in a cold-flow model of the reactor. A mathematical model was also developed for the reactor, based on the kinetic data of an iron-based catalyst. The present modeling approach employed enabled the computation of the extent of gas contraction due to reaction. Six sets of experimental runs were carried out to validate the model, the last utilizing biosyngas, produced by the gasification of willow. The model developed was suitable to predict the performance of the reactor, with rate parameters adjusted, necessitated by the fact that catalyst activity changes with time-on-stream. The effect of a number of selected parameters on the Fischer-Tropsch process was also investigated.

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GCEN O-02 rec

Design and Study of Ru/Carbon Catalysts for Processes of Wastewater Treatment

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The development and examination of Ce-promoted carbon-supported Ru catalysts in wet air oxidation (WAO) of phenol, aniline and acetic acid are the objectives of the consideration in this work. The choice of a catalytic system is justified by results of studies of variety catalytic systems (oxides and supported noble metals Ru-, Pt-, Pd-/C), shown the highest efficiency of Ru-CeO_2/ Sibunit (the combination of activity in deep oxidation of a carbon chain and selectivity of formation of molecular nitrogen or sulfates) for oxidation of various sulfur-, and nitrogen-containing compounds at T = 160 – 200 ^oC, P_{O2} = 0.3 - 1.0 MPa.

The carbon material of Sibunit family is favorably differs from known active carbons by the high stability in aggressive and oxidizing mediums. So it was used in the present study as universal support, and as an adsorbent simultaneously.

Catalytic WAO of 1 g/L organic solutions was carried out in agitated autoclave (0.6 MPa of partial O_2-pressure). Pure Sibunit samples were shown to be active catalysts for phenol and aniline oxidation. The conversion of phenol and selectivity to CO_2 increased after the carbon has been treated with H_2O_2. Therefore it can be concluded that this treatment introduces additional functional groups active for the oxidation reaction.

In the phenol oxidation the catalytic activities follow the series: Sibunit < H_2O_2-oxidized Sibunit <Ru-CeO_2/Sibunit. A total oxidation to CO_2 is obtained with the 5.3wt% Pt catalyst; however Ru-containing catalysts, giving 70% selectivity to CO_2, are more economically valuable because of the low amounts of noble metal involved.

The stability of various WAO catalysts ((0.6% Ru+5% CeO_2/Sibunit, 0.6% Ru+8% CeO_2 /Sibunit, Sibunit-4) in phenol and acetic acid oxidation was investigated for about 300 h in a continuous trickle-bed reactor. The activity was very stable in all cases of phenol oxidation, and significantly decreased as a function of time on stream of acetic acid after 100 h of tests.

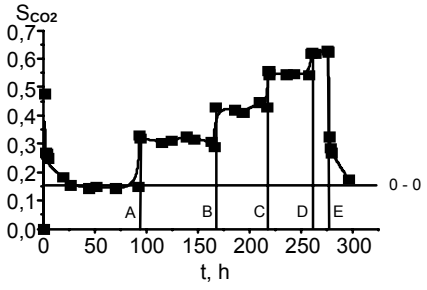


Fig. 1. Selectivity of CO_2 formation in long term test of Ru-CeO_2/C catalyst in phenol oxidation. (m=1.0 g, C_{PhOH} =1.00 g l^{-1}, 180 ^oC, P=5 .0 MPa, V_{air}= 5 l h^{-1}, V_{liq}= 1.0 ml min^{-1}). Recycling after 92 (A), 165 (B), 216 (C), 257 (D) hours; fresh solution after 276h (E). Line 0-0 - initial level of activity.

Acknowledgment:
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An Experience of Catalyst Design Using Mathematical Modeling

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The report concerns an approach is called “kinetic assisted design of catalysts” that widely used in the literature during last ten years. Several examples of mathematical modeling application in catalyst design are presented.

Ratio of different active centers

The roles and ratio of active centers of “metallic” (Pt^{o}) and ionic platinum (Pt^{n+}), and acid centers of Al_2O_3 (AC) in naphtha reforming catalysts are discussed. The combination of kinetic experiments (pulse technique) and its mathematical simulation allows to establish the roles of Pt^{o}, Pt^{n+} and AC in reforming reactions – naphthenes dehydrogenation and isomerization; paraffins isomerization, cyclization and hydrogenolysis. The results give the possibility to develop the new generation of reforming catalysts with high selectivity and stability.

Localization of active component

Modern techniques of catalyst preparation allow synthesizing the supported catalysts with non-uniform distribution of active component in porous support – along the radius of pellet (macro-distribution), and among the pores with different size (micro-distribution). The regulation of macro-distribution is widely used in practice, While, the regulation of micro-distribution is relatively new problem. Possible effects of non-uniform micro-distribution are analyzed in this report using mathematical modeling. The optimal micro-distribution of Pt in reforming catalyst is worked out in order to improve their selectivity and stability.

Catalyst porous structure

The influence of catalyst porous structure on catalytic process is rather diverse. In this report, the affect of porous structure on the reactions accompanied by capillary condensation of some reagents is considered. Again, the combination of special experiments and mathematical modeling is used. It was shown that capillary condensation affects reaction kinetics, rate dynamics in transient regimes, and catalyst deactivation. This exerts influence on the optimal porous structure in some processes, for example, in hydrodesulfurization of petroleum derivates.

Pellet size and form

The combination of catalyst pellet size and forms is the main way in optimization of pellet effectivity and pressure drop in catalyst bed. It is demonstrated in the report that different forms may be optimal depending on optimization criterion (productivity of catalyst, productivity of bed, pressure drop, and other).

Solid inert in catalyst bed

The application of solid inert in catalyst bed (“dilution” of the catalyst) has an effect only in unsteady-state regimes. It is shown that in cycle processes: reaction-regeneration (such as olefines dehydrogenation) the effect depends on coke concentration deposited on the catalyst. In this case, the solid inert can accumulate the additional heat of coke burning during catalyst regeneration.

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GCEN O-04 rec

Efficient Bleaching of Cotton With Hydrogen Peroxide Using a New $[Mn_2O_3(tmtacn)]^{2+}$ Catalyst Reaction System

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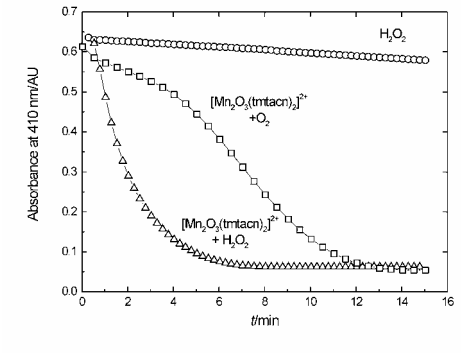
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This study outlines fundamental aspects of the performance of $[Mn_2O_3(tmtacn)]^{2+}$ catalyst (dinulclear μ-oxo bridged Mn(IV) complex of the ligand 1,4,7-trimethyl-1,4,7-triazacyclononane) as a process intensificator for bleaching of cotton with H_2O_2. This catalyst and related complexes have proven to be very active in the catalysed, and often selective, oxidation of organic substrates with H_2O_2 in non-aqueous systems [1a] and provide stain bleaching activity in detergent formulations under alkaline conditions [1b].

Catalytic bleaching of cotton takes place in a heterogeneous aqueous reaction system in which it is difficult to study physical and chemical phenomena. To study intrinsic kinetics and chemical mechanism, it is necessary to exclude the influence of transport phenomena that exist in such a heterogeneous reaction system. In order to eliminate these effects, we have developed homogeneous model system containing specific polyphenolic substrates (mainly flavonoids) as model compounds to mimic cotton fibre coloured matter. The primary model pigment chosen is morin, owing to its presence in native cotton fibre.

The oxidation of model compounds over $[Mn_2O_3(tmtacn)]^{2+}$ catalyst is carried out in batch mode. The influence of reactant and catalyst concentrations, reaction temperature and reaction pH is investigated. The results show that the addition of very small quantities of $[Mn_2O_3(tmtacn)]^{2+}$ leads to a tremendous increase of the reaction rates at lower temperatures (30-40^oC) by providing a new mechanism with lower activation energy of bleaching.

Through the use of a homogeneous system, we have revealed the ability of $[Mn_2O_3(tmtacn)]^{2+}$ to use O_2 present in the aqueous system as ultimate oxidant. Figure compares the reaction profiles of the uncatalysed (H_2O_2) and $[Mn_2O_3(tmtacn)]^{2+}$ catalysed morin oxidation by H_2O_2 or O_2 recorded by UV-Vis spectrophotometry at 410 nm (25^oC and pH 10). A decrease of absorbance with time corresponds to oxidative degradation of morin and can be considered as a measure for the catalytic activity of $[Mn_2O_3(tmtacn)]^{2+}$. The catalytic oxidation activity of $[Mn_2O_3(tmtacn)]^{2+}$ is confirmed to be superior compared to the activity of "free" manganese catalyst [Mn(II)]. Reaction rates are pH dependent, reaching a maximum value at *ca.* pH 10.5 and without significant change until *ca.* pH 11. Generally, the results obtained from both systems (heterogeneous and homogeneous) correlate well. When $[Mn_2O_3(tmtacn)]^{2+}$ is present in the bleaching system, the process efficiency is improved, the oxidation proceeds rapidly even at ambient temperatures, whereas bleaching system with hydrogen peroxide only, shows almost no reaction under the same conditions.



We thank Dr. R. Hage (Unilever Research, the Netherlands) and Dr. W. R. Browne (University of Groningen, the Netherlands) for helpful discussions on the reaction mechanisms.

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Experimental Investigation of Partial Oxidation of Ethane to Ethylene in Fluidized Bed Reactor

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Olefins, which are the main feedstock in industrial organic chemistry, are mainly produced by thermal cracking. This process is highly endothermic and requires construction of large cracking furnaces which should be shut down periodically to remove coke deposit. Due to those disadvantages, in the recent years many efforts were made to investigate catalytic oxidation of alkanes as an alternative process for obtaining olefins. Development of catalytic oxidation would give the opportunity to utilize the natural gas instead of oil and to perform the process with large saving of energy.

In this work catalytic oxidation of ethane to ethylene was studied. The catalytic oxidation of ethane is complex reaction and the formation of ethylene as intermediate product is limited by consecutive and parallel deep oxidations. The aim of this work was to investigate the influence of type of catalyst, temperature and residence time on conversion and selectivity to ethylene.

The reaction was carried out in fluidized bed reactor with cross-section area of 100×100 mm. Two types of catalyst particles were employed: pure γ-Al_2O_3 and V_2O_5 impregnated on γ-Al_2O_3, both of 1,8 mm in diameter. Reaction was performed at atmospheric pressure, in the range of temperatures from 400-600 ˚C, in dilute system with inlet ethane concentration of 1 mol % for different masses of catalyst and superficial gas velocities.

Experimental investigations indicate that pure γ-Al_2O_3 shows better activity as catalyst but V_2O_5/γ-Al_2O_3 shows much higher selectivity to ethylene. This difference comes from different acid/base and redox properties of catalysts. Increase of the temperature and residence time leads to decrease of ethylene selectivity. Higher temperature favors deep oxidation and higher residence time causes ethylene loss through consecutive reactions.

Experimental results for ethane conversion and ethylene selectivity obtained in fluidized bed reactor were compared with those in packed bed reactor from literature. Fluidized bed reactor shows better performances for exothermic catalytic oxidation due to temperature uniformity.

GCEN O-06 sep

Separation of Ascorbic Acid by Reactive Extraction With Amberlite LA-2

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CANCELED

Ascorbic acid, or vitamin C, is one of the well-known vitamins, being biosynthesized by microorganisms, plants and most of animals, but not by human organism. Due to its antioxidant properties, vitamin C plays a vital role in protecting the body. Its deficiency leads to scurvy, a disease characterized by weakness, small hemorrhages throughout the body that cause gums and skin to bleed, and loosening of the teeth.

Vitamin C is a water-soluble compound, being obtained by extraction from plants, by chemical synthesis, by biosynthesis and by mixed chemical/biochemical methods. The industrial manufacture of vitamin C is carried out by two ways: biosynthesis combined with chemical synthesis (Reischstein process) and two steps fermentation. The annual production is over 70.000 t, China being the most important producer with 43.000 t/year. Indifferent of the method used for vitamin C production, its separation and purification require a lot of difficult stages, with high material and energy consumption. For these reasons, the selective separation of vitamin C from 2-keto-gluconic acid by an original technique, namely reactive extraction with Amberlite LA-2, was studied. These studies were initially carried out for individual separation of vitamin C and 2-ketogluconic acid from aqueous solutions, and then for their separation from mixtures. In this paper the results obtained for individual reactive extraction of vitamin C with Amberlite LA-2 dissolved in butyl acetate are presented.

These studies indicated that the separation occurs by means of an interfacial reaction of first order between the two components. The extraction process is controlled by the extractant concentration in organic phase and pH-value of aqueous phase (Figure 1).

Figure 1. Influence of the pH-value of aqueous solution on vitamin C extraction degree

For Amberlite LA-2 concentration of 160 g/l and acidic pH-domain, the extraction degree of vitamin C reached 90%, as the result of the solubilization of interfacial product by solvation or by entrapping into aminic micelles formed in organic phase.

The separation efficiency was enhanced by addition of a phase modifier, namely 2-octanol, the extraction yield being increased with about 6 - 23%. This variation indicated that the increase of solvent polarity exhibits a favorable effect on interfacial formed compound solubilization into organic phase.

Cyclic Operation of Adsorption Column - Fast Estimation of Periodic Quasi-Steady States Based on Higher Order Frequency Response Functions

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Cyclic operation of an adsorption column with periodic modulations of the inlet concentration or/and adsorbent temperature was used as a case study for testing a new method for fast approximate calculation of quasi-steady-states of periodic processes. The method is based on the concept of higher order frequency response functions. The system inputs are represented in the form of Fourier, and the output in the form of Volterra series. For practical applications, both the input and the output series are approximated by finite length sums. In this way, the approximate periodic quasi-steady state of the system output is calculated analytically, without long numerical integrations.

The necessary frequency response functions of the adsorption column up to the third order were derived, based on the equilibrium dispersion model. The method was tested for sinusoidal and rectangular input changes. Three cases were considered: Case 1 - for periodic modulation of the inlet concentration, Case 2 – for periodic modulation of the temperature of the entire column and Case 3 – for simultaneous, out-of-phase, periodic modulations of both inputs. The approximate solutions based on the derived higher order frequency response functions were calculated for different input frequencies and amplitudes and compared with the numerical solutions. Very good agreement was obtained.

As illustration, in Figure 1 we give a sample of the simulated results, corresponding to a laboratory column and adsorption of Tröger's base (-) enanthiomer on microcrystalline cellulose triacetate from ethanol. These results were obtained for rectangular input(s) with adsorption to desorption half-cycle ratio 3:2, period 628 s, input amplitudes 25 % for the inlet concentration and 3.2 % for the adsorbent temperature and steady state values: 0.005 mol/dm3 for concentration and 315 K for temperature. The higher order FRFs up to the third order and the first four harmonics of the inputs were used to calculate the approximate quasi-steady state response of the column, shown by solid lines in Figure 1. The dashed lines correspond to the exact response, obtained by numerical solution of the model equations.

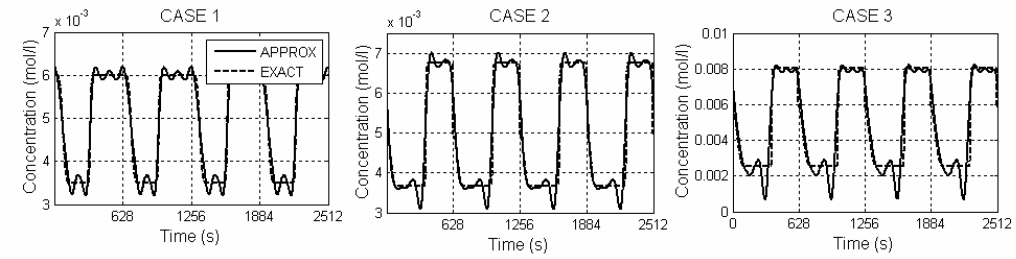


Figure 1. Comparisson of the approximate and exact outlet concentrations for Cases 1, 2, and 3 (period 628 s, steady state: C_s=0.005 mol/dm^3, T_s=315 K, amplitudes: concentration - 25%, temperature - 3.2%)

GCEN O-08 sep

Three Dimensional Finite Element Modelling for Fluid Flow Through a Wire Mesh

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CANCELED

Wire mesh screen is used as the separating medium in filters or to enhance the integrity of the filter medium in, for example, filter cartridges. In this paper we present the progress of an ongoing research project aimed at simulating the non-Newtonian fluid flow through a wire mesh. Due to the complex geometry of a wire mesh, three-dimensional modelling is deemed necessary to correctly visualise the described flow. The modelling in a three-dimensional domain was handled using a finite element method which is known to cope with the complex geometry of the described flow domain very effectively. The governing equations of continuity and momentum were solved by a continuous Penalty finite element method and in conjunction with implicit theta time stepping scheme for temporal discretization. The simulation results were found to be in good agreement with experimental data and theory, showing the developed model is capable of generating accurate results in solving three-dimensional non-Newtonian flow problems.

Solids Flow Pattern in Gas-Flowing Solids-Fixed Bed Contactors

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In gas-flowing solids-fixed bed contactors fine solids particles are introduced at the top of the packed bed column, while gas can be introduced either at the bottom for countercurrent contacting or at the top when cocurrent operation is desired. The flow of fine solids through a fixed bed deviates from plug flow for two reasons: axial mixing and the presence of static solids holdup which exchanges solids with the moving solids particles (dynamic holdup). Solids residence time distribution (RTD) was determined experimentally in the countercurrent gas-flowing solids-fixed bed contactor by the response analysis to a step change at the flowing solids inlet. Mathematical model, which can describe the overall flow pattern, was developed.

In step change experiments fine alumina particles of different color (all other properties being the same) were used as a tracer, and the RTD was obtained by the color analysis of the outlet. The 58.8 mm inner diameter glass column was used and packed with 16 mm glass spheres. The apparatus (at the bottom) contained a narrow sample tube in which solids were accumulated after step signal, representing the "frozen" response. The step response curves were obtained that relate the fraction of the tracer (digital photo analysis – calibration curve) with corresponding time (via sample tube height calibration). Four sets of experiments were carried out, in order to investigate the influence of operating conditions (solids flux and gas velocity) on the solids flow pattern.

Differential model based on two material balances, one for fast moving particles and the other for stagnant particles (settled on packing) was developed. Model presumes axial dispersion in fast moving zone, represented with Peclet number, and exchange of mass between dynamic and stagnant zone, represented with a frequency of exchange. Other parameters of model are: dynamic and static holdup and "dead" fraction of particles. Well known Dankwert's boundary conditions were used for model calculations. Simulation results are in very good agreement with experimentally obtained response curves. Sensitivity analysis was performed which showed the significance of each model parameters. Experimental results as well as model simulations confirmed a minor dependence on gas velocity and considerable influence of solids flux on solids flow pattern. Proposed model predicts well the residence time distribution data for countercurrent gas-flowing solids-fixed bed contactors.

Modelling of Simultaneous Ultrafiltration and Diafiltration with Real Flux

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The classical diafiltration process is carrying out with constant volume. Disadvantages of this process are large consumption of liquid for purification (usually water) and decreasing flux. In order to save water different modes of diafiltration was examined. The diafiltration in two stage [1] has show significant water saving (the permeate of second step use in first step for washing with addition a fresh water). The process with variable volume [2] (liquid for purification is continuously added at a rate less then the permeate flow rate-volume overhead membrane successively decreasing) makes possible to save larger volume of liquid [3].
In this work the mathematical model of diafiltration with variable volume, real membrane and decreasing flux has been presented. The equations for flux were taken from literature and they are based on different theories. In this work the time dependence of macrosolute concentration, amount of liquid for purification, the purification degree of microsolute and dependence purification degree of microsolute of relative diafiltration volume have been investigated. Result show that achieving of high concentration of macrosoluts, needs more time, and liquid for purification. In order to remove small amounts of microsolutes one must use higher amount of liquid for purification. For high purification degree velocity of process is getting higher, the amount of liquid for purification is decreasing. It has been observed that the rejection coefficient decreasing, versus micromoles penetration through membrane, causes decreasing of process velocity.
The model with variable volume has been compared with the model with constant flux. As expected, the model with variable volume predicts larger volume of liquid for purification and more time. The variable volume models with different equations for flux have been also compared. Numerical limitation of models has been also investigated. It has been observed that the difference between rejection coefficient and α must be in the range 0.1 and 0.5.

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The Removal of CO_2 With Activated Solutions of Tertiary Amines

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The (bulk) removal of CO_2 from industrial gases, e.g. natural gas, is usually realized with a reactive absorption technique in which (non-)aqueous solutions of alkanolamines are used. From the point of absorption rate primary or secondary amines are preferred. However, in case costs of regeneration are taken into account, tertiary amines are much more attractive. In order to combine the specific properties of tertiary and primary/secondary alkanolamines respectively, mixtures of both types of compounds are used. A well known example is the activated MDEA-process in which MDEA is mixed with (small amounts) of activator (the fast reacting compound, e.g. piperazine). In this study a matrix of several tertiary amines with several activators is studied with respect to the performance of CO_2-bulk removal from natural gas. The absorption process has been carried out in a tray column. For some typical industrial cases the impact of the activator on the total number of trays has been simulated. From these simulations the optimal number of trays in combination with the composition of the solvent (mixture of a tertiary and a primary/secondary amine) can be determined. Furthermore, insight is obtained on the mechanism of the absorption steps in mixed amine solutions. It will be demonstrated that the working action of the activator is substantially influenced by the partial pressure of CO_2 in the gas mixture. Moreover, this effect is strongly depending on the molar fraction of the accelerator.

Experimental Treatment of Porous Solids by Simplified Dusty Gas Model: Steady-state Isobaric Multicomponent Transport

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The transport of gaseous components into porous media could be described according to the well-known Fick model and its modifications. It is also known that Fick low is not suitable for predicting the fluxes in multicomponent gas mixtures, excluding binary mixtures. This model is still frequently used in chemical engineering because of its simplicity. Unfortunately, besides the Fick model there is no generally accepted model for mass transport into porous media (membranes, catalysts etc.). Numerous studies on transport through porous media reveal that Dusty Gas Model (DGM) is superior in its ability to predict fluxes in multicomponent mixtures. Its wider application is limited by more complicated calculation procedures comparing to Fick model. It should be noted that there were efforts in order to simplify DGM in order to obtain satisfactory accurate results. Moreover, there are also two other models which are used in the literature (mean transport pore model - MTPM and friction model -FM). They vizualize the gas diffusion in pores in a different way but they are very similar.

One of the applications of DGM model is to determine transport characteristics (transport parameters) of porous solids. The classical approach for experimental investigation of diffusion through porous media is by using Wilke-Kallenbach (W-K) cell. This cell consists of two flow-through compartments separated by porous material under study. The experiment is performed under steady-state isotermic and isobaric conditions. Binary or ternary mixtures of unabsorbable inert gases are used (eg. H_2, He, N_2, Ar). The measured net fluxes through porous material are fitted with DGM governing system of ODE in order to obtain the characteristic parameters (model parameters): mean pore radius, tortuosity factor and permeability. It is common practice to use the original DGM model for this procedure.

In this paper we propose using the simplified DGM model in the analysis of experimental data by W-K cell in order to obtain the characteristic parameters of the porous material. Published experimental data are used in testing the accuracy of the linearized procedure. It is shown that this simplified procedure is accurate enough compared to the standard more complicated calculations. On the other hand, this procedure allows more insight into the obtained experimental data.

Eco-Chemical Knowledge, Behaviour and Engagement of the Workers Employed in the Industry of the Mineral Fertilizers in Novi Sad

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The level of enviroment pollution is influenced by knowledge, behaviour and ecological engagement of the individual and society as well. The industry of the mineral fertilizers represents one of the potential sources of pollution. The issue examined in this study is the level of eco-chemical knowledge, behaviour and ecological engagement of the workers employd in the industry of the mineral fertilizers in Novi Sad. The results obtained could be used for the selection of methods to enhance eco-chemical knowledge of the employees and influence their increased engagement in solving the enviromental issues. The survey used in the research was constructed of the set tasks:

1. The analysis of eco-chemical knowledge level of the employees
   - The analysis of effects that family,education system, enviroment, workplace and media have on the employees' eco-chemical knowledge.
   - The analysis of effects that the curriculum contents of the subjects such as biology, chemistry and ecology have on eco-chemical knowledge.
   - The analysis of effects that eco-chemical contents in printed and electronic media have on the level of employees' eco-chemical knowledge

2. The analysis of eco-chemical attitudes of the workers employed in the industry of the mineral fertilizers in Novi Sad
   - The analysis of effects that media have on the employees' ecological awareness.
   - The analysis of effects that enviroment (family, education system, media, surroundings and workplace) have on the employees' attitudes toward it.
   - The analysis of the employees' attitudes toward enviroment pollution.
   - The analysis of the employees' attitudes toward the existing ecological magazines, brochures, ecological events, exhibitions within their company.

3. The analysis of eco-chemical behaviour and engagement of the workers employed in the industry of the mineral fertilizers in Novi Sad
   - The analysis of the employees' ecological engagement
   - The analysis of the employees' ecological activity
   - The analysis of the employees' participation in ecological associations
   - The analysis of the exchange level of the knowlegde and experience asquired between the employees and their enviroment

How to Use the Software for Education Purposes

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There has been computer revolution in engineering education. Computers have greatly increased the ability of students and practicing engineers to perform calculations. Since simulators allow professors and students to do much better job at calculation, they have been widely adopted in engineering education.

The aim of this work is to combine the possibilities of three software to create simulation flowsheet for the sulphuric acid production process. Two of them are equation solving oriented (Polymath and E-Z Solve for CRE and Kinetics), and one is simultaneous modular oriented (HYSYS).

The step of oxidation of SO_2 in the production of sulphuric acid is chosen as example. The examination of the kinetics of the reaction and its equilibrium is performed using E-Z Solve for CHE and Kinetics. The reaction rate expression is used from the literature. This software produce 2D plots, the most important X-T reaction plan, and 3D plots, r (X,T), that is the space where the reaction can take place. These plots are very useful for determination the conditions or part of the space where the reaction occurs according to the design requirements.

Two types of converters; heat exchange reactor and multibed reactor can be designed using Polymath.

HYSYS was used to simulate absorption column in sulphuric acid separation section.

The case study presented in this work shown how can use the simulators in the process of synthesis the reactor and separation sections, as well as the analysis of the reactor.

Problems and Possibilities of Education of Blinds for Professions in Chemistry

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The blinds and generally, the persons with poor vision, have very narrow space in employment. In society with equal chance there is a need to equalise the handicapped with others. The chemistry requires good perception and good reactions. The gap with blinds could be overdue by means of modern technology, using joint instruments with computer. On that way the most sensitive information could be worked out and transferred to the user in different forms. For blinds the computer information goes trough programs with tonality. On that way could be followed the chemical reactions, measured the quantity of chemicals, to read out and write the formulas. For identification of the chemicals useful also the bar code with text reader. In the professional education helps instead of books the CD with tonality. If any books will be used, there is a need for text reader according to the use font. We suggest that the programmes will be free.

We propose operative programme **JOZ for Windows** accommodated for blinds, **Voice Navigator** as voice commander, **Narrator** as text reader and **Magnifier**, for persons having poor visions. Besides many of technical solution with load speakers on measuring devices and computers there are many problems to solve them. One of basic problems is the synthetic speech. Especially the Screen reader makes problems. For this computer tool used software JAWS, Window-Eyes, Simply Talker, VIR 60 and Win Vision the mentioned programmes are accommodated to the English language. For East-European languages could be used only the JAWS and Window-Eyes.

Also problem is the complicated navigation and many details and links. One of the solutions is the conversation on natural and synthetic speech. The other solution is the synthetic speech for book reader or for any printed materials based on scanner-OCR-Generator of synthetic speech. The current devices of this type are VERA, OVATION, GALILEO and KURZWEIL 1000. To take notes are good Brailen'n Speak and Type'n Speak.

The next problem is with manipulative nature. Trough the work with the instruments has great importance the signalisation. For that is suggested a pulsed tone with 880Hz frequency with 1HZ repetition. It helps to find things in laboratory and workshop. The orientation, navigation and alarm are the logistics between computers, printed texts, devices and the operators. The basic information comes from printed Text. Great help gives the PC trough INTERNET supported by telephone, which makes could control and led in the process of activity. The telephone support is necessary on the case of PC programme problem in conversation with centre

GCEN P-04 ece

Motivation Models for Food-Processing Branch Students in Learning Chemistry at Advanced Education Level

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The aim of this research was to find and suggest motivation models to students, so that they should learn chemistry in an efficient way. The suggested model was their independent choice and chemical experiment elaboration. This kind of model was verified in practice.
Pedagogic experiment, with two parallel groups, was conducted (control group of 50students and experimental group of 50 students). This experiment was included in the process of regular lectures and it presented an integral part if everi day chemistry curriculum, according to Inorganic Chemistry Curriculum for food-processing branch, at Advanced Technological School in Šabac. The students' tasks were to chose and elaborate appropriate experiments, which should be included in total number of lectures, according to anticipated curriculum. The students from the experimental group were divided into two groups - 25 students in each, and each group was divided into subgroups-5 students in each (according to their own will). Each subgroup had its representative who was distinguished by his knowledge and skills.
Mutual comparison of thes two groups (control and experimental) was done by testing hypothesis of equality of two sample proportions. Significant difference was noticed according to freedom degree and critical table values for probability degrees from 0,05 and 0,01.
The course of experiment consisted of initial evaluating (srandardizing control and experimental groups), introducing experimental factor-active chemistry learningin experimental group and continuing the common way of working with control group, conducting experiments (effecting experimental factor-active learning), final evaluation of students' success and passing conclusions. This model demanded the following activities: studying literature and collecting information, exchanging collected information, "for and against" chosen experiment, waking a short list of experiments, team working of subgroups in checking chosen experiments, waking a final list of experiments, doing regular practice classes, testing students' knowledge in the fields (Stehiometry, Dispersion systems, Chemical kinetics).
According to the total results of this research, it was concluded that the suggested model was efficient and that it significantly influence on students' success, being our future food-processing engineers.

Catalytic Incineration of Ethylene Oxide in the Packed Bed Reactor

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The removal of ethylene oxide (EtO) from numerous emission sources (EtO production plants, manufacture of ethylene glycol, polymers, surfactants, food and pharmaceutical sterilizing units) is very important due to its mutagenic, teratogenic and cancerogenic effect on human health. Generally, it is considered that exposure to EtO at any level is harmful to health.
Different technologies can be used to treat EtO emissions: wet scrubbers, thermal oxidizers, catalytic oxidizers and dry-bed reactors and theirs appropriateness for the specific application depends on several factors such as: efficiency, energy consumption, secondary pollution, capital investments etc. The principal advantages of catalytic oxidation are high efficiency of the process, lower energy consumption than thermal oxidizers and absence of secondary pollution (NOx or liquid or solid waste). The supported noble catalysts are widely used for catalytic oxidation of organic vapours, particularly platinum, because of its high selectivity, resistance to poisoning and low ignition temperature. A preheater must be used to bring the inlet gases to the appropriate initiation reaction temperature.
Investigations of catalytic incineration of ethylene oxide (ETO) over Pt/Al_2O_3 catalyst have been conducted on laboratory and pilot scale level. The main conclusion drowns from packed bed investigations is that conversion overreached 99.9% when the inlet temperature of the reaction mixture was higher than 180°C. With a relatively high EtO concentration at the inlet, the reactor could operate autothermally by the use of appropriate heat exchanger since heat of combustion is sufficient to for preheating inlet gas mixture to the ignition temperature. This would mean that external heating is necessary only during the start-up period. EtO inlet concentration should be maximum 30% of the LEL (lower explosion limit) due to the safety requirements. The LEL for EtO is 3 vol.%. Our experiments showed that the optimum catalytic oxidation parameters are: space velocity 17000 h^{-1}, inlet temperature of the reaction mixture 200°C and inlet EtO concentration 0.82 vol.%. Under these conditions, the exit gas temperature is 550°C. The measurements of the reaction rate conducted under gradientless conditions have been used to evaluate kinetics parameters valuable for reactor modeling. A reactor model is proposed which could a priori predict behavior of catalytic convertor under various operating conditions (inlet temperature, inlet pollutant concentration and space velocity) based on the kinetics parameters and mass and energy balances. The results show satisfactory agreement between predicted and experimental values of conversion and temperature profiles along the catalyst bed.

GCEN P-06 rec

Batch Dissolution of SiO_2 in NaOH Aqueous Solution – Kinetics Models

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Kinetics of SiO_2 particles batch dissolution in aqueous NaOH, corresponding to the ratio $SiO_2/Na_2O=2$, was investigated at elevated temperatures and high pressure. It is desirable to have a simple model for predictive purposes. In this study several kinetics models were developed, and compared with experimental results. As a first approximation, the silica particles were assumed to be smooth spheres, which decreased in size, as dissolution proceeds. The influences of the particle size, the operating temperature and the hydroxide ion molality on the kinetic rate were studied. It is certain that these models can be used to correlate the experimental data on dissolution.

On the Ozone Absorption in Mechanically Stirred Reactor

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Ozone absorption in water was investigated in a mechanically stirred reactor of Rushton type, using both batch and continuous mode of operation. Absorption is accompanied by chemical reactions in a liquid phase. In the case of ozone absorption in distilled water only the ozone self-decomposition reaction occurs. The rate of this reaction can be easily determined by measuring the ozone concentration in inlet and outlet gas flow, as well as in the liquid phase.
However, the experimental determination of the ozone volumetric mass transfer coefficient requires the ozone concentration in liquid phase, which is in equilibrium with the ozone partial pressure in the gas phase, to be known. This concentration is a product of ozone solubility ratio and average ozone concentration in gas bubbles present in gas-liquid dispersion in reactor. The problem arises since a variety of data for the ozone equilibrium concentration in water is reported in the literature. From the other side the average ozone concentration in gas bubbles depends upon the mixing status of the gas phase, which is unknown. This problem is successfully overcame in this work and a model for precise determination of ozone volumetric mass transfer coefficient is developed. It was found that both liquid and gas phase are completely mixed and that volumetric mass transfer coefficient changes with the square of the impeller speed. The same behavior was noticed during oxygen absorption in water.From the other hand, volumetric mass transfer coefficient vary with the third root of gas superfacial velocity. Previously obtained correlation for oxygen transfer in stirred tanks seems to hold for ozone transfer as well:

$$K_L a = const \cdot \left(n^3 \cdot d^2\right)^{\frac{2}{3}} \cdot u_G{}^{\frac{1}{3}}$$

The suggested expression is in well agreement with some of literature data, but differ significantely from the other data. The possible reason for that difference may lie in different experimental conditions, that is in different flow regimes in stirred reactor.

Kinetics of Lipase-Catalyzed Esterification in Reversed Micellar Reaction System

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During the last two decades lipases attract great research attention as biocatalysts in various reactions. In nature, they act as hydrolyses of triacylglycerols but also reveal a broad substrate compatibility involved in reactions of esterification and transesterification of esters. Recently, in oleochemistry, a special attention has paid to fatty acid alkyl esters because of their utility as lubricants, plasticizers and emollients. The currently common commercial production method involves chemical synthesis from alcoholysis of oils by acidic or alkali catalysts with high pressure and temperature. Considering the inherent merits of enzymatic reactions, e.g., moderate conditions, less pollution and the trend in consumer preferences toward natural products, also, enzymatic production of such products for different uses has been extensively studied.

Lipase-catalyzed synthesis is preferably carried out in anhydrous media (e.g., in organic solvents). Absence of water eliminates the competing hydrolysis as well as competing nucleophile. But in contrast, lipases are not soluble in most organic solvents and in general, water benefits the intrinsic activity of lipases. In addition, the lipase regioselectivity has been shown to strongly depend on the level of hydration, solvent medium used, and the type of substrate chemistry (i.e., acylating agent). Thus, the optimization of the reaction medium composition is a multiple task.

The scope of the present work is to study the kinetics of lipase-catalyzed esterification realized in a reversed micellar reaction medium. On a macro scale, such system combines the heterogeneity in one phase. It provides a considerable interfacial "oil-water" area needed for lipase interfacial activation.

The studied system was composed of the *substrates* (oleic acid) and i-amyl alcohol in the continuum of an organic solvent where the *lipase* enzyme (***Candida cylindracea***) was incorporated into the reversed micelles of a *quaternary ammonium salt* (Cetyl Pyridinium Chloride). The effects of the system constituents were examined in the frame of kinetic series to determine the initial reaction rate and conversion profile. The following data on initial reaction rates were determined:

- curves of *substrates' molar ratio* (acid to alcohol) *at different concentrations' level*;
- dependence on the *initial water content at different substrates ratio and concentrations level*;
- *lipase concentration* per system volume unit regarding initial water content;
- effect of *solvent used* in terms of its *type and polarity*.

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Volumetric Oxygen Mass Transfer Coefficient in a 16.6 cm Multiphase Reciprocating Plate Column

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Reciprocating plate columns (RPC) has more favorable mass transfer properties than the bubble columns and gassed, stirred tanks. The previous studies of oxygen mass transfer, carried in the 2.54 and 9.2 cm i.d. RPCs have showed that the volumetric oxygen mass transfer coefficient depends on the vibration intensity (product of amplitude and frequency of reciprocating movement), the superficial gas velocity and the solids content.[1] Continuing the previous work, the oxygen mass transfer was studied in a 16.6 cm i.d. RPC in order to find if a criterion for scaling-up this type of multiphase contacting devices could be based on the volumetric oxygen mass transfer coefficient. The reciprocating agitator consisted of a set of perforated plates (number of plates,15; hole diameter of 8 mm; plate free area of 46.6 %) fixed on the common shaft. A number of polypropylene spheres (diameter of 8.3 mm) were uniformly placed in each interplate space, the volume of the solids content being 3.8 or 6.6 %. Air was fed into the liquid, arranged as a batch, through four nozzles at the column base at the superficial gas velocity of 0.5, 1.0 or 1.5 cm/s. The oxygen mass transfer rate was measured by the sulfite method using a 0.8 M sodium sulfite solution and copper(II) sulfate as catalyst (10^{-4} M) at room temperature. The volumetric oxygen mass transfer coefficient was found to increase with increasing both the vibration intensity and the superficial gas velocity for both solids contents, due to the contribution of increased power input to the break-up of gas bubbles and the increased gas holdup, respectively. The increase of the solids content positively affected the break-up of gas bubbles, enhancing the oxygen mass transfer rate, compared to the gassed column in the absence of the spheres. The volumetric oxygen mass transfer coefficient, s^{-1}, could be correlated with the specific power consumption, W/dm^3, and the superficial gas velocity, m/s, using the well-known equation:

$$k_l a = 2.33\left(\frac{P_{sr}}{V_l}\right)^{0.803} u_g{}^{0.572} \quad (r^2=0.935;\ \pm 15.6\%)$$

$$k_l a = 0.60\left(\frac{P_{sr}}{V_l}\right)^{0.572} u_g{}^{0.316} \quad (r^2=0.9295;\ \pm 7.8\%)$$

for the volume of the solids content of 3.8 and 6.6 % respectively. Compared to the columns of smaller diameter (2.5 and 9.2 cm), the volumetric oxygen mass transfer coefficient was higher in the 16.6 cm i.d. column.

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GCEN P-10 rec

Drop Size Variation During Transesterification of Sunflower Oil

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The transesterification process, applied for biodiesel production, is affected by a number of factors, such as: type of molar ratio of alcohol to vegetable oil, type of catalyst, temperature, presence of free fatty acids and moisture and agitation intensity. Poor mass transfer between two phases and the low solubility of methanol in the vegetable oil limit the rate of transesterification reaction during its early stages. In order to increase contact between the vegetable oil and methanol in production of biodiesel, mechanical agitation is normally applied.

The present work dealt with the drop size variation during the alkali-catalyzed transesterification of sunflower oil with methanol in a batch reactor. The main goal was to elucidate the effect of variable interfacial area on the reaction rate.

A 6:1 molar ratio of methanol to sunflower oil was used in all experiments. Potassium hydroxide (1 g per 100 g of oil) was dissolved into a certain amount of methanol before use. The 1 L glass reactor, filled with 820 cm^3 of emulsion, was immersed in a thermostated glass chamber. The reaction was carried out at 20 ^oC. The reactor was equipped with concentric two flat-blade paddle agitator; the impeller diameter and blade width were 75 and 25 mm, respectively. The distance of the agitator from the bottom was 36 mm. The kinetics of the reaction of transesterification and the drop size variation was followed at two agitation speeds, namely at 90 and 150 rpm; in the former case, a fraction of methanol was not dispersed by the agitation in the beginning of the reaction. The concentration of triglycerides and methyl esters was estimated by a HPTLC method. Drop size was measured photographically. The photographic system consisted of a 500 W light source and an AF Nikon F-801 camera with an AF Micro Nikkor lens (f = 60 mm; light power 1:2.8). Data were recorded on a Konica film (Centuria Super 100). The negatives were scanned by a Film Scanner (Sony UY-S90) in order to get digitized images, which were then processed using image software for determining drop size.

It was observed that drop size reduction parallels ester formation. The Sauter mean diameter was unchanged at the beginning of the reaction, when the ester formation was small, then rapidly decreased (from 1,2 and 0,7 mm at 90 and 150 rpm, respectively) in a relatively short period (5 to 10 minutes) of the fast triglyceride disappearance and methyl ester formation and finally reached approximately the same size (about 60 μm). The decrease of drop size at constant agitation intensity was explained by stabilization of smaller drops by the formed mono- and diglycerides which were well-known for their emulsifying action. The significant increase of the interfacial area due to the drop size reduction and the decrease of viscosity of the reaction mixture as the reaction progressed were believed to be responsible for the enhancement of methanol mass transfer from alcoholic to oil phase and thus for “autocatalytic” nature of the reaction.

Influence of Water and Steam Affecting the Activities and Characteristic of High Temperature CO Conversion Catalyst by Steam

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During the production of ammonia by natural gas reforming, the CO conversion section by steam affects to a large extent the economic aspect of the process due to the reduction of the quantity of CO in the process gas also, due to the increased quantity of hydrogen used for ammonia synthesis.

Technical problems concerning the working conditions and the condition of the equipment consequently led to the damage of the high temperature conversion catalyst due to its exposure to water. Exposure to wet conditions endangered the process. In order to analyze the process of catalyst wearing out period, also the influence of water affecting the activities and characteristics of the high temperature conversion catalyst, it was laboratory tested. Testing was performed on wetted catalyst samples in the laboratory reactor at ambient temperature before and after the reduction and during the reaction of CO conversion by steam vapor at 360-100°C. Each test was performed in one wetting/drying cycle or in three wetting/drying cycles.

Results of laboratory tests showed that sample catalyst wetting caused the changes in its characteristics (in texture), leading to catalyst decreased activities.

Catalyst wetting in ambient temperature, regardless of the fact that it was performed before of after the reduction, led to catalyst decreased activities for 12,29 % ie. for 10.59%. Simultaneously, total porosity and specific surface increased resulting in decreasing of the average diameter of the pores. (See Table below). By increasment of the number of wetting (3x), porosity and surface area decreased, pores grew larger, followed by 13,76 %, decreased and slowered activities for the samples wetted before and by 16,10 % for the samples wetted after reduction.

Catalyst wetted at higher temperatures (350-100 ^{0}C) during the reaction of conversion is more active then the catalyst sample wetted in the ambient temperature which is showing the decrease in activity for 4,89 %. When the number of wetting is increased, the endency to decreasement of pores is noticed, which is leading to catalyst decreased activites for 12,15%.

Wetting did not led to decreased crushing streangth of the catalyst. Changes that are evident are in accordance with the changed porosity (See Table below).

Wetting affecting the physical characteristics of HTS catalyst

Character	Samples wetted before reduction		Samples wetted after reduction		Samples wetted during reaction of conversion		New sample after activities determination
	1x	3x	1x	3x	1x	3x	
Density (g/cm^3)	34,919	4,679	11,935	3,120	3,273	2,153	4,756
Pores volume (cm^3/g)	0,337	0,363	0,307	0,332	0,312	0,304	0,308
Porosity (%)	62,69	51,00	76,50	49,50	50,27	39,45	59,38
Surface area (m^2/g)	48,36	15,47	46,19	36,97	48,35	66,78	41,23
Pores average diameter (Å)	139,4	46,9	132,9	134,1	129	91,0	149
Crushing streangth (kg/grain)	5,24	5,02	5,34	5,19	6,00	6,00	4,75

GCEN P-12 rec

Liquid Biofuels Produced By Transesterification of Vegetable Oils

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Introduction

A liquid bio-fuel (Biodiesel) is a "mono-alkyl ester-based oxygenated fuel" with clean-burning properties, produced by converting the triglyceride oils to methyl (or ethyl) esters.

Material and Methods

In our experiments we produced Biodiesel methyl esters from rapeseed oil and from used frying oil. To make biodiesel fuel efficiently from used vegetable oils and rapeseed oil we had to avoid one major problem: soap formation. We used base catalysis in the experiment with rapeseed oil. In the experiment with used frying oil, we performed a two-step transesterification reaction. The first-stage process is not transesterification, but pure and simple esterification. Esterification is followed by transesterification [2]. The first step uses a one-phase acid-catalyzed process to convert the free fatty acids into methyl esters, before using base catalysis to convert the triglycerides, in the second step.

Results and Discussion

The quality parameters of the oils and of the produced biofuels are presented in Table 1. Viscosity is an important quality parameter of Biodiesel since the aim of the transesterification reaction is to reduce the viscosity of the vegetable oil. The acid value (AV) also met the German (0.5max) and US standard (0.8max) [1]. The yield in Biodiesel was greater and the reaction time was shorter when rapeseed oil was used (Figure 1).

Table 1. Quality parameters of the feedstocks and of the biodiesel

Parameter	Feedstock		Biodiesel from	
	Rapeseed oil	Used frying oil	Rapeseed oil	Used frying oil
AV (mg KOH/g)	0.7	5.32	0.08	0.15
Viscosity (cSt)	43.9^{40^o}	46.3^{40^o}	4.8^{40^o}	5.13^{40^o}
Specific gravity	0.921^{20^o}	0.924^{20^o}	0.89^{15^o}	0.89^{15^o}

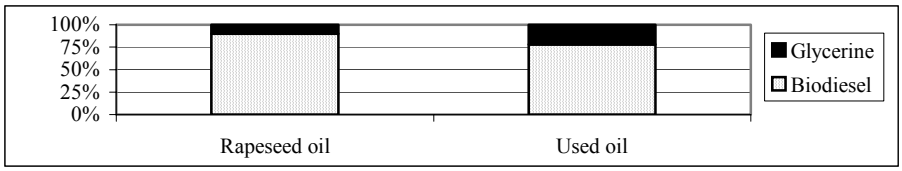


Figure 1. Volume percentage yields of reaction products

Conclusions

The transesterification of recycled oils with methanol was performed with a maximum biodiesel yield of 78.04%. The used frying oil contains FFA and water, which might reduce the yield in Biodiesel by forming by-products (soaps). A greater yield in Biodiesel was obtained when rapeseed oil was used (90%).

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Drag Coefficient for Single Sphere Settling in Stagnant and Counter-Current Fluid and Rising in Stagnant and Co-Current Fluid

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The settling and rising velocities of single test sphere 9.85 mm in diameter were measured in stagnant and flowing water using column 40 mm in diameter. The settling and rising particles had different densities (340 to 1990 kg/m^3) and the fluid in settling and rising experiments in stagnant and flowing liquid was water. Additional experiments in stagnant fluid were conducted using various water-glycerol solutions.

Experimental results indicate that the effective drag coefficient in turbulent regime depends both on directions of movement as well as on water velocity. In stagnant water, the effective drag coefficient for rising particles is significantly higher than the drag coefficient for settling ones, at the same Reynolds number. This result agrees with the work of Karamanev and Nikolov and Dewsbury et al. With increase in fluid viscosity the differences between the effective drag coefficients for rising and settling particles decreases, indicating that bellow Reynolds number of about 200 the direction of particle movement becomes unimportant.

Experiments for rising particles obtained by keeping particle density constant but varying the water velocity, show that the effective drag coefficient increases with a decrease in test particle density, if the velocity of rising particles (v_R) is higher than water velocity (U). If the rising particle velocity is lower than the cocurrent water velocity, the particle moves through the wake. In this case the effective drag coefficient for constant densitz of perticles increases with an increase in the ratio v_R/U. Experiments for both rising (v_R>U) and settling particles obtained at constant water velocity but varying test particle density shows that the effective drag coefficient increases with an increase in water velocity.

GCEN P-14 rec

Platinum Catalyst Nature and Energy Efficiency of Naphtha Reforming

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The catalyst, as a vital part of chemical process, has very important influence on energy efficiency. From that point of view, the study of parameters that contribute to energy consumption of some catalytic process can play significant role in process economy through adequate catalyst choice. But, it seems, that such investigation approach is not enough established.

The main process criteria selected to define catalyst energy efficiency in naphtha reforming are temperature levels needed to reach desired research octane number and reformat yield.

The data collected from reforming simulation process in laboratory reactor (100 cm^{-3} catalyst volume) using several catalyst types with different platinum and other metal content are shown in this paper.

Another important aspect of energy efficiency of process as a whole is catalyst energy consumption during catalyst regeneration. The main factor influencing in that phase is the nature of coke deposited on deactivated catalyst.

The same catalyst samples used in process simulation were studied to define the coke quality and to correlate the coke texture with the fresh catalyst properties.

The forming of so called „soft" coke, desirable for easy elimination and better catalyst regeneration, depends on fresh catalyst characteristics. The energy consumption during soft coke combustion could be more than 30% less and results of catalyst properties revitalization are much better.

Such investigations that contribute to establish the criteria of catalyst energy efficiency are significant for catalyst design as will as for real catalyst choice in industry.

Interfacial Area in a Gas-Liquid-Solid Reciprocating Plate Column

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Having favorable mass transfer characteristics and a relatively small power input per liquid volume, reciprocating plate columns (RPCs) have widely been used as gas-liquid and gas-liquid-solid contacting devices. The mass transfer in RCPs is improved by the presence of the solid spheres in interplate spaces, compared to the corresponding gas-liquid system.[1] In a continuing study of the hydrodynamics and mass transfer, only spheres (3.8 and 6.6 % by volume), placed in interplate spaces, have been used so far. There is an evidence that the gas holdup[2] and mass transfer in RPCs can also be enhanced by the presence of Rashig rings.[3] The present work dealt with the specific interfacial area in a 9.2 cm i.d. RPC (number of plates: 15; hole diameter of 8 mm; plate free area of 45.4 %) with Rashig rings (made of aluminum; height and diameter: 8 mm) placed in each interplate space, corresponding to the solids content of 0.35 to 3.20 vol. %, respectively. The main goal was to reflect the effects of the operating conditions (vibration intensity and superficial gas velocity) and the content of Rashig rings on the specific interfacial area. The sulfite method was used to measure the specific interfacial area (sodium sulfite solution: 0.8 M; cobalt sulfate as catalyst: 0.001 M) at room temperature. The superficial gas velocity was 0.5, 1.0 or 1.5 cm/s. The specific interfacial area was found to increase with the increase of both the power input and the superficial gas velocity, independently of the content of Rashig rings, due to the increased power input, which enhanced the breakage of the gas bubbles, and the increased drag to the gas flow through the plate holes, respectively. The specific interfacial area was correlated with the specific power consumption and the superficial gas velocity.

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GCEN P-16 rec

Pressure Drop and Dynamic Holdup Predictions for Gas-Flowing Solids-Fixed Bed Contactors

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Gas-flowing solids-fixed bed contactors are novel type of equipment suitable for adsorption, gas purification, heat recuperation, and for catalytic chemical reactions with separation *in situ*. In these contactors fine solids particles (flowing solids) are introduced at the top, while gas is introduced at the bottom of the packed bed column. They flow counter-currently through the fixed bed of larger solids particles (second solids phase). Basic design parameters are: pressure drop, flowing solids holdup and axial dispersion.

In this work empirical, semi-empirical and fundamental models for dynamic holdup and pressure drop are compared and commented. For dynamic holdup predictions three models are presented. The first one is strictly empirical and the correlation contains all significant variables grouped in dimensionless numbers. The second model is fundamentally based, but it contains one empirical parameter. The dynamic holdup was calculated from average solids velocity which was predicted. Terminal slip velocity, which can not be reached in packing voids, was corrected with empirical factor to take into account the unsteady-state conditions. The third dynamic holdup model is simple, fundamental model which also predicts average solids velocity. The solids velocity was calculated from differential equations, based on force balance, for the solids paths in packing interstices. The average bad void was approximated with simple geometry of vertical double cone. All three proposed models are based exclusively on parameters known a priori and do not require any experimental data from actual system.

For pressure drop two models are offered. The first model presents two empirical dimensionless correlations, one for preloading regime and the other for loading regime. The second pressure drop model is fundamentally based and it assumes that there are two major contributions for overall pressure drop: resistance of the packing, and drag due to complex interactions between gas and flowing solids. Both models contain parameters known in advance, except dynamic and static holdup which can be measured experimentally, or can be predicted with proposed models.

The results of all offered models were compared with our own data and data available from the literature. The data included various types and dimensions of packed bed column with different packing elements, a variety of flowing solids materials, and a wide range of solids and gas flow rates (over 400 data points). In general, empirical models have somewhat smaller error, but they might be unreliable in the case of extrapolation. On the other hand, fundamental models can be used for broad range of system conditions, and they present the physical picture of phenomena. General recommendations for practical use of different type of models are offered.

Flowing Solids Exchange between Stagnant and Flowing Zone in Gas-Flowing Solids-Fixed Bed Contactors

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The idea of contacting gas and fine solids particles (flowing solids) inside a packed bed of other solids was patented more than fifty years ago. The first realization was in France for heat recovery, but many other applications were under consideration in recent years. They include various separation processes, as well as catalytic chemical reactors with separation *in situ* and integrated processes with heterogeneous chemical reaction and simultaneous heat exchange in a bed of catalyst.

In this type of equipment fine solids particles are introduced at the top of the column containing a packed bed, while gas is introduced at the bottom. A fraction of solids flows downwards through the bed (dynamic holdup), while the other fraction of solids particles is resting on the packed bed elements (static holdup).

In this work the tracer technique was applied in order to confirm that there is an exchange between particles that are temporary settled on packing elements, and those flowing through the bed. Fine alumina particles of different color (all other properties being the same) were used as a tracer in a step change experiments. After stagnant flowing particles were separated from the packing elements, the mean value of the tracer fraction in static holdup was determined by the color analysis of digital photographs. Experiments were repeated for different time intervals (after a step change), giving the fraction of tracer in the static holdup as a function of time. Different solids flux and gas velocities were used in order to investigate the influence of operating conditions on the rate of exchange.

It was found that the exchange exists for a major part of static holdup. However, a part of stagnant zone (static holdup) does not take part in the exchange process, and should be considered as a dead zone. A simple mathematical model was developed and employed to determine the frequency of the exchange rate, and dead fraction of static holdup.

GCEN P-18 rec

Static Holdup in Gas-Flowing Solids-Fixed Bed Contactors

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Gas–flowing solids–fixed bed contactors can be considered as two phase or three phase systems. In the first case, gas and flowing solids are the contacting phases, while the packing serves only to enable better contact between the flowing phases. In such a case there are no limitations in geometry and design of packing elements. In the other case, the packing elements could be considered as an additional, third phase, as in heterogeneous catalytic reactors with *in situ* separation. In these cases the geometry of packing elements is limited by the process requirements, i.e. by the shape of catalyst particles. Therefore, flowing solids static holdup plays an important role and can not be minimized by adequate design of packing.

In this investigation flowing solids static holdup was experimentally determined. After reaching the steady state in counter-current gas-flowing solids-fixed bed contactor, inlets of gas and flowing solids were simultaneously closed. The content of column was discharged and sieved in order to separate the stagnant flowing particles from the packing elements. The flowing solids that remained in the bed were weighted, and the static holdup was calculated. The experiments were performed in two different column sizes: bench-scale contactor (inside dia. 0.059 m), and pilot-scale system (inside dia. 0.111). In the latter column, three types of packing elements were used: Raschig rings (12x12x2.4), ceramic beads (19mm) and crushed stone (8-11 mm). In these experiments, flowing solids materials were: sand (mean dia. 0.254 mm) and propant (mean dia. 0.642) in the vide range of flowing solids fluxes and gas flow rates. Bench-scale contactor was filled with glass beads (dia. 16 mm) and two types of flowing solids particles were used: glass (mean dia.0.7 mm) and alumina (man dia 0.291). Several different solids fluxes and gas flow rates were employed in the bench-scale system.

The obtained results were discussed and compared with scarce literature data. An empirical correlation for prediction of flowing solids static holdup was offered. The equation contains all major variables which can be known a priori and do not require any experimental measurements. Correlation is in a good agreement with experimental data, and it shows a significant influence of packing geometry and dimensions on static holdup.

Kinetic Studies of Immobilization of Some Chromotropic Acid Derivatives onto Anion Exchange Resin

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The kinetics of the adsorption of pyrazol- (PACA) and imidazol-azo-chromotropic acid (IACA) on Dowex 1-X8 resin, with respect to the initial dye concentration, temperature and pH, was investigated. The optimal conditions for adsorption were obtained at pH 4.5. The intraparticle diffusion model, pseudo-first- and second-order kinetic models were used to describe the kinetic data. The kinetic data don't fit well to intraparticle diffusion model. The obtained results fit well using the pseudo-first order kinetic model in the initial stage of the adsorption process and using the second-order kinetic model for all stages of adsorption process. These models have been tested to predict the rate constant of adsorption, equilibrium adsorption capacity and equilibrium concentration by the fittings of the experimental data. The adsorption rate constants were found to be in order of magnitude 10^{-2} min^{-1} for all used kinetics models. The adsorption capacity increases with increasing initial dye concentration and with change of solution pH it doesn't change significantly. The values of calculated equilibrium adsorption capacities, q_e are in relatively good agreement with obtained experimental data (from 0.60 to 1.28 μmol dye/g of resin in the case of pseudo-first order kinetic model and from 0.77 to 1.03 μmol dye/g of resin in the case of second order kinetic model, for investigated temperature range). The investigation of adsorption kinetics at different temperatures (in the range from 0 to 25°C) exhibits increase in the rate of adsorption and adsorption capacity with the increase in temperature. The energy of activation was determined using the Arrhenius dependence. The adsorption mechanism is shown to be the electrostatic interactions between the dye and resin beads.

GCEN P-20 rec

Influence of Silicate Material Type Applied in a Cigarette Blend on Pyrolitic Temperature

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Tobacco smoke composition and particularly reduction of harmful smoke compounds, such as TAR, CO, NOx and PAH could be control by cigarette pyrolitic conditions. In nowadays practice the concentration of harmful compounds is changed with different adsorbents applied mostly in cigarette filter. The new, modern approach, still in the research phase, is introduction of different catalyst types directly to tobacco blend.

In this work, four different silicate materials: sedimentary SiO_2 (SIL) and zeolite catalysts (Z-14, LZ-Y62, and CVB100) were added directly to the tobacco blend in the quantity of 3% on tobacco mass. This is the very first time of such experiment being carried out with zeolites.

The cigarettes were industrially manufactured (MOLINS-9) and smoked on the smoking machine (BORGWALD RM20/CSR) according to the standard procedure ISO 3308.

Solid phase temperatures in burning were recorded by IC camera ("FLIR" therma CAM 675). Char temperature during puffing was determined by thermocuple Fluke 52/K-Type (Chromel-Alumel).

Experimental results indicated that application of different silicate materials caused different pyrolitic temperature profiles in combustion zone in the smoldering as well as in puffing.

In comparison with standard (control) cigarette, addition of sedimentary SiO_2 (SIL) caused explicitly increase of temperature in smoldering for 75^oC and in puffing for 14^oC.

Decrease of burning temperatures has been notified by addition of zeolite catalysts. The largest decrease of temperature in smoldering (37,4^0C) was noticed with addition of catalyst CVB 100, and the least in addition of Z-14 catalysts (23,3^0C). Temperature decrease with added zeolite catalysts is more extensive in puffing. The largest decrease of temperature in puffing (for 61^oC) has been caused with CVB100 catalyst applied. The least decrease of temperature in puffing was noticed in test with Z-14 catalyst (for 38,1^oC).

The obtain results were indicated that zeolite catalysts in existing conditions are working as catalysts of hydrocarbons cracking reactions which are endothermic and for that reason the temperatures in smoldering are necessarily lower. The final result is significant modification of smoke composition.

Photocatalytic Degradation of Methyl-Tertiary-Butyl-Ether

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During the past decades, the effects of the majority of different technologies used for the prevention and control of pollution, as well as degradation of pollutants already present in the environment, had unfortunately been recognized as damaging on the environment. This fact outlines a need to develop a new and environmentally friendly technology, acceptable and efficient from all relevant aspects: sustainability, physical and chemical reliability, energy efficiency and cost effectiveness, and finally of purification effectiveness on the contaminated atmosphere, hydrosphere and soil.

The subject of this research is photocatalytic degradation process of toxic organic pollutants. We investigated the effects of several parts of specter of concentrated solar radiation simulated with different artificial lights performed in laboratory measurements on the selected samples. The degradation of toxic organic pollutants was performed in the presence of titanium-dioxide and hydrogen-peroxide as catalysts. The photocatalytic efficiency was investigated on the water samples containing methyl-tertiary-butyl-ether (MTBE). Conventional and sol-gel obtained titania were used. The measurements were done on samples in liquid phase of water in laboratory conditions and with simulated solar radiation. Detection of MTBE degradation was measured with gas chromatographs (GC) equipped with flame ionization (FID), as well as infrared (IR) spectroscopy. The results of the experiment were presented in analytical forms, also suitable for the process optimization. The investigation was performed with special concern to develop "clean" photocatalytic degradation of MTBE. The degradation process was completed with carbon-dioxide and water as the only degradation products followed by other non-toxic compounds. Finally, the results of our investigation showed that the photocatalytic degradation processes could be used as superior system for a series of other toxic organic pollutants originated from different sources.

GCEN P-22 tph

Wall-to-Bed Mass Transfer in Particulate Fluidized Beds and Vertical Hydraulic Transport

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Mass transfer coefficient in: single phase flow, liquid fluidized beds and vertical hydraulic transport of spherical inert particles have been studied experimentally using columns 40 mm and 25,4 mm in diameter. Mass transfer data were obtained by studying transfer from tube segment of benzoic acid to water using the dissolution method. In all runs mass transfer rates were determined in the presence of spherical glass particles 1.2-2.98 mm in diameter.

Influence of different parameters like: liquid velocity, particles size and voidage on mass transfer in fluidized beds and in hydraulic transport is presented. Our experiments show that with increasing liquid velocity mass transfer coefficient is practically constant in fluidized beds and increases in vertical hydraulic transport of spherical inert particles.

Wall-to-bed mass transfer in particulate fluidized beds and in vertical hydraulic transport are higher then in single phase flow for Reynolds number of column less then 10000. For high Reynolds number there is no significant difference between single phase flow and hidraulic transport.

The data for mass transfer in all investigation systems were correlated using general form of Colburn type equations $j_D=f(Re)$. Mass transfer factor as function of particle Reynolds number depends on particle size in fluidized beds and in vertical hydraulic transport.

The data for mass transfer in particulate fluidized beds and for vertical hydraulic transport of spherical particles were correlated treating the flowing fluid-particle mixture as a pseudofluid by introducing modified mixture Reynolds number (Re_m).

New correlation for mass transfer factor in fluidized beds and in vertical hydraulic transport is proposed.

Wall-to-Bed Heat Transfer in Particulate Fluidized Beds and Vertical Hydraulic Transport

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Heat transfer coefficient in: single phase flow, liquid fluidized beds and vertical hydraulic transport of spherical inert particles have been studied experimentally using column 25,4 mm in diameter. Heat transfer coefficient was determined from overall heat rate between fluid and wall. Experiments were conducted using a cooper column equipped with a 700 mm long jacked. Saturated steam at atmospheric pressure was supplied to the steam jacked and heat wall of the column. In all runs heat transfer rates were determined in the presence of spherical glass particles 1.2-2.98 mm in diameter.

Influence of different parameters like: liquid velocity, particles size and voidage on heat transfer in fluidised beds and in vertical hydraulic transport is presented. Experimental data shows that the curve, which represent heat transfer coefficient as a function of superficial velocity or bed voidage, has a maximum in fluidized beds. With increasing liquid velocity heat transfer coefficient increases in vertical hydraulic transport.

The data for heat transfer in all investigation systems were correlated using general form of Colburn type equations $j_H=f(Re)$. Heat transfer factor as function of particle Reynolds number depends on particle size in fluidized beds and in vertical hydraulic transport.

The data for heat transfer in particulate fluidized beds and in vertical hydraulic transport of spherical particles were correlated treating the flowing fluid-particle mixture as a pseudofluid by introducing modified mixture Reynolds number (Re_m).

New correlation for heat transfer factor in fluidized beds and in verical hydraulic transport is proposed.

GCEN P-24 tph

Performance of Rashching Super Ring Packings in Distillation of Ethanol-Water Mixture

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The Raschig Super Ring packings are modern high efficient random packings for realization of absorption and distillation processes. The purpose of this work is to investigate the efficiency of this packing in distillation of the important industrial system ethanol-water mainly in the high alcohol concentration range. Due to particular system equilibrium, a prevailing part of the column operates in this concentration range.

The experiments are carried out in an installation including a column 0,213 m in diameter with 2,8 m packing height. Column heating is done by electric resistance heaters with total power of 45 kW, which can be gradually changed. The installation construction enables operating with constant and variable reflux ratio.

Three types of Raschig Super Ring packings made of metal are studied: No.No. 0,5; 0,7; 1. A part of the experiments are carried out in total reflux regime in the vapor velocity range from 0,253 m s^{-1} to 0,936 m s^{-1} and density of irrigation from $4{,}44 \cdot 10^{-4}$ $m^3/(m^2\ s)$ to $1{,}63 \cdot 10^{-3}$ $m^3/(m^2\ s)$ respectively.

Also experiments are carried out with variable reflux ratio realized by: constant density of irrigation and variable vapor load; constant vapor load and variable density of irrigation.

The results are presented as height of a transfer unit (HTU) and height equivalent to a theoretical plate (HETP) as function of the phases' velocities. Comparison of the efficiency of the investigated packings with another high efficient packing - HOLPACK, used in distillation of the same system, was made.

Simulation of Gas Distribution in Packed-Bed Columns Accounting for the Discrete Structure of the Packing

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An enhanced mathematical model of the gas distribution in packed-bed columns is proposed. It takes into account the packed bed inhomogeneity due to the discrete structure of the packing and the difference between the local geometry in the bulk and in the wall zone.

The real maldistribution factor can be expressed as a result of superposition of the maldistribution factor derived from the dispersion model for isotropic medium and a "noise" maldistribution ones due to the packing inhomogeneity. It is shown theoretically that the superposition can be present as additivity of the squares of above mentioned maldistribution factors. The "noise" factor is considered as a sum of static and dynamic components. The static component reflects the influence of the packing discrete structure and the dynamic one – the influence of height of packing on the ratio between the bulk and the wall zone gas permeability. The definition of the both components is given.

The application of the enhanced model requires an experimental data for change of maldistribution factor with the packing height and also the minimal value of maldistribution factor (uniformity limit) for some height (penetration depth). It is shown that the uniformity limit represents the static "noise" component and characterizes the packing discrete structure. The influence of dynamical component is demonstrated in the model based on the experiments, for which the maldistribution factor is investigated after the penetration depth.

The model is tested with the author's experimental data for modern high-effective random packings and structured ones as well as for results from other literature published.

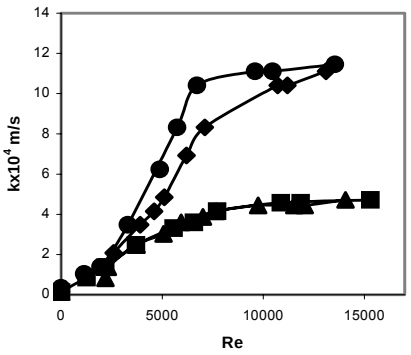
Modeling of Interfacial Mass Transfer Using Neutral Network

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The mass transfer of a solute between two immiscible liquids is an important method for separation and purification, having numerous industrial applications, even if the process has a very complex phenomenology. Difficulties associated with the construction and the solution of phenomenological models necessitates exploration of alternative modeling formalisms. Neural networks possess the ability to learn what happens in the process without actually modeling the physical and chemical laws that govern the system. Therefore, they are useful for modeling complex nonlinear processes where process understanding is limited.

This work deals with the potential applications of artificial neural networks to modeling of interfacial mass transfer. Experimental data, consist of the variation of the individual mass transfer coeficients when single or both phases are stired were used in building and training neural networks. The experiments were performed in an improved Lewis cell operating in continuous mode, made out of two baffled compartments equipped with separate driven agitators. Each compartment contains stirred or non-stirred phase. The transfer of the solute can be carried in the two directions through an interface of constant area created between the two phase. The inputs of the neural networks were Reynolds number (Re) and Schmidt number (Sc) and the output variable was individual mass transfer coeficients (k). The topology of the networks was selected by training a wide range of networks with the well-known back-propagation algorithm, and selecting the one that best balanced generalization performance against network size. Consequently, feed-forward neural networks with two hidden layers were selected because they had errors smaller than 1 % in the training phase. A comparison between the results of neural networks (continuous line in figure below) and training (experimental) data (points in the figure) prove that the networks learned well the behavior of the process. The generalization ability of the artificial neural networks are then evaluated using a test dataset distinct from the training data (table below). Based on the good results obtained in the training and validation phases, the neural models were used to make prediction for different values of Re and Sc number. Because the experiments are laborious and require long time, the neural network predictions are recommended to be use for practical proposes.



Re	Sc	kx10^4	k×10^4 neural network	Relative error
1100	1032.51	0.346	0.420048	-0.0015
4885	995.023	6.24	5.744362	-0.3584
7016	952.034	3.871	3.949422	-0.1529
9050	1025.84	10.41	10.20725	-1.0626
11850	862.113	4.576	4.377916	-0.2003

Mass Transfer Phenomena Investigation of the Azeoptopic Extraction

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A new mass transfer phenomena of the azeotropic extraction was examined[1,2]. Dynamics of the methanol and the ethyl-acetate azeotrope formation in the determination ratio was investigated. The investigation was performed by experiments and computer simulation.
The mathematical model of the molecules migration to the azeotrope formation was derived in the multicomponent mixtures. The diffusivity coefficient for multicomponent mixture were determined from the diffusion coefficients of their binary mixtures. Binary diffusion coefficients are determined by Leffer-Cullinan equation.
Experimental investigation was performed by methanol separation from the liquid mixtures with adding ethyl-acetate. The experiments were carried out with mixture of the methanol-ethanol-ethyl-acetate-water in a laboratory conditions at the atmospheric pressure and room temperature. The component concentrations were measured in the mixtures by gas chromatograph, before and after extraction.
Phenomena progress were simulated with derived mathematical model. Process analysis was performed by dynamic simulation of the azeotrope formation and separation of the new liquid phase by extraction for various conditions.
The obtained results show successful separation of the methanol from the liquid mixtures by azeotropic extraction. No, methanol and ethyl-acetate detection in the mixture after the azeotrope extraction.
The obtained results implicate this separation method can be used for the others substances. Also, the investigated results in this paper can be applied in the others domain.

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GCEN P-28 sep

Batch Sorption Study of Cs^{1+}, Sr^{2+} and Co^{2+} Immobilization by Natural Clinoptilolite

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Regarding radiation and toxic effect, among the most hazardous pollutants identified in the liquid wastes are Co^{60}, Cs^{137} and S^{90}. The objective for the present preliminary study was to evaluate the effectiveness of the local clinoptilolite from Serbia, in reducing contaminant (Co, Sr, Cs) solubility. The results may be used as a starting point in waste water treatments, treatments of secondary waste that result as a byproduct from processing of nuclear wastes and decontamination activities, reducing the metal mobility prior to excavation and storage, or in-situ treatment of polluted soils. The influence of initial metal concentration was studied using batch equilibration technique. Under defined experimental conditions (solid/liquid ratio 1:200, 24 h of equilibration, room temperature, initial pH=5) calculated capacities per 1 g of clinoptilolite, using linear form of Langmuir adsorption isotherm, were 2,93 mg Co^{2+}; 9,80 mg Sr^{2+}; 49.02, mg Cs^{1+}. Since clinoptilolite exhibits the best sorption properties towards monovalent Cs, additional study of the effects of contact time (15 minutes – 3 days) and solid to solution ratio (2.5 – 40 g/dm^3) were also performed for initial Cs^{1+} concentration of 300 mg/dm^3. Rapid metal uptake with increasing equilibration time is followed by slower phase of sorption process and then saturation. Approximately 6 hours is required to reach the equilibrium. A good agreement between experimental results and pseudo-second order reaction model was observed. The increase in clinoptilolite to liquid ratio causes the increase of the percents of sorbed metal. At the ratio of 10 g/dm^3 98.3% of Cs^{1+} is removed from the solution, reaching 99.9% at the ratio of 40 g/dm^3.

The Ammonia Scrubber Mathematical Model

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Multistage absorption operation in the ammonia absorber was investigated. The vapor -liquid equilibrium parameters for ammonia and water were determined based on literature experimental data. The mathematical model of the absorber for for the steady state and dynamic operation conditions simulation was derived. This model performs real time plant operations on various levels with the aim to waste minimization.

In this paper process intensification was applied to environment protection. With process system technique the identification process model was created from input and output data, eliminating the need for detailed knowledge of the process system.

The investigation was performed by computer simulation and experiments. The experiments were carried out by industrial scale. Computer simulation was provided for various operation regions and object functions with the aim to reduce ammonia emission.

Optimization of the examined scrubber was performed. The optimal values for absorption operation conditions were determined. Absorber optimization requests maximum flow, minimum cost flow, concern the assuagement problem and software implementation that yields maximum profit.

The obtained results illustrated plant operation system for process operation improvement, conflict resolution and real- time optimization.

The obtained results in this paper can be applied to the environmental problems created by atmospheric emission, leading to carbon smog, acid rain, the green effect and ozone layer damage.

Solvent Extraction of Pd(II) with Calix(IV)Erenes

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Calixarenes and their amino-, amido- and ketonic derivatives have been attracting much attention as novel types of interesting extractants. Their ability to recognize and discriminate metal ions is one of the most remarkable features making them suitable as specific receptors [1-3]. Solvent extraction properties of these derivatives were investigated for metal ions complexation (at the beginning for alkali and earth alkaline, but latter for some heavy- and noble metals).

The aim of this work was to investigate the ability of both calix[4]arene-tetramide and calix[4]arene-thiotetramide to extract palladium nitrate from aqueous solutions, acidified by nitric acid. Based on experimental data some information about the process were derived, as: about the process stoichiometry i.e. about the capacity of subjected calix[4]arenes; about their selectivity particularly against silver; in one word, about the extraction efficiency and parameters affecting the process itself.

Experiments of the solvent extraction were carried out in a classical way. That means by using equal volumes of both the aqueous and the organic phase, putting them in a closed vessel, and after shacking for 5 min, to leave the emulsion for phases settling. After that, samples for analysis on the metal content in the aqueous phase have been issued. The analysis on palladium has been done by means of AAS method.

Concentration of calixarene in dichloromethane was a parameter of the process and was changed in the range of 10^{-4} to 10^{-3} M. Concentration of palladium was kept at $1x10^{-3}$ M. All experiments were performed at an ambient temperature.

High extraction degree is achieved with both extractants. In case of calix(4)arene thiotetramide the extraction degree was higher than 99.5% by adding extractant and palladium in 1:1 stoichiometric ratio. By employing the other extractant, the extraction degree does not exceed 30% even at the organic : aqueous phase ratio twice higher than the stoichiometric one. Distribution ratio was calculated and plotted against extractant : palladium ratio. The other relevant data have also been evaluated from experimental results.

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A New Method for Determination of Adsorption Isotherms Based on Nonlinear Frequency Response – Experimental Confirmation

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A new method for determination of adsorption isotherms, based on nonlinear frequency response of a chromatographic column and the concept of higher-order frequency response functions (FRFs) has been developed theoretically[1]. Determination of adsorption isotherms using this method is performed by estimation of the 1st, 2nd, 3rd, etc. derivatives of the isotherm in a chosen point, from the low-frequency asymptotes of the corresponding FRFs[1]. By estimating these derivatives for several points, the complete isotherm can be reconstructed[1].
In this paper the adsorption of ethyl benzoate and 4-tert-butylphenol as single solutes was studied on Octadecyl Silica (C18) using methanol and water (60:40, v/v) as the solvent. The experiments were performed using a standard HPLC system, which enables periodic changes of the feed concentration at the inlet of a column filled with the C18 during the experiment. Simulations of the response of a chromatographic column were performed for inlet concentration changes in sine wave form. In the experiments, sine wave form was approximated with stair case function. The amplitude that gives the best agreement between the reference[2] and the estimated coefficients is selected based on simulations. Simulated and experimental results will be presented, as well as the explanation of the experimental procedure.

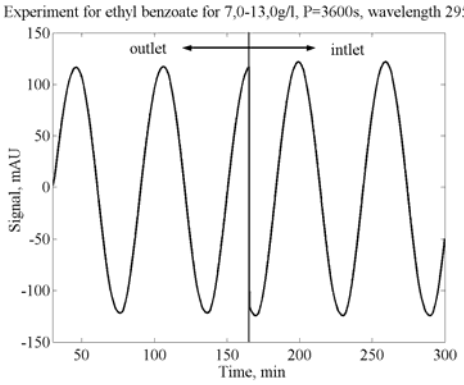


Figure 1. A sample of raw experimental data (steady-state concentration 10g/l and amplitude 30%)

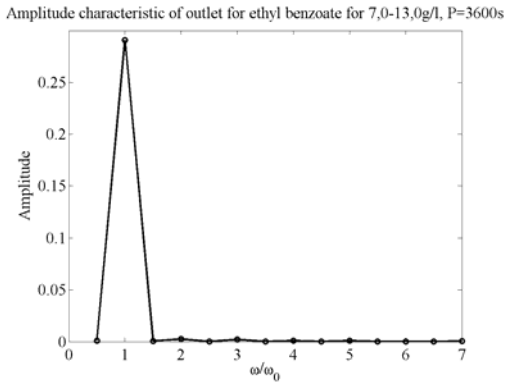


Figure 2. The corresponding amplitudes of the Fourier transform of outlet concentration

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GCEN P-32 sep

Strategies for Water Adding in Diafiltration Processes: Influence on Process Time and Water Consumption

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Membranes provide a simple and effective way of concentrating and purifying a macromolecular solutions. The classic approach to achieving macrosolute concentration and microsolute removal is to use two separate processes: batch ultrafiltration (UF) and constant volume diafiltration (CVD).

This paper presents a model that enables investigation of various strategies for time dependent water adding in a variable volume diafiltration (VVD) process, in the view of process time and water consumption. Fresh water flowrate introduced in the system is expressed as a fraction of permeate flowrate in terms of the parameter α. By the introduction of the time dependent α, governing the system through variety of different states is enabled. This may reduce the process time as well as the water consumption.

By the selected expression for the permeate flux, influences of both component concentrations are involved. In the material balance, the rejection coefficients for both components are included resulting in a system of three ODE. The additional ODE for water consumption can be separately solved.

Step, linear and hyperbolic tangens $\alpha(t)$ functions were examined. By particular cases of step function some of the classic processes (UF/CVD, UF/VVD etc.) are represented. Calculations were performed for the albumin-ethanol separation process. The results showed that by the same combinations of the functions parameter values (starting point and height of the step function, slope and intercept of the linear function, and three parameters characterizing the position, height and slope of the hyperbolic tangens function) the minimum of both time and water consumptions is provided. As for linear function, a negative slope should be excluded, that indicates that any time decreasing water adding could not be recommended. The limiting values of intercept (minimum) and slope (maximum) that satisfy the demands for final micro- and macrocomponent concentrations proved to be optimal. Similarly, the optimal step function parameters are the maximal starting point time and the maximal height. The least time and water consumptions are provided by the optimal step function. The performances of optimal hyperbolic function are somewhat lower than those of the optimal step function, that could be expected as the hyperbolic function could be interpreted as a distorted step function. The results showed that if the optimal linear function was replaced by optimal step function, the reduction of the calculated process time up to 8% and water consumption up to 50% was obtained.

Adsorption and Electrothermal Desorption in Annular - Radial Flow Adsorber – Mathematical Modeling Using FEMLAB

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The idea about regeneration of used adsorbents by direct heating of the particles by passing electric current through them (Joule effect), was first published in the 1970s [1]. The desorption process based on this principle, which was later named electrothermal desorption [2], has been recognized as a perspective way to perform the desorption steps of TSA cycles [2].
Recently, a new TSA process with electrothermal desorption step, based on an adsorber composed of one or several annular, cartridge-type, fixed-beds, integrated with a condenser, has been developed [3]. The cartridge-type adsorption bed is schematically shown in Figure 1. The gas flow through the adsorption bed is in the radial direction. During the desorption step, electric current is passed through the adsorbent bed in the axial direction, causing heat generation, heating of the bed and desorption. The desorbed adsorbate is carried by the radially flowing gas stream to a cylindrical wall of the adsorber, where it is cooled, condensed and drained out of the system.

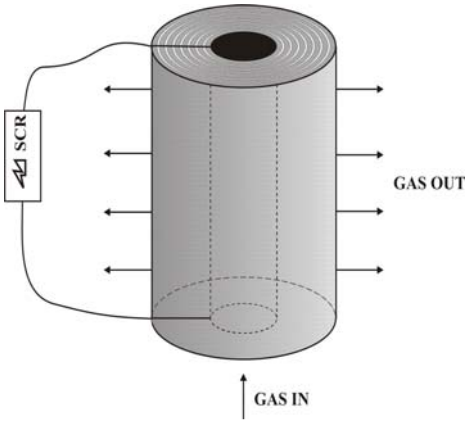


Figure 1. Schematic representation of the annular - radial flow – adsorption bed

In order to get a better insight in the process, which would help detecting the potentials for its improvement, reduce the need for experimental trials and enable optimization of the system based on computational analysis, mathematical modeling of the system has been performed. The analyzed system is very complex with a number of different phenomena, such as gas flow in tubes and porous beds, heat and mass transfer in one- and two-phase media and heat generation, simultaneously taking place in a complex geometry. Owing to that, very complex mathematical models, consisting of coupled sets of nonlinear PDEs, ODEs and algebraic equations are needed to describe it.
The mathematical models presented in this paper were obtained using FEMLAB, a relatively new modeling software based on finite-element method for solution of PDEs. The models describing adsorbers with one and two cartridges, in which adsorption and electrotrhermal desorption is taking place, have been developed. Velocity, pressure, concentration and temperature fields in the adsorbers, obtained by solving the models, will be presented.

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Modeling and Simulation of the Crystallization of $NaHCO_3$ from the System $NaCl-NH_4HCO_3-NaHCO_3-NH_4Cl-H_2O$

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In the carbonation process, during the production of sodium carbonate according to the Solvay procedure, sodium bicarbonate, previously formed by the following reaction, crystallizes:

$$NaCl + NH_4HCO_3 = NaHCO_3 + NH_4Cl$$

By adding CO_2 to the already ammonized sodium chloride solution, $NaHCO_3$, which has low solubility, crystallizes until equilibrium is established. Simultaneously, CO_2 is absorbed, the carbonized solution cools and $NaHCO_3$ crystallizes. The basis for analyzing the carbonation is the equilibrium of the multicomponent system $NaCl-NH_4HCO_3-NaHCO_3-NH_4Cl-H_2O$. Keeping in mind the complexity of the process occurring in carbonation columns, it was necessary to derive equations that described the process. On the basis of these equations it was possible to determine the retention time of the system components in the column, as well as the column dimensions.

An algorithm of the mathematical model of the carbonation process represented by a classic technological scheme is discussed in this paper. The optimal parameters of the technological process, the mass and energy balances of the process and basic column design parameters can be determined on the basis of the algorithm.

The mathematical model of the process in the carbonation column includes a system of independent equations. The variables of the technological regime can be determined by the simulation on the basis of a certain number of fixed (inlet) parameters. The type and number of parameters, the type of system of equations constituting the mathematical model and the algorithm are discussed in detail. The results of the simulation using the model are parameters that define the retention time in the column (τ), the amount of humidity in the $NaHCO_3$ crystals (w_c), the amount of absorbed CO_2 and NH_3 in the process, the amount of gas introduced into the process and other parameters that define the mass and energy balance of the process.

The methodology of calculating the basic parameters of the carbonation process and equipment dimensions that can be applied in the design of equipment in a broad range of liquid phase loads is presented as a result of the simulation and mathematical model derived in this study.

Electrically Enhanced Crossflow Membrane Separation

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Flux decline due to concentration polarization, filter-cake formation, and membrane fouling is a large problem in membrane filtration of inorganic and biological suspensions, and colloid solutions. Different anti-fouling methods have been applied to improve the performance of the pressure driven membrane separation such as feed pre-treatment, hydrodynamic intensification through turbulence promoters, gas sparging, high cross-flow velocities, etc. The combination of a membrane filtration with an electrophoresis opens new perspectives in this direction. If an electric field with sufficient strength and appropriate direction (opposite to the convective pressure-driven force) is applied during the crossflow filtration, the trajectories of charged particles can be changed away from the membrane surface and a "clear" boundary layer at the membrane-solution interface can be created.
In this study, the behaviour of two different solute systems during the cross-filtration through a polymeric membrane in electric field was investigated:

- System 1: mineral suspension (aqueous suspension of SiO_2)
- System 2: protein (bovine serum albumin) aqueous solution

An electrical field was applied across different flat sheet micro-filtration membranes in a plate module. Both electrodes, which represent a titanium mesh coated with a thin platinum layer, were situated on both sides of the membrane in two chambers separated from the feed and permeat streams by ion-permeable membranes. The electrodes were rinsed continuously by a salt electrolyte solution to protect the process streams from any changes through gas formation or other electrochemical reactions.
Hydrodynamic and concentration factors influencing both the permeate flux and the separation efficiency were investigated. The effects of operation parameters such as trans-membrane pressure (1-3 bar), cross-flow linear velocity (0.1-0.34 m/s), applied voltage (0-200V), feed concentration (1-5 wt.%), conductivity (up to 20 mS) and temperature (15-50°C) were examined and evaluated.
Appropriate operation conditions were found for both systems at which a significant enhancement of the membrane flux compared with the flux with no electric field was reached. Apart from the flux enhancement, the quality of the permeate was substantially improved by applying an electric field.

GCEN P-36 sep

The Influence of pH on Pb^{2+}, Cd^{2+}, Zn^{2+} and Sr^{2+} Removal from Aqueous Solutions by Hydroxyaptite

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Sorption of different ionic species, especially heavy metals, on calcium-hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$, (HAP) and other apatite minerals plays an important role in environmental chemistry and practical applications of these materials. As HAP particles exhibit pH dependent surface charge, and the percent of various heavy metals hydrolytic species depend on pH, it is evident that pH significantly influences sorption processes.

In this work, the point of zero charge (pH_{PZC}) of HAP was determined using batch technique. The measured amounts of HAP and inert electrolyte (KNO_3) solutions of different initial pH were equilibrated, on a horizontal shaker. The initial pH values were adjusted from ~4 to ~12, by adding minimum amounts of HNO_3 or KOH. After 24 hours of contact time, suspensions were filtrated, final pH values were measured, and pH_{PZC} was estimated from the plateau part of the plot pH_{final} vs. $pH_{initial}$. A large buffer capacity of HAP surface was observed. For initial pH in the range 4-10, final pH was the same and equal to 6.1±0.1 (pH_{PZC}).

Sorption behavior of Pb^{2+}, Cd^{2+}, Zn^{2+} and Sr^{2+}, at the same initial concentration, equilibration time, solid/solution ratio and temperature, was studied as a function of pH. The plateau part of pH_{final} vs. $pH_{initial}$ plots, corresponding to pH range where the buffering effect of HAP surface takes place, becomes shorter in the presence of Pb^{2+}, Cd^{2+}, Zn^{2+}, while in the case of Sr^{2+} plateau part is the same as for inert electrolyte. Also, the decrease in pH_{PZC} values was observed, in the order Cd>Zn>Pb>Sr.

A substantial difference in the sorption behavior of Pb^{2+} and other cations was observed in respect to pH. The influence of final pH on Pb^{2+} soprtion was insignificant. In the entire pH range, sorption was higher than 99%. Generally, the concentration of other metals in liquid phase decreased, at the different extent, with an increase of pH, due to both sorption and precipitation processes. The order of HAP affinity towards examined metals was: $Pb^{2+}>Cd^{2+}>Zn^{2+}>Sr^{2+}$. The sequence of pH_{PZC} decrease follows the sequence of HAP affinity towards examined metals, except for Pb^{2+}, indicating a different sorption mechanism.

In conclusion, HAP buffer properties must be underlined. In addition to good sorption properties towards various metal cations, HAP will buffer most waters to final $pH=pH_{PZC}$, which is particularly important for its possible practical application (treatment of acid rock drainage, acid mine drainage and wastewater from chemical processing).

The Kinetics of Ultrasonic Extraction of Oil from Tobacco (*Nicotiana tabacum L.*) Seeds

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The ultrasonic extraction kinetics of oil from tobbaco seeds (*Nicotiana tabacum L.*) of Preševska Otlja type, collected in the sourordings of Surdulica, South Serbia in 2001 was sudied. Both native and ground seeds were used. The seeds were dried, packed in paper bags, stored in a dry, dark place at room temperature and milled before use. n-hexane and petrol ether were used as solvents. The extraction was carried out with indirect sonification in a ultrasonic bath (40 kHz, 3x50 W) at room temperature, 40 °C and at boiling temperature, with the plant material-to-solvent ratios 1:3, 1:5 and 1:10 w/v, for 2,5; 5; 10; 20; 40 and 60 minutes. The extraction was found to occur in two main stages: first, the dissolution of oil near the particle surface (washing or fast extraction) and the second, diffusion from the pores of the solid to the outside of the particle and transfer of the solute to the bulk of the extract (slow extraction). The theory of unsteady diffusion through plant material and the empirical equation of Ponomaryov were used for modelling the kinetic of ultraosnic extraction. The extraction rate and the yield of oil were found to be affected by the type of solvent, the solvimodul, the plant material-to-solvent ratio, the tobacco seed preparation (comminuted or not) and the operating temperature. The maximal yield of tobbaco seed oil (23 g oil per 100 g ground seeds) was obtained using *n*-hexan and the ratio of plant material to solvent of 1:10 w/v at boiling temperature in 60 minutes.

Prediction of Excess Volumes from Experimental Refractive Index of Binary Mixtures

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Density and refractive index have been experimentally determined for binary liquid mixtures: water + propionic acid and toluene + propionic acid at 292.15, 299.15, 305.15, 311.15 and 317.15K and normal atmospheric pressure. Densities were measured with Anton-Paar digital precision densimeter operating in static mode and capable of a precision better than 0.01 kg m^{-3}. Refractive indices of the pure liquids and solutions were measured to an uncertainty of $\pm$ 2x10^{-3} with an RA-510 M at the wavelength of D line of sodium, 589.3 nm. Excess refractive indices were calculated and fitted to a Redlich – Kister function (fig. 1). The estimated error in n_{exc} is $< 3\times10^{-5}$. Using some mixture rules (Lorentz – Lorentz, Dale – Gladstone, Eykman, Oster, Arago – Biot and Newton), prediction for Vm_{exc} at 292.15K have been made and compared with experimental data (fig.2). It can be seen that the estimations obtained employing the modify Eykman function are better than the other ones.

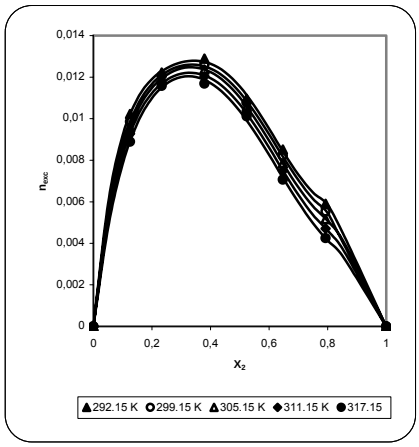
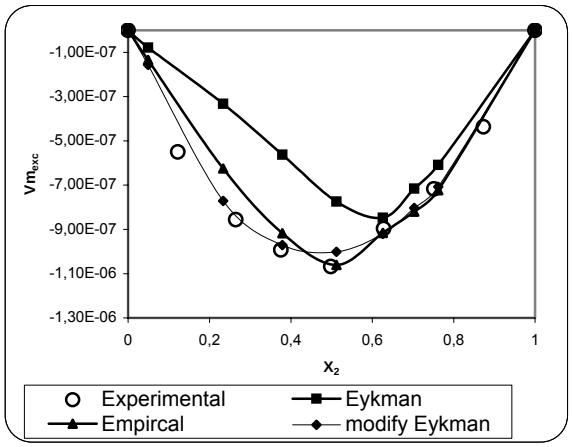


Fig. 1 Experimental and calculated refractive index for water – propionic acid mixtures



f(n)	Function
$(n^2-1)/(n+0.4)$	**Eykman**
$(n^2-1)/(n^2-5)$	**Empirical**
$(n^2-1)/(n+20)$	**modify Eykman**

Fig. 2 Comparison between experimental and predicted excess molar volumes for water – propionic acid mixtures

The refractive index of liquids, n, can be easily measured with a high precision in a wide range of temperatures being only necessary a small volumes of sample, so it is convenient to use n for calculating other liquid properties.

Volumetric Properties of the Ternary System Methanol + Chloroform + Benzene: Experimental Data, Correlation and Prediction by Cubic EOS Mixing Rules

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Volumetric properties of liquid mixtures are very important for the design of separation processes and equipment for chemical production. Also, knowledge of these properties is a potential source of information about the molecular structure of mixtures.
This paper belongs to our systematic study of the volumetric properties (density and excess molar volume) of ternary mixtures and their binaries constituents [1, 2].
Densities of the ternary system methanol + chloroform + benzene (for which literature data are not available at investigated conditions) and corresponding binaries have been measured with an Anton Paar DMA 5000 digital vibrating tube densimeter at various temperatures (288.15, 293.15, 298.15, 303.15, 308.15, 313.15 K) and under atmospheric pressure. The excess molar volume, was calculated from the measured data from the equation:

$$V^E = \sum_{i=1}^{n} x_i M_i \left[(1/\rho) - (1/\rho_i) \right]$$

where x_i is the mole fraction of component i in the mixture, M_i its molecular weight, and ρ and ρ_i the measured densities of the mixture, and the pure component, respectively. The V^E of binary and ternary data were fitted using the Redlich-Kister and Nagata and Tamura equation, respectively. The correlation of the binary data was performed by the PRSV CEOS using the selected mixing rules: (i) the composition dependent van der Waals one-fluid (vdW1) and (ii) the modern mixing rules which incorporate the excess free energy model (G^E) recently developed by Twu and co-workers (TCBT). Correlation and prediction of volumetric properties of ternary system were performed by the same vdW1 and TCBT models. Figure 1 shows the isolines of the excess molar volume for the ternary system at 303.15 K.

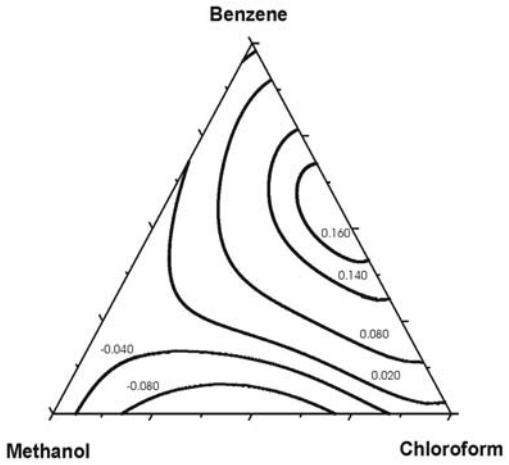


Figure 1. Curves of constant V^E for the ternary system at 303.15 K under atmospheric pressure.

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The Introduction of Thermodynamics in Explanation of Biochemistry in Seed Germination Proccess

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The thermodynamics approach in biochemical aspects of seedling growing is possible through differences in water absorption at two average daily temperatures: T_1 and T_2. The assay is established on seeds of four soybean varieties grown in sand, with saturated conditions. The limits in application of thermodynamics in biochemistry of living systems are non-existing of time and a total reversibility, as category [1]. It could be overcome by analysing the seedlings in a point of growth where the differences are underlined, determined by convention of ISTA with chair in Zurich [2] and including of the seed rest, as irreversible sequence of the whole seedling system.

Table 1. The water content in seedlings presented as average values of sorts growing in saturated environment.

Environment	Unit	Seedling	The sequence of seedling			
			Cotyledons	Plant	Root	Shoot
T_1	mmol	52.05	22.14	30.00	14.74	15.38
T_2	$part^{-1}$	58.83	23.11	36.01	16.82	18.89

The absorption of the different water volumes at T_1 and T_2 (Tab.1) allowed the calculation of differential: Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) of seedlings and their sequences for each examined variety. It was demonstrated that ΔG, ΔH and ΔS of seedlings could be dependent on a relation: phosphorus content in seed and weight of the same (P : Sd).
The arising of waterfront activates at first, hydrolytic and other enzymes in seed, successively.
A critical mass of Σ hydrolysate introduces Σ biosynthesis "*de novo*" in embryo; first in root to continue water absorption, then in shoot. According to constants of: Σ hydrolysis, Σ biosynthesis at T_1 and T_2, the differential free energy, ΔG, of germinating and substance devasting were calculated as: $\Delta G = - R\Delta T \ln \Delta k$[3]. The individual sensitivity of varieties to temperature variation during germination was expressed.
Generally, thermodynamics categories of differential free energy, enthalpy and entropy based on biochemical parameters of water absorption, hydrolysis and biosynthesis (supported by previous reaction) have expressed better resolution among soybean varieties, germinating at two different environmental temperatures. Hence, this assay showed that such, combined approach of thermodynamics and biochemistry could be established as analytical method, with ecological background, as a test for resistance to lower, sub-optimal temperatures in breeding and selection of new varieties in crop production.

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Section:

Process Engineering

PREN

PREN X-NN yyy

X = KN – Keynote lecture
O – Oral presentation
P – Poster presentation

NN = Number

yyy = Topic:
hpp - High Pressure Processes
fst - Food Science and Technology
poc - Process Operation, Automation and Control
ppi - Process and Product Innovation
mci - Management in Chemical and Process Industry
pin - Process Intensification
psd - Process Synthesis and Design

Supercritical Fluid Extraction of Essential Oils – Results of Joint Research

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In contrast to conventional steam distillation or hydrodistillation yielding partially hydrolyzed and degraded essential oil (EO), supercritical fluid extraction (SFE) with supercritical carbon dioxide (SC-CO_2) as solvent enables isolation of authentic EO. Compared to conventional extraction, the SC-CO_2 extracts contain less ballast substances and no residuals of liquid solvents. Nevertheless, dry leaves and flowers are covered with cuticular waxes and contain residual water; as both substances dissolve in SC-CO_2, they are co-extracted with EOs. The solubility of EOs extracted with SC-CO_2 from leaves and flowers is reduced by solute-matrix interaction, presumably by EO adsorption on solid lipids. We studied three topics:

Phase equilibrium essential oil + fatty oil + CO_2

When EO is extracted from seed, its solubility in SC-CO_2 is reduced due to the presence of fatty oil. The reduction was measured at 40 ˚C and modelled with the Soave-Redlich-Kwong cubic equation of state[1]. The EO, represented by limonene, was distributed between the liquid phase rich in fatty oil and the vapour phase rich in CO_2, and its equilibrium concentration in the latter decreased with the diminishing limonene-to-oil ratio in the extractor. A detailed explanation of the three-component system behaviour observed was provided by thermodynamic modelling. The most appropriate extraction pressure for an efficient SFE of EOs from seeds was found to be approximately 20% above the critical pressure of the EO+CO_2 binary mixture.

Extraction curves for total extract

Extraction yield was measured in dependence on the amount of SC-CO_2 passed through the extractor[2]. One or two extraction periods were distinguished according to the solvent loading. For higher EO content in plant (1.85 wt. % in peppermint leaves), almost pure EO was extracted the first period. The extraction then continued at a lower loading; the EO extraction rate was reduced due to EO-matrx interaction, and water and cuticular waxes prevailed in the extract. If the EO content in plant was lower (1.03 wt. % in thyme herb), EO solubility was affected by its interaction with matrix and the extract was rich in water and waxes from very beginning.

Essential oil yield and composition

Gas chromatography was used for analysis of SC-CO_2 extracts from yarrow[3] and sage[4]. Extraction yields of individual EO components were plotted against solvent amount and compared with their yield by hydrodistillation. Monoterpenes as the most soluble and volatile compounds were extracted most rapidly but they partially escaped from separator, dissolved in CO_2. Monoterpene esters and sesquiterpenes were extracted slower but their yield was in the end of extraction run several times higher than their yield in the distillate.

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The Chemical Engineering Analysis – a Prospective Support for Regional Food and Bioproduct Processing Industry

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In view of strengthening and extending the regional European research area and decisive productive potentials, the subject of food and bioproduct processing will be used to review possible ways of chemical engineering support for the local sustainable economy. A brief overview of regional production will be given. Referring to specific production systems, examples of chemical reaction engineering science support for industrial reactor effectiveness will be presented in detail. Production of animal food additives and mixing of fermentation bio-fluids will be considered. As effective tools, the use of structural reactor modeling and computational flow modeling will be discussed in the paper.

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PREN O-01 hpp

Energy Utilization in Supercritical Carbon Dioxide Extraction of Essential Olis from *Lamiaceae* Family Species

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In present work reduction of energy consumption in supercritical carbon dioxide extraction of essential oils from leaves of *Lamiaceae* family species due to oprimal pretreatment of herbaceous material was studied. Essetial oils of *Lamiaceae* family species are stored in peltate glandular trichomes on the leaf surface, and the optimal pretreatment for this type of secretory structure includes grinding followed by supercritical carbon dioxide batch (non flow) pretreatment prior to continuous flow extraction[1]. Extraction of peppermint (*Mentha piperita*) leaves was performed at 313 K and 10 MPa, including only grinding pretreatment as well as optimal pretreatment. Reduction of energy consumption refering to the mass unit of produced essesntial oil was experimentaly determined and veryfied by the mathematical modelling on he micro-scale which observed secretory structures behaviour during the extraction process. Phenomena that the exposure to supercritical CO_2 led to disruption of a fraction of peltate glands that stayed untouched by grinding process, and the essential oil release had been used as a basic hypothesis of the mahtematical model and was further verified by Scanning Electron Microscopic analysis of treated plant material[1]. The model was also applied on the literature experimental data on supercritical CO_2 extraction from grinded plant material to simulate optimal supercritical carbon dioxide extraction from basil, rosemary and marjoram[2] and pennyroyal[3] leaves. Reductions of energy consumption were in range from 34 to 68 kJ per gram of produced essential oil.

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Apparatus With a Vibrating-Rotating Mixer for Osmotic Dehydration of Fruits and Vegetables

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Although the osmotic dehydration of horticultural products has been known since 1966[1] there are no available data on industrial application. One of the reasons for that is unavailability of suitable apparatus for continuous operations. In our earlier publications[2,3] we have reported a bench scale vibrating plate column as equipment for continuous contact of apple pieces and concentrated sugar solution. The modified and improved pilot-plant extraction column has been constructed and continuous experiments of osmotic dehydration of various fruits (apples, cherries, sour cherries, raspberries, strawberries etc.) and vegetables (mushrooms) have been done.

Good apparatus for industrial application, of osmotic dehydration process must fulfil several requirements: continuous mode of operation, sufficient contact time (1.5 – 3 h) of solid phase to reach required moisture content, solid phase plug flow, large solid phase hold-up etc. To eliminate resistance to water mass transfer in a liquid film around a fruit piece, intensive mixing of the liquid phase is necessary. All these requirements are accomplished on this apparatus. The solids were fed by hydraulic transport through the feed leg. The fruit pieces flow upward by buoyancy and the syrup flows counter currently. The counter current flow of syrup through the column and through heat exchanger is maintained by a pump. The flow rate and the temperature of the syrup were measured and controlled. Two types of mixers (vibrating plate and vibrating-rotating plate mixers) have been investigated. It was found out that maximal flow rate of solid phase through the column was larger with vibrating-rotating mixer i.e. when vibrating mixer was at the same time rotating. Also asymmetrical reciprocating movement of plates (the plates moved slowly up and quick down) was better then symmetrical sinusoidal movement.

Flow of solid phase (fruit or vegetable pieces) through the column is completely segregated flow. Under continuous operation of extractor with vibrating and vibrating-rotating mixer in which osmotic dehydration (extraction of water from fruits) takes place, the residence time distribution of fruit pieces was determined experimentally. The hydrodynamic conditions (mild vibration intensities, counter-current flow rate when the convective resistance to water mass transfer was eliminated) has been found under which the residence time distribution of fruit pieces can be described by **n** cells with ideal mixing model, with **n** =10-20 what is near plug flow.

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Optimal Control of a Free-Time Batch Stripper for Low Relative Volatilities

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CANCELED

Batch distillation received, in the last years, a growing interest because of its applicability to small scale production of specialities, characterized by high value and lower capital cost[1]. A batch distillation column whose products are collected from its bottom is called a stripper. Finding the optimal control for batch distillation columns is not trivial, even when the operating time is fixed; when this is free, a supplemental variable to be optimized appears. Free-time optimal control means to compute both the minimum working time and the appropriate time profile for the control variable under the penalty of matching a given performance index, such as the mean product concentration in the residue (for the batch stripper) or distillate (for the batch rectifier). From several popular choices when it comes to batch distillations, the reflux was used as command variable.

If the free-time optimal problem is considered as optimization over a set of stages, iterative dynamic programming (IDP) could be used with proven success. According to this method, both time and control variables are discretized to a predefined number of values, particular to a stage. A systematic backward search method in combination with the simulation of the system model equations is used to find the optimal path through the defined grid. Unfortunately, IDP cannot be used for the batch stripper, since the objective function computation should assume a known condenser concentration profile, which permits the actual reboiler profile to be computed. But, there is no a priori knowledge of this kind.

To overcome these drawbacks, an evolutionary optimization strategy could be used, based on Genetic Algorithms (GAs). The GAs became a reliable optimization tool for strong nonlinear systems with many variables[3]. They are based on natural evolution processes, where selection results in species that fit the best. Variation in the population is achieved by genetic crossover and mutation. Because of the non-linear structure of a batch distillation, given by the thermodynamic vapour-liquid equilibrium, the use of GAs to calculate a piece-wise step-like trajectory of the control variable is appealing. A stage is defined as a period of constant reflux. The reflux indirectly influences the duration of this stage, which is computed using the reboiler heat flow also. All the stages are encoded in the chromosome. The population, formed by individuals with different chromosomes, is restricted naturally to the feasible region through the mechanisms of reproduction or mutation. A balance between the convergence to the global minimum and the calculation efforts by choosing the population size and selection mechanism was sought.

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PREN O-04 ppi

Novel Areas and Future Trends of Computational Fluid Dynamics Software Applications in Chemical Engineering

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The advanced computer aided design and analysis tools are gradually replacing the classical working methods of chemical engineers. Among these, the Computational Fluid Dynamics method, or CFD, has grown and changed rapidly during the past twenty years. Many physical models have recently become available as commercial codes. Combined with the increased capabilities of today's computers, they have contributed to expanding CFD modeling into many new application areas of Chemical Engineering.

The paper presents a brief overview of advanced novel applications and future trends of CFD software in Chemical Engineering, based on numerous examples of the authors' experience and reference tasks from the literature. The example problems are described in parallel with visualized results.

Among the cases of major importance, single phase turbulent flow, as well as multiphase flow models are reviewed.

Referring to single phase flows, the LES and RANS approaches are described and illustrated. The RANS approach is revealed as the most popular and inexpensive method for analysis and solving of technical tasks. The paper reports on two recent modeling applications, namely, CFD facilitated design of a new mixing impeller, and CFD characterization of impeller mixing efficiency.

Multiphase models of increased sophistication describing solid, liquid and gas flows with simultaneous mass transfer between the phases are summarized with emphasis on their applications to describe evaporation, condensation and multiphase reacting flows. The CFD method emerges as a powerful tool, for examining the real behavior of distillation towers' mass and heat transfer, as well as chemical reactions in bubble columns and fluidized beds.

The future trends and directions in Computer Aided methods for analysis of Chemical Engineering processes incorporate developments, such as the integration of various pieces of software including flow sheet modeling, CFD modeling and complex reaction and thermodynamic models.

PREN O-05 ppi

Adaptive Neural Fuzzy Inference System to Modeling of Flux and Fouling During Ultrafiltration of Skimmed Milk

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CANCELED

A neural fuzzy inference system (ANFIS) is simply a neural network- learning algorithm. The ability of ANFIS was investigated for the dynamic modeling of cross flow ultrafiltration of milk. This paper presents application of a class of hybrid neuro-fuzzy network to the solution of a nonlinear complex process. It aims to predict permeate flux and total hydraulic resistance as a function of transmembrane pressure, PH, temperature, fat, molecular weight cut off, and processing time. Dynamic modeling of ultrafiltration performance of colloidal systems (such as milk) is very important for designing of a new process and better understanding of the present process. Such processes show complex non-linear behavior due to unknown interactions between compounds of a colloidal system. The ANFIS approximation gave advantages over the other methods. The results showed that there is an excellent agreement between the checked data (not used in training) and modeled data, with average errors very low. Also the trained ANFIS is able to accurately capture the non-linear dynamics of milk ultrafiltration even for a new condition that has not been used in the training process (tested data). In addition, the results show that neural fuzzy systems are efficient in terms of better performance time and lower error rates while compared to pure neural network approach. The primary objectives are both to investigate the capability of adaptive neuro-fuzzy networks and to justify their application to predict the Jp and Rt characteristics of milk ultrafiltration. Successful implementations of neuro-fuzzy predictors are described and their performances are illustrated using the results obtained from adaptive neuro-fuzzy networks and showed data in figures. In this paper, ANFIS is compared to Multilayer perceptron. The results of modeling showed that the protein rejection at each value of condition is almost constant with time, but the rejection of other components has increased significantly with time. In addition, the fouling has been increased at first and then decreased with the TMP, because the membrane pores were closed. Nevertheless, the fat rejection at each value of PH is constant with time.

PREN O-06 ppi

A Multi-Criteria and Fuzzy Logic Based Methodology for the Relative Ranking of the Hazard of Chemical Substances and Installations

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Hazard assessment of materials, process units or installations is actually a multi-criteria problem. No single property can be used for assessing the fire hazards of chemical substances and materials; different methods use different fire hazard properties in their assessment. On the other hand, current methodologies and classification systems usually use linguistic variables, corresponding to specific range of values, for the classification of different hazards. Moreover, many uncertainties are present in the assessment of industrial hazards or industrial accidents consequences.

A new approach for the rapid assessment and relative ranking of the hazards of chemical substances, as well as units and installations, is introduced in this paper. It is based on the employment of a multi-criteria decision-making technique, the Analytic Hierarchy Process. The multi-criteria approach aims in better incorporating the different properties or parameters in hazard assessment. The proposed approach is also based on fuzzy logic, since fuzzy logic is considered better for dealing both with linguistic variables and uncertainties.

Based on the proposed methodology, a number of indices have been developed and are presented here: the *Substance Fire Hazard Index, (SFHI)*, which is focused on the major-accident hazards of the substances, and the *Facility Hazard Index (FHI)*, for the ranking of chemical installations based on their 'consequences potential'.

Finally, the challenges and limitations of using the multi-criteria approach for the development of relative ranking and assessment indices are also discussed.

PREN O-07 ppi

Methods for Product Quality Standards Development

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Methods for product quality standards development were investigated. These examinations involve analytical, adaptive and statistical methods for quality products and process parameters control. The investigation was performed by industrial experiments and computer simulation.
Analytical methods for quality control were derived for selection of systematic errors, stochastic errors, and synthesis basic errors into inductive errors.
Statistical methods for quality control were carried out based on sample functions parameters values estimation and statistical hypothesis. Statistical analysis of empirical sets and methods for experimental data reduction were provided. Stochastic modeling for management quality product and process quality control was performed.
The experiments were carried out with optimal evaluation experimental design. Process analysis and quality design was performed by computer simulation for various conditions.
Statistical lists and probability diagrams were derived for quality system in producing plasticable products. Method of checking lists were used for evaluation quality standards.
The adaptive quality control involves structure and functions system examination. Functions of the product quality were determined and models for standard development of the plasticable products were derived.
The obtained results show that these results can be used for standards development of the others products . Also, the investigated results in this paper can be applied in the others domain.

PREN O-08 ppi

The Oxidative Dehydrogenation of Propane Using MoO_3/Ga_2O_3 Catalysts – An Overview and First Experimental Results

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The Oxidative De-Hydrogenation (ODH) of propane over MoO_3/Ga_2O_3-based catalysts offers an interesting alternative for propene production. The good alkane activation properties of Ga_2O_3 in combination with the selective oxidation function of MoO_3 make it possible to obtain high propene yields at much lower temperatures than usually applied when using other catalysts such as those mentioned in *Figure 1.*

The reactor used in this study was designed in such a manner that the contribution of homogeneous reactions to the overall conversion of propane can be quantified. Experiments are carried out to examine the influences of temperature, propane/oxygen ratio and total pressure on propene yield. It is known that gas dopes such as CO_2 and N_2O can affect the oxidation state of a catalyst in such a way that the formation of undesired carbon oxides is hindered. Experiments with such dopes are also carried out.

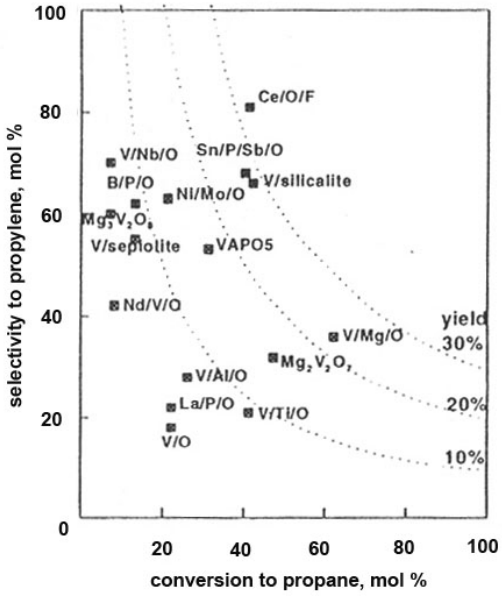


Fig. 1. Best yields to propene in ODH of propane reported in literature, for various catalysts; [1].

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PREN O-09.ppt

Making High Octane Fuel from Juice of Sweet Sorghum

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Technological process for high octane machine fuel production from the juice of sweet sorghum "*succrosorgo 405rt"* was postulated and developed.
The basic stages of the established technological process are as follows: obtaining the sweet sorghum juice; sugar fermentation from the sorghum juice in ethanol on the immobilized cells S*accharomyces cervisiae,* making higher concentrations of the ethanol solutions by adsorption and catalytic conversion of ethanol to high octane motor fuel.
Catalytic conversion of ethanol to high octane motor fuel was performed in duration of two hours on the zeolite type catalyst KAG-350 in stainless steel reactor with fixed catalyst layer. Gaseous and liquid reaction products were analyzed using standard gas-chromatography GC methods.
In this research was investigated the influence of following technological parameters: a) reaction temperature within the temperature interval from 650K to750K; b) pressure of the reaction system (0.5-5MPa); c) contact time with raw materials (0.1 to 1 hour) and d) water content in ethanol (5-50%) on the ethanol catalytic conversion, as well as on the selectivity of this process: yield of the gaseous carbohydrate products (C_1-C_4), diethyl-etar, gasoline, "LCO" and "coke", and researcher octan numbers of the obtained gasoline fraction (RON).
It is shown that under the optimal choice of the technological parameters of the investigated process was possible to achieve complete conversion (100%) of the 92% ethanol solution into gasoline with the research octane number RON 99%.
Techno-economical benefits of the high octane gasoline from juice sweet sorghum production, as well as the possibilities of the faster applications of this process to the countries of South-eastern Europe were examined.

PREN O-10 mci

Strategies for Integration of large Industrial Accidents, Environmental and Quality Management Systems

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This paper focuses on the analysis of the implementation process of an integrated management system and on which have been the basic requirements for its success in an Greek Pesticides formulation Industry of average dimensions. Since the main set of rules for the environment (*ISO 14001 and EMAS*), industrial safety (Seveso Directive Safety Management System) and quality (*VISION 2000*) have the same statement and provide for analogous rules, it is possible to apply a system having some common fundamental procedures (*Environmental Quality System EQS*) and some specific procedures (*Environmental Management System EMS*) (*Safety Management System SGS*). Up to now, the main variables for an industrial reality – environment, safety and quality- have been separately managed and this rose problems in terms variable, by determining, therefore, a difficult retrieval and use of them. If, on the one hand, this "integrated" approach has brought benefits in terms of the organization of the activities, on the other hand it has determined a great effort from the whole personnel. A great work is necessary in order to organize the documentation, making it easy to retrieve, to understand and to use. The enterprises operating in sectors with an high degree of ecological intensity and being insensitive to the environmental aspects of their own activity are in a high risk position, since they have not taken a crucial area of business management into consideration. On the other hand, the enterprises that adopt a suitable environmental strategy for the context in which they operate, will get a greater competitive and economic success.

PREN O-11 mci

The Process Plant Management System Development

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This paper presents plant management system investigation and development. Process plant management system which including managament support system, decision support model, and investment, costing and profitability analysis was provided. The networks optimization requests maximum flow, minimum cost, concern to assigment problem, the matching and the minimum spanning trees, computer implementations and heuristics.

Management operation system aimed at helping engineers and managers optimize all phases of process plant operations. Plant operation provides optimal process conditions, equipment services life, troubleshooting, advances process control, waste minimization and hazard analysis. Process operation makes history database of manipulates and object variables, performs dynamic simulation and detect process disturbance before they cause significant disruption. Optimization requests maximum flow, minimum cost flow, concern the assignment problem, the matching and the minimum spanning trees, computer implementations and heuristics with the aim to find the path toward an automated intelligent tool that yields maximum profit.

Automatically create plant process models requires software tools for system identification which claimed management to enable users automatically create high fidelity mathematical models of physical systems, process and plant. System identification is technique that creates model of a plant or process from input and output data, eliminating the need for detailed knowledge of the process system. The new estimator automated the process, enabling engineers to perform modeling and simulation studies without having to create the underlying mathematical models from first principles.

As a case study the ethanol recovery distillation plant was used. Database plant management system was developed as a relational data base system for the top and bottom of the linked column. Database protocol manages all data bases, reports and tables as a linking objects.

The computer supported cooperative work with databases management and mathematical modeling and simulation of the process plant provides intelligent plant management support system. The plant manager workflow software can be used for the new product quality design, to build the model network optimization, generating new database, on-line expert systems and specified tools. Real time software need to build intelligent process management applications.

Clays Utilization in the Manufacture of the Dairy Products

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CANCELED

This work purpose consists in studying the influence of adding basic clays in the process of milk coagulation for obtaining yogurt and cottage cheese. The milk coagulation process is considered the principal phase of yogurt and cottage cheese manufacturing. In that stage, the milk (in liquid phase) is processed into a gelled mass which presents elasticity. Basic clays have the property to intervene in the kinetics of milk fermentation reaction. Utilizing hydrotalcite clay the lactate anion can be fixed, conductive to the multiplication of lactic bacteria's. The alkalinity developed by clays can decelerate the negative influence of the lactic acid formed in fermentation process and can accelerate milk fermentation. In this paper are presented the resultants obtains consequence by dependence relation between clay quantity - acidity of the final products and clay quantity – conversion level in coagulum.

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Effect of Nitrogen Supply on Correlation among Quality Parameters in Different Winter Cultivars

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A study has been providing with four winter wheat cultivars differing on technological quality potential. Novosadska rana 2, Sremica, Lasta and Pobeda is domestic cultivars developed at the Institute of field and vegetable crops on Novi Sad. The cultivars were grown in the following different treatments of nitrogen fertilization: 0, 60, 120 kg N ha^{-1} during three years. The goals were to investigate correlations among quality parameters in the cultivars grown at different levels of nitrogen supply. The following quality parameters were study: Protein content, sedimentation value, bread volume and crumb quality value.

Assessments included the contribution of 30 years of wheat breeding and importance of nitrogen fertilization for the utilization of genetic yield potential of the studied treatments. Finally, interactions among the studied treatments were assessed with respect to their influence on the studied characteristics of wheat.

It was found that nitrogen significantly affected the utilization of genetic yield potentials and most of the quality characteristics of the study cultivars. Regarding the direct indicators of technological quality, bread volume and crumb quality number, no significant interaction were found between year of growing and nitrogen nutrition. Correct nitrogen nutrition further increases the stability of the quality characteristics.

Effects of Limited Hydrolysis on Traditional Soy Protein Concentrate

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The influence of limited proteolysis of soy protein concentrates on protein solubility/extractability, the composition of the extractable proteins and their emulsifying properties were investigated. Traditional concentrate (aqueous alcohol leached concentrate) was hydrolyzed using trypsin and pepsin as hydrolytic agents. Polyacrylamid gel electrophoresis (PAGE), SDS-PAGE and size exclusion gel-HPLC chromatography were used to detect differences in soluble protein composition between traditional concentrate and hydrolysates. Emulsifying activity and stability of modified concentrates were measured by a turbidimetric method at the same level of the soluble proteins and were expressed as the Emulsifying Activity Index (EAI) and the Emulsion Stability Index (ESI).

The limited proteolysis is an effective way to improve the traditional protein concentrate solubility. All hydrolysates showed better solubility than the original traditional protein concentrate, while trypsin induced hydrolysis caused significantly better emulsifying properties of modified concentrates. Due to the alcohol induced denaturation, traditional alcohol-washed concentrate had low soluble protein content (247.01 ± 1.26 mg/g). The soluble protein content of modified samples varied from ca. 46% to 66%, depending upon the enzyme used. Trypsin increased the solubility most efficiently during the initial 30 min of incubation, reaching about two fold rise (507.4 ± 0.75 mg/g). After that, a slightly lower increase was observed. The average protein content of 90 min-treated samples was 660.50 mg/g. It is interesting to note that the control samples treated at pH 8.0 without enzyme adding had higher soluble protein content (304.30±0.46) than the initial concentrates. This indicates that the improved solubility of trypsin-modified samples is the result of the enzyme activity, but partly could be due to the hydrolytic effect of mild alkali hydrolysis. Solubility of traditional concentrate was also improved with pepsin; although the effect was lower (466.40 mg/g). Trypsin-induced hydrolysis significantly ($p<0.001$) improved emulsifying activity index (EAI) from 41 to 88, 110, 105 and 97 m^2/g for 30-, 60-, 90 min trypsin-treated samples and pepsin modified concentrates, respectively. Trypsin treatment also significantly ($P<0.05$) improved the ESI (Emulsion Stability Index) of traditional concentrate from 18.72 to 27.85, 34.37 and 30.72 min for 30-, 60- and 90-min.-treated samples, respectively. In opposite, pepsin acting increased EAI of traditional concentrate, but the emulsions prepared with these samples were less stable than those prepared with the unmodified concentrate.

In conclusion, the limited hydrolysis is a simple and effective method for the improvement of the functional properties of traditional soy protein concentrate. Better properties are the result of the enzyme induced alterations of the major soybean proteins.

Isolation and Characterization of Starch from Different Maize Genotypes

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Maize is the most important raw material for the production of commercial starch not only in our country but in the world too. The aim of the contemporary technology of maize wet milling or starch processing of maize grain is to obtain as high yield as possible and to utilise highly valuable products simultaneously with as complete separation of grain constituents as possible.
Twelve ZP maize genotypes of different both, genetic background and the length of the growing season, were used in the studies of physical, chemical and wet-milling (processing) properties of maize grain in starch processing. Starch yield, recovery and purity, then the protein content in the recovered starch, are the most important parameters for the evaluation of wet-milling properties of maize hybrid grain. It was determined that genotypes with the highest starch yield did not as a rule have the highest starch recovery and that the increase of starch yield and recovery resulted in the decrease of gluten yield. Starch yields of studied maize genotypes ranged from 58.8% in ZP 633 to 69.0% in ZP 808, while the highest (13,5%), i.e. lowest (5,3%) gluten yields were detected in ZP 633, i.e. ZP 808, respectively. The protein content was low in recovered starches (<0,3%) pointing out to high quality of produced starches. Furthermore, the content of amylose and amylopectin in these starches is also characteristic for the standard maize starches. There was a difference in rheological characteristics of recovered starches of ZP maize genotypes and commercial maize starch (pasting temperatures of recovered starches were lower). The basic chemical composition of the grain did not significantly affect the starch yield and recovery, while physical traits of the grain (test weight, kernel density and the proportion of soft endosperm fraction) significantly affected these processing properties. Hybrids with a lower test weight and a greater proportion of soft endosperm fraction had a higher yield, recovery and purity of starch. Equations of linear and multiple regression analyses were determined and they can be applied in the prediction of the grain wet milling properties, i.e. of starch yield, recovery and purity but the additional studies with a greater number of hybrids of different physical and chemical properties are still necessary.

Thermal Analysis of Whey Concentrates

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Whey is valuable by-product of dairy industry. Usage of whey products is common in food industry. Production of whey components (proteins, lipids, lactose) could transform these by-products into products with high nutritional and technological values.

Thermal stability of crude whey and obtained whey fractions: concentrated whey, whey lipid-protein fraction and dry whey protein concentrate has been analyzed by Differential Scanning Calorimetry (DSC), performed by Du Pont Instruments 910 Differential Scanning Calorimeter, sensitive DSC, performed by MicroCal MC-2 Scanning Calorimeter, MicroCal Inc. Northampton, MA and thermogravimetric analysis (TGA), performed by Du Pont Instruments 951 Thermogravimetric Analyzer. Partial characterization of prepared fraction and information on thermal stability of sample, valuable for technological process, were obtained. Temperatures of transitions for crude whey, and whey fractions in solution were: T_{m1}=302.8 K, lipid thermo tropic transition, T_{m2}=345.7 K and T_{m3}=356.7 K, protein unfolding and for dry whey protein fraction: T_{m1}=373.3 K, water evaporation, T_{m2}=421.9 K, lipid melting and T_{m3}=476.5 K, protein degradation.

From thermodinamical parameters obtained (T_m-temperature of transition midpoint, ΔH^{cal}-calorimetric enthalpy) it can be assumed that that thermal denaturation process (followed by DSC), off whey proteins from crude whey and separated fractions didn't differ regarding T_m and ΔH^{cal}, meaning that proteins didn't udergo denaturation in the process of concentration. Comparing the shapes of DSC curves, it can be concluded that different proteins of whey were separated in obtained fractions.

Application of Brewers Yeast in Bread Production

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Possibility of debittered brewer's yeast (*Saccharomyces cerevisiae*) application in the bread making industry, without changes in the technological process, has been investigated. Laboratory examinations of fermentation activity revealed synergism between brewer's and baker's yeast.

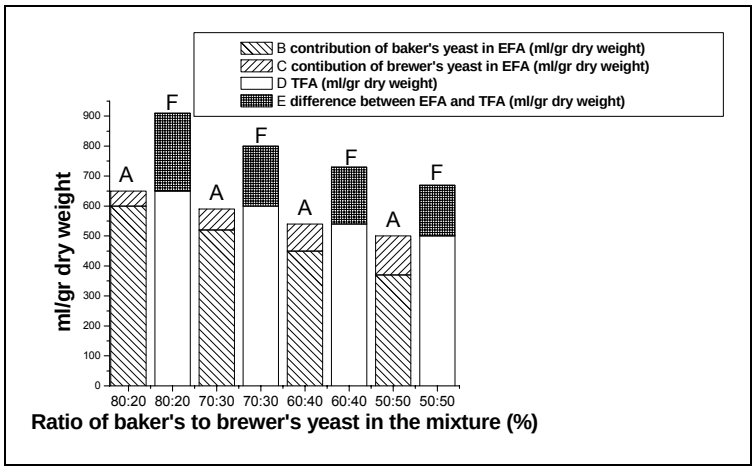


Fig. 1 Fermentation activity of baker's and brewer's yeast mixtures obtained theoretically-A (TFE) and experimentally-F (EFA).

Fig. 1. represents the fermentation activities of baker's and brewer's yeast mixtures measured volumetrically. Each combination of baker's and brewer's yeasts is represented by two histograms. First (A) corresponds to theoretical value of fermentation activity (TFA), obtained as a sum of contributions of baker's (B) and brewer's (C) yeast. Contributions are calculated separately according to the formula:

$$TFA = \frac{EFAbe \times \%BE}{100} + \frac{EFAbr \times \%BR}{100}$$

where the first fraction of histogram (A) represents contributions of baker's while the second represents contribution of brewer's yeast.

The second histogram (F) represents experimental fermentation activity (EFA). For each combination of baker's and brewer's yeast increase of experimental activity compared to theoretical is obtained (E-difference between EFA and TFA).

Based on these results, partial or complete replacement of baker's yeast with brewer's yeast has been tested in bread making under industrial conditions. It has been found that baker's yeast could be partially substituted with brewer's yeast. Bread obtained by substituting 40 % of baker's yeast with brewer's yeast, besides bigger volume and better organoleptic remarks, has prolonged freshness, compared to the bread made with baker's yeast only.

Energy Improvement Comparison Between Sugar and Sugar - Ethanol Coupled Manufacturing Processes

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The paper presents the possibility to redefine the streams in a technological flowchart by means of process simulators and pinch analysis specialized software. SuperPro Designer simulator was chosen due to its facilities concerning the definition of unit operation and procedures in bio-industries. The simulator environment offers a large database to characterize the material streams in food industry, a variety of equipments and tools for economic analysis in this field. This study focuses on sugar and sugar – ethanol coupled manufacturing processes.

The technological processes is characterized by preheating units for several intermediate streams (solutions and juices) and that is the reason why by rearranging the energetic streams a more efficient design can be found. The optimization of energy balance was the main objective of the present work. Restrictions referring to specific parameters of the technological process were also considered.

The simulated flowsheet of sugar beet manufacturing process starts with the extraction unit of sucrose from sliced sugar beet. The last operations considered in both cases are the crystallized sugar packing and dehydrated ethanol filling. Due to the availability of the raw material, annual operating time of 3960 h/year is considered for the sugar and sugar-ethanol coupled manufacturing processes. In both cases, several sections and branches have been defined to facilitate reporting of results for costing, economic evaluation, and raw material requirements of large processes.

The concept of co-production is based on biophysical, industrial and economic principles. Molasses and/or beet juice are valued for the fermentable sugars that can be converted into ethanol, as well as being used as industrial and agricultural inputs. Molasses obtained as byproduct in sugar manufacturing process can be used as major raw material for ethanol manufacturing by fermentation. The value of molasses from a sugar factory is generally much greater as an ethanol feedstock on-site than the value of exporting the molasses to a separate distillery. In ethanol manufacturing process (as well as in sugar factories), low steam utilization technologies have been introduced through heat integration using waste heat in heat exchangers, which is then reused to increase the temperature and/or pressure of other processes.

The improvement of the sugar and sugar – ethanol coupled manufacturing processes were considered for both saturated steam and hot water as hot utilities. The results obtained proved that the use of saturated steam is more efficient in both cases. The optimized heat exchanger (HX) network in case of sugar manufacturing process engages only 11 HXs (compared with 24 HXs when using hot water). In the case of coupled manufacturing process only 10 HXs (compared with 19 HX when using hot water) are necessary.

Total costs for sugar and sugar – ethanol coupled manufacturing processes are not very different because in the second case a compromise must be made between the distillery and utility costs.

The analysis of the optimized flowsheet reveals an increase of some preheating duration (up to 50%) but the batch time is not significantly modified (76 hours in the optimized solution and 72 hours in the initial configuration).

Application of Commercial Yeast Strains in the Analysis of Biotin in Sugar Beet Molasses

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Sugar beet molasses represent a basic raw material for the production of baker's yeast *Saccharomyces cerevisiae*, and biotin is an essential growth factor in it. The content of biotin in molasses is not sufficient for the development and growth of yeast. Sugar factories need routine and inexpensive method for determination of biotin in molasses. It is important for yeast producers to develop a method that enables the utilization of their own yeast strain as a test organism in determination of biotin activity in molasses.

In the investigation, two commercially available yeasts, A and B, aged 7 days, were used, supplied from inside manufacturer. The yeast samples were suspended directly. The content of biotin was determined in 15 samples of molasses according to Danielsen and Eriksen. The results of biotin content calculated graphically and by Mathcad software package were statistically computed using SPSS8.0 and compared using F-criterion.

The analysis of variance of measured parameter was carried out to calculate the effects of yeast strains and molasses for the level of significance of 5%.

The results undoubtedly confirmed that the content of biotin, having been signicantly different in the investigated samples of molasses, varied depending on:

- the sample of molasses (F=107.268);
- the type of commercial yeast strain (F=344.748). The comparison of mean values by calculation of least significant differences (LSD) revealed that there was a significant difference in biotin content within sample A (0.0551 μg/g, 1 replicate) and sample B (0.07284 μg/g) and sample A (0.05379 μg/g, 2. replicate) and sample B;
- the interaction within molasses samples and yeast strains (F=23.082).

PREN P-09 fst

Influence of Some Zeolits on the Growth of Mycelia of Industrial Fungi *Agaricus bisporus, Ganoderma lucidum, Pleurotus ostreatus* and *Lentinus edodes*

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Mineral zeolite is today successfully used in adsorption, ion exchange and dehydratation processes. More than 40 natural and more than 150 artificial types of zeolite are used in fields such as agriculture and stockbreeding, pollution control, energy applications and mining and metallurgy. The word **zeolite** comes from *boiling stone* (from Greek words *zeo* - boiling and *litos* - stone), named by Swede mineralogist Fredrich Cronstdet in 1756. Its main structure is constituted by SiO_4 and/or AlO_4. Most significant features of this structure are the huge amount of gaps and cavities with their ability to release water at high temperatures without losing its original form and availability of loosely bounded, exchangeable cations.

One of the possibly use of zeolit is as mushroom growth accelerator. We found very interesting influence of two kinds of zeolit on the growth of some industrial mushrooms. *Agaricus blazei*, *Ganoderma lucidum*, *Pleurotus ostreatus* and *Lentinus edodes* were cultivated without and in the presence of different zeolit's concentration-0.25%, 1% and 2%. Mycelium growth was monitored six days in Petri dishes with malt agar media and diameters of mycelia growth were measured.

In all cases growth without zeolit were significantly slower. By addition of 0.25% of zeolit growth of all four kinds of mushrooms were faster and with addition of 1% of zeolit, too. The best results were obtained with addition of 2% of zeolit, when growths of micelium were 2-4 times faster in the same period in comparison with growth without zeolit.

Zeolit 1 (Minazel) showed very strong stimulation on growth of mycelia *Agaricus blazei* in all used concentration (0.25, 1 and 2%); in case of *Ganoderma lucidum* in concentration of 2%; *Lentinus edodes* in concentration of 1% and with *Pleurotus ostreatus HK*-35 in concentration of 0.25% on the second day of cultivation.

Zeolit 2 (Minazel plus) showed very strong stimulation on growth of mycelia *Ganoderma lucidum* in concentration of 0.25% and 1%, in case of *Lentinus edodes* in concentration of 0.25 and 2% and with *Pleurotus ostreatus Hk*-35 in concentration 1% and 2% on the second day of cultivation.

The strongest stimulation were obtained after sixth day of cultivation in *Agaricus blazei* growing with addition of zeolit 1 in concentration of 2%, *Lentinus edodes* growing with zeolit 2 in concentration 2% and *Ganoderma lucidum* with zeolit 2 in concentration 2%.

The investigation indicated very interesting and useful role of zeolite in shortening the time for mycelium growth. Because of those facts we believe this investigation should be continued because of its possible impact on industrial mushroom growing.

Effects of High Temperatures in the Course of Micronisation and Extrusion on Changes in Nutritive Values of Soybean Grain

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Different technological processes that satisfy, to a smaller or a greater extent, requirements for elimination of antinutritional factors as better as possible, on the one hand, and for damages of essential grain constituents as less as possible, on the other hand, are the necessary prerequisites for soybean utilisation in food and feed.

In the present study, the grain of soybean cultivars Bosa and ZPS 015 was subjected to treatments of micronisation and dry extrusion. Depending on the technological process applied, grain was subjected to the temperatures ranging from 100°C to 150°C for 25-30 to 40-60 seconds during extrusion and micronisation, respectively. The content of oil, fatty acids, total proteins, water soluble and proteins soluble in salt solutions, available lysine, trypsin inhibitors and activities of the isoenzyme of lipoxygenases 1, 2 and 3 and urease were analysed in the obtained products.

Considering that applied treatments have different sources of heat, the exposure of grain to high temperatures causes various processes within the grain what lead to changes in the chemical composition, i.e. changes in nutritive values.

Depending on the genotype the lipoxygenase activity 1 decreases over increased temperatures. The same regularity was observed in trypsin inhibitor and urease. The applied thermal treatments did not affect more essentially changes of total protein contents, but the temperature increase in the both processes caused a drop of protein solubility down to a certain limit. Micronisation had the greater effect on the reduction of lysine availability. Dry extrusion, occurring within a closed system in which increased humidity has a special effect, caused much smaller changes of the available lysine content. Thermal treatments had an unexpected effect on the activities of the isoenzymes of lipoxygenases 2 and 3. The higher temperature of the thermal treatment the higher isoenzymatic activities.

PREN P-11 fst

Growth of *Fusarium* Spp and Zearalenone Production during the Micromalting Process

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CANCELED

Two samples of two rowed winter brewer's barley (SSK3 and SSK6), harvested in the year 2003 in Serbia were investigated on the presence of *Fusarium* species and their toxic metabolite - zearalenone (ZEA) during the micromalting process.
Isolation and determination of *Fusarium* spp. were done before and after 1st and 3rd day of germination (green malt), after kilning and in malt samples. All samples were tested on the presence of ZEA too.
Determination of *Fusarium* species were carried out according to Nelson et al. (1983) and ZEA by using a fluorometric method (Fluorometer Vicam, series 4, USA).
During these experiments following *Fusarium* spp. were isolated: *F. avenaceum*, *F. culmorum, F. poae, F. sporotrichioides, F. tricinctum* and *F. verticillioides*. The most frequent *Fusarium* sp. found to be *F. poae*.
Is was established that barley samples before malting process were contaminated with ZEA (SSK3- 9.7 μg/kg, SSK6- 9.2 μg/kg). Concentrations of ZEA varried from 12.47 to 86.47 μg/kg during the malting process.

Influence of Fermentation Temperature and Wort Composition on Modelling of Attenuation and Diacetyl and 2,3-Pentandione Concentrations in Beer

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A mathematical model for calculating attenuation and diacetyl and 2,3-pentanedione concentrations was developed based on experimental data obtained in 10 laboratory-scale lager beer fermentation carried out at 8°C and 14°C using worts of various compositions. Worts were produced from malt and with 10, 20, 30 and 40% of corn grits. The real and apparent attenuation were determined according to EBC Analytica. Diacetyl and 2,3-pentanedione concentrations were determined by GC/MS method with the extraction using SPE columns.

On the basis of experimental results a functional dependence in the form of an analytic expression was derived that allowed the calculation of the real and apparent attenuation. The change of the value of this quantity as a function of time has an exponential form with a high degree of significance. It was concluded that the presence of corn grits in the wort did not influence significantly the real and apparent attenuation. On the other hand, the fermentation temperature had an essential effect on the real and apprent attenuation.

On analyzing the experimental results it could be observed the congruence of the increase/decrease of diacetyl and 2,3-pentanedione concentrations with certain functional forms of an exponential character. From a number of exponential forms the function chosen for description was the one based on the Weibull distribution with two parameters. The values of the parameters were obtained by heuristic search. The acceptability of the parameters and coefficients was estimated on the basis of the lowest χ^2 value of the experimental and theoretical results.

Maximal diacetyl concentration for the worts with all contents of corn grits in the fermentation at 8°C was achieved on the fifth day of fermentation, whereas the analogous value in the fermentation carried out at 14°C appeared on the third day of fermentation. Maximal 2,3-pentanedione concentration obtained in the case of the worts with all contents of corn grids in the fermentation at 8°C was achieved on the fifth day of fermentation, whereas the corresponding values in the fermentation at 14°C were attained on the third day of fermentation. The appearance of maximal diacetyl and 2,3-pentanedione concentrations is in agreement with the achieved intensity of fermentation at the given temperatures that is with the real and apparent attenuation.

Attenuation and concentrations of diacetyl and 2,3-pentanedione, that is their production and reduction during fermentation, could be calculated on the basis of the kinetic equations derived in this work. The proposed mathematical dependence can also be used in calculation the diacetyl and 2,3-pentanedione production and reduction in the course of the industrial beer fermentation.

Comparative Study of the Supercritical Non-Catalytic and Subcritical Alkali-Catalyzed Processes of Biodiesel Synthesis

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The main advantages of the application of biodiesel fuel in the internal combustion engines are: its renewability and biodegradability, better quality exhaust gas emissions and the fact that it does not contribute to a rise in the overall level of carbon dioxide in the atmosphere. These facts have led to the increased interest in the production and application of biodiesel fuel worldwide. Commonly applied technology to produce biodiesel is the alkali-catalyzed synthesis, which proceeds at moderate temperature and ambient pressure. The drawback of this technology is the necessity to neutralize and remove homogeneous catalyst from the reaction mixture. The non-catalytic process however, proceeds at elevated pressure and temperature but without presence of a catalyst. Both processes were simulated using Design II simulation software and their main features were analyzed and compared. The advantages of the supercritical non-catalytic process are the absence of the catalyst removing and neutralization units as well as the ability to process feedstock (triglycerides) with higher free fatty acids contents. On the other hand, the advantages of alkali-catalyzed process are its moderate operating conditions and low energy consumption.

The Influence of the Sunflower Oil–Methanol Mixture Phase Equilibria at Elevated Pressure and Temperature on the Non-Catalytic Biodiesel Synthesis

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Biodiesel synthesis under supercritical conditions proceeds at elevated pressures and temperatures without presence of a catalyst. The knowledge of triglycerides-methanol phase equilibria and its influence on the reaction kinetics would be useful for process optimization due to the high pressure and temperature of the synthesis. The phase equilibria of the binary system triglycerides-methanol was measured at different temperatures between 473 and 503 K, and a range of pressures between 10 and 56 bar. The experimental data were correlated using Peng-Robinson (PR), Soave-Redlich-Kwong (SRK) and Redlich-Kwong-Aspen (RK-ASPEN) equations of state, and different mixing rules. The best results were obtained with RK-ASPEN equation of state and Van der Waals mixing rule, which were then used to calculate the phase equilibria at pressures and temperatures common for biodiesel synthesis under supercritical conditions. Phase equilibria data and kinetic data from the literature indicated that binary mixture critical point governs the reaction kinetics and that reaction proceeds in the supercritical phase.

PREN P-15 hpp

Lipase-Catalyzed Synthesis of Fatty Acid Fructose Esters in Organic Media and in Supercritical Carbon Dioxide

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Sugar fatty acid esters are non-ionic surfactants, which are mostly used for personal care products, cosmetic applications and as emulsifiers for food. Fructose monoesters can be also applicable to food additives as antibacterial agents that suppress the cell growth causative organism of dental caries.

Chemical synthesis of fatty acid sugar esters is usually performed as a high temperature esterification in the presence of an alkaline catalyst, which is accompanied by high energy consumption, low selectivity toward the various hydroxyl groups in sugars and coloring of products. In recent years, the use of enzymes as an alternative for the synthesis of sugar fatty acid esters has been investigated, emphasizing the synthesis of regioselective products. Carbohydrate fatty acid esters can be enzymatically synthesized from renewable substrates in mild reaction conditions, which compared to the chemical process minimize side reactions. Moreover, the enzymatic synthesis can be performed in less toxic solvents compared to those of chemical synthesis.

Supercritical fluids (SCF) can offer many advantages over organic solvents and are therefore attracting much interest as possible media for enzymatic reactions. Supercritical carbon dioxide (SC CO_2) is the most suitable SCF because of its relatively low critical pressure and temperature (7.3 MPa and 31 °C) and its low cost. Being completely nontoxic and nonflammable, carbon dioxide is interesting to the food and pharmaceutical industries as a safe SCF medium. Another advantage of SC CO_2 compared to the organic media is that the addition of molecular sieves, which are necessary for the removal of water generated during the esterification, is not required. Addition of molecular sieves is not practical on a larger scale, because it increases the reactor volume and mass transfer is limited due to difficult stirring. SC CO_2 has a high diffusivity, low viscosity and zero surface tension which allows easy penetration into macro and microporous materials. These enhanced transport properties makes it attractive when mass transfer in the immobilization matrix is rate limiting. Another advantage is the ability to control the solubility of solutes by regulating temperature and pressure. Stability of immobilized enzymes in SC CO_2 has proven to be good and similar to that obtained in liquid organic solvents. Since it is gas at room temperature, the solvent can be easily removed without leaving any residues in the product. Easy separation of the unreacted fatty acid from the sugar ester product seems to be feasible in this system. However, the solubility of apolar compounds, such as fructose, in carbon dioxide is limited and because of that various methods have been suggested, like addition of co-solvents or preadsorption of the polar compound onto an inert material with high internal surface.

In present research, reaction parameters of lipase-catalyzed synthesis of fructose fatty acid esters in organic solvent, such as temperature, biocatalyst concentration, stirring rate and molecular sieve concentration were optimized in a batch reactor at atmospheric pressure. The highest obtained conversion in 2-methyl-2-butanol using 10% (w/w of substrates) of lipase from *Candida antarctica B* and 12.14% (w/w of reaction mixture) of molecular sieves at 60 °C and 600 rpm was 78%. At optimized reaction conditions, previously defined at atmospheric pressure, lipase-catalyzed synthesis of fructose palmitate was performed in SC CO_2. Effect of temperature on enzyme activity was studied.

Solubility of Menthol in Pressurised Carbon Dioxide Experimental Data and Thermodynamic Modelling

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Introduction

Naturally occurring (-)-menthol (or *l*-menthol), $C_6H_9OHCH_3C_3H_7$, is a saturated secondary alcohol, which, together with menthone, is the major component in peppermint oil - the popular flavour used in a wide range of sugar confectioneries, chewing gums, toothpastes, chocolate fillings, pharmaceuticals and liqueurs. One appealing possibility for obtaining peppermint oil from vegetable material is extraction with supercritical carbon dioxide. However, the design of a viable supercritical extraction process with a possible industrial application requires an in-depth understanding of the phase equilibria of the system, and knowledge of the solubility of the components of interest in the supercritical solvent. This study reports new information on the solubility of menthol in pressurized CO_2, analyses solubility data published by other authors and assesses their reliability, as the agreement of the data from the different sources is rather poor. Furthermore, we model and validate against experimental data obtained the solubility of pure menthol in pressurised CO_2, and present for the first time experimental and modelling results for the melting point depression of menthol.

Solubility measurements

The solubility of menthol in dense CO_2 was measured using a flow-type apparatus in the temperature range 30-60 ^oC and in the pressure range 66-144 bar. The experiments for the melting point depression of menthol in the presence of carbon dioxide are carried out in a view cell by changing the pressure from 15 to 70 bar, and the temperature from 283 to 313 K. Determining the melting point depression is very important for this system as the difference between the critical temperature of the solvent CO_2 (304.2 K), and the melting temperature of the solute menthol (316.65 K) is less than 13 K, and hence it is of great importance to know in which region of the thermodynamic phase space the measurements are actually performed – in the vapour+solid region or in the vapour+liquid one.

Thermodynamic modelling

In our study we used the Soave-Redlich-Kwong (SRK) cubic equation of state (EoS) with the one fluid van der Waals mixing rule to model the melting point depression of menthol, and its solubility in pressurised carbon dioxide. To trace the SLV line for CO_2+menthol, a strongly non-ideal system of equations, which may have several solutions, must be solved. Taking into consideration that the equality of chemical potentials represents a necessary but not a sufficient condition for equilibrium, a stability analysis routine, based on a modified tangent-plane function criterion, and a phase identification procedure are employed, which guarantee that the phase configuration with the minimum Gibbs energy is found. This is particularly important in regions of the thermodynamic phase space where the EoS has multiple roots as is the case around the SLV conditions.

Extraction of Essential Oil from Yarrow with Supercritical CO_2: Effect on Antiradical Activity

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Yarrow with white flowers is the most abundant subspecies of Achillea millefolium L. in Macedonia. It is well known as medical plant with wide spectrum of healing activities. Its essential oil possessing antioxidant and antimicrobial properties is used in medicinal, veterinary and cosmetic applications[1]. In this work, supercritical CO_2 extraction was used to isolate essential oil from yarrow as an alternative technique to hydrodistillation. Carbon dioxide is a safe, colorless, odorless, nontoxic and readily available solvent, and the supercritical CO_2 extraction offers through alteration of pressure and/or temperature possibility of selective recovery of plant solutes. With aim to find the most appropriate conditions for obtaining essential oil free of waxes, SC-CO_2 extraction from yarrow flowers was performed at pressure of 10 MPa and temperatures of 40-60 ºC. The flowers were intact or ground, of different particle size. Essential oils extracted at different operating conditions were tested for antiradical DPPH scavenging activity, compared with the activity of essential oils obtained from flowers and leaves using hydrodistillation and of synthetic antioxidants BHA, BHT, and TBHQ. Additionally, residues after SC-CO_2 extraction were successively extracted with solvents of increasing polarity: hexane, ethylether, ethylacetate, ethanol and water and the extracts were evaluated for antiradical activity. The extract obtained with SC-CO_2 at 40°C contained large amount of co-extracted waxes; the yield of essental oil was 87% of the hydrodistillation yield. The extract obtained at 60°C contained less waxes but the yield of essential oil was lower (52% of hydrodistillate)[2]. Antiradical activity of essential oils obtained by both SC-CO_2 extraction and hydrodistillation was very similar but lower than that of synthetic antioxidants. The extracts isolated with non-polar solvents from the residues after SC-extraction have shown antiradical activity dependent on the selectivity of the previous extraction with SC-CO_2. Ethanolic extracts exhibited quite strong DPPH radical scavenging activity similar to BHT activity.

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PREN P-18 hpp

Extraction of Fennel (*Foeniculum vulgare* Mill.) Seeds with Supercritical CO_2: Comparison with Hydrodistillation

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Fennel (*Foeniculum vulgare* Mill.) is annual, biennial or perennial plant, depending on the variety, belonging to Apiaceae family and is native to the Mediterranean area. Fennel is known since antiquity as a medicinal and aromatic herb, commonly used to flavour liqueurs, breads, fishes, salads and cheeses.

The drug consists of the dry, ripe, whole cremocarps and mericarps (commonly called seeds), which contain 1-4 vol% of volatile oil whose major constituents are the phenylpropanoid derivative *trans*-anethole and fenchone. The oil is used as an ingredient of cosmetic and pharmaceutical products for its balsamic, cardiotonic, digestive, lactogogue and tonic properties.

Ground fennel (*Foeniculum vulgare* Mill.) seeds (particle diameter size of 0.9 mm), growing wild in Montenegro, were extracted with supercritical carbon dioxide (SC-CO_2) at a flow rate of 0.2 kg CO_2/h in order to determine yield, composition and organoleptic characteristics of extract. The extracts obtained were compared to fennel seed oil isolated by hydrodistillation.

The extracted material was characterized by gas chromatography using flame ionization and mas specrometic detection. In the SC-CO_2 extracts as well in the hydrodistilled oil the major compounds were *trans*-anethole (73.3-75.0%) and (62.0%), methyl chavicol (6.63-6.74%) and (4.90%), fenchone (8.57-11.4%) and (20.3%), respectively. A comparison between the hydrodistilled essential oil obtained by hydrodistillation and SC-CO_2 extracts showed that in latter technique some undesired higher molecular weight compounds (waxes) were co-extracted with essential oil. At extraction pressure of 100 bar with temperature varied from 40 to 57°C, it was found that, for the selected herb material, the optimal conditions of SC-CO_2 extraction (the high percentage of *trans*-anethole, with significant content of fenchone and reduced content of methyl chavicol and co-extracted cuticular waxes) are: pressure, 100 bar; temperature, 40°C; extraction time, 120 min.

The organoleptic tests confirmed that hydrodistilled oil possessed a less intense fennel seed aroma then extracts obtained by SC-CO_2.

PREN P-19 hpp

Enzyme-Catalyzed Reactions in Different Types of High-Prssure Enzymatic Reactors

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Enzymatic catalysis has gained considerable attention in recent years as an efficient tool for synthesis of natural products, pharmaceuticals, fine chemicals and food ingredients.
The realization that most enzymes can function perfectly well under nearly anhydrous conditions and, in addition, display a number of useful properties, e.g., highly enhanced stability and different selectivity, has dramatically widened the scope of their application to the organic synthesis. The use of monophasic organic solvents can be problematic because of toxicity, flammability, and increasing environmental concerns. Therefore, supercritical fluids (SFCs) have attracted much attention in recent years as an alternative to organic solvents for carrying out enzymatic reactions.
Most of the time enzymatic reactions are carried out in a classical enzyme batch reactor at controlled temperature. However the industry, in particular, favours continuous processes because they are more cost efficient and the reactors can be kept smaller in size. This reduction in size reduces both costs and safety problems of the high-pressure equipment needed for SC reactions.
Enzyme-catalyzed hydrolysis of carboxymethyl cellulose (CMC) was performed in two kinds of reactors; in a high-pressure batch stirred-tank reactor, operating at atmospheric pressure as well as in supercritical carbon dioxide (SC CO_2) and in a high-pressure tubular membrane reactor with the aim to find optimal reaction parameters for the reaction performance. In all cases cellulase from *Humicola insolens* was used as biocatalyst. In the high-pressure reactors aqueous SC CO_2 was used as a reaction medium.
Glucose production in the high-pressure batch stirred-tank reactor was faster at supercritical conditions than at atmospheric pressure. At atmospheric pressure 30 °C was found to be the optimal temperature while in SC CO_2 it was 32 °C. External diffusion limitations were prevented by proper mixing of the reaction mixture.
The application of tubular ceramic membranes in the high-pressure reaction system was studied on the model reaction of hydrolysis of CMC at atmospheric pressure and in SC CO_2. The reaction was catalyzed with on the surface of ceramic membrane covalent linked cellulase from *Humicola insolens*. Hydrolysis of CMC in SC CO_2 and atmospheric pressure was performed for a long-time period. Reaction carried out in SC CO_2 gave higher productivity than reaction, performed at atmospheric pressure. In both cases, the concentration of product slowly decreased with time.

PREN P-20 mci

Planning and Scheduling Leading to Optimal Loading the Systems of Resource Consumption in Case of Multipurpose Chemical Plants and Complex (Supply Chain Management)

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The presented work studies the problem of optimal control of multipurpose and multiproduct batch chemical plants. This problem has been great interest the last few years. This is due to the fact that while in resent past more attention was paid to the optimal functioning of a separate unit, without take in the consideration the complex interaction in the chain provider, transport, producer, distributor and user, in the present moment stable economic results can not be achieved without optimal collaboration of the elements of the whole chain. In this work the stress put on specific characteristic of the business in this stream, which consists in the process of uniting the multiplicity of similar multipurpose plants into corporations for which the important thing is reaching stable high economic results for the whole system, and not for the separately taken unit of it. The object of the research are the unions pharmaceutical plants for which to be observed all the above mention characteristics and the problems arising during there optimal functioning at the present stage of work.

The main goal which is achieved this work is the conception of a strategy for planning and scheduling of batch plants which consider the flexibility and the changes in the market. The main problem which is solved is the construction of a new system for planning and distribution of production portfolios for complicated production complexes, which aims to meet the requirements of the market at maximum profit for the whole system. The subject strategy for solving the problem is based on the decomposition approach. According to this approach the task of optimal control of multipurpose complexes is solved on two subsequent levels. On the first level the problem of determining the optimal production portfolios for each of the plants of the studied complex is solved. This task is formulated as a problem of a mixed integer stochastic programming in case of vector criteria for quality, including maximum profit and optimal loading the system of resource consumption of each of plants in the complex. The next level is connected with determining optimal production schedules for a implementing the production portfolios that were produced on the first level for each of the plants of the complex. This task is formulated as a problem of the mixed integer nonlinear programming in case of optimal loading of the systems of recourse consumption. For the solution of both problems are used the common approaches for modeling of the batch productions and complexes.

This work gives a short description of the conceived user oriented software for permitting the solution of the task for determining of the optimal production schedules of the work of separate plant during the implementation of a given production portfolio in case of optimal loading of the systems of resource consumption.

PREN P-21 ppi

Complex Process Analysis of Obtaining Non-Transparent SiO_2

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Complex analysis of process production of electro-fused non-transparent SiO_2 based on the temperature tracking of the reactor working space is shown in this paper. Experiments were carried out in the electro-resistance furnace. The melting was performed in the furnace chamber due to horizontally placed graphite electrode. The electrode is moved during the melting in order to obtain block of optimal capacity. Initial raw material was floated quartz sand with very high purity. The electrode is fed via monophase transformer of 50 kW, the current intensity of 1000-2000 A and the voltage of 12-15 V. The melting point, which is in the temperature interval of 1713-1850°C, was reached by gradually increasing voltage and current intensity. The furnace is kept in the mentioned temperature interval for several hours.

During the melting process, the temperature distribution on the reactor wall was quantified by the thermo-vision measurements as a source of visual information. Temperature was monitored and recorded by thermo-visual (IR) camera, type AGEMA 9000. The camera was significantly modified for the experiment. The camera realizes non-contact measurements of temperature in the range of –40-2000°C. ThV camera gave the information of surface temperature distribution. The process was considered as dynamic non-stationary process since many gaseous bubbles were produced as result of numerous accompanying reactions during the process. Based on the visual and thermal images, isotherms and temperature distribution in relation to time were also presented in the paper.

New approach to analyze non stationary process of single component melting with a movable heater as well as obtaining of information related to changes of surface temperature distribution in time are presented in this paper. On the basis of this temperature analysis, development of working model of time-temperature profile during the process could be realized, too. In the further research, the model could be used as the base of the process optimization.

PREN P-22 ppi

Mathematical Model of Moisture Homogenization in Clay-Water System

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Mathematical model proposed in this paper describes the homogenization of moisture in plastic raw materials. The model requires data of maximal initial in-homogeneity of moisture in the mixture clay–water and temperature dependences on the diffusion coefficient of water. The model was verified experimentally for the natural mineral montmorillonite. Good agreements were found between the model and experiment. The homogenization times and their temperature dependences were calculated for Na-, Ca- and natural montmorillonite. Appropriate information about water transfer in plastic raw materials (clay minerals) is preconditioned to the proper control and optimization of their processing technology. Quantitative description of the process based on mathematical modeling gives access to the range of necessary information in mixtures clay mineral-water. The homogenization of moisture was studied experimentally on test pieces prepared from natural kaolinite (the natural ionic form of kaolinite). Pieces with inhomogeneous initial moisture distributions were formed by extrusion of the mixture in the vacuum auger. The initial moisture distribution, mean moisture C, maximal difference C_{max} and the inhomogenity dimension were determined after forming for one series of samples. Samples of the other series were insulated and homogenized at temperature of 308 K. The moisture distribution and the maximal difference C_{max} were determined in the samples after 10 h. The diffusion coefficients of water in various ionic kaolinite types and their temperature dependences must be known to calculate and verify the model.

Assuming that the moisture transfer only occurs in the liquid state, the proposed model allows description of the homogenization of water in clay pastes and in soils. The time required homogenizing moisture in the temperature range $T \in (303\ K, 323\ K)$ increases in the sequence: Ca -kaolinite natural kaolinite Na-kaolinite.

PREN P-23 ppi

The Influence of Technological Variables on the Texture and Thermoisolation Properties of Aerogel SiO_2

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A new synthetic method for aerogel SiO_2 preparation was developed. In this process water glass is used as raw material and hydrogel conversion into aerogel is performed at atmospheric pressure. The influence of the basic technological variables of the different stages of the process: hydrogel synthesis, degree of water removing from hydrogel, sylilation degree, type and method of thermal treatment) on the texture properties: specific area - SA; bulk density –BD; porosity – P; mean pore diameter -d_p and thermo-isolation properties (coefficient of the thermal conductivity - *K*) were determined. It was found that changes in the technological parameters of the particular stages of the process, gave the possibility to change the texture properties of the SiO_2 aerogel relatively easy, within the following intervals of values:

SA= 200-2500m^2/g
P= 80-95%
d_p=5-32nm
BD= 50-300kg/m^3
K=0.01-0.08W/mK

The possibilities of SiO_2 aerogel applications in various industrial processes and benefits of energy reduction are discussed.

PREN P-24 ppi

Comparative Analyze of Drying Suspensions in the Fluidized Bed and Spouted Bed with Draft Tube

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Drying of suspensions is the very important process in the chemical, pharmaceutical and food processing industries. This unit operation is most energy consuming industrial operation. Although there are hundreds of variants actually used in drying, the research efforts over the world are associated with the development of more sophisticated systems. For slurries, spray dryers are usually preferred equipment to yield products of reasonable quality, but at the economics disadvantages of high investment and operating costs. Particularly, with respect to the drying of solutions, suspensions and pastes, the use of fluidized, spout-fluid, vibrofluidized and agitated beds of inert particles are very important alternative to the classic drying technologies.

An efficient drying system should meet several conditions: high values of heat and mass transfer coefficients, high contact area, high input of heat carrier gas, uniform temperature distribution over the drying chamber, the use of concentrated suspensions (as high as possible) in order to minimize water amount which should be evaporated and the use high inlet air temperature, as much as possible. However, many of these conditions are conflict each to other. The only drying concept that meets majority of the mentioned conditions is drying in an agitated bed of inert particles. Several systems (fluidized, spouted, spout-fluidized and different modifications) are at various stages of development.

The fluid-dynamic characteristics and evaporation capacities for spouted bed with a draft tube (DTSB) and fluidized bed (FB) dryers were compared in this paper. The influence of the drier type to drying capacity, fluid-dynamic parameters and quality of dried product was investigated. Drying experiments were carried out with suspensions of pesticide Cineb [$(CH_2\text{-}NH\text{-}CS_2)_2\text{-}Zn$], inorganic compound Calcium carbonate, organic compound Calcium stearate (only in DTSB), Copper hydroxide (only in FB) and pure water, used as a referential material. The presence of fluids (water or suspensions) increased the fluid-dynamic parameters over the values when only the inert particles were present in the beds. In general, the drying capacities of fluidized bed dryer are higher than those observed in the spouted bed with draft tube dryer under similar conditions, while the suspensions, which contain organic and biological compounds, can be dried in the spouted bed with a draft tube dryer, which is its important advantage.

PREN P-25 pin

An Experimentally Preconditioning Process for Extended Passivation of Alloyed Lead Anodes in Chemical Industry "Zorka", Šabac

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The preconditioning process consist in anodizing silver alloyed lead electrodes in the presence of a fluoride as an acitivating agent, produced thereby a thin PbF_2 interlayer, which further catalytically affects the transformation of the isolating $PbSO_4$ layer into the protecting β-PbO_2 layer. It laso hinders crystalization of α-PbO_2, which exhibits much lower protecting features. The protective layer in zinc electrowinning undergoes further transformation into a glassy deposit of mixed oxides β-PbO_2-MnO_2, that exhibits advanced protection properties, hinders production and precipitation of sludgy MnO_2 upon the substrate surface and extends the life-time of alloyed anode by three to four times. A plant-cell employing lead anode and cathodes has been operating at plant current density (600 A/m^2). An acid fluoride bath (43 g/dm^3) with sulphate (39 g/dm^3) is used. Operating temperature of preconditioning process for given ration and cell volume was 35°C. Hydrogen is generated at the cathodes, while ohygen evolution took place at the anode along with the gradual formation (8 to 12 hours) of a dense, thin and hard β-PbO_2 coating. Such a preconditioned anode has been operating with advanced passive features and used for zinc electrowinning in pilot-plant Chemical Industry "Zorka", Šabac, so that the resulting content of lead in produced zinc deposits was lowered down to between 2 and 4 ppm. Thus zinc of higher purity for application in cathodic protection has been produced straight in the electrolytic process with no common refining procedure.
A view of plant equipment in industrial production of zinc electrowinning with preconditioning anodes is shown in Fig.1.



Fig. 1. A view of plant equipment in industrial production of zinc electrowinning with preconditioning anodes

The effect of lead on zinc deposit morphology and features has also been considered and pointed out in the work. A detailed display both of plant equipment for preconditioning and the procedure of anodizing passivation has been given and discussed.

PREN P-26 pin

Flow Field Characteristics of Modified Flat-Blade Mixing Impellers

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The flow field generated by flat-blade mixing impellers with modified blades is studied. The work is focused on designs with specific alterations – slots and flips. Three types of flat-blade geometry are examined – a general type of a trapezoidal flat blade, termed TFB, a shielded TFB, i.e. STFB, and extended TFB, i.e. ETFB with the largest 'wall-to-fluid' contact area. Some blades' parts are inclined at 45 degrees to the horizontal plane. A vessel of 0.4 m diameter is used. Flow differences have been sought in order to determine the correspondence between shape performance and impeller application requirements. The problem was solved by CFD using FLUENT commercial software for fluid dynamic analysis. A RANS 'k-ε' model was employed. The flow field parameters, such as velocity, strain rate, turbulence intensity and static pressure are determined both for the impeller and the bulk. The parameters relevant to the different shapes are compared. The modified flat blades are found to exhibit higher turbulence intensity than the general type of a blade. On the other hand, the area differences are directed to highly viscous systems. The results are used in a discussion of possible application area.

PREN P-27 pin

A Mathematical Model of the Ion-Exchange Process in a Fluidized Bed Air-Lift Apparatus with External Liquid Recirculation

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CANCELED

Air-lift apparatus with liquid external recirculation, with fixed or fluidized bed of inert or active solid particles, represents an efficient [illegible] having numerous applications in process as well as in environmental engineering.

In this paper, based on the experimental data for the ion-exchange process (cationic resin in H^+ form – diluted aqueous solution of NaOH) in an air-lift apparatus, with three-phase fluidized bed, a mathematical model was elaborated that shows the variation of the non-dimensional concentration, $C_L/C_{L,0}$, as well as that of the degree of use of the ion-exchange capacity, U, as a function of the operation period, *t,* for different values of the supe rficial gas velocity, w_G, and of the solid mass loading of the column, q_S.

The physical model used presents the following simplifying hypotheses:

- quasihomogeneous structure for the resin particle;
- mass transfer realized through ionic diffusion, accompanied by irreversible, instantaneous chemical reaction;
- ionic diffusion expressed quantitatively through Nernst equation;
- interface resistance to mass transfer is negligible;
- finite volume and perfect mixing of solution.
- Solving of the system of equations and restrictions for the binary ion-exchange process resulted in the following relations:

$$\frac{C_L}{C_{L,0}} = exp\left\{-7\cdot 10^{-3}\; q_S\, t\left[\frac{1}{\left(1-1.32\, w_G^{\,0.71}\right)^2}+3.676\right]^{0.41}\right\} \qquad (1)$$

$$U = 4.26-\left(1-C_L/C_{L,0}\right)/q_S \qquad (2)$$

The values obtained with relations (1) and (2) have an error of less than 10% when compared to experimental data for the domain of variation of operation parameters:

$w_G=(0.0082\div 0.0164)\ m/s,\ q_S=(2.45\div 9.82)\%wt$ and $t\le 180s$

Relationships (1) and (2) can be used for the process design of an air-lift apparatus in fluidized bed with liquid external recirculation, for the ion-exchange process of residual waters with low NaOH content.

Monitoring Traces of Corrosive Ions in the Water-Steam Cycle in the Power Plants

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Introduction

One of the primary concerns of all power plants is to ensure high-purity of water. It is essential to monitor the presence and movement of ionic impurities in various water samples such as feed water, boiler water, steam, and cooling water. The presence of corrosive ionic species in the process water streams, even at low-μg/l levels, has negative corrosion effects. The minimization of the concentrations of corrosive ions in the boiler feed water and in steam reduces the corrosion damages to various system components. The measurement and control of ionic impurities can provide valuable information regarding the source of contamination, the likely rates of contaminant build-up, and probable rates of corrosion.

Experimental

In this work Ion Chromatography (IC) and Atomic Absorption Spectrometry with Electrothermal Atomisation (Graphite Furnace AAS, GF-AAS) as sensitive methods are investigated and applied for determination and control of corrosive ions in the water-steam samples in thermal power plant "Nikola Tesla" (TPPNT). Anions, cations, transition metals were monitored in raw water, demineralizer influent/effluent, process steam, boiler feed water, boiler blow down water and high and low pressure steam condensate.

Results and conclusion

In this paper, an ion chromatographic method was developed for the determination of inorganic mineral anions and cations at trace levels in water samples. In this method, samples were injected using a high-volume direct injection technique (large sample loop volume up to 1000 μl). The method detection limits for analyte ions ranged from 70 to 200 ng/l. The relative standard deviations (RSD) of peak area and peak height of analyte ions were ranged from 0.1 to 5.0 %. Heavy metals, that is copper and iron ions have been analysed by the GF-AAS method. The detection limit was the most serious problem while determining these ions, due to rather low concentrations of these ions in samples. Concentrating technique by method of standard additive was applied. RSD for target ions for five replicates (n=5) were less than 5 %. Overall analysis was done of the series of representative samples from TPPNT, sampled in different plant operation modes (normal operation phases and block movements). Optimum number of ions for analysis was chosen, which directly indicate required water quality, specifically: cations (Na^+, Ca^{2+}, Mg^{2+}, Cu^{2+}, Fe^{3+}) and anions (F^-, Cl^-, PO_4^{3-}, SO_4^{2-}). Obtained results proved that in the phase of normal operation mode almost all ions had been under allowed limits, with the exception of calcium the content of which increased in all samples. In the phase of block moving, the ion concentrations increased: Na^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}. Particularly high concentrations were recorded for Ca^{2+}-ion in all samples, while Na^+, Cl^- and SO_4^{2-}- ions were mostly represented in the samples of steam condensate.

Scientific contribution of this investigation is reflected in developing and establishing the method to determine ion traces; practical contribution lies in finding solution to problems of ion species monitoring, in particular for natrium and chloride-ions which represent indicators of corrosive processes in thermal power plants.

PREN P-29 poc

Singular System Theory Applied to the Evaporator Dynamics of a Once - Through Subcritical Steam Generator: The Differential Discrete Mathematical Modelling Based Approach

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The once – through subcritical steam generator considered in this analysis is a typical one of those used in gas-cooled nuclear power plants. It contains a large number of differently located metal tubes. Some of them can be treated as counterflow and some as crossflow heat exchangers. In this paper the latter case is of particular interest. In the focus of this investigation is the classical steam generator evaporator with time – varying boundaries. In that sense, we disscuss displacements of evaporation beginning and ending coordinate within the formal construction boundaries of evaporator. Hot gas (primary coolant) is circulated in such manner that crosses perpendicularly over tubes surfaces, transferring thermal energy from the primary coolant to the secondary coolant (homogenous steam vapour) through the tube walls.
The evaporator section contains a water-steam mixture. To describe its dynamics two cases may be considered. In the case of complete evaporation, saturated water enters the evaporator, enters the evaporator tube and leaves it as a saturated steam The exchange of thermal energy results in the cooling of the hot gas and production of saturated steam on the tube side. Simulation results have been presented and compared with the real behavior of evaporator dynamics.
Here, the idea of physical discretatization *is extended* to the continuous case of three-section model of whole once- through steam generator with time – varying phase boundaries, first time presented in *Ray*, *Bowman* (1976).
Singular systems are systems covered by a mixture of differential and algebraic equations and are of particular significance in studying of feedback control systems.
Theirs description in state space is as follows:

$$E\dot{\mathbf{x}}(t) = A\mathbf{x}(t) + B\mathbf{u}(t), \;\; \mathbf{x}(0) = \mathbf{x}_0 ,$$

with matrix E necessarily singular.
An intensive investigation of this class of systems begun in 1974.
The problems of existence, uniqueness, consistent initial conditions and impulse behavior are the fundamental questions which must be solved in prior to any investigation of systems dynamics.
The once through model has been derived in the form of model that corresponds to the class of Linear Singular Systems.
An adequate analysis has been performed in order to calculate significance system transient performances.

PREN P-30 poc

Exponential Stability of Dicrete Time Delay Technological Systems with Nonlinear Perturbations

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In industrial processes, time-delays often occur in the transmission of information or material between different parts of a system. Chemical processing systems, transportation systems, communication systems, and power systems are typical examples of time-delay systems. Since the presence of time-delay often causes serious deterioration on stability and performance of the system, considerable research has been devoted to control problems of time-delay systems.
It is obvious that there are much more published papers in the area of continuous than discrete time delay systems. This is mainly due to the fact that such systems can be transformed into augmented systems without delay. This augmentation of the systems is, however, inappropriate for systems with unknown delays or systems with time-varying delays.
In practice, to satisfy the performance specification and to have a good transient response of the system, the controlled system is often designed to possess a stability degree. If the controlled system has a stability degree α, we say that the system is exponentially stable.
We consider the following unforced discrete time-delay system with nonlinear perturbations

$$x(k+1)=\sum_{j=0}^{N}A_j x(k-h_j)+\sum_{j=0}^{M}f_j\left(x\left(k-h_j\right),k\right) \qquad (1)$$

where $x(k)\in\mathbb{R}^n$ - state vector,

h_j - time delay,

$A_j\in\mathbb{R}^{n\times n}$, $0\le j\le N$ - real square matrices and

$f_j\in\mathbb{R}^n\times\mathbb{R}\to\mathbb{R}^n$ - nonlinear perturbation, which satisfy condition

$\left\|f_j\left(x\left(k-h_j\right),k\right)\right\|\le b_j\left\|x_j\left(k-h_j\right)\right\|$.

The main results of the paper are expressed by next theorem.

***Theorem* 1**. If the condition

$$\alpha\|A_0\|+\sqrt{N\sum_{j=1}^{N}\alpha^{2(h_j+1)}\left\|A_j{}^T A_j\right\|}+\sqrt{(M+1)\sum_{j=0}^{M}\alpha^{2(h_j+1)}b_j^2}<1$$

is satisfied, then the system (1) is exponential stable with stability degree α.
The proof of this theorem is based on Lyapunov's second method.
Derived results present new delay-independent sufficient condition for the exponential stability of discrete time delay systems with nonlinear perturbations.
A numerical example has been working out to show the applicability of results derived.

PREN P-31 poc

Asymptotic Stability of Linear Discrete Time Delay Systems Using Lyapunov Second Method

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Time-delays are important phenomena in industrial processes, economical and biological systems. For instance, they appear as transportation and communication lags and also arise as feedback delays in control loops. Because time-delays have a major influence on the stability of such dynamical systems, it is important to include them in the mathematical description, leading to a modeling with delay differential or difference equations.
In this paper we consider the stability of discrete systems described by following difference equation:

$$x(k+1) = A_0 x(k) + A_1 x(k-h) \tag{1}$$

with an associated function of initial state

$$x(\theta) = \psi(\theta),\ \theta \in \{-h, -h+1, \ldots, 0\}. \tag{2}$$

where $x(k) \in \mathbb{R}^n$ - state vector, h - time delay, $A_j \in \mathbb{R}^{n\times n}$, $0 \le j \le 1$ - real square matrices.
The main results of the paper are expressed by next theorem.

Theorem 1. If for any given matrix $Q = Q^T > 0$ there exists matrix $P = P^T > 0$ such that the following matrix equation is fulfilled

$$\left(1 + \frac{\|A_1\|_2}{\|A_0\|_2}\right) A_0^T P A_0 + \left(1 + \frac{\|A_0\|_2}{\|A_1\|_2}\right) A_1^T P A_1 - P = -Q, \tag{3}$$

then, system (1) is asymptotically stable.
The proof of this theorem is based on Lyapunov's second method.
Derived results present new delay-independent sufficient condition for the asymptotic stability of discrete time delay systems. This result is less conservative than those in existing literature.
A numerical example has been working out to show the applicability of results derived.

PREN P-32 psd

Alternative Approaches of Increasing Low Density Polyethylene Plant Capacity: Process Simulation Analyses

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Field of polyethylene production is a complex one characterized by very wide range of different products types, based on different manufacturing processes. In last few decades polyethylene production is constantly being increased, making polyethylene the major tonnage plastics material worldwide. Growing demand for different types of polyethylene products in world market require from polyethylene manufactures to consider increasing their production. In principle, production development can be based on two options: building new plant or modifying the existent one by increasing its capacity. Presented dilemma is present in HIP Petrohemija, Pancevo, one of the biggest petrochemicals producers in South Eastern Europe. After terminating of PVC production in 1999 the company has decided to increase the production capacities of low density and high density polyethylene plants. Described goal is vital, because the factory has huge surplus in ethylene plant production which should be prefabricated at the same site in mentioned polymers.

In this paper alternative approaches of increasing capacity of existing low density polyethylene production plant for will be considered. In the first part of the paper critical parameters of process and plant have been analyzed in order of future design alternatives definition. Result is establishment and description of two alternative approaches related to the future process design. Both approaches require addition of new reactor. First approach considers sequent order between new and existing reactor and the second one approach considers that reactors will be in parallel positions.

Result of comparative process simulation analyses for two process design alternatives has been presented in the second part of the paper. The advantages and disadvantages of both approaches have been discussed. In conclusion, a comprehensive proposal related to the future increasing of LDPE plant capacity in Pancevo has been presented.

PREN P-33 fst

Microbiological Fouling of Ion Exchange Resins

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CANCELED

A general problem for industrial applications of ion exchange resins is the tendency for bacteria, fungi, viruses and algae to be attached to them. The ion exchange resins can also act as supportfor microbiological growth. In certain cases, biological growth can be so extreme that it interferes with flow patterns resulting in channelling and pressure drop across the resin bed. In food applications the bacterial growth is unacceptable because of hygienic reason. Understanding of initial microbial adhesive interactions is crucial for control of bacterial fouling. In this research work the two type of anion exchange resins were infectioned by gram positive *Bacillus cereus* and gram negative *Escherichia coli*. Bacterial adhesion experiments were conducted by batchwise procedure at the different ionic strength of surrounded liquid media. Bacteria cell surface and resins were examined by zeta potential measurements. In addition,hydrophobicity of bacterial surface was examined by adhesion to hydrocarbon method (MATH). Results showed that deposition of bacteria mostly depended on the bacterial cell hydrophobicity and ionic strength of electrolyte. Moderately hydrophobic *Bacillus cereus* had more attraction to resins bead than extremely hydrophilic *Escherichia coli*. Degree of adsorption of bacteria onto anion exchange resin was function of ionic strength of surrounded media. Bacterial adhesion decreased rapidly with the increase of electrolyte concentration

Section

Polymers and Interfacial Phenomena

PIPH

PIPH X-NN yyy

X = KN – Keynote lecture
O – Oral presentation
P – Poster presentation

NN = Number

yyy = Topic:
icp - Interfacial and Colloidal Phenomena
pol - Polymers

Development of New Polymer Electrolytes for High Temperature Fuel Cell Applications

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Polymer electrolyte membrane fuel cell (PEMFC) technology has been receiving increased attention due to its high energy efficiency and environmentally friendly nature. Among the different technologies developed, PEMFC which operate at temperatures above 150 ^{o}C show certain advantages, which result in improvement of the overall performance and simplification of the system. The polymer electrolyte membranes in high temperature PEMFCs must enable proton conduction and at the same time have mechanical, thermal and oxidative stability at the operational conditions.

The state of art material used in high temperature PEMFCs is polybenzimidazole (PBI), which is widely studied after doping with various strong acids. In the case of phosphoric acid, PBI exhibits high acid uptake, resulting in highly conductive materials. However PBI shows moderate mechanical properties, especially in cases where low molecular weight fractions are included. Thus research effort has been devoted to improve its mechanical properties. Other drawbacks, such as the reduced oxidative stability, limited availability and high cost of PBI have stimulated an increasing search effort for development of alternative polymeric structures. An ideal polymer electrolyte should exhibit thermal stability, high acid uptake and ionic conductivity, as well as high mechanical and oxidative stability and low cost.

Among recently developed polymer electrolyte membranes, our group reported the synthesis of aromatic polyethers containing polar pyridine units in the main chain[1,2]. These new materials have been used as polymer blends in combination with PBI or in PBI free systems that have been thoroughly characterized in respect to the critical parameters for their application in Fuel Cells. Furthermore, single cells based on MEA's constructed from these new materials have been tested at temperatures higher than 130°C.

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PIPH O-01 icp

The Effect of Salt on the Interfacial Tension of Aqueous Biopolymer-Surfactant Mixtures

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The effect of sodium chloride on the interfacial tension (σ) of aqueous pullulan and sodium dodecyl sulphate (SDS) phase separated systems was investigated. The interfacial tension of mixtures of varied pullulan and SDS concentrations was measured for the NaCl concentrations of 0.25 M and 0.5 M. An increase in the interfacial tension was observed with increasing pullulan and SDS concentrations. A small increase was also observed as the NaCl concentration was increased. In all systems the measured interfacial tension was of the order of μN/m in agreement with comparable aqueous polymer-polymer phase separated mixtures. Interfacial tension σ plotted against the difference in pullulan and SDS concentrations between the phases (ΔC_{Pul} and ΔC_{SDS}) and also the tie-line length (TLL) on a log-log scale was found to yield straight lines for both salt concentrations.

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Kinetics Study of Bulk Free-Radical Dimethyl Itaconate Polymerization with Cage-Complex Initiation Mechanism

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During the last few years, interest in the properties and applications of monoesters and diesters derived from itaconic acid has increased, not only because itaconic acid is obtained by a fermentation process but also as a consequence of great variety of polymers that can be prepared owing to the existence of two lateral esterifiable groups in the monomers. Dialkyl itaconate esters (DRIs) are radically polymerized at moderate rates to yield polymers of high molecular weight in spite of their two bulky substituents. The overall rate of polymerization of dimethyl itaconate (DMI) is reported to be proportional to the square root of initiation concentration , whereas the kinetic order with respect to monomer concentration is higher then unity.

This kinetics order could be incorporated into a kinetics scheme by the empirical setting of initiation efficiency proportional to the monomer concentration. Although such an empirical model did provide a reasonable fit to experimental monomer conversion data, it did not provide mechanistic insights into the initiation process.

In this study, the free-radical bulk polymerization of dimethyl itaconate (DMI) is analyzed with the objective of interpreting the kinetics of the process through model that incorporates the hybrid cage-complex initiation mechanism. The proposed kinetic model, describes the experimental polymerization data, which reveal an overall polymerization kinetics order ranging from 1 to 3/2 with respect to monomer conversion. The excellent fits to the experimental data (over a wide range of conditions) suggest that the proposed initiation mechanism provides an adequate description of polymerization kinetics.

Mathematical Modeling of Free Radical Polymerization by Monte Carlo Method

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Introduction
Monte Carlo technique, due to complexity of Moments method[1,2], is used to simulate polymerization reaction with long chain branching [3]. In Monte Carlo method, instead of total reaction volume a selected volume is used to modeling of reaction.

Theoretical
The free radical solution polymerization with long chain branching governed by the following stage of elementary reactions [2]: initiation, propagation, terminal double bond polymerization, termination and chain transfer to polymer, monomer and solvent. For simulation, the probability of reactions which selected radical chain can be contributed in them, is calculated by division of occurrence reaction into all of the reactions that can be happened. Then a random number between 0 and 1 is generated and by comparing the random number and selection probability of reactions, it will be found that which reaction will be occurred[4]. After each reaction, the new concentration of species should be determined and then simulation algorithm will be repeated.

Results and Discussion
By Monte Carlo method very detailed information such as molecular weight distribution and average molecular weight are obtained. The validity of Monte Carlo modeling is justified by comparing the results from well-established method as shown branching density in figure1.

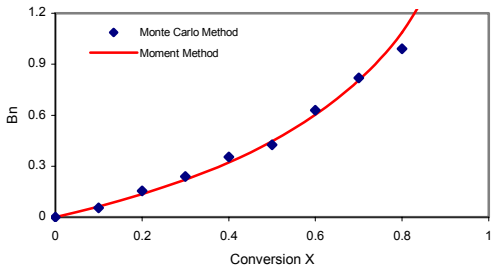


Figure 1. Number average branching density from Monte Carlo modeling and method of Moments [1]

Conclusion
In Monte Carlo simulation method only by the mean of random number generation and level of probability without any need to solve moment equations, very detailed information about the structure and properties of polymer are determined.

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Electron and Momentum Transfer Phenomena at Developed Deformable and Liquid/Liquid Interfaces

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A new idea, using deterministic approach, has been applied for the elucidation of the electron and momentum transfer phenomena at, both rigid and deformable interfaces in finely (micro, nano, atto) dispersed systems. The behavior of e.g., liquid/liquid interfaces (emulsions and double emulsions) is based on three forms of "instabilities"; these are rigid, elastic, and plastic. The events are understood as interactions between the internal (immanent) and external (incident) periodical physical fields. Since the events at the interfaces of finely dispersed systems have to be considered at the molecular, atomic, and/or entities level it is inevitable to introduce the electron transfer beside the classical heat, mass, and momentum transfer commonly used in chemical engineering. Therefore, an entity can be defined as the smallest indivisible element of matter that is related to the particular transfer phenomena. Hence, the entity can be either differential element of mass/demon, ion, phonon as quanta of acoustic energy, infon as quanta of information, photon, and electron. A number of theories that describe the behavior of liquid/liquid interfaces have been developed and applied to various dispersed systems e.g., Stokes, Reiner-Rivelin, Ericksen, Einstein, Smoluchowski, Kinch. A theory of electroviscoelasticity, based on a new constitutive model of liquids describes the behavior of electrified liquid/liquid interfaces in finely dispersed systems considering droplet or droplet-film structure (collective of particles) as a macroscopic system with internal structure determined by the way the molecules (ions) are tuned (structured) into the primary components of a cluster configuration. How the tuning occurs depends on the physical fields involved, both potential (elastic forces) and nonpotential (resistance forces). All these microelements of the primary structure can be considered as electromechanical oscillators assembled into groups, so the excitation by an external physical field may cause oscillations at the resonant/characteristic frequency of the system itself (coupling at the characteristic frequency).Up to day, there are three possible mathematical formalisms discussed related to the theory of electroviscoelasticity. The first is tension tensor model, where the normal and tangential forces are considered, only in mathematical formalism, regardless to their origin (mechanical and/or electrical). The second is Van der Pol derivative model. Finally, the third model comprise an effort to generalize the previous Van der Pol differential equations, both, linear and nonlinear; i.e., the ordinary time derivatives and integrals are now replaced by corresponding fractional-order time derivatives and integrals of order $p<1$. Both, the presented model and theory can facilitate the understanding of entrainment problems in solvent extraction, developed interfaces in colloid and interface science, chemical and biological sensors, electro analytical methods, biology/biomedicine (hematology, genetics and electroneurophysiology). Also, this knowledge may be implemented in studies of structure; interface barriers/symmetries, -surface (bilipid membrane cells, free bubbles of surfactants, Langmuir Blodgett films), -line (genes, liquid crystals, microtubules), -point (fulerenes, micro-emulsions), and -overall (dry foams, polymer elastic and rigid foams**).**

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A.M. Spasic and J.P. Hsu (Eds.) ***Finely Dispersed Particles: Micro-, Nano-, and Atto-Engineering***, Marcel Dekker/CRC/Taylor and Francis Group, LLC, Boca Raton, Florida (In Press, To appear 2005).

Emulsion Creaming Process: Fractal Dimension Measurement

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Chaotic dynamics may be said to have started with the work of French mathematician Henri Poincare at about the turn of the 19th century. Poincare's motivation was partly provided by the problem of the orbits of three celestial bodies experiencing mutual gravitational attraction. Considering the behavior of orbits arising from sets of initial points, Poincare was able to show that very complicated, now called chaotic, orbits were possible. In spite of this work, however, the possibility of chaos in real physical systems was not widely appreciated. Reasons for this were the first that a mathematical papers were difficult to read for workers in other fields, and the second that the theorems proven were often not strong enough to convince researchers in other fields. The situation has now changed drastically, and much of the credit for this can be prescribed to the extensive numerical solution of dynamical systems using digital computers. Using such solutions, the chaotic character of the time evolutions in situations of practical importance has become dramatically clear. Furthermore, the complexity of the dynamics cannot be blamed on unknown extraneous experimental effects, as might be the case when dealing with an actual physical system**.** In this paper the emulsion creaming was analyzed in purpose to quantify the effects of additives on the creaming process. As the experimental set up the modified Sommerer and Otto cell equiped with the CCD camera was used. The standard emulsion was used and the influence of the four additives (surface active materials, SAM) was analyzed by the fractal dimension measurements. The flow is periodically pulsed, and fluid instabilities lead to strong azimuthally dependence of the flow velocity. For the calculations of the fractal dimensions D_i, the box

$$D_i = \lim_{\varepsilon \to 0} \frac{\sum_{\varepsilon=1}^{N_\varepsilon} i \ln i}{\ln \varepsilon}$$

counting method, was used. The resulting droplets distribution was determined by taking the intensity, i, of the light measured in a given camera pixel as proportional to the number of oil drops. Using boxes of varying size ϵ, the numerator was then plotted versus the denominator. The result was well fitted by a straight line down to the smallest accessible value of ϵ, and Di was then estimated as the slope of this line.

For this experimental set Di was estimated to be from 1.538 to 1.734, regarding to the used SAM. Experiments presents the correaltion of SAM type and mesured fractal dimendsion. Another conclusion could withdrawn from these experiments and that is that floating droplets initially distributed on the surface are compressed and tend toward some point as the time increases, and that point is an attractor for the dynamical system. This means that the atrctor could be seen, and could be used as the measure of system stabilty. At this point it is important to note, that with slightly more complicated time-dependent flows, the atractor for this dynamical system could be fractal. Here, the phase space is the set of actual physical coordinates of surface particles. Consequently, the fractal in this case is a real physical object and is, accessible to direct visual inspection.

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Inffluence of Organic Dispersants on Rheological Parameters of Suspensions

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Rheological parameters of cement suspensions and suspensions with mineral fillers have been studied for a long time. The precision and reproducibility of measurements depend on number variables (on the water/solid ratio, type of additives or parameters of cement and mixing process). The variation in the obtained values of viscosity of cement suspensions can be caused by the rate of chemical reactions (hydration) and segregation of phases if the water/solid ratio is high [1 to 3]. On the other hand, plastic flow in the shear gap might be not sufficient or interrupted if this ratio is low. Nevertheless, shearing tests are also connected with the destruction of the formed structure [4]. It seems that there are still a number of questions which must be dealt with, in spite of concentrated effort in this area of research.

In this work, rheological parameters of suspensions (yield point, shear stress, water/solid ratio, distance between particles) with calcium carbonate filler modified with different doses of Gecedral Fluid 10.1 (PC), Melment (F10X), naphthalene-formaldehyde condensate (NF) and ligninsulfonate (LS) type of additive were tested by a new alternative method of centrifugation [5]. The aim of this method is to minimize influences mentioned above. Calcium carbonate was used to avoid the influence of chemical reactions in the suspensions. The sorption of organic molecules of additives on $CaCO_3$ particles was also followed.

It was found that affinity (sorption) of organic molecules of dispersants to the surface of solid particles decreases in the order: PC, LS, NF, F10X. The rheological effectiveness of additives is in order: PC>MF>NF>LS. The results indicate that repulsive forces between the charged particles increase mainly when the critical micellar concentration of organic molecules in the interparticle solution of suspension is reached. Moreover, yield point, shear stress, water/solid ratio and distance between particles depend on the dose of additive and on the magnitude of centrifugal forces. It seems that the method of centrifugation could be used for determination of dispersing effectiveness of additives or rheological parameters of suspensions in general.

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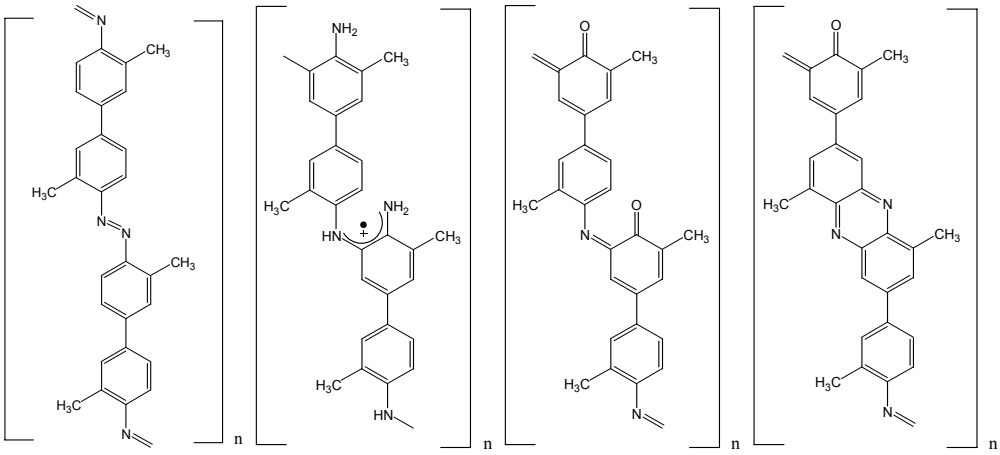
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Oxidative Chemical Polymerization of 3,3'-Dimethyl-Biphenyl-4,4'-Diamine

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Novel homopolymeric materials were synthesized by oxidative chemical polymerization of 3,3'-dimethyl-biphenyl-4,4'-diamine (*o*-tolidine) using ammonium peroxodisulfate as an oxidant, in acidic aqueous solutions at room temperature. Poly(*o*-tolidines) obtained using various oxidant/monomer molar ratio in range 1.25 to 3.0 were characterized by elemental analysis, gel-permeation chromatography, infrared spectroscopy and conductivity measurements. Elemental analysis revealed the oxygen incorporation in the macromolecular structure. This oxygen content was explained by hydrolysis of intermediary formed *o*-iminoquinonoide. New substitution patterns shown by IR spectroscopic analysis combined with MNDO-PM3 semi-empirical quantum mechanical calculations revealed N─N and N─C_5 coupling reactions as dominant. Quinonoid and benzenoid structures were observed by IR spectroscopy. Influence of oxidant/monomer ratio on phenazine structural unit formation was examined.



N─N dimer unit azo form | *N─C_5 dimer unit polaronic form* | *N─C_5 dimer unit hydrolysed o-iminoquinonoid form* | *N─C_5 dimer unit phenazine form*

Polyurethane Rigid Foam Production Through Chemical Recycling of Polyester Waste Material

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Chemical recycling of polyester-fibre production waste (oligoestercondensate) was performed by the means of transesterification and further processing of the synthesised polyesterpolyols into polyurethane rigid foam. Transesterification was done using diethyleneglycol and dipropyleneglycol in a temperature range of 200-230 ^{o}C during a period of 2-8 h. Synthesised specimens were purified from excess glycol and characterised concerning their hydroxyl number, acid number, viscosity and molecular mass (osmommetrically). The specimens with appropriate hydroxyl number and viscosity, considering the application, were chosen to be processed further into polyurethane rigid foam. For the production of polyurethanes were used: methylene-tris-(4-phenyl-isocyanate) as an isocyanate component, combination of dimethylethanolamine and triazine as catalysts and water as a coreactant. The produced polyurethane rigid foams were examined with respect upon their dimensional stability at 110 ^{o}C and 130 ^{o}C. Some of the foams demonstrated good results and displayed acceptable dimensional stability on 130 ^{o}C.

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Poly(Acrylic Acid) Hydrogels Synthesized Using Microwave Irradiation

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Hydrogels are three-dimensional crosslinked polymeric structures that are able to swell in an aqueous environment. Due to characteristic properties such as swellability in water, hydrophilicity, biocompatibility, and lack of toxicity, hydrogels have been utilized in a wide range of biological, medical, pharmaceutical and environmental applications.

In this investigation hydrogels of crosslinked poly(acrylic acid) were synthesized in the microwave field by the simultaneous free radical polymerization and crosslinking of acrylic acid in the presence of a multifunctional crosslinker N,N'-methylenebisacrylamide (NMBA) and using VA-044 as the initiator. Reactions were carried out in a homogeneous microwave field of 2.45 GHz frequency of CEM microwave focused reactor.

Kinetics of the isothermal preparation of poly(acrylic acid) hydrogels at temperatures of 303, 3130 and 323 K in the microwave field of 2.45 GHz frequency with input powers from 30W to 300W and reaction times from 2 to 30 minutes was investigated. Kinetics curves of hydrogel yield were determined. Significant increase of the investigated process under the influence of microwave irradiation in comparison to the conventional process is recognized. Based on the changes of determined rates constants for the investigated process of simultaneous free radical polymerization of acrylic acid and crosslinking of poly(acrylic acid) with temperature under the influence of microwaves, kinetic parameters of this process under the influence of microwaves were determined.

Mechanism of the investigated simultaneous polymerization of acrylic acid and crosslinking of poly(acrylic acid) under the influence of microwaves was investigated.

Optimization of a Polymerization Process Using Genetic Algorithms and Neutral Networks

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The optimization of the free-radical polymerization is multiobjective in nature, since it normally has several objectives (often contradictory) that must be satisfied at the same time. One of the most important problems related to this type of optimization are the combination of the proposed objectives into a scalar or vectorial function, the development of the model included in the optimization procedure, and the choice of the solving method - classical computer-aided optimization techniques or evolutionary algorithms. We explored the feasibility of an optimization control scheme for free radical polymerization of methyl methacrylate using, comparatively, different scalar objective functions and different solving methods: a traditional technique based on sequential quadratic programming (SQP), a simple genetic algorithm (GA) and a hybrid method that combines the first two approaches. It seems that the GA provides very good initial starting point for SQP. The objective functions which are minimized include the total reaction time and the polydispersity index and, simultaneously, end-point constraints to attain desired values of the monomer conversion and the number average polymerization degree. The control variables used are the temperature in the reactor consisting in two or more isothermal steps, and the initial concentration of the initiator. The hybrid method represents an improved technique for multiobjective optimization of these complex processes.

In the above methods, we have included the phenomenological model of free radical polymerization of methyl methacrylate (MMA) associated with gel and glass effects and achieved in a batch bulk process. Developing complete mechanistic models for polymerization reactors is not an easy task. The difficulties lie with the complex reactions occurring simultaneously inside the reactor, the large number of kinetic parameters which are usually not easy to determine, as well as the poor understanding of chemical and physical phenomena for mixtures involving polymers. To overcome the difficulties in the mechanistic modeling of polymerization processes, data-based empirical models can be used. Neural networks possess the ability to learn the trends of the process without actually modeling the physical and chemical laws that govern the system. Therefore, they are useful for modeling complex nonlinear processes where process understanding is limited.

Feed-forward neural networks with reaction conditions (temperature and initiator concentration) as inputs, and conversion and polymerization degrees as outputs were developed for MMA polymerization. These models were included in the optimization procedure carried out with different solving methods (SQP, GA, HM). It is interesting to evaluate a method that combines two instruments of artificial intelligence – neural network for modeling and genetic algorithm for optimization. Finally, a hybrid model was used with genetic algorithm. The hybrid model contains a simplified mechanistic model that does not consider the gel and glass effects of the free radical polymerization and neural networks, built to characterize these effects, which are one of the most difficult parts of polymerization modeling. Optimal reactor temperature control policies are then calculated using the hybrid neural network model.

The results of all optimization methods were compared from two points of view: accuracy of the results and simplicity in use.

The Effect of Starting Components on Some Characteristics of Flexible Polyurethane Foam

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Flexible polyurethane foams were synthesised using: polyol (PO), toluene-diisocyanate (TDI), catalyst system comprising organic-metallic compound and tertiary amine, water, surfactant and filler ($CaCO_3$). Investigation concerning the influence of the amount of TDI, water and filler on duration of the synthesis and on some basic characteristics (density, tensile strength, elongation at break, splitting, compression module of elasticity and water absorption) of the synthesised polyurethane flexible foams was performed.

Increase of the amount of water and TDI in the reaction system caused reduction in duration of the synthesis and density of the synthesised polyurethane flexible foams.

Optimal physical-mechanical properties were displayed by polyurethane flexible foams with density of 25 and 30 kg/m^3.

Addition of filler in amount of 5 till 10% (based on the amount of PO) contributed in improvement of certain properties of the synthesised polyurethane flexible foams.

Considering the experimental results, a correlation between the amount of certain components in the system and characteristics of the synthesised polyurethane flexible foams was withdrawn.

Investigation of the Buffer Diffusion into HEMA Based Hydrogels

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In the modern medicine, polymeric materials have been used for a wide range of applications because much of them are biocompatible with blood, tissues, cells, i.e., the human body. Hydrogels agree well with the actual tendencies, directed towards the materials that are assimilated by the organism producing minimum collateral effects.

Gels based on 2-hydroxyethyl methacrylate and small amount of itaconic acid were prepared by free-radical polymerization in aqueous solution at 60 ^{o}C using potassium persulfate as initiator and ethylene glycol dimethacrylate as the cross-linking agent. The dynamic and equilibrium swelling properties of all networks were studied as a function of pH in buffer solutions of pH 2.20, 4.50 and pH 6.80. In order to study the diffusion process buffers with different pH values, corresponding to those in physiological liquids, were used in swelling experiments, conducted for short and longer times.

For the early stages of the swelling process, when the thickness of the sample can be considered as constant, equation (1) was used in order to determine the type of diffusion in different buffers:

$$M_t/M_\infty = \qquad (1)$$

where M_t and M_∞ are the amounts of buffer solution in the hydrogel at time t and at equilibrium, respectively, k is a characteristic constant for the system, and n is the exponent related to the type of transport of the buffer solutions. The value of n = 0.5 indicates a Fickian diffusion process, but for 0.5 < n < 1 non-Fickian or anomalous diffusion takes place. In the special case in which n = 1, the transport mechanism is named Type II diffusion. The diffusion coefficients for the early stages of swelling were obtained from the slope (k) of the straight line ln M_t/M_∞ vs. $t^{1/2}$, using the equation (2):

$$k=4(D_i/\pi l^2)^{1/} \qquad (2)$$

where D_i is the diffusion coefficient in the glassy region and l is the thickness of the sample. For long diffusion times the different relation (3) can be used:

$$\ln((M_\infty-M_t)/M_\infty)=\ln(8/\pi^2)-(\pi^2 D_f t/l^2) \qquad (3)$$

where D_f is the diffusion coefficient for long diffusion times, t-time and l-sample thickness.

For the early stages of swelling at 25 ^{o}C, an increase of the itaconic acid content in the hydrogel, i.e., of the number of carboxylic acid groups, leads to greater water absorption and to higher values of diffusion coefficients in all buffer solutions investigated, due to the hydrophilic COOH groups. This effect is enhanced for pH values higher than the pK_a values of itaconic acid, due to the ionization of carboxylic groups, which leads to more hydrophilic COO^- groups. For longer times diffusion, the trend of diffusion coefficients (D_f), is similar to the case of D_i. However, D_f values are higher than the D_i values.

Analyzing the diffusion process in hydrogels, it can be concluded that the expansion of the network volume is slower for the early stages of the process, since the gel is transformed from xerogel (glassy state) to hydrogel form.

Section

Environmental Engineering
ENEN

ENEN X-NN yyy

X = KN – Keynote lecture
O – Oral presentation
P – Poster presentation

NN = Number

Reclamation of High TDS Effluent Using Microfiltration and Composite Membrane Reverse Osmosis: Possible Application in the West Balcan Region

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Large parts of the world are experiencing "water stress", both in terms of quantity and quality. In the coming decades, economic and population growth will exacerbate this situation. Since its humble beginnings in the 70s, membrane technology has grown to be one of the choice separation technologies for a wide variety of areas including water and wastewater treatment, mining, dairy and food processing, gas separations, biomaterial and environmental applications. Given its potential, the City of Los Angeles implemented membrane technology for a major water reclamation program at its Terminal Island Treatment Plant. The plant is a nominal 18 mgd (68,140 Nm3/day), secondary plant with supplemental multi-media filtration, but no disinfection. Plant effluent is high in salts, averaging about 4,000 mg/l total dissolved solids (TDS), because of seawater intrusion. An Advanced Wastewater Treatment Facility (AWTF) plant has been designed using reverse osmosis (RO) to remove TDS and prepare the water for indirect potable reuse by injection into a system of barrier wells used to prevent seawater intrusion.

This project implements membrane technologies that span the exciting and challenging interdisciplinary interface between science and engineering. The City of Los Angeles 5 mgd (18,930) AWT Facility, recipient of the 2003 Los Angeles Society of Engineers and Scientists Award has demonstrates the "real world" application of this important, emerging technology through several years of operation. The presentation examines: technology transfer, engineering, water quality and regulatory challenges.

Modeling Indoor Pollution Using a Comprehensive CFD Model

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This work which is part of an Occupational Health and Safety Assessment study of a major Chemical Industry and presents a methodology of assessing the indoor dispersion of a toxic chemical substance using Computational Fluid Dynamics techniques. A mathematical model , using CFD Code PHOENICS and based on solving the full 3-D Navier-Stokes equations and scalar conservation equations together with turbulence modelling, is used to predict the toxic substance dispersion in a geometrically complex industrial area. The source emissions, as well as the effect of the geometrical details of the building structure were studied. The PHOENICS® code is used as the general Computational Fluid Dynamics (CFD) environment where the model was developed.

Experience from Road, Ports, Airports and Railways Environmental Projects in Greece. Linking Transport Simulation Models with Emission Estimation and Air Dispersion Models

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This work presents a summary of technical and methodological problems from 15 years of experience with Air Dispersion Problems in Transport Environmental Assessment Studies Projects in Greece. The main problem that is addressed in this work is the effective linking of transport simulation models, with emission estimation models and air quality models. All the above transport projects address tough problems: they are complex, dynamic, and involve large volumes of data as well as spatially distributed 3D phenomena and models. They also involve problems of communicating difficult technical concepts and data to a largely non-technical audience, and of assisting non-technical users with complex analytical tools

ENEN O-01

Application of Recycled Wool Based Non-Woven Material for Removal of Heavy Metal Ions from Wastewater

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Nowadays, strict ecological legislation concerning the concentration of heavy metal ions imposes rigorous requirements for control and purification of wastewater. Although many different sorbents have been developed, wool seems to be an interesting alternative to commercially available sorbents due to the ability to effectively bind some metal ions and its high biodegradability. The possibility of using recycled material for wastewater purification is of great importance from the resource preservation and cost-effectiveness point of view. Thus, the aim of this study was to investigate the sorption properties of a recycled wool based non-woven material for heavy metal ions. In order to improve sorption properties, the material was treated with low-temperature air plasma (LTP) and/or biopolymer chitosan (CHT). CHT has been established as a relatively cheap and extremely good metal ion sorbent due to its amino groups, but the main problem with CHT application is that it is weakly bound to wool. It is assumed that protonated amino groups of CHT interact electrostatically with the available anionic groups in wool and that hydrogen bonding between hydroxyl or amide groups of wool and similar groups of CHT is established. Therefore, to enhance CHT binding, it is necessary to promote the formation of new anionic and hydroxyl groups on the fibre surface. To achieve this, the LTP treatment of the wool was applied before coating with chitosan. The rate and the extent of the uptake of metal ions by wool, the kinetics of adsorption and the influence of metal ion concentration on the sorption process were determined. It was found that wool even as a recycled material efficiently bound heavy metal ions in all investigated cases.

Study of the Air Pollution Episodes in the Winter of 2005. in Belgrade Central Zone

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Introduction

This paper presents level of ambient air pollution that cause serious exposure of citizens of Belgrade in February 2005. in the aim of investigation the influence of local meteorological parameters as well as orography on the observed air pollution episode.

Materials and Methods

As part of municipal air pollution monitoring network, Public Health Institute of Belgrade established four automatic stations for measuring air pollution and meteorological parameters in Belgrade city center in summer 2003. Air pollutants as NO_2 and SO_2 are registrated at four sites, while O_3, CO and PM_{10} are measured per one station. Analytical instruments are Horiba's detectors that are recommended as standard instrumentation for pollution monitoring according to EC directives requirements. Meteorological parameters including ambient temperature, pressure, relative humidity, wind speed, wind direction and solar radiation flux were also monitored concurrently atop a 10-m tower at the mobile station.

Results

In Table 1 there are assigned days when episodic air pollution occured in the surrounding of measuring sites.

Table 1. Period of 24 hour episode for specific air pollutants

air pollutant / measuring site	SO_2	NO_2	CO	PM_{10}
29. novembar	9-12.2	10-12.2	11-12.2	
mobilna	10-12.2	9-12.2	11-12.2	6.2, 9-12.2
Ohridska	2.2, 5-12.2, 21-22.2, 24.2	6-7.2, 10-12.2		
N. Beograd	11-12.2	11-12.2		

Daily characteristics of relevant meteorologic parameters can be summised as:

- wind speed was less than 0.5 m/s in period of 6-7.2, 9-12.2
- athmospheric pressure was above 1000 mbar in period between 2-11.2
- relative huimidity was less than 80% in period 4-5.2, 7-13.2, 19-22.2

Discussion and Conclusion

According to the current domestic regulations and EU limit value for PM_{10}, observed concentrations of SO_2, NO_2, CO and PM_{10} approve that ambient air pollutants in wider central zone of Belgrade were above limit values on February 11 2005. In part of city center located at the right bank of the rivers there were several days with air pollution episode. It was observed only two days duration of air pollution episode in city zone located on northwesten part in the plain at the left bank of river Sava (N. Beograd). Analysis show that a limited days of such episodes that occurred in February 2005. are mainly in conjunction with periods of high-pressure system, inversioins and low wind speed. Local orographies also contribute to air pollution levels. There are also shown differences of usual time-series plots of the one hour concentrations for NO_2 and SO_2 revealed that peak concentrations often registrated during morning and afternoon rush hours in comparison of days when air pollution episode occured.

Portable Analyzers for Olive Oil Quality Assessment

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High analysis rates: 20- Flow Injection **(FI)** analyzers developed for the quality assessment of olive oil will be presented. The [illegible] and data acquisition and control. Reagents are continuously pumped by a micro-pump through PTFE micro-tubes of 0.8 mm inner diameter. Micro-quantities of olive oil are automatically injected in the flow using a chromatography injection valve. Samples are mixed with the reagents and incubated while flowing to the detector. For methods based on slow reactions, a **Parallel Flow Injection (PA-FI)** multichanell analyzer based on a stream selection valve and ten incubation coils was developed. While stored samples are incubated, new samples are injected and mixed with the reagents. Then, incubated samples are aspirated in the detector flow reversal. After measurement, samples are driven to waste. The PA-FI analyzer allows automation of methods that require long incubation times without loss of sampling rate. The developed automated analyzers provide determination of the following parameters: **Acidity**, **Peroxide value**, **Iodine value**, **Thiobarbituric acid reactive substances** and **Anisidine value**.

Advantages of the developed flow injection analyzers are:

- 100 samples per hour.
- **Full automation:** Sampling, weighting, sample pretreatment, analysis timing, data acquisition and calculations proceed at the press of a button. Lack of human intervention results in **increased precision and accuracy**.
- **Low cost:** 0.2-7 ml of organic solvents are consumed per analysis. The low solvent consumption and the replacement of chlorinated solvents renders the developed methods **environmental friendly**.
- **Low sample consumption:** 0.0012-0.2 ml per analysis.
- **Good agreement with time consuming official methods**.
- **Protection of reagents from light and atmospheric oxygen**.
- **Miniaturization is easily achieved through integrated microconduits**.

Plans for the development of prototype for commercialization will be discussed.

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Removal of Zn(II) and Cd(II) Ions from Aqueous Solutions by Granular Activated Carbon and Natural Zeolite

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Many toxic heavy metals have been discharged into the environment as industrial wastes, causing serious soil and water pollution. Zn(II),Cd(II), Pb(II) are especially common metals that tend to accumulate in organisms, causing numerous diseases and disorders.
The adsorption ability of natural zeolite (NZ) and Granular Activated Carbon (GAC) was investigated for the removal of Zn(II) and Cd(II) from single (non-competitive) aqueous systems. Batch experiments were conducted to study the main parameters such as adsorbent concentration, initial adsorbate concentration, contact time, kinetic, pH solution, and stirring velocity on the sorption of Cd(II) and Zn(II) by NZ and GAC. The equilibrium of a solution between liquid and solid phases is described by Langmuir, Freundlich, Langmuir-Freundlich and Redlich-Peterson model. The parameters in the adsorption isotherms were estimated from the experimental equilibrium data using non-linear regression software. From the Langmuir isotherms, maximum adsorption capacities of the NZ and GAC towards Zn(II) and Cd(II) were determined.
Comparing the values of q_m for adsorption of Zn(II) and Cd(II) onto GAC and natural zeolite, it can be concluded that both heavy metals show 2,3 times greater affinity for GAC than for natural zeolite. The initial part of the isotherm curves for adsorption of Zn(II) and Cd(II) onto GAC practically coincides with the ordinate axis. This indicates that for low concentrations, Zn(II) and Cd(II) is almost completely removed from the solutions using GAC. For the investigated heavy metals the results show that the recovery is in the range 90% to 99.9% for both used adsorbents. In order to reach this removal efficiency different amounts of adsorbents are necessary.

ENEN P-02

Modeling of Cadmium(II) Ions Adsorption Kinetic on Natural Zeolite and Granular Activated Carbon

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The isotherms and kinetics of cadmium adsorption from aqueous solution onto Granular Activated Carbon and natural zeolite has been studied using an agitated batch adsorber. Maximum adsorption capacities of GAC and natural zeolite towards Cd (II) from Langmuir adsorption isotherm have been determined using the adsorption equilibrium experimental data.
Series of experiments were undertaken to study the influence of initial Cd(II) concentration, mass of adsorbents, agitated speed for both investigated systems i.e. Cd(II)-GAC and Cd(II)-natural zeolite on uptake curves. The results of contact-time studies are average solid phase concentration (q_{av}) versus time plots.
The single Cd (II) uptake curves have been described by the homogeneous solid diffusion model (HSD-model) combined with external mass transfer resistance. In the homogeneous solid diffusion model, the range of varying the external mass transfer coefficient k_f has been estimated assuming a linear isotherm and negligible interpartical diffusion. The range of varying the solid diffusion coefficient D_s has been defined by single resistance model assuming non-linear isotherm and negligible external mass transfer resistance. For performing the kinetics simulation study the computer program based on the proposed mathematical model and developed using gPROMS, was used. As two-mass transfer resistance approach was used, two model parameters were fitted during the simulation study. For any particular system Cd(II) - adsorbent, k_f was constant except the lowest initial concentration, while D_s was found to increase with initial concentration. This means that if the diffusion model with the concentration dependent diffusion coefficient will be used, the model is able to predict the adsorption data regardless of the variation of concentration in the adsorption processes.

Appliance of »Complex Splitter« in Plating Wastewater Treatment

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Introduction

Stable complexes formation caused by usage of complexing agents as aditive in plating solutions, made wastewater treatment aggravated and expensive. The investigation results of samples which contain maximal concentrations of some cathions expected in waste waters from this type of facilities, are presented in this paper.

Inductively Coupled Plasma Optical Emission Spectroscopy is used for wastewater samples analysis.

The precipitation of disolved heavy metals (Ni, Fe, Cu, Cr, Zn, Sn) by neutralization is the most common method used in industrial conditions.

In the presence of EDTA – Disodium Salt and Ammonium hydroxide (strong chelator), above mentioned procedure treated wastewater do not give requested results. Toxic metals content at the outage, prior to discharge into the city sewerage system exceeded Law permited maximal concentration.

Experimental procedure and results

The effluent water from all processes are collected into chromate, spent/stripping acids, cleaner and acid – alkali (rinse) sumps. Hexavalent chrome is reduced to trivalent chrome with sodium bisulfite and sent to the neutralization tank. The pH is raised with sodium hydroxide. Small addition of lime facilitates the metal hydroxide precipitation. In high ammonia media hydroxide precipitation alone is not sufficient, but »Complex splitter« CS – 1 addition at the neutralization stage assure complete removal of metals. Precipitated solids are treated with coagulants and after flocculation and clarification decants in a sand filter.

Table 1. Plating wastewater samples analysis before treatment

Ni	Fe	Cu	Cr	Zn	Sn	EDTA	NH_4OH
g/dm^3							
20	3	14	40	5	7	1	2,5

Table 2. Plating wastewater samples analysis after »Complex splitter« CS – 1 addition

Ni	Fe	Cu	Cr	Zn	Sn	EDTA	NH_4OH
mg/dm^3							
0,3	-	0,2	0,1	0,1	0,1	-	-

Table 3. Plating wastewater samples analysis prior to discharge into the sewer

Ni	Fe	Cu	Cr	Zn	Sn	EDTA	NH_4OH
mg/dm^3							
0,1	-	<0,1	<0,1	<0,1	<0,1	-	-

Conclusion

Neutralization process modified by addition of 2 mole »Complex splitter« CS – 1 per 1 mole bivalent metal, with unchanged retention time and pH 9.0±0.2 results the Law permitted wastewater quality.

ENEN P-04

Retention of the Pollutants on H-Montmorillonite of Romanian Source

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Abstract

In this paper is proposed a method unconventional for depollution of water infested with metal cations and heavy metals. The microporous material used for the montmorillonitic retention of the pollutants is clay of romanian source. The clay was characterized by analyses for the determination of BET surface and the surface acidity was determinate by "Thermo Programmed Desorption" method. To increase specific surface, the clay structure was modified by pillaring process. There were realized kinetic tests on cations (Cr, Ni and Pb) to show the retention capacity of H-montmorillonite clay for pollutants. The resultants show that the pillared clay from romanian source is a performant material for unconventional depollution of waste water.

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Solidification of Radioactive Sludge by a Research Reactor

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In the last forty years, in “Vinca” Institute, as a result of two research reactors operation, named RA and RB, and as a result of the radionuclides application in the medicine, industry and agriculture, radioactive waste materials of different levels of specific activity were generated. As a temporary solution, radioactive waste materials are stored in two interim storages. Radwaste materials that were immobilized in the inactive matrices are placed into the concrete containers, for further manipulation and disposal. The present paper reports the results on preliminary removal of sludge from the bottom of the spent fuel storage pool in RA reactor, mechanical filtration of the pool water and sludge conditioning and storage.

Presently, the reactor RA spent fuel storage pool is in very bad condition. Water in the pool is dirty and its chemical parameters are not maintained to minimize corrosion. Following the recommendations obtained from International Atomic Energy Agency (IAEA), the “Vinca” Institute elaborated a project incorporating the following steps: preliminary removal of sludge and other debris from the bottom of the pool in RA reactor, washing of deposits from all the surfaces in contact with the pool water, venting of the aluminum barrels, mechanical filtration of the pool water, final removal of the sludge, sludge conditioning and storage at the waste repository at the “Vinca” Institute site.

Cleaning the research reactor RA spent fuel storage pool appeared to be a more difficult, more time consuming and certainly more expensive operation than originally estimated. However, the results achieved so far, extraction of the sludge from the bottom of the pool and its immobilization and conditioning – the first stage of the cleaning, are a sound basis to conclude that the task shall be accomplished successfully.

After the operations explained above have been performed, necessary elements for planning further stages of pool and water cleaning, and treatment of the spent fuel should be obtained. Through many years research and development in radioactive waste immobilization and conditioning performed experimental experience gave the possibility to choose the best formulation for cement mixture and results gave us certainty to claim that described methods and used matrix materials will serve as a barriers to preserve radionuclides migration to the surroundings for at least 300 years. Optimization of the processes and matrix-radwaste mixtures is in further progress and we hope that this work will influence the design of the future Serbian disposal center, shallow land burial type for low and intermediate level radioactive wastes.

All performed steps in removing sludge from the bottom of the spent fuel storage pool, pouring the sludge from the sedimentation vessel to the concrete cask, cask with a sludge transportation to the laboratory for immobilization and conditioning, and immobilization and conditioning of the radioactive sludge in a cement matrix have been done in accordance with all relevant requirements for radiation safety and radiation protection .

ENEN P-06

A New Photo-Fenton Catalyst Based in a Pillared Clay Nanocomposite

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Photoassisted Fenton reaction proved to be the most effective process for the degradation and the mineralization of organic pollutants in water [1]. However, the homogeneous photo- Fenton reactions have a big drawback: the large volume sludge generated at the end of the treatment by neutralization and precipitation of Fe ions. The recovery of Fe ions by separation and re-dissolution is rather costly. To eliminate this major disadvantage studies have been done to find a solid support for the Fe catalyst. The Nafion-based catalysts, studied by Fernandez et al.[2] , proved to have a low catalytic activity, and to be too expensive for an industrial application. Pillared clay minerals have been used as catalyst supports because of their particular properties and structures as well as of their abundance and low cost[3]. A laponite RD-based Fe nanocomposite has been recently synthesized and tested for the Orange II degradation in water by the photo- Fenton reaction [4]. But they did not compare the results with those for the homogeneous photo-Fenton process in similar conditions.

The first objective of this work was to prepare the laponite RD clay-based Fe nanocomposite by the pillaring technique experimented previously for montmorillonite [5]. The XRD characterization of the product revealed the crystallites of Fe_2O_3 as pillars and of $Fe_2SiO_{10}(OH)_2$. The second objective was to taste the photocatalytic activity of the Fe-Lap-RD nanocomposite for the degradation of the Monuron herbicide in water. Kinetic curves have been generated for a 0.2 mM aqueous Monuron solution at pH 3, UV-C (254 nm) radiations, 9 mM H_2O_2 dose, and catalyst doses between 0.1 and 1.0 g/L. Parallel probes have been taken for the homogeneous process , in identical conditions, but using doses of soluble $FeSO_4$. The pollutant, analysed by HPLC, has been almost completely removed after 60 minutes in both processes. The mineralization degree (% TOC removal) after 120 minutes of irradiation reac hed 65% in the heterogeneous, while only 51% in the homogeneous process, under the optimal conditions. Despite the encouraging results a major question arises: how many cycles the catalyst could be reused?

Acknowledgements:
The physical tests of the catalyst have been done in the Chemistry Laboratory, University of Oslo.

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Simulation of a Pollutant Accidental Discharge Scenario in a Danube Tributary by Using a Diffusion Model

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In order to simulate a hypothetical river contamination with BOD-organics, when failure of a municipal Waste-Water Treatment plant occurs (see WWT risk analysis of Maria et al., 2000, 2001), a pollutant diffusion stationary model is adopted (Whelan & McDonald, 1996):

$$u\frac{\partial C}{\partial x} = D_y\frac{\partial^2 C}{\partial y^2} - r \;;\; \left.\frac{\partial C}{\partial y}\right|_{y=0}^{y=B} = 0 \;;\; C|_{y=B} = 0 \;;\; C|_{x=0}^{y=0} = C_o \;;\; C_o = C_{fond} + Q_{poll}/Q_{river}$$

(C_{fond}, C = pollutant concentration before and at contamination source; x = longitudinal distance from source; y = lateral distance from middle-river; B = river half-width; Q_{river}, Q_{eff}, Q_{poll}= river, effluent, pollutant flow-rates; $Q_{river} + Q_{eff} = u \cdot 2B \cdot h$; u = water-flow avg. velocity; h = river depth; D_y= radial dispersion coefficient; r = pollutant biodegradation rate). The small size discharge source is located in the middle of the river, while constant flow-rates, quasi-uniform river-size, dispersion coefficient, and biodegradation rate in the analysed site have been considered ($Dy = 0.06hu$, Fischer, 1974). Simulation results for the case study, i.e. the pollutant fate and transport in a Danube tributary pathway, are presented in Figure 1. The model can be used to assist the environmental risk assessments in a river contamination area, the WWT-plant analysis, and the river-pollution monitoring.

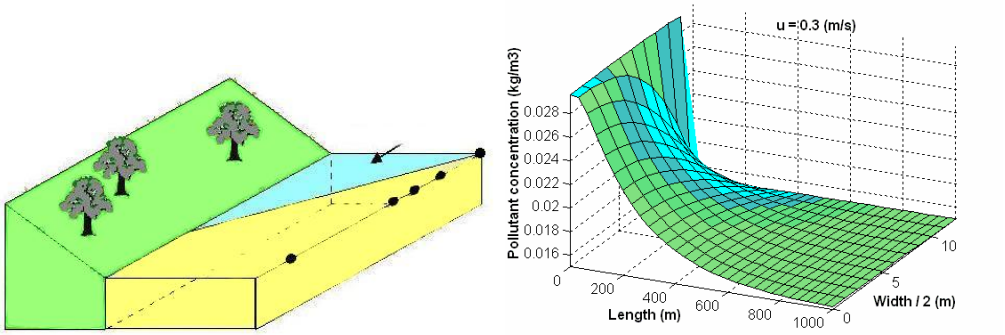


Fig. 1. Riverside contamination pathway (left). Pollutant distribution (right) ($0<x<1$km, $0<y<B=12.5$ m, $h=5$m, $Q_{river}=35m^3/s$, $Q_{poll}=0.55kg/s$, $Q_{eff}=2.5m^3/s$, $C_{fond}=0.015kg/m$, $r=kC$, $k=0.05\ day^{-1}$).

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ENEN P-08

Total Cellulase Activity of Carboxymethyl Cellulosse Degrading Mycoflora

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Total cellulase activity was investigated for the following fungi: *Fusarium oxysporum* (Schecht), *Trichoderma harzianum* (Rifai), *Aspergilus niger* (Van Tighem) and *Alternaria alternata* (Fr. Keissler).

The fungi *Fusarium oxysporum* and *Trichoderma harzianum* were isolated from the waste water of the "Tetrapak" printworks after standing in basins for about 90 days. Cultures obtained from the waste water were reseeded on potato-glucose agar (PGA), on which they developed for 7 days at room temperature of 20°C under alternating day-night light conditions. Afterwards, the fungi were reseeded on a new PGA base where they developed for another 7 days. The reseeding procedure was performed four times in order to obtain pure cultures needed for determination.

The fungi *Aspergilus niger* and *Alternaria alternata* were derived from the material of the mycological collection of the Faculty of Science in Kragujevac. These two cultures were isolated from different grades of paper, according to scientific references (Das et al. 1997, Klamer et al. 2004).

The ability of indicated fungi to utilize carboxymethyl cellulose and similar organic molecules, as a source of carbon for their metabolic reactions was tested by measuring the scope of cellulase activity. The influence of CMC on cellulase activity was investigated in 100 mL of nutrient mineral base, after addition of 2 g of aqueous CMC solution and 1 mL of the spore suspension (1 x 10^5 spores). The enzyme activity was examined between the 3rd and 21st day of the test period, not including inoculation.

The unit of enzyme activity was defined as the amount of protein necessary to produce 1 mmol of reducing sugar per minute in the reaction with dinitrosalicilate.

Results for the test period between 3rd and 21st day indicate following value ranges of cellulase activity of the fungi:

0,68 – 2,58 U/ml for *Fusarium oxysporum*
0,60 – 1,20 U/ml for *Trichoderma harzianum*
1,60 – 3,50 U/ml for *Aspergilus niger*
0,20 – 1,50 U/ml for *Alternaria alternata*

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Decolorization of Coloured Textile Wastewater After Wool Dyeing by Several Processes

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Wastewater is the major environmental issue of the textile industries besides other minor issues like solid waste, and the like. Variations in the fabric quality and treatment process results into large fluctuation in daily flow rates and pollutants concentrations. Dyes and dyestuffs find use in a wide range of industries but are of primary importance to textile manufacturing. During textile processing, inefficiencies in dyeing result in large amounts of the dyestuff being directly lost to the wastewater, which ultimately finds its way into the environment.

The decolorization of the dyes in water after woolen dyeing was investigated in laboratory-scale experiments, using two advanced oxidation processes: Fenton, and UV/H_2O_2. Degradation of six different dyes in aqueous solutions by the processes was performed. The coloured textile wastewater was obtained from the textile factory "Leteks", from Leskovac, Serbia and Montenegro. The wastewater was collected after wool dyeing. These dyes include three types: acidic, reactive, and chrome dyes. The six dyes tested were Bemacid Blau GW, Supramin Blau GW, Drimaren Blau X-3, Lenaset Blau, Diamantchromacht Gelb KE, and Bezacrom Schwarz T-FD. All it is to use for wool dyeing.

The quickest decolourisation was obtained when H_2O_2 was activated by Fenton's reagent (average time 30 min); satisfactory decolourisation times were achieved using H_2O_2/UV (about 60 min). Decolourisation with Fenton's reagent was performed in an acidic medium (pH=3), whilst docolourisation with H_2O_2/UV took place in an alkaline medium (pH=11). The optimum ferrous sulfate and chloride concentration are 0.8g/l. For peroxide, that is 10g/l. Flocculates that are produced because of neutralization using the H_2O_2/Fe^{2+} process can precipitate non-decomposed dye. Although decolourisation with H_2O_2/Fe^{2+} was fastest, and the costs of such a process are low, it is not really suitable for environmental reasons, namely the formed sludge needs to be removed. The best experimental results for the Fenton process proved to the following: after 10 min of reaction time the removal of color was equal to 85% and more than 90%, respectively.

Each dye solution was scanned from 300 to 800nm and its maximum absorbance was determined. The color removal was based on the change of the maximum absorbance. After 15 min of reaction, 65% decolorization was achieved, and after 30 min of reaction time, the degree of decolorization was 95%, by $H_2O_2/FeCl_2$ process. It is like with $H_2O_2/FeSO_4$ process. The color removal of dye solution by Fe^{2+}/H_2O_2 was higher and greater than by H_2O_2/UV process which the colour remove at amount 35.1%, 53.5%, 80.6%, 92.1%, during 15, 30, 45, 60 min, respectively.

Decolourisation with H_2O_2/UV is an environment- friendly procedure. It causes no sludge and no additional water pollution because of the physical activation of hydrogen peroxide while the COD values were low, but investment and operating costs are high.

ENEN P-10

Modeling of Biological Nitrification Based on Graph Theoretical Methods

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A kinetic study of the biological nitrification carried out in aerobic conditions was performed. The experimental data were generated in a laboratory scale fed-batch reactor. The reactor was seeded with activated sludge from a municipal wastewater treatment plant. The simultaneous process of nitrification and denitrification (N/D) was carried in the same reactor. The data utilized for the model implementation were taken during the aeration period in which nitrification reaction occur. Three sets of data were obtained at different experimental conditions. Each value represents the mean value of three parallel runs conducted at the same operational conditions. In order to make a more reliable decision, additional experimental data from the literature were evaluated .

Besides, a large number of hypotheses for the mechanism of the autotrophic biological nitrification and respective kinetic models have been generated by using graph theoretical methods and chemical information for reaction intermediates. A model discrimination procedure was performed based on the experimental data and different statistical criteria. The experimental results for the biological nitrification have been fitted to the kinetic models derived. The discrimination between the alternative kinetic models was performed by considering: sum of squares of the residuals at the optimum, mean percent error and randomness of the residual distribution. The parameters of kinetic models are estimated by using an efficient parameter estimation method in mathematical models represented as a set of ordinary differential equation.

One of the kinetic models obtained describes the kinetics of the reaction appropriately. The model is in correspondence with the mechanism including the reaction step of formation and decomposition of an intermediate complex between the microorganisms and ammonia.

The Process Plant Hazard and Risk Reducing System

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Process plant risk reduction system which including hazard identification, frequencies analysis, consequence analysis and hazard cost was investigated. Hazard identification method was used in different ways to model part of the incident scenario of a possible accidents. A systematic cause event analysis gives the results which are summarized in the form of a fault diagnosis decision support system.

Despite increased concern and safety standards, accidental situations throughout the industry occur, influencing very often large environmental damage. Regardless weather the reason for accidents is human error or technical failure, it is necessary to take an action in order to prevent them.

As a case study the sulfurdioxide plant was used. The sulfurdioxide oxidation plant makes environment protection producing by product ammonium sulfate.

Process safety analysis begin with system definition. Definition includes system components, topology, input and output attributes, state variables, behavior rules and initial scenarios. Process safety analysis includes hazard identification, frequencies and probability analysis, consequence analysis and hazard cost analysis.

Hazard identification methods can be used in different ways to model part of the incident scenario leading to a possible accident. A systematic cause event analysis gives the results which are summarized in the form of fault three. It follows the structure of a generic fault tree point to the release of materials, chemicals and of an event tree from this point to the release on people, the plant and the environment.

It purpose is to discover and locate the disturbance or faults which could lead to accidental situations. The fault diagnosis model was derived. The obtained results indicate the influence of a single disturbance to registered symptoms, as well as to the safety of the whole plant.

Model for risk reduction analysis and prevention of accidental situation for sulfurdioxide plant is realized through development of a logical frame. Its knowledge base is composed of information streams, and database of occurred symptoms and faults at a single units.

In this paper consequence model was developed for troubleshooting system and formalizing hazard report to creates recommendation to correct hazard.

ENEN P-12

Study of the Ammonium Sulfate Aqueous Solution Electrodialysis

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This work aims to study the application of ED to the recovery of ammonium sulphate , a valuable fertilizer, from fermentation waste liquors. A synthetic solution of analytical grade ammonium sulphate and deionised water (1.2 %) was used in this study. A five cell pair stack was assembled with AMX and CMS ion echange membranes , with an effective area of 200 cm^2 each .

The experimental kinetic curves C (molar concentration of NH_4^+ in dilute, and in concentrate) versus time have been generated for three flow rates and four potentials (132 experimental points) at a constant temperature (303 K). These primary results have shown that the separation time is remarkably reduced as the potential increases from 5 V to 12 V at all flow rates.

A phenomenological mathematical model describing the variation of the dilute concentration with time has been derived. The integrated model includes the two experimental factors (dilute flow rate Q_D, applied potential E), two constants (Farday number F, volume of the diluted solution tank V_D) as well as three empirical constants (*a, b, c*) originated from the semiempirical dependences of of the mass transport coefficient on the flow rate, and of the solution/membrane electrical resistance on the concentration.The model predictions of C versus time have been compared to the experimental points, and the three "constants" (*a, b, c*) have been identified. Taking c = 0.5 (the exponent of the Reynolds number) the average values of *a* and *b* have been found: $a = 4x10^{-4}$ and $b = 2.8x10^{-6}$.

The specific power consumption (SPC, kWh/ m^3 solution) has been further calculated for each set of potential and flow rate, using the validated model. This SPC does not include the pumping energy. The results revealed a drastical influence of the potential on SPC which increased from 0.12 to 0.48 kWh/ m^3 as E varied from 5 to 12 V, while the flow rate (between 0.1 and 0.2 m^3/h) had a negligible influence.This is not in agreement with previous results predicting an optimal flow rate in the desalination plants[1-3].

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Dyes in Textile Wastewaters Problems and Solutions

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CANCELED

There are a large number of pollutants in textile wastewaters. Among these an important place is taken by synthetic dyes. The fixation of dyes on textile fibers depend on the structure of the dye, as well as is compatibility with the textile material. Solutions for dye elimination are presented.
The general characteristics of textile wastewaters are the followings [1]:

- pH: 4-12 (4.5 knitted wool, 11.0 cotton);
- COD: 150-250 mg/L;
- BOD: 80-500 mg/L;
- BOD/COD: 1/3 - 1/5;
- Color: 500-2000 Pt-Co units;
- Suspended matter: 30-400 mg/L, sometimes 1000 mg/L;
- Cr (VI): 1-4 mg/L;
- Sulfide: 0-50 mg/L.

The problems generated by the presence of dyes in the wastewaters are:

- Color, leading to the decrease of water transparency for the sunlight diminishing the photosynthetic process - ecological impact;
- High values for TOC, COD, BOD, due to the presence of dyes and auxiliaries;
- Toxic metals present in some dyes;
- Toxicity of the dyes and their degradation products (amines) [2]

Usually, there are three steps in wastewater treatments [3]:

- physico-chemical treatments (screening, filtration, equalization, aeration, coagulation, flotation, neutralization, oxidation, etc);
- biological treatments (aerobic, anaerobic, plant degradation, enzymes);
- physico-chemical post-treatments (sorption, membrane filtration, oxidation, etc.)

The biological treatments are a relatively inexpensive way to remove dyes from wastewaters. The dyes belonging to the largest class of dyes, the azo-dyes, are suitable for bacterial biodegradation.

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From Sequential Extraction to Quantification of Uranium Sorption to Contaminated Soils

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Desorption test using a sequential extraction method were used to characerize and quantify uranium sorption to contaminated. Soils collected from Bratoselac, (11.14 gU/t) which was target of depleted uranium ammunition during the NATO aggression in Serbia and tailing (16.76 gU/t) from closed uranium mine, Kalna in Southeast Serbia. Test were conducted to provide geochemical information relevant for selecting appropriate remediation technologies for contaminated site. Advantages of desorption Kd values compared to traditional sorption Kd values for estimating appropriate values to use in transport calculationas:

- Desorption is often the rate limiting process governing contaminant release into the mobile aqueous phase.
- In desorption experiments, it is possible to capture the ″aging″ process between the radionuclide and sediment.

For determing the geochemical fractionation of uranium in soils and tailing we are used sequential extraction protocol *(Fig. 1.)*.

Metal mobility ↑

EXTRACTANT	DESIRED FRACTION
Deionized water/surface water	water soluble
IM $CaCl_2$	EXC hangeable
1M NaAc	metals bound of carbonates
30%H_2O in 0.1M HNO_3	metals bound on organic matter
0.01M NH_4OH-HCl in 0.1 M HNO_3	metals bound on amorphous Fe/Mn oxides
0.5gNa-ditionate in 0.15M $Na_3H_5G_6O_7$+0.05M	metals bound on crystalline Al/Fe oxide
$HF+HNO_3$	Strucural (residual metals)

↓ Leachant stregth

Fig.1 Sequential extraction protocal

Concentration of uranium in each fraction were quantified by fluorimetric method after extraction with sinergistic mixture TOPO (tri-n-octilphosfin oxide) in ethil acetate.
Desorption Kd values were calculated using Equation 1.

$$Kd_{desor} = \frac{C_{exch.} + C_{org.} + C_{amorf}Fe_{oxide} + C_{carb}}{C_{liquid}} \quad (1)$$

The four extracts exchangeable, organicaly bound, bound on carbonates and amorphous Fe-oxide, used to define C_{solid} for Kd_{desorb} are expected not to recover contaminats occulted in silicates, alumosilicates, crystalline Fe-oxides of Mn-oxide or contaminats that were precipitated this fraction would contribute to future contaminant plumes in investigated area.
Obtained results shows that uranium were associated with labile fractions and were not concentrated with the smaller sediment particles. These finding suggest that phyteremediation or heap leaching and not soil washing are viable remediation approaches for this site.

Enviromental Protection from Influence of Liquid Phase from the Red Mud Disposal

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The aim of this paper was to investigate the possibility of treatment process of the liquid phase (water) from the red mud disposal site of the aluminium production. The water from the red mud disposal site was treated, so that is could discharge into recipient - river Morača. Treatment of liquid phase achieved the following: 1) reduction of environment pollution, and 2) reduction of raw water consumption, which contributed to the preservation of this major environmental resource.

The treatment process of liquid phase from the disposal site was based on the neutralization by acid (H_2SO_4, HNO_3, HCl, H_3PO_4) and separation of the solid products from that process by filtration. As materials of filtration used: in once case anthracite in combination with sand, and in second case sand different granulation.

The results show that optimal reagent for neutralization is sulphuric acid concentration of 1,0 mol/l. The important criteria for selection of this reagent was low cost and accessibility on our market in compare to another reagent for neutralization (HCl, HNO_3, H_3PO_4).

The results obtained will be useful in the protection of potable well-water located in vicinity, south of the Aluminium Plant in Podgorica.

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ENEN P-16

Phytoremediation Arsenic from Drinking Water Using Maidenhair Spleenwort (*Asplenium trichomanes* L.)

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Arsenic-contaminated soil and other waste materials is one of the major arsenic sources for drinking water. Arsenic species are bioactive and toxic. Long term expository to low concentrations of arsenic in drinking water can led to non-cancer and cancer disease. The primary anthropogenic input derives from combustion of municipal solid waste, fossil fuels in coal and oil-fired power plants, release from metal smelters and direct use of arsenic-containing herbicides by industry and agriculture. Technologies of cleanup arsenic from water have significant deficiency, such as high cost, generating high volumes of toxic sludge and brine, and low water recovery. Phytoremediation, an emerging, plant-based technology for the removal of arsenic contaminants from water, has been renewed attention. The recent discoveries of brake fern (*Pteris vitata*), which can hyper accumulator for arsenic, open the new phytoremediation options. In this study, fern maidenhair spleenwort (*Asplenium trichomanes L.*) samples growth one week in an arsenic-contamined water (50, 100 and 500 mg/l). This fern demonstrated the ability hyperacumulations arsenic and transfers rapidly from water to rhizomes and fronds with elevate concentration arsenic of some hundreds more than the control. This results open new opinions of phytoremediatin arsenic from water using some ferns, outside from genus *Pteris*, and proposal newly technologies for decontamination arsenical drinking water.

Lead Removal from Wastewater by Complexation-Membrane Filtration Process

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Removal, separation and enrichment of heavy metal ions in aqueous solutions play an important role for environmental remediation of wastewater. Among the various processes for heavy metal removal from water, the technique of complexation-membrane filtration proved to be a promising alternative to technologies based on precipitation and ion exchange. The basic idea is a fixation of metallic ions on macromolecular species, which is performed to increase their molecular weight. These compounds, which then become bigger than the pore size of the selected membrane, can be retained whereas water is then purified. However, the choice of water-soluble macroligands remains important for developing this technology. Water-soluble polymeric ligands have shown to be powerful substances to remove trace metals from aqueous solutions and industrial wastewater through membrane processes. Polymers with carboxylic or amine groups have been extensively studied for this purpose. The aim of the present study was to evaluate the applicability and the efficiency of selected macroligands (polyethylene glycols 5000, diethylaminoethyl cellulose and dextrin). The research was conducted on model wastewater containing Pb(II) ions. Lead is recognized as one of the serious environment contaminants because of its high toxicity, accumulation, and retention in the human body. It is a cumulative toxicant causing chronic poisoning; therefore its removal from water is very important.

Retention coefficients of Pb(II) complexes, depending on type of complexing agent, pH value and applied pressure were investigated. The concentration of heavy metal ions in aqueous solution was determined using atomic absorption spectroscopy (AAS). It was observed that bonding process was more efficient at alkaline conditions than at neutral or acidic conditions. Lowest retention coefficient, as expected due to its low molecular weight, was obtained with dextrin. Polyethylene glycols showed as more efficient complexing agents, but highest retention coefficient was achieved using diethylaminoethyl cellulose.

ENEN P-18

Enzymes as Cotton Dyeing Auxiliaries

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CANCELED

Classical textile processes generate high pollution due to finishing operations generating waste-waters with an acid or alkaline pH, as well as production, in same cases, of chlorinated organic compounds.
In textile field enzymes have many possible applications starting with the raw material work-up. The enzymatic finishing has now been applied in a number of processes in cotton finishing like: bio-polishing, bio-stoning, etc. Many attempts have been done also for applying biotechnology for wool finishing or synthetic fibers finishing technology.
These procedures are recommended due to the ecological aspects. Thus, the use of enzymes in textile processing seems to be a real solution for a sustainable development in textile industry.
A study concerning the action of a Cellulase on cotton knitted fabric is presented in order to obtain more information on the influence of the enzyme in the dyeing process and the color aspects of the fabric. Two procedures have been experimented. A one stage finishing-dyeing treatment of cotton with a Cellulase and Reactive dyes in the same bath was proposed. Secondly, an enzymatic treatment before the dyeing was proposed.
The experimental conditions were in agreement with the enzyme demands (pH, temperature).
The influences of enzyme concentration and of the treating time on the process were evidenced.
The enzyme action on cotton fabrics was measured by measuring the weight loss due to the hydrolytic process.
The influence of the enzyme upon the color attributes: lightness, chroma and hue has been studied by measuring the light remission. The weight loss was measured with a Mettler Toledo high precision balance. The treatment with IndiAge SuperL led to a small weight loss of the cellulosic substrate.
The tristimulus value, the L^* a^* b^* coordinates and color differences have been calculated using the CIELAB equation. The light remission was determined with Specord 20 UV-Vis apparatus. The enzyme treatments led to minor modifications of the color parameters.
A more accurate illustration of enzymatic action was given by the SEM analyses performed with Hitachi S-3000N apparatus.
A comparison between the results obtained in the one stage treatment and those in the two stage experiments has been done. The experimental data revealed the possibility to realize the dyeing and finishing of knitted cotton in a one step process.
The enzymatic treatment did not damage the fiber surface and is compatible with the reactive dyes.

Desulfurization to Produce Exceptional Quality Biogas 15 Years from Concept to Proven

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Fermentation (biogasification) of raw biosolids to biogas, and use of the biogas as a renewable fuel, is a major part of the City of Los Angeles' biosolids management program. For the City to beneficially use its biogas, some form of desulfurization is required to reduce the normally high H_2S concentration associated with raw biogas and, thereby, prevent the formation of SO_x emissions during fuel firing. The City began implementation of a desulfurization process in 1980, eventually selecting a regenerative, liquid redox, scrubbing system based on designs used in the natural gas industry. A series of process problems were encountered with the original plant, primarily caused by the relatively high CO_2 content of biogas. Bench and pilot scale studies were required to develop solutions to these problems which were then implemented in the full-scale plant. The modified plant has proven to be efficient, economical and reliable. The purpose of this paper is to discuss the City's experiences and present the design criteria and operating characteristics of the desulfurization process now in operation at Hyperion.

The City of Los Angeles Nitrogen Removal Conversion Program: Assessment of Nitrogen Removal, Dephosphatization and By-Product Formation

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CANCELED

The City of Los Angeles is implementing a major biological nitrogen removal conversion program at its Los Angeles Glendale (LAG) Water Reclamation Plant and Donald C. Tillman (DCT) Water Reclamation Plant to meet new effluent quality discharge limits established by the California Regional Water Quality Control Board (CRWQCB). The design criteria for conversion to biological nitrogen removal mode are established based on full-scale pilot plants data.

The full scale pilot plants were successful in implementing processes for biological removal of carbon, nitrogen and phosphorus compounds. Processes tested included step feed and MLE. The separation of anaerobic zones for SVI control (selector) and "free" biological dephosphatization, anoxic zones for denitrification; aerobic zones for nitrification and oxidation of carbon compounds to remove biogenic compounds more efficiently was explored. The presentation examines particular full scale results including simultaneous nitrification and denitrification (SND) identified as function of dissolved oxygen, availability of suitable carbon source, biomass floc size, "free" phosphorus removal and by-product formation triggered by utilization of cationic polymer for a foam control.

Adsorption of Heavy Metal Ions From Multi-Metal Solution by Silica-Immobilized *Medicago sativa* Biomass

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Preliminary screening laboratory batch experiments to determine the binding ability of *Medicago sativa* shoots and sprouting seeds showed good heavy metal ion binding characteristics of the biomasses studied. Sprouting seeds proved to be more efficient and less pH dependent.

In an attempt to remediate metal-contaminated waters, the ability of the *Medicago sativa* biomass to bind metal ions was further investigated under flow conditions. The Pb(II), Cu(II), Ni(II), Zn(II), Cr(III) and Cd(II) binding properties were studied. In order to avoid clumping and to obtain a uniform flow rate, the biomass was immobilized in a silica matrix. The experiments included pH profiles, time dependencies and metal binding capacities of the biomass. Results showed high affinity of biomass for metal binding around pH 5.0 within a time period of approximately 5 min for all the metal ions studied. Column experiments with the silica immobilized biomass proved that this material was capable of removing considerable amounts of metal ions under flow conditions.

The pH dependence of the metal ions binding to the biomasses suggested that it might be possible to recycle the system much like an ion-exchange resin. By treatment with dilute HCl, the bound-metal ions were recovered in approximately 90%, except for Cr. Recovering the metal ions from the biomass using a dilute acid, demonstrated the potential of reusing the metals. Once the metal is recovered, the immobilized polymer is biodegradable, causing no harm to the environment. Obtained data will be useful for development of an environmental friendly and cost-efficient technology for remediation of heavy metal-contaminated waters.

ENEN P-22

Influence of Sulphate and Chloride Ions to Potentiometric Stripping Analysis of Lead, Cadmium and Zinc in Waste Water

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Stripping analysis is a sensitive electrochemical technique for measuring trace metals. Potentiometric stripping analysis involves two steps: electrodeposition and stripping. During electrodeposition the analyte-metal cation reduces and forms an amalgam. During the stripping the metal oxidizes by dissolved oxygen and redissolves in the solution. In this paper the influence of sulphate and chloride ions on potentiometric stripping analysis of lead, cadmium and zinc was investigated. All stripping analysis were performed by using a commercially available computerized analyzer[1]. The electrochemical cell comprises a processing vessel bowl, a mechanical stirrer and a three-electrode system. A glassy carbon disc working electrode was used as an inert support for the mercury film. The mercury film was formed electrolytically[2]. An Ag/AgCl electrode was used as the reference and a platinum wire as a counter electrode[3]. Standard sollutions of metal ions were suprapure, all other sollutions were proanalysis. The content of sulphate ion less then 100 μg/dm^3 has no influence on the determination of lead, cadmium and zinc by potentiometric stripping analysis. Content of sulphate ion greater then 1000 μg/dm^3 strongly effects stripping analysis, because micro amounts of insoluble sulphate compounds were made. Content of chloride ion has greater influence on determination of lead and cadmium then zinc. Content of chloride ion less then 30 μg/dm^3 has no influence to the determination of lead and cadmium ions. Accuracy of determination is low if content of chloride ion is greater then 300 μg/dm^3. The reason is forming of some lead and cadmium complex with chloride compounds which are not electroactive during stripping step. The results obtained in this work shows that both, sulphate and chloride ions have some efects to the determination of lead, cadmium and zinc by potentiometric stripping analysis. Sulphate ion strongly interferes the determination if the content is greater then 1000 μg/dm^3. Accuracy of PSA determination of lead and cadmium is very low if concentration of chloride ion is greater then 30 μg/dm^3.

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Biogeochemical Cycle of Microelements in Sea Water of Boka Kotor Bay (Southern Adriatic) I

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The aim of this research was to determine the content of microelements in seawater, marine sediments and marina mussels (*Mytilus galloproviucalis)*. The cycles of microelements between seawater, marina sediments and marina organisms were monitoring at three different places in the Boka Kotor bay: Kotor, Tivat and Herceg Novi. The samples were collected in spring 2005, from February to April. Microelements in samples of marine sediments were determined directly on the grinded sample *via* EDPXRF techniques. The experimental results of microelements in sea water and marina mussels are obtained by using AAS and GF-AAS methods. The traces of elements in examined marina mussels were determined after usual sample preparation by previously decomposing organic matter with mineral acids.

The content of microelements in sea water and marine mussels is higher in the samples of Tivat and Herceg Novi then in Kotor samples, but it is opposite in the samples of sediments. The samples of sediments in Kotor have much higher concentrations of examined microelements than the sediment samples of Tivat and Herceg Novi.

The obtained results of sediments can be explained by high intensity water movement in Tivat and H. Novi bays, because of the open sea, causing bottom erosion, while in Kotor bay there is almost no water movment at all, causing fine particles sedimentation.

Higher concentrations of the examined microelements into Tivat and Herceg Novi water and mussels, than into Kotor samples, can be explained, beside water movement, by strong anthropogenic influnce from cost, especially from shipbuilding industry in Tivat bay.

At the same time, there is impact on the obtained results of incoming river's fresh water and spring water from the Kotor bay bottom.

ENEN P-24

Sorption Modelling of Chloro- and Nitrophenols by Natural Materials

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The usage of natural mineral sorbents for wastewater treatment is increasing because of their abundance and low price. The bentonite and the perlite used for the investigations were taken from deposits in the southern part of Bulgaria. They have been characterized by their chemical composition, specific surface area and particle size distribution. The kinetic and equilibrium experiments of p-chlorophenol (p-CP), 2,4-dichlorophenol (2,4-DCP), 3,5-dichlorophenol (3,5-DCP), 2,3,6-trichlorophenol (2,3,6-TCP), o-nitrophenol (o-NP), p-nitrophenol (p-NP) and 2,4-dinitrophenol (2,4-DNP) were carried out using their single model solutions at 20±2°C and pH 6.5-7.0. The concentrations of the phenols studied were determined using a Perkin-Elmer 323 UV-VIS-NIR spectrophotometer at definite wave length. An adsorption contact system with standard configuration was used for the kinetic study. The intensive mixing of the sorbent particles in the liquid phase was performed by a two-bladed impeller with a Heidolph RZR 2100 motor. The isotherms were determined by shaking of single model solutions with definite sorbent quantity on a platform shaker.

The sorption of chloro- and nitrophenols onto bentonite and perlite from their aqueous solutions has been studied in terms of pseudo-first order, pseudo-second order and intraparticle diffusion models. The batch sorption model based on the assumption of a pseudo-second order mechanism has been developed to predict the rate constant of sorption, the equilibrium capacity and initial sorption rate with the effect of initial phenol concentration, sorbent particle size, mass of the natural material used and agitation rate. An equilibrium capacity of sorption has been evaluated with the pseudo-second order rate equation as well as the Langmuir and Freundlich isotherms.

If the rate of sorption is a pseudo-second order mechanism, the corresponding kinetic rate equation given in its linear form is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\,2}} + \frac{1}{q_e}.t$$

where q_e and q_t are the sorption capacities at equilibrium and at time t, respectively (mg g^{-1}) and k_2 is the rate constant of pseudo-second order sorption (g mg^{-1} min^{-1}). The initial rate of sorption can be expressed as:

$$h = k_2 . q_e^{\,2}$$

The straight line plots of t/q_t against t have been analyzed. The values of k_2, q_2 and the correlation coefficient R^2 under different working conditions were calculated from these plots.

The rate parameter of intraparticle diffusion can be defined as:

$$q_t = k_i . t^{0.5}$$

where k_i values were calculated from the slopes of the straight line regions of the respective plots q_t against $t^{0.5}$.

The theoretically predicted curves by means of the second order parameters show an extremely high degree of correlation with the experimentally obtained data. Thus, the limiting step may be chemical sorption involving valency forces through exchange of electrons between the sorbate and the sorbent.

Section

Bio and Pharmaceutical Engineering

BIPE

BIPE X-NN yyy

X = KN – Keynote lecture
O – Oral presentation
P – Poster presentation

NN = Number

yyy = Topic:
bce - Biochemical Engineering
bim - Biomaterials
bme - Biomedical Engineering
phe - Pharmaceutical Engineering

The Improvement of Oxygen Transfer in Vitamin B_{12} Biosynthesis Process by n-Dodecane Addition

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CANCELED

Vitamin B_{12}, known as cyanocobalamin, cobolamin and also known as the energy vitamin is one of the most studied vitamin, being widely used in diet supplementation. The main producer of vitamin B_{12} at industrial scale is *Propionibacterium shermanii* by aerobic fermentation on glucose.

The oxygen supply into the broths constitutes one of the decisive factors of *P. shermanii* growth and can play an important role in the economy of vitamin B_{12} production. The aim of our work is to study the influence of n-dodecane, used as an oxygen-vector, on oxygen transfer in stirred bioreactors for vitamin B_{12} biosynthesis process, respectively for *Propionibacterium shermanii* broths.

The addition of n-dodecane allows enhancement of the oxygen mass transfer rate in broths, without any supplementary energy consumption for mixing intensification. By studying the oxygen mass transfer by submerged and surface aeration in the presence of n-dodecane as oxygen-vector for *P. shermanii* broths in a stirred bioreactor, it was recorded an increase of k_La up to 9 times compared with bacterial broths without hydrocarbon, depending on hydrocarbon concentration, biomass amount, mixing intensity and aeration rate (Figure 1).

Figure 1. Influence of n-dodecane concentration on amplification factor (v_S = 8.36x10^{-4} m/s).

By adding n-dodecane, the contribution of surface aeration to overall mass transfer of oxygen into the broth was greater than for the systems without hydrocarbon, but inferior to that obtained for simulated broths without biomass (the maximum contribution of surface aeration was of 1.6% for biomass concentration of 30.5 g/l d.w., superficial air velocity of 8.36x10^{-4} m/s and specific power input of 1790 W/m^3, that value being for about 3.2 times lower compared to the case of simulated fermentation broths at same viscosity and experimental conditions).

Microcapsules/Microparticles Loaded with Biologically Active Molecules for Medicine

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Development of T-vaccines protecting from intracellular pathogens, such as viruses, micobacteria, mycocoplasma and others is one of complicated challenges in immunology. Encapsulation of antigens (protein and protein coding DNA) are supposed to induce a better activation of both humoral and cellular responses, and therefore can be considered as a promising approach to the development of T-cell vaccines. Encapsulation could allow**:** 1) to easily entrap in microcapsules specific ligands ensuring a targeted interaction with cell receptors; 2) to encapsulate several DNA plasmids or proteins in one microcapsule; 3) to protect DNA from serum nuclease cleavage; 4) to mask a protein and DNA from preexisting antibodies enabling effective priming of immune response. To encapsulate protein or protein coding DNA, we have suggested an original universal technique based on layer-by-layer (LbL) adsorption of oppositely charged macromolecules onto a surface of inorganic colloid particles. Hollow microcapsules loaded with biologically active molecules can be easily prepared by decomposing an inorganic core, while the microcapsule wall can provide desired release properties. Multilayer microcapsules containing immobilized protein Asp f 2 and its coding DNA (DNA-Asp f2 under CMV promoter) are suggested as a novel delivery systems for the development of vaccines against intracellular pathogens.

The use of various polymer materials allows a proper shell design, in order to adjust required stability, biocompatibility and affinity properties of the microcapsules. The polymers used for entrapment of proteins/peptides, DNA have to be biocompatible and have to provide bioencapsulation procedure under mild conditions. In our research for preparation of microparticles/microcapsules we proposed both natural materials (alginate, chitosan) and synthetic polymers, such as poly-L-lysine (PLL) and poly(d,l)lactide-co-glycolide (PLGA).

Thrombin receptor agonist peptide (TRAP-6) was entrapped in biodegradable biocompatible polymer microparticles based on poly(d,l)-lactide-co-glycolide (PLGA) using w/o/w double emulsion-evaporation technique. The morphology of empty and TRAP-6 loaded microparticles was evaluated using scanning electron microscopy (SEM). *In vitro* release kinetics profile of TRAP-6 from microparticles was evaluated by both HPLC and biological assay. Biological activity of the peptide as well as its sensitivity to various organic solvents was investigated by platelet aggregation test. The obtained results can allow to optimize immobilization procedure and to encounter a new promising approach to development of novel controlled drug release delivery systems for wound healing, in particular to treat inner wounds.

Modeling of Aromatic Compound Degradation by *Pseudomonas putida*

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Before being discharged environmentally**,** aniline and phenol containing industrial effluents require proper previous treatment. Conventional methods, such as solvent extraction, activated carbon adsorption, and chemical oxidation suffer from serious drawbacks including high costs and formation of hazardous by-products. On the other hand, recently there has been a pronounced interest in biodegradation. Several bacteria degrading aromatic compounds either as a sole or as co-metabolic substrate have been described in literature [1-6].
In the present work, aniline degradation by *P. putida* intact cells in a stirred batch reactor is studied. Since such kinetic data are of significant importance in view of the strain use in large-scale bioreactors, the biodegradation reaction has been considered thoroughly. A mathematical model of the process is proposed. The model consists of differential equations describing the time-course of biomass *(X*) growth and simultaneous aniline utilization *(S), as well as* the initial instantaneous substrate adsorption by the cells*($(X-X_m)^n$* or *$k(X-X_m)$)*:

$$\begin{cases} \dfrac{dX}{dt} = \mu X \\ \dfrac{dS}{dt} = -\dfrac{\mu X}{Y} + \left(X - X_m\right)^{n_d} \end{cases} \quad \text{or} \quad \begin{cases} \dfrac{dX}{dt} = \mu X \\ \dfrac{dS}{dt} = -\dfrac{\mu X}{Y} + k\left(X - X_m\right) \end{cases}$$

The kinetic parameters are determined by using an adapted numerical procedure. In this procedure, the yield coefficient (*Y*) is considered a variable.
The model proposed is adequate to the experimental results delivered both from the study and from the literature. The model is compared to several reference models from the literature concerning biodegradation reactions. Bearing in mind that no other model from the literature describes the initial phase of substrate degradation, this specific part of the model proposed is significant for control of the exponential phase of fermentation.

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BIPE O-02 bce

Chromatophore Based Cytosensor: Responses to Various Biologically Active Aagents

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The design, operation and performances of a cytosensor based on living chromatophores isolated from *Betta splendens* Siamese fighting fish are presented here. The cytosensor was used to test several classes of biologically active agents including neurotransmitters, adenyl cyclase activators, cytoskeleton effectors, cell membrane effectors, and protein synthesis inhibitors. Detection was accomplished by monitoring motor-protein mediated movements of cellular pigment in chromatophores at both the gross population level as well as in singly imaged cells. Characteristic responses were optically analyzed and quantified based on the change in cell area covered by pigment and/or change in the optical density of the treated cell samples and untreated control cells. Chromatophores showed remarkably strong reactivity to agent which act as neurotransmitters, adenyl cyclase activators and cell membrane effectors. Conversely, protein synthesis inhibitors did not cause significant effect on chromatophores. Particular response features such as mode of response, its magnitude, kinetics, sensitivity and dose dependence for different classes of agents were monitored and could be used as a basis for mathematical modeling of these responses. The results confirmed that the cytosensor have a great potential for the use in food and water testing and in pharmacy.

Control Challenges in Photobioreactors

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Photosynthetic microorganisms like microalgae and cyanobacteria have a high potential in a wide range of applications (Richmond, 2000) such as pharmaceutical (bioactives molecules, toxins) and cosmetical applications (pigments), aquaculture (as feed for larvae and molluscs), environmental remediation (wastewater treatment and CO_2 removal), or renewable energy production (H_2). But, despite this well-known potential, examples of industrial valorisations remain scarce, mainly because of the difficulty to propose adapted process, called photobioreactors (PBR) that permits to reach sufficient productivity (Tsoglin and Gabel, 2000).
Whether the operation mode is batch or fed-batch, the main challenge in industrial applications involving photosynthetic microorganisms remains how to design and operate photobioreactor for photoautotrophic intensive cultivation. Biomass composition, growth rate, and product spectra depend strongly on the cultivation conditions. Important factors are medium composition, temperature, pH, CO_2 and O_2 supply, and most important of all: illumination.
The specific biological needs of photosynthetic microorganisms, like the light supply, pose fundamental challenges to the design and control of photobioreactors (PBR). Conventional engineering methods hit a complexity barrier due to the existing interactions between an important number of biological and physical parameters.
The principal goal of this study is to employ the advances towards the understanding of photosynthetic microorganisms metabolism together with recent advances in control science dealing with adaptive and nonlinear systems to elaborate reliable control strategies for photobioreactors.

BIPE O-04 phe

A Novel Stepwise Approach to Optimizing the Biocompatibility of Implantable Microcapsules

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Introduction

The implantation of microcapsules containing cells that secrete therapeutic products is a promising method for treating a range of diseases. In principle, the semi-permeable membrane of the microcapsule protects the enclosed graft from immune rejection by blocking out antibodies and immune cells, while tiny pores allow the free diffusion of therapeutic products and cell nutrients, ensuring the proper function and survival of the transplanted cells.

Problematic

Although the concept of immuno-protection by microencapsulation has proven to be feasible, clinical trials have been extremely limited. A lack of reproducible biocompatibility of the microcapsules is a primary reason for this slowed progress. Only recently, it's been recognized that the best way to achieve real success is to adopt a rational, step-wise approach (vs. trial and error) to optimizing the biocompatibility and functionality of the microcapsules.

Objective and Approach

This research focuses on the use of physicochemical analyses to optimize the biocompatibility of alginate-poly-L-lysine-alginate (APA) microcapsules, the most popular design for cell encapsulation. Following a stepwise approach, we [1] evaluated the purity level and biocompatibility of the alginate, [2] examined the interactions between the alginate and poly-L-lysine (PLL) within the microcapsule membrane, and [3] analyzed the microcapsule surface chemistry since surface properties generally govern the biological response to implants.

Results

[1] Using standard assays for purity in combination with X-ray Photoelectron Spectroscopy (XPS), we showed that commercially available alginates contain traces (up to 2 at%) of elemental impurities, despite their purification after purchase. More importantly, the presence of these contaminants, particularly proteins, correlated with a stronger immune response to implanted alginate gels. [2] The interactions between the alginate and PLL within the membrane of APA microcapsules were investigated using Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR). We demonstrated that their degree of interaction is variable. The result is relevant since unbound PLL is known to induce immune reactions. [3] To verify whether PLL, or other immunogens, were exposed at the microcapsule surface, we applied XPS and Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS). XPS provided quantitative information while the extreme surface sensitivity of ToF-SIMS allowed us to evaluate, for the first time, the composition of the outer monolayer of the microcapsule. We proved that PLL, in the form of a PLL-alginate complex, is exposed at the microcapsule surface in significant amounts. Since the degree of alginate-PLL interaction is variable, this result implies an increased risk that unbound PLL is in contact with the host tissue and compromising the biocompatibility of the APA microcapsule.

Conclusion

This research demonstrates the effectiveness of using physicochemical analyses as tools for understanding and explaining the biocompatibility of implantable microcapsules. Such analyses are a crucial aspect of the rational, step-wise approach to optimizing the microcapsule biocompatibility so that reproducible results may be achieved *in vivo* and the microencapsulation method may be used regularly in clinical applications.

Biodegradable Polymeric Carriers for Controlled Release Systems

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Low molecular weight poly(lactic acid) was synthesized by direct polycondensation of lactic acid. The oligomers were characterized by viscosimetry, Light Scattering, and Gel Permeation Chromatography (GPC). The swelling behaviour of tablets made of the above polymer immersed in buffer solutions (pH: 5.4 & 7.4) and deionized water at 37°C was studied. In the same experiments, the hydrolytic stability of D,L-PLA was assessed by measuring the weight loss after drying the tablets. In order to inhibit any degradation due to bacteria, formaldehyde was added in the solution as biostatic factor. The results obtained from this work showed that degradation seems to be purely chemical and proceeds faster in deionized water and acidic buffer. PLA samples immersed in buffer with pH 7.4 show much better stability and water transport tends to obey Fick' law.

The release of model drugs such as hydrochloric propranolol, sodium salt of diclofenac and sulfasalazine incorporated into D,L-PLA slabs, was recorded as a function of time in buffer solutions of pH 5.4 and 7.4. It was found that the incorporation of drug in D,L-PLA tablets increases their swelling index, probably due to the creation of additional porosity to the specimens or other interaction between drug and polymeric matrix.

The observed differences in the release profile of the above drugs in the different buffers show that release is affected not only by the PLA degradation in the various liquids but also by interactions between the drug and the surrounding buffer. The fast release of diclofenac in pH 7.4 shows that the drug diffusion is favoured in this area whereas in the buffer with pH 5.4 diffusion rate is slower. On the other hand differences in the release of propranolol can be attributed to variations in the PLA stability into various buffers.

BIPE O-06 bim

Modified Polyethylene as a Matrix for Paper Fiber Reinforced Composites

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Compounding of polyethylene with paper was achieved by dispersion of paper fibers into the appropriate hot polymer solution followed by co-precipitation of the components by cooling at room temperature. The above method was found suitable for the proper dispersion of fibers in the polymeric matrix, as compared with melt compounding. The density, hardness, tensile and impact properties were measured in composite specimens prepared by compression moulding, with filler content ranging from 10 to 40% (w/w). Unmodified low density polyethylene (LDPE), modified with maleic anhydride grafted linear low density polyethylene LLDPE and an acrylic acid and n-butyl acrylate polyethylene copolymer were used as matrices for the preparation of paper fiber reinforced composites. The incorporation of polar groups into the polyethylene chain modifies the dissolution/co-precipitation behaviour of their solutions. Composites based on modified LDPE showed improvement on their mechanical properties. The Takayanagi model, applied to predict the Young's modulus of composites, was in very good agreement with the experimental data.

Dehalogenating Activity of New Isolated Bacterial Consortium BM1. Comparison Between Free and Immobilized Culture

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Biodegradation is the main process by which xenobiotics disappear from the environment, because of their low concentrations presence. 1,2-Dichloroethane, also called ethylene dichloride, is a manifactured chemical that is not found in the nature. The toxic chemical released to the environment is released into the rivers, lakes soil and underground water. It breaks down very slowly in the water and most of it evaporates to the air, where 1,2-dichloroethane can stay more than 5 months. It causes liver and kidney diseases, damages of the immune and has a cancerogenic effect .Bacterial consortium BM1 capable to metabolize 1,2-Dichloroethane was isolated from activated sludge taken from petroleum refinery ''Lukoil-Neftochim''- Burgas, Bulgaria. Its dehalogenating activity was tested toward of various of concentrations of 1,2- Dichloroethane used as main substrate. Batch mode experiments were carried out where BM1 was included as: a) free culture, in shaking flasks under aerobic and anaerobic conditions; b) immobilized culture, where active carbon was used as solid carrier. Immobilized cells showed several times higher and faster dehalogenating activity than free ones. Concentrations over 0.25 g/l of 1,2- Dichloroethane inhibit the growth of free bacterial cells, while 0.6 g/l of the substrate were successfully degraded by the immobilized culture. The process of dehalogenation is followed of chloride ions release. Liquid medium MMV containing $Na_2HPO_4.12H_2O$, KH_2PO_4, $(NH_4)_2SO_4$, $MgSO_4.7H_2O$, was used for cultivation, T= 30 ^{0}C and pH 7-7.5. No vitamins or yeast extract were added as biostimulators.
Finally, in a local wastewater treatment plant a biotreatment of halogenated aliphatic compounds by BM1 using poor mineral medium can be applied successfully.

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BIPE O-08 bim

The Use of Multi-Parameter Flow Cytometry for Characterisation and Monitoring of Insect Cell-Baculovirus Fermentations in a Mechanically-Agitated Bioreactor

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Bacteria and mammalian cells have been traditionally used as hosts for commercial recombinant protein production. In recent years, the insect cell-baculovirus system has emerged as a potentially attractive recombinant protein expression vehicle. This route is attractive because baculovirus-infected insect cells are able to perform post-translational modification while accommodating very abundant expression of recombinant protein. Although flow cytometry has been used widely for analysis of mammalian and microbial cell physiology and morphology, there is very little information on applications of this powerful and highly efficient technique in insect cell culture.

Here we have compared cell ratiometric counts and viability of Sf-21 cell cultures using a flow cytometer to those determined by more traditional methods using a haemocytometer and the trypan-blue exclusion dye. There was good agreement between the two counting methods but the former technique proved to be a more reliable and statistically robust viability indicator (stains used: propidium iodide and calcein AM).

Flow cytometry has also been used to monitor various parameters during fermentations of Sf21 cultures infected with the recombinant *Autographa californica* Nuclear Polyhedrosis Virus (AcNPV). This recombinant baculovirus contains the inserted nucleic acid sequence amFP486 coding for AM-Cyan coral protein, which emits natural green fluorescence. A good correlation has been obtained between parameters such as mean green fluorescence and AmCyan positively stained cells linked to cell viability. Additionally, DNA content, cell size and granularity have proven to be good indicators of baculovirus infection.

We have also simplified and optimised methods of cell treatment prior to flow cytometric analysis.

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Bioreactors with Interstitial Fluid Flow for Cartilage Tissue Engineering

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In vitro cultivation of functional tissue equivalents may address the clinical problem of tissue failure and provide physiologically relevant models for *in vitro* studies of cells and tissues under normal and pathological conditions. Tissue engineering based on the integrated use of chondrogenic cells, biodegradable scaffolds and bioreactors was proposed for *in vitro* cultivation of functional cartilage tissue equivalents. In this approach, biodegradable scaffolds provide a structural and logistic template for cell attachment and tissue regeneration, while bioreactors maintain control of the *in vitro* conditions designed to mimic the *in vivo* environment and promote chondrogenesis.

Efficient and controlled delivery of biochemical signals is one of the main requirements especially in cultures of precursor cells such as bone marrow derived chondrogenic cells (herein referred to as bone marrow stromal cells BMSC). Cultures of these cells require additional biochemical regulatory signals to induce chondrogenic differentiation as compared to cultures of differentiated chondrocytes. Bioreactors based on perfusion of cultivated tissues by culture medium present an attractive design option providing enhanced mass transfer directly to the cells.

In this work, we have utilized two bioreactor designs providing interstitial flow through the cultivated tissue. Perfusion cartridges (1.5 mL volume, Millipore, Bedford, MA) were used for cultivation of murine BMSC seeded on porous polyglicolic acid (PGA) scaffolds (10 mm in diameter x 5 mm thick disks). The scaffolds were secured between two rubber gaskets such that medium flow was forced through the cultivated tissue at a velocity of about 100 μm/s. The perfusion was periodically applied in order to provide efficient mass transfer at regimes imitating the *in vivo* environment.

The second bioreactor design was based on packed bed reactor configuration and the use of particulate cell supports with BMSC entrapped within the support matrices. Electrostatic droplet generation technique was used for cell immobilization in alginate microbeads 600 μm in diameter. Packed bed bioreactors, 1 mL volume, were designed as glass cylinders, 10 mm in diameter, with porous sintered glass plates at the bioreactor ends to support the bed of microbeads and distribute the medium. The medium flow was applied continually at an interstitial velocity of 100 μm/s.

The bioreactors with interstitial fluid flow were placed in a humidified 5 – 10 % CO_2 incubator and cartilaginous tissues were cultivated for up to 3 weeks. Effects of medium flow and mass transfer were evaluated by analyses of distribution and differentiation of cultivated cells, deposition of cartilaginous components, and structural properties of the engineered tissues.

BIPE O-10 bim

Combined Fed Batch and Continuous Operating Regimes for the Hybridoma Bioreactor

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CANCELED

Hybridoma cell cultures are used for the production of monoclonal antibodies (MAbs). These have many applications in the analysis and *in vivo* diagnostics, therapeutics, instrumentation and affinity chromatography. Production of MAbs in industrial quantities is a demanding task and involves high costs. As operating mode, the batch culture was the primary choice, due its robust control and simplicity in operation. Afterwards, the continuous mode was preferred, using either suspended cells with external recirculation or immobilized cells in hollow fiber type reactors. This allows a longer functioning time and, also, higher cells densities.

In two previous studies (Lavric, 2005; Ofiteru, 2005) the performance of both fed-batch and continuous hybridoma reactors was analyzed and optimized. The fed batch mode cannot be used for a long period because of the accumulation of dead cells. To be efficient, the continuous mode should start from high living cells concentration. Taking these into account, the present study focuses on the sequence fed batch – continuous operation which can give an improved performance of the whole system. Three test runs were performed, for the same switch time from fed batch to continuous. The chosen cases were the best, the worst and the base case of the fed batch runs, as presented in Lavric et al., 2005.

Figure 1. MAb's concentration in time (left) and the ratio MAb/dead cells (right)

The switch to the continuous mode is made when the dead cells concentration rate becomes too high. For the allowed fermentation time, the system tends towards steady state, except for the dead cells concentration, which needs a much longer period. The combined mode preserves the hierarchy of the fed batch, improving the overall performance of the system without an excessive accumulation of the dead cells (Figure 1, left). If the cost of the cells is important, a better performance criterion is the ratio between the MAb and dead cells concentrations (Figure 1, right). For long operating times, this ratio shows that the worst case becomes better than the other two. An optimal control of the whole system is mandatory.

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Pharmaceutical Packaging - Handling the Problem of Humidity

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Pharmaceutical dosage forms can be harmed by many environmental factors, mostly by humidity. This work reports that, for sensitive products, such risks can be drastically minimized by choosing appropriate packaging materials and methods. In our study, we focused on barrier polymers, since they represent attractive packaging solutions, especially because they offer the advantages of light weight and formability [1]. Although many thermoformable foils are used in pharmaceutical blister packages, those made with PVC are most common. Nevertheless, there are increasing demands on the packaging industry to develop foils that are extremely good barriers to moisture. The moisture vapor barrier for packaging foil is expressed in terms of water vapor transmission rate (WVTR) [2]. A blister package's ability to limit water vapor permeation depends on the material used (fig. 1). Our work deals with the comparison of different blister foils (cold form, PVC and PVC/PVdC) and their product protective ability against moisture, in the course of accelerated stability studies.

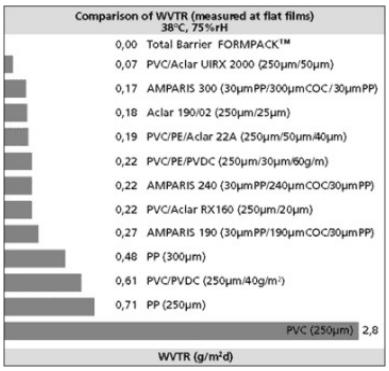


Fig. 1 Pharmaceutical blister foils

Furthermore, tubes and desiccant stoppers were taken into consideration as an ideal moisture protection for effervescent forms. The desiccants currently used for pharmaceutical packaging are usually silica gel and molecular sieves. Each desiccant has different properties under various temperature and humidity conditions. When tested at constant temperature, silica gel's absorption capacity for water is relatively small at low humidity levels, but rises with increasing humidity, while molecular sieves react rapidly at both high and low humidity levels (fig. 2). Nevertheless, molecular sieves could be difficult to handle in uncontrolled manufacturing environments. Absorption capacity is one of the key measures of desiccant performance, and it was used in this study to calculate the amount of silica gel necessary for maintaining the required relative humidity level during shelf life of the product of interest.

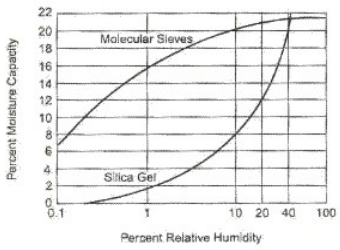


Fig. 2 Moisture capacity vs. RH

In the course of this work, the variety of packaging options available were considered in order to ensure integrity and keep the quality of the specific product. Medical grade blister-packaging foils can protect many medicines against moisture, but packaging systems with desiccants were also taken into account to reach a final goal of finding an optimal packaging solution for the tested products.

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BIPE O-12 phe

Crystallinity of Chiral Omeprazole Alkaline Salts

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Summary

The physical properties of drug substances may affect stability, manufacturing, dissolution, and bioavailability. This study thus reports on the physical and thermal characterisation of crystallinity versus amorphous part of the alkaline salts of chiral omeprazole (S- and R-omeprazole), and has confirmed that the physical properties of enantiomers are different, that may have an impact not only on the bioavailability but also their therapeutic efficacy. SEM results indicated a smaller and more uniform particle size for the S-enantiomer, while the low level of crystallinity of both enantiomers was confirmed by DRIFT spectroscopy. µTA shows different topographical images for S- and R-omeprazole, while results from DSC analyses confirmed S-omeprazole to be predominantly amorphous. Thermal stability of chiral omeprazole sodium salts was better compared to neutral omeprazole.

Introduction

There is a constant need within the pharmaceutical industry to characterize the physical properties of different batches of drug substances, in terms of the polymorphic form and degree of crystallinity. In the first instance, there are many circumstances whereby the amorphous drug form has advantages over that of the crystalline system, in terms of improved dissolution and bioavailability. However, generation of amorphous material on particle surfaces during processing (e.g. mixing, milling) may also result in significant changes in the behaviour of the system and was also examined in the current study after compression of drugs into the disks.

Results and Discussion

The IR spectra of R and S-omeprazole (for various weight ratios) clearly differ from each other over the entire spectral range (Fig. 1) where intensity is plotted against wavenumbers. Most bands are, however, overlapping and the largest peaks can be seen at around 1370 and at 2900 cm^{-1} for S and R-omeprazole respectively. A key characteristic of semi-crystalline materials is the degree of crystallinity (Ic) here calculated as a ratio of intensities of absorption bands at 1372 cm^{-1} CH groups (disorder) and covalent vibrations of CH_2 and CH groups at ~2900 cm^{-1} (order). The crystalinity indices were calculated to be 1.9 and 1.2 for S- and R-omeprazole respectively (these values are relatively low as expected).

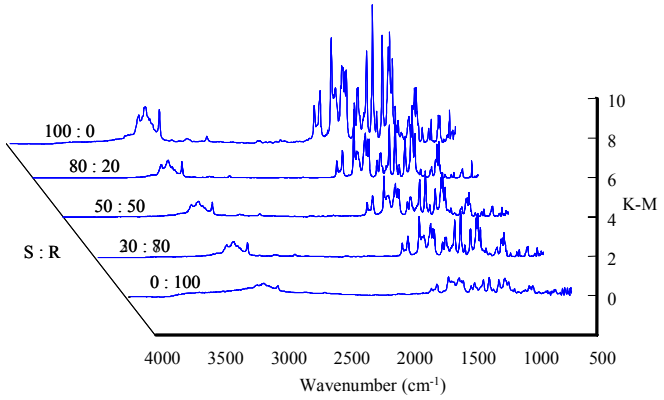


Figure 1. DRIFT spectra as a function of the S-: R-omeprazole w/w ratio in physical mixtures.

Production of Yeast Biomass with Increased Content of Zinc

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The work dealt with the production of yeast biomass with the increased content of zinc in a bubble column at different operating conditions (the gas flow rate and type of bioreactor: a) batch bioreactor with initial concentrations of glucose and zinc of 20 g/dm^3 and 5 mM, respectively, b) feed-batch bioreactor with constant glucose and zinc concentrations of 20 g/dm^3 and 5 mM, respectively, and c) feed-batch bioreactor with continuous addition of glucose and zinc). The oxygen mass transfer rate did not affect the specific yeast growth rate (0.16 h^{-1}) in the batch bioreactor. Somewhat higher specific yeast growth rate (0.19 h^{-1}) was obtained in the feed-batch bioreactor when the glucose and zinc concentrations were maintaned at constant levels. The highest specific yeast growth rate (0.25 h^{-1}) was achieved in the fed-batch bioreactor when glucose and zinc were continuously added. The amount of the absorbed zinc was reduced with the increase of the oxygen mass transfer rate. The highest content of zinc in the yeast biomass (1.28 %) was obtained at a low oxygen mass transfer rate in the batch reactor at the initial zinc concentration of 5 mM.

BIPE P-02 bce

Methodology for Characterization of Residence Time Distribution in Inverse Fluidized Beds

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Three phase fluidized beds are commonly used in industrial applications, such as chemical and petrochemical industry and in biological reactors. Among them, inverse fluidized beds are commonly used for microbial and enzyme encapsulation. Such cases involve light solids. The bed is being expanded downwards by the flowing liquid. A gas phase is rising counter-currently to the liquid, thus achieving high bed uniformity. Due to the bed organisation and the uniform phase distribution, the oxygen mass transfer rate is high [1].
The study is focused on liquid maldistribution in inverse fluidized bed. The phenomenon may or may not depend on column design. The latter case is dependent merely on bed fluid dynamics and could be treated by using the methodology of the residence time distribution theory. The paper describes such a methodology based on the general experimental tracer technique extended by a new systemic modelling approach. The approach is based on a Mellin-modification of the Laplace transform over the relevant equations. A transfer function with delay time, i.e. $\frac{k\exp(-T.p)}{(1+\tau.p)^n}$, is used to solve the problem. In this function, k is the static gain, T is the time delay, τ stands for time constant, and n indicates the system order. These parameters are identified based on a least squares approximation of the experimental and modelling time-courses. Variable p represents the Laplace operator[2]. Experiments on RTD in a lab-scale column of *ID* 0.1m and bed height up to 0.8 m. have been carried out. The method allows zero-time solutions for fast identification analysis. Unlike the diffusion model approximation, the technique considered allows exact approximation of the RTD curves with circulation. The Mellin transformation proposed represents adequately bioreactor liquid maldistribution thus allowing fast overview of the studied reaction and prompt feed back control on the physical situation.

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Endo-Pectinase Inactivation in a Ceramic Membrane Filtration System

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The functionality of enzymes is usually dependent on their tertiary structure. Deforming or destroying the tertiary structure to a certain extent, coming as a consequence of e.g. a shearing treatment under different regime such as stirring, can lead to enzyme inactivation. That is why it is desirable to investigate the stability of commercially important enzymes under different conditions of production, downstream processing and application.

Pectinases are enzymes that degrade pectic substances by different mechanisms and are produced at the commercial level mostly in submerged aerobic cultivation conditions. Pectinases have wide application in food industry and lately one of the components of pectinase enzymes complex, endo-pectinase, renewed great attention because of its involvement in the production of functional food.

In the presented work the loss of endo-pectinase activity due to its inactivation during ceramic membrane cross-flow ultrafiltration was investigated. During filtration under operation conditions that provided sufficient permate flux, the significant loss of activity was observed: 66% after 120 min of operation. The use of Kenics static mixer as a static turbulence promoter provided operation at similar flux values at lower cross-flow velocity, which resulted in moderate decrease of activity loss; the loss of the enzyme activity was 43% after 120 min of operation. Replacing of the membrane tube with nonporous tube proved that shear stress created by the pump and circulation through the system represents the main source of the enzyme inactivation. Modification of the feed solution enabled filtration with sufficient permeate fluxes with the loss of enzyme activity as low as 10% after more than 200 min of operation.

Comparison of Lipase-Catalyzed Ester Synthesis in Organic Solvent and Solvent-Free System

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Lipase-catalyzed syntheses of esters of various lengths, structures and applications in organic solvents are well documented. Although the synthesis of esters with the lower melting points is feasible in solvent-free system, reports on related studies are scarce. The advantages of reactions in solvent-free system are savings in reactor design in large-scale process and reduction of separation costs due to avoiding solvent recovery.

The aim of this study was to investigate catalytic activity of porcine pancreatic lipase in synthesis of several valuable aroma esters, in solvent-free system and in isooctane. The reactions were performed at 45°C, with 0.1% (v/v) of added water with 0.5% (w/v) of lipase from porcine pancreas and with equimolar concentrations of reactants.

Lipase showed good catalytic properties in each of performed esterifications. Yields over 90 % were achieved after 48 h of esterification. By comparison of results of esterification in solvent-free system and in organic solvent, it can be concluded that addition of isooctane significantly changes lipase activity and specificity. In solvent-free system lipase showed low activity towards the synthesis of esters of butyric acid (final yields around 10 %), while exhibits high activity in synthesis of esters of caprylic acid (yields over 90 %). On the contrary, in reactions performed in isooctane, lipase showed greater affinity towards butyric acid. Discrepancies between affinities were significantly lower in system with isooctane. Kinetics of reaction in both systems was tested. Obtained initial rates of esterification were in good agreement with ping pong bi-bi kinetics for bisubstrate enzymatic reactions.

It can be concluded that lipase from porcine pancreas showed significant esterification activity in synthesis of various aroma esters in solvent-free system, especially for synthesis of esters of caprylic acid. This is probably due to the fact that lipase denaturation occurs in solvent-free system when shorter and more polar acid is applied as acyl donor.

Cell Immobilization in PVA Microbeads for Wastewater Treatment

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Immobilized cell systems are widely investigated in different fields of biotechnology and successfully utilized at industrial scale in wastewater treatment and production of biopharmaceuticals and fermented beverages. Some of the advantages of cell immobilization over conventional free cell systems are containment of cells within a limited space at higher concentrations, higher conversion rates, and easy separation from the fluid phase.

One of the approaches to cell immobilization is entrapment within porous carrier matrices such as hydrogels, which provide cell retainment while allowing metabolite diffusion. Among various carrier materials, polyvinyl alcohol (PVA) is a promising support since it is nontoxic and mechanically stable. It is a synthetic, hydrophilic polymer, which can form hydrogels by creation of hydrogen bonds between hydroxyl groups of neighboring polymer chains. The mostly used gellation method is multiple freezing and thawing of PVA solutions resulting in PVA cryogels, which have been successfully applied for cell and enzyme immobilization.

In this work, we have investigated possibilities for production of PVA microbeads with immobilized activated sludge by an emulsification method followed by freezing and thawing, aimed for wastewater treatment. PVA solutions (10 – 20 % w/w) containing cells were poured in a hydrophobic phase under vigorous mixing resulting in formation of a stable emulsion system. The emulsion was then frozen at – 20°C for 18 – 24 h, followed by thawing at 0°C. Emulsion composition and regimes of freezing and thawing were varied in order to obtain uniform, mechanically stable microbeads. Depending on the operating conditions, microbeads ranging from 200 μm to 1 mm in diameter were produced. The viability and activity of the immobilized cells were investigated in treatments of wastewater from a starch factory. Decrease in COD, although slower as compared to batches with suspended cells, indicated preserved activity of the immobilized activated sludge. Results of this study indicated potentials of the applied method for controlled production of PVA microbeads with immobilized biomass.

BIPE P-06 bce

Production and Characterization of the Dextranase From *Penicillium funiculosum* TFZ 94

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Dextranase (1,6-α-D-glucan 6-glucanohidrolase, EC 3.2.1.11) is an extracellular enzyme of bacteria, microscopic fungi and some yeasts. This enzyme catalyses the reaction hydrolysis of dextran, a polysaccharide in which more than 95% of the D-glucosyl units are α-1,6 linked. Dextranase is a inducible enzyme, and one from the best inducers is his substrate, dextran. Dextranase is important because of its possible application in pharmaceutical, cosmetical and food industry. In this work we investigated production and some properties of the dextranase from *Penicillium funiculosum* TFZ 94.

Submerged cultivation of the fungi *Penicillium funiculosum*, strain TFZ 94, isolated from soil, was performed on the reciprocal shaker at 28°C. Composition of nutrient medium was: native dextran 1%, $NaNO_3$ 0,1%, K_2HPO_4 0,08% and $MgSO_4 \cdot 7H_2O$ 0,12%, with initial pH value 6.0.

Dextranase activity was determined through the increase of the amount of reducing groups with dextran T100 as substrate, at pH 6.0 and temperature 37°C. Reducing groups were determined by a modified ferricyanide method, with glucose as a standard. The unit of the dextranase activity (U) represents a quantity of enzyme producing the amount of reducing groups equivalent to 1 μmol of glucose per minute. Kinetic constants K_m and V_{max}, optimal temperature for activity and stability, optimal pH for activity, and efects of some inhibitors has been investigated.

The maximum of dextranase activity (78 U/ml) was obtained in the course of the seventh day of cultivation. Kinetic constants for dextran T100 K_m=73,3 mM and V_{max}=2,5 $\mu mol \cdot ml^{-1} \cdot min^{-1}$ was established. Enzyme showed the optimal temperature 48°C, E_a =30,1 KJ/mol, and optimal pH=5.8-6.4 for activity, and it was stable up to 50°C. Inhibitory effects of Cu^{2+}, Hg^{2+}, Fe^{3+}, and N_3^- ions was detected.

Bioprocess of the Polyester Fabric by Lipases

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Polyesters are manufactured synthetic compositions comprising any long chain synthetic polymer composed of at least 85% by weight of an ester of a substituted aromatic carboxylic acid, including but not restricted to substituted terephthalic units. In the textile industry, polyester has certain key advantages including high strength, soft hand, stretch resistance, stain resistance, machine washability, wrinkle and abrasion resistance. However, polyester is not so optimal in terms of its hydrophobicity, pilling, static, dyeability, softening or wettability enhancing compounds.

We have used a 100% polyester fabric, homopolymer poly (ethylene terephthalate) and lipases in this study. We use tree lipases, different origins, which are commercially products from Biocatalysis. Treatments, i.e. interactions of enzymes and the PES fabric are done in aqueous buffer solutions. We have selected the inorganic phosphate buffer and used it throughout this study; because, it gives best conditions for correction several properties of polyester fabric. In most cases, the primary biological attack is an enzymatically catalysed hydrolysis of ester in the polymers, e.g. PES fibers. This first step of depolymerization is a surface erosion process (enzymes can not penetrate into the polymer bulk).

The results of sorption characteristics, i.e. water absorption and penetration, for different treatments of the PES fabric have larger values than the raw samples of the same fabric. Two of the three lipases significantly improve the water penetration and absorbent properties of regular polyester fabric. All treatments have caused increase weight loss reducing wear resistance of PES fabric and partly decreasing quality the final goods.

Under the same reaction condition two lipases significantly improves the water wetting decreasing the contact angle (55°) according to control sample (76^0).

Spectral distribution of reflection curves, i.e. the intensity of reflection energy is different relative to the applied enzymatic treatments, which signals different quantity of fixated dye for the fabric. Presented spectral K/S values show that previous biomodification of polyester fibers influences a contribution to the increase in tint depth. Surface polyester fibers modification has caused better dye uptake but probably better sorption characteristics.

The breaking tenacity and strain from the lipases treated polyester fabric indicating insignificant differences to control samples.

Lipases improve the hydrophilicity much more than the alkaline hydrolysis reaction in a significantly shorter time. The improved water wettability is accompanied by full strength retention compared to the significantly reduced strength and mass from alkaline hydrolysis.

BIPE P-08 bce

Enhencement of Protolytic Enzymes Production in Batch Cultivation of *Bacillus subtilis:* Optimization of Oxygen Transfer Condition

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The paper presents investigation of production of extracellular enzymes resulting from decomposition of proteins from the nutritive medium during vegetative growth, as well as metabolic processes during the sporulation phase of *Bacillus subtilis* G. The fact that energy-providing reactions during growth and sporulation differ considerably (Hanson and et al, 1962), indicates that oxygen requirements during these phases also differ. Since phases of vegetative growth and sporulation take place synchronously with different intensity, they in fact condition the production of proteolytic enzymes. The goal of this research was to increase the production of proteolytic enzymes by providing the optimum level of oxygen saturation of the medium by combining a certain level of aeration and stirring speed adapted to the need of microorganisms during specific physiological states.

Process optimization for production of proteolytic enzymes of probiotic *B. subtilis* G bacteria was done on a fermentor with a 20 l volume under various conditions of oxygen transfer characterized by oxygen transfer rate (OTR; 6-50 mM/l h). Bacterial growth and enzymes production during 40 hours of incubation in a semisynthetic nutritive substrate (corn steep liquor, molases), were monitored via the number of colony forming units (CFU), spore number (X), culture pH, and proteolytic enzyme activity. Since the phenomen of transition from the vegetative to the sporulating cycle is reflected in changes in pH of the medium as a consequence of accumulation of acetic and pyruvic acids during vegetative growth, changes of pH as an indicator of physiological changes in cells were left to take place naturally during the first phase of these investigations.

Results of our investigations show that implemented aeration and stirring regimes, and oxygen consumption resulting from the speed of growth and proliferation, as well as bacterial sporulation, have a significant influence on the intensity of proteolytic enzymes production. For this reason, the defining of aeration and stirring conditions has a signignificant importance for the development of this new procedure for the industrial level.

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Ionic Liquids as (Co) Solvents for Enzymatic Reactions

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Ionic liquids are salts that are liquid at room temperature. Their use as catalysts and catalytic support has been studied extensively. They are also being considered as "green solvents" for various separation processes.

Generally, the term "ionic liquids" stands for liquids composed of ions. Ionic liquids mainly comprise organic cations such as 1,3-dialkylimidazolium, tetraalkylammonium, tetraalkyl-phosphonium, N-alkyl-pyridinium. The common anions which lead to neutral and stoichiometric ionic liquids are $[PF_6]^-$, $[BF_4]^-$, $[CF_3SO_3]^-$, $[(CF_3SO_2)_2N]^-$, …

Ionic liquids are attractive as potential solvents for a number of reasons:

- they have essentially no vapour pressure and thus serve as potential replacements for volatile organic compounds in the chemical industry;
- they possess good thermal stability and do not decompose over a large temperature range;
- they are able to dissolve a wide range of organic, inorganic and organometallic compounds;
- they serve as a good medium to solubilise gases such as H_2, CO, O_2 and CO_2;
- they generally do not co-ordinate to metal complexes, enzymes and different organic substrates;
- their ionic character enhances the reaction rates to a great extent in many reactions including microwave-assisted organic synthesis;
- they show a high degree of potential for enantioselective reactions as a significant impact on the reactivities and selectivities due to their polar and non-coordinating properties can be achieved;
- the viscosity of 1-alkyl-3-methyl imidazolium salts can be decreased by using highly branched and compact alkyl chain, as well as by changing the nature of anion.

Ionic liquids can be used in biotechnology for enzyme catalysis as pure solvents, as co – solvents in aqueous phase, or as a two – phase systems together with other solvents. But not all ionic liquids are suitable for biocatalysis. Enzymes are usually active in ionic liquids containing BF_4, PF_6 and $(CF_3SO_2)_2N$ anions and not in ionic liquids containing Cl, NO_3, CF_3SO_3, trifluoroacetate or acetate anions. The majority of enzymes reported to be active in ionic liquids belong to the class of lipases – *Candida Antarctica* lipase type B, *Candida rugosa* lipase, *Pseudomonas cepacia* lipase, *Pseudomonas fluorescens* lipase.

Biocatalytic reactions in ionic liquids have shown higher selectivity, faster rates and greater enzyme stability.

In order to use ionic liquids as reaction media in enzyme catalyzed reactions two different ionic liquids, i.e. 1-butyl-3-methylimidazolium tetrafluoroborate and 1-butyl-3-methylimidazolium hexafluorophosphate have been synthesised.

BIPE P-10 bce

Anion Effect on Antimicrobial Activity of Metal Complexes with Benzimidazole Derivates

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Benzimidazole derivatives with substituents such as methyl and chloro in different positions have been found to posses inhibitory effect on the development of several yeasts and bacteria. Various benzimidazoles are effective inhibitors of the growth of lactobacilli, vaccinia virus, influenza virus and HIV-virus. Many different benzimidazoles have such activities as analgetics, anticarcinogens, sedatives, etc.

In view of previous observations [1-3] that presence of the metal ions considerably enhance the biological activity of organic molecules, we now study and report the anion effect on antimicrobial activity of copper(II) and zinc(II) complexes with 1-(4-chlorobenzoyl)-2-methylbenzimidazole.

Chloride and nitrate of copper(II) and zinc(II) react with 1-(4-chlorobenzoyl)-2-methylbenzimidazole to give complexes of the type $ML_2A_2 \cdot nH_2O$ (M=Cu or Zn; A=Cl^- or NO_3^- L=1-(4-chlorobenzoyl)-2-methylbenzimidazole; n=0, 1 or 2. The antibacterial activity of the 1-(4-chlorobenzoyl)-2-methylbenzimidazole and its complexes was evaluated against three gram positive bacterial strains: *Bacillus* sp.*, Staphylococcus aureus* and *Sarcina lutea,* one gram negative isolate: *Pseudomonas aeruginosa* and yeast: *Saccharomyces cerevisiae*.

The minimum inhibitory concentration (MIC) was determined for ligand and its complexes. It was found that tested compounds were more active against gram-positive than gram-negative bacteria. None of the compounds were significantly effective against yeast *Saccharomyces cerevisiae,* except $CuL_2Cl_2 \cdot 2H_2O$, which moderately inhibited the growth of yeast. ZnL_2Cl_2 complex was found to be slightly active against *Saccharomyces cerevisiae.* The same complex showed the lowest MIC value of 60 μg/ml against *Pseudomonas aeruginosa,* as well as 125 μg/ml, against *Bacillus* sp*. and Sarcina lutea.* The MIC value of $CuL_2(NO_3)_2 \cdot H_2O$ was 60 μg/ml against *Pseudomonas aeruginosa.* $ZnL_2(NO_3)_2$, showed the lowest MIC value of 60 μg/ml against *Staphylococcus aureus.* The effect of anion on the antimicrobial activity was discussed.

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The Study of Fermentation Process on Binding Capacity of Yeast Biomass with Microelements

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Recently there is an evident expansion of the market position for products based on various microorganisms (bacteria, fungi, etc.), with bonded bioelements. Cell structure and the negatively charged surface of the biomass, are very suitable for bonding metal cations of zinc, chromium, magnesium, iron, cobalt, and selenium.

The goal of the paper was to investigate the effect of fermentation process parameters under industrial conditions on obtaining high yields of brewer's yeast cell biomass and on maximum capacity of bonding available iron to macromolecules.

Semisynthetic nutritive medium was seeded with a culture of brewer's yeast *(Saccharomyces cerevisiae)*obtained in the industrial beer production process. Under dynamic conditions of biomass production, ferrosulphate as the source of iron was used.

Industrial "scale up" of the fermentation process is based on optimal laboratory parameters and results of investigations with initial scale-up under semi-industrial conditions.

Experiments were done in the selected interval of air flow and degree of utilization of fermentor capacity. Biomass production and quantity of organically bonded Fe were investigated as a function of derived states variables of the fermentation process: aeration intensity and efficiency of stirring of the fermentation suspension.

Results of mentioned investigations will be used to optimize the fermentation process, as a segment of the technology for obtaining brewer's yeast with bonded iron.

Distribution of Distances of Connected Amino Acid Pairs in Proteins

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It is considered that two amino acids are connected if distance between their non hydrogen atoms is less than 4.5Å. The models of energies for amino acids contacts in proteins were analyzed, while all contacts of amino acids that are connected were treated uniformly, regardless of the amino acid distance [U. Bastola et al, PNAS, 97, 3977—3981, 2000]. Because of that, in order to investigate the reliability of the mentioned model, it is interesting to analyze a distribution of distances between amino acids that are in contact.

In order to analyze a distance distribution, we developed a software tool that enables a range of computations on protein data. Our tool calculates distances between pairs of amino acids in the protein, under different sorts of additional restrictions. In addition, the average and dispersion of distances between pairs of amino acids can be computed. Two kinds of distances are considered: between Cα atoms, and minimal distance between non hydrogen atoms of two amino acids. The results are presented in a tabular and graphical form. As a data set we used proteins from PDBSELECT.

We noticed that for some amino acid pairs, average distances are notably smaller. Also, histograms of distance distribution for some amino acid pairs have two or more local maxima, implying that in the range considered (<4.5 Å) there are more connection types with different contact energy.

Stabilisation of Probiotic Strains by Microencapsulation

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The application of microorganism called probiotics has been a trend in production of fermented foods. Probiotics are live microbes which can act benefically in host by improving its gastrointestinal microbial balance. Pobiotic strains must have a suitable level of viable cells during the product's shelf life, at the time of consumption and maintain their viability throughout the gastrointestinal tract.

The current research is based on microencapsulation of probiotics in order to improve their stability and viability in food products as well as in gastrointestinal tract. The paper gives an overview of the actual techniques and support materials for probiotic cells microencapsulation. The encapsulation techniques have been investigated for probiotics applied in fermented foods can be classified into two groups: extrusion (droplet method) and emulsion or two phase system. In the emulsion technique a small volume of the cell suspension (discontinuous phase) is added to a large volume of a vegetable oil (continuous phase). The common used supporting materials are alginate, starch, hitosan, carragenan, and gelatin. The investigations that are done in this field concerning both techniques demonstrated that micronencapsulation of probiotics improve their viability by up to 80-95%.

BIPE P-14 bce

Investigation of Bioethanol Production from *Helianthus tuberosus,* Grain Sorghum and Sweet Sorghum

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We investigated the possibility of growing *Helianthus tuberosus* on different types of soil in Vojvodina, particularly on those that were out of regular production. In addition, the possibility of cultivation in the same time with the ordinary crops used in the ethanol production was considered and compared. In order to investigate the properties of the biomass and carbohydrates of the *Helianthus tuberosus* in comparison with other crops (maize, sugar beet, potatoes and sorghum) we performed parallel trials on tree location (chernozem, black sand and brown sand). The results indicates that the *Helianthus tuberosus* cultivated on the high–quality soils can produce 3 times more carbohydrates than potatoes and approximately twice as much as maize. For ethanol production from *Helianthus tuberosus* the most interesting problem is hydrolysis of inulin. Enzymatic hydrolysis was carried out by inulinase (2,0 units of inulinase per 1 gr of inulin). We also studied the fermentation conditions by two microorganisms *Saccharomyces cerevisiae* and *Kluyveromyces marxianus*. By using *Saccharomyces cerevisiae,* inulin from *Helianthus tuberosus* was hidrolysed with inulinase. Using *Kluyveromyces marxianus* fermentation can be conducted without prior either acid or enzymatic hydrolysis. For ethanol production the best utilization is achieved by using *Kluyveromyces marxianus*. This microorganism did not need heat energy in the preparation of *Helinathus tuberosus*. On the location of brown sand we obtained the smallest quantities of ethanol. We could, therefore, conclude that the yield of ethanol per hectare depended on the type of soil.

Grain sorghum represents one interesting raw material for ethanol production, due to the fact that it is easily cultivated on poor soils and even under unfavourable climate conditions. There are also hybrids which could be cultivated as the second crop on the soil from which grain has been harvested. Mind of the fact that the duration of vegetation period could be of vital importance in selecting five groups of sorghums with different vegetation periods (on chernozem) very early maturing sorghum, early maturing sorghum, medium early maturing sorghum, late maturing sorghum and very late maturing sorghum varieties. The quantities of ethanol that could be produced per unit of area, depend on the vegetation period of specific varieties. These results indicate that we were able to produce increased quantities of ethanol with the varieties that had longer vegetation periods. In the case of the late maturing varieties the average yield was 4371 dm^3/ha, whereas in the case of other varieties we obtained considerably smaller quantities of ethanol (from 700-800 dm^3/ha). When selecting sorghum as the raw material for the production of fuel ethanol these differences could be of vital importance.

Sweet sorghum is an interesting raw material for the ethanol production as it has a short period of cultivation. and it can be sown after picking-up some other crop, e.g. wheat or barley. About twenty sweet sorghum varieties and hybrids were tested over a period of several years.

Fracture Toughness and Brittleness of Some Biovitroceramic Coatings on Metallic Substrates (Titanium) Obtained from Vickers Hardness Measurements

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The paper presents biovitroceramic covering layers obtained by enameling procedure on metallic substrates used in implantology, particularly titanium. Biovitroceramic layers belong to the oxidic system: SiO_2-CaO-P_2O_5-Na_2O-K_2O-Li_2O-MgO-B_2O_3-TiO_2. Such layers must be adherent to the metallic substrate, to have high fracture toughness and small brittleness and to form an hydroxyapatite layer on their surface at the contact with the human body fluids. The enameling procedure and the obtaining conditions of these couples are presented in the previous papers [1-3]. The aim of this article is to determine the fracture toughness and the brittleness of the ceramic coatings belonging to the above system, from the Vickers hardness measurements. The indentation prints were obtained both in the ceramic coatings and at the interface, *Fig. 1.*



From analyzing and measure of cracks propagated from the indentation print corners together with the diagonals of the prints obtained at a certain penetration force the fracture toughness was determined using certain formulas. The brittleness was calculated also with the aid of a formula in which the Vickers microhardness and the fracture toughness values enter.
From examination of the indentation prints obtained at the interface vitroceramic coating-metallic substrate information about the adherence of the coatings were obtained.

Fig. 1. Optical micrographs of a cross section in a biovitroceramic coatings-metallic substrate (titanium) couple. Indentation prints obtained in the metallic substrate and in the ceramic coating at a penetration force P = 100 gf. Without metallographic etching.

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BIPE P-16 bim

Candida antarctica Lipase B Immobilization onto Hybrid Organic - Inorganic Mesoporous Materials

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CANCELED

Based on MCM-41, three different [illegible]ganic mesoporous materials were produced. Functionalization and hydrophobization of MCM-41 with 3-aminopropyl-triethoxysilane (APTES), trimethylcholosilane (TMCS), and propyltrimethoxysilane (PTMS), respectively were carried out by post - synthesis method after removal of surfactant template, hexadecyltrimethylammonium bromide. The effect of organosilanes on the mesostructural properties of the resulted hybrid materials was systematically controlled by different techniques such as X-ray diffraction (XRD), N_2 adsorption isotherms, FT-IR and ^{29}Si MAS NMR.

The activity of the new biocatalysts was measured in the alcoholysis of ethyl acetate with two alcohols (1-hexanol and 1-butanol) and compared with that of the free enzyme. The kinetics of alcoholysis reaction with free enzyme was investigated and it is agreed with *Ping Pong Bi Bi* mechanism in which the inhibition by both substrates alcohol and ethyl acetate was identified. All reactions were performed in organic media using n-hexane as solvent.

Prolonged Anesthetical Effect of Biomedical Fibers

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Local anesthetics reversibly block impulse generation and propagation in the tissues that contain nervous structures. The local anesthesia effect, as a rule, stopped before pain disappear, and using of absorbent cottons, gauzes and tampons with incorporated anesthetic agent could be great important for a patient. Our idea was to obtained control releasing anesthetic fibrous system that could be suitable for application in medical and dental practice. [1-2,4]

Biologically anesthetic activated fibers used for local anesthesia can be obtained by the chemisorption of anesthetic preparations into different fibrous sorbents. In this paper, cation-exchanged PAN fibers in H- and Na-form with ion-exchange capacity of 2.0-2.8 mmol/g, as well as plasma activated nonwoven blend PP/viscose, were modified by the application of procaine hydrochloride and lidocaine water solutions during different periods of modification.

A procaine hydrochloride concentration of $3.5x10^{-3}mol/dm^3$ was selected because, according to the literature [3], the recommended concentration of anesthetic agent is 1.5 times the value of the ion-exchange capacity of the fibers. The obtained results show that selected fibrous materials possess excellent sorption ability for procaine hydrochloride and lidocaine. The maximum obtained amount of bonded anesthetic agents by fibrous material is over 100 mg per gram of fibers. The gained results show that it is possible to obtain a biologically activated complex of fibers and anesthetic agent that achieves a satisfactory anesthetic effect (according to literature data [3], fibers with a local anesthetic agent concentration of 5-15% show anesthetic activity during 4-72 hours).

Desorption of bonded procaine hydrochloride and lidocaine was studied in vitro in the distilled water as well as physiological solution. Desorption of anesthetic drug in the distilled water did not occur, which means that the procaine hydrochloride and lidocaine are bonded chemically and cannot be washed away. The local anesthetic slowly released from this complex into the physiological solution. About 10% of the incorporated anesthetics were released in the first 2 hours of desorption. The gained results indicate the possibility of obtaining an anesthetic delivery system with controlled-release. The results of the imposed experiment encourage further investigations concerning the behavior of anesthetic biomedical fibers in the organisms of experimental animals.

Ministry of Science and Environmental Protection of the Republic Serbia through Project TR-6713 B financially supported this work

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Prolongated Action of Biomedical Antimicrobial Fibres

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Biomedcal antibacterial textile materials have become necessary in many areas as protective and health care and medical therapy. For protective and medical propose, biocidal functions, especially rapid and efficient inactivation of a broad spectrum of microorganisms, are required.
In this paper was presented antimicrobial action of biomedical fibers and textile the broad spectrum of activity. The in vitro bioactivity of the fiber and textiles was tested on different types of gram-positive and gram-negative bacteria: Staphylococcus aureus, Klebsiella pneumoniae, Eschrechia coli, Candida albicans and Pseudomonas aeruginosa i during the period of 1- 30 days. The bioactive fibers have very high antibacterial activity and prolongation effect.

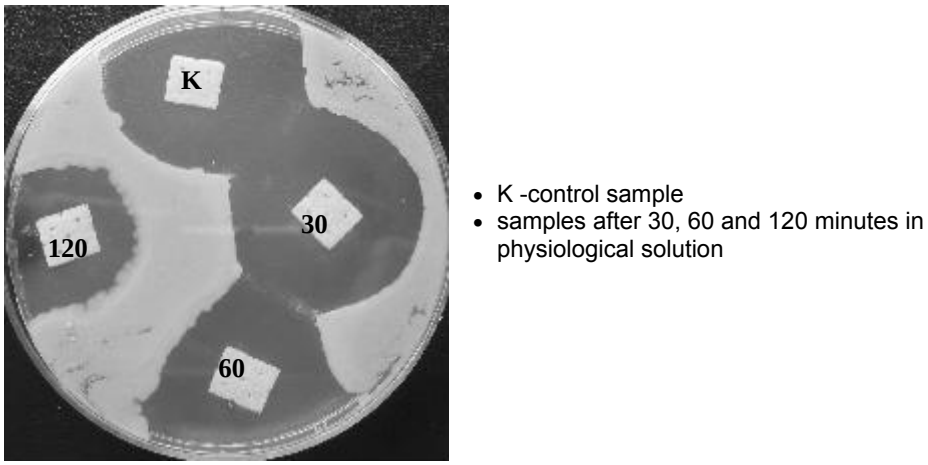


Figure 1. Antimicrobial effect of fibrous material on Staphylococcus aureus

In this study, a gentamicin sulfate and fusidic acid sodium salt incorporated textile materials for medical application was prepared and evaluated. The phenomenon of continuous and sustained release of gentamicin sulfate and fusidic acid sodium salt is clinically very important. Since agents that function by constant, prolonged release of gentamicin sulfate are more clinically effective in both preventing and treating infections than are agents that release rapidly. These experiments indicate that textile materials were biocidal in vitro for all five test organisms. The inactivation performance was seen as a function of time (5, 10, 15, 30, 60, 120 and 1440 minutes as 30 days, figure 1.

Ministry of Science and Environmental Protection of the Republic Serbia through Project TR-6713 B financially supported this work.

Flow Cytometry as a Tool for Process Monitoring of Virus-Cell Systems

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Physiological and morphological changes upon infection by viruses have been observed in many cell lines used for the production of proteins and viruses. Here we demonstrate the utility of single-cell analysis to monitor various cellular parameters in insect cells-baculovirus and HEK293-adenovirus systems, including DNA content, cell size and cell granularity and their correlation with the propagation of virus and production of recombinant protein. Analysis of infected cells at the single-cell level by flow cytometry was shown to be an effective method to monitor the changes in virus titre and intracellular protein. In the HEK293-Ad5GFP system the better parameters to monitor virus titre are DNA content and cell size, giving R2 values 0.91 and 0.84 respectively when correlated with Ad5GFP titre. Naturally fluorescing reporter gene product, GFP showed a good correlation between the mean fluorescence and the proportion of GFP positive cells and viability in heterogeneous populations. There was also good correlation between virus titre and the two parameters up to 48hrs post infection giving R2 values between 0.8 & 0.9. Insect cell-baculovirus systems are highly efficient for the production of recombinant protein. The optimum level of r-protein can be monitored by following the cell size & granularity parameters. The accumulation of r-protein and increase in cell size & granularity as determined by flow cytometry are consistent with the mechanism of DNA replication and protein synthesis. The results show that flow cytometry is an effective tool for process monitoring of virus-cell systems that allows the design of optimum harvest strategies. Understanding and prediction of the virus infection and multiplication process are possible with the aid of DNA, cell size and cell granularity analysis which can also provide the data necessary to address the problem of modelling cell population-virus infection dynamics. For example by measuring the DNA content, the replication of adenoviruses and baculoviruses in cells can be monitored and specific control actions recommended.

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The Luciferin/Luciferase Enzymatic Reaction as Microbiological Testing Technique

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Introduction

The firefly luciferin-luciferase reaction is the most efficient bioluminescent reaction for ATP determination. It requires D-luciferin as cofactor and Mg^{2+} for activity, when a yellow-green light (max. 562 nm) is emitted [1]. We used the ATP assay as a method for measuring biological activity, since ATP is found in all living cells (eucaryotic and procaryotic).

Material and Methods

The ATP analysis time is reduced to approximately 30 seconds when a luminometer Bioscan Monitor RHS 055 is used. This detects light emitted and translates the light intensity into a measurement called a Relative Light Unit (RLU), which is proportional to the ATP in the sample and is, therefore, a direct measurement of the amount of living matter in the sample.

Results and Discussion

The experiments were carried out on milk and water samples. Water samples were analyzed for colony forming units (CFU) and RLU, and milk samples were analyzed for CFU, somatic cell count (SCC) and RLU. The correlations were made based on the logarithmic values and the regression coefficients (r) were calculated (Figures 1 and 2). Total ATP does not correlate very well to the CFU values in experimental conditions, because the ATP method measures all of the microbiological organisms in the sample. Total aerobic plate counts measure aerobic bacteria which accounts for only a part of the ATP content. We observed a high correlation in milk between RLU and the sum SCC and CFU (r=0.9590). We calculated the proportion of bacterial and non-bacterial ATP in water.

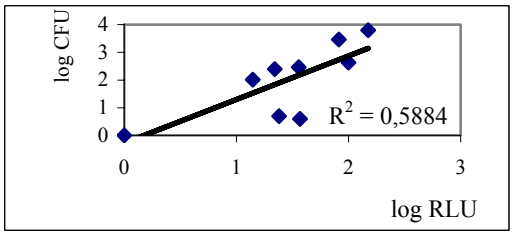


Figure 1. Correlation between the logarithmic RLU's and CFU's of water samples

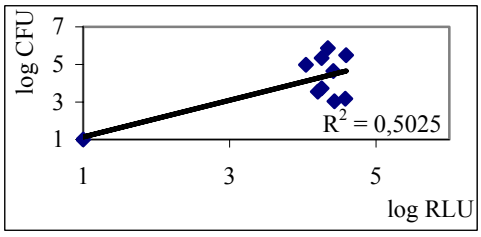


Figure 2. Correlation between the logarithmic RLU's and CFU's of milk samples

Conclusions

The determination of total ATP by the luciferin/luciferase enzymatic reaction may be used as an indicator of water and milk microbiological quality. This technique has the advantage of rapid measurement of all of the microbiological organisms in the sample, in comparison with the traditional colony count techniques, which determine only aerobic bacteria and require lengthy incubation periods.

High milk RLU values indicate either a subclinical mastitis or a bacterial contamination.

Water samples with high RLU and low CFU contain greater amounts of non-bacterial species (molds, algae, etc).

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Yeast Cell Immobilization on Wood Chips Aimed for Beer Fermentation

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Immobilized cell systems offer many advantages as compared to traditional fermentation processes such as higher cell densities and cell loads, increased volumetric productivities, possibility for continuous operation, reuse of same biocatalysts for prolonged periods of time and, above all, much higher fermentation rates. Systems with immobilized brewer's yeast cells are nowadays successfully applied for beer maturation and industrial production of alcohol-free and low-alcohol beers. However, application of such systems for main beer fermentation is still restricted to laboratory or pilot levels mainly due to mass transfer limitations within cell carriers causing an unbalanced flavor profile of final beers.

Wood chips are attractive for cell immobilization especially for use in fermentation processes due to biocompatibility, mechanical stability, large surface area for cell adsorption, and low price. In these carriers cells are adsorbed at surfaces and directly exposed to the fermenting broth thus avoiding internal diffusion limitations. Although wood chips were successfully utilized in several cases of beer production, data on carrier characterization and performance are missing.

The aim of this study was to develop and standardize the method of yeast immobilization on wood chips and to investigate potentials of this carrier for use in main beer fermentation. Immobilization efficiency and yield of brewer's yeast *Saccharomyces cerevisae* on aspen chips were investigated at different pH levels and cell concentrations. Activity of the immobilized cells was investigated in batch fermentations of plant wort of 11,7% extract in shaken flasks and a packed bed reactor.

Yeast immobilization in physiological saline solution over approximately 24 h resulted in efficiency of about 80 % and a cell concentration of 5 x 10^8 cell/g of carrier. Scanning electron microscopy showed that cells covered wood surfaces and large pores. During fermentations that lasted approximately 48 h, apparent attenuations exceeding 85% were achieved, reaching the maximum of 89,2%. In addition, concentrations of cells immobilized on carriers and suspended in medium increased over time reaching final overall concentrations of about 2 x 10^8 cell/ml. These results indicated high fermentation activity of immobilized yeast cells and significant potentials for applications of wood chips as cell carriers in brewing industry.

SARS CoV Spike Protein Polymorphism: Bioinformatics Study

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Severe acute respiratory syndrome (SARS), potentially fatal atypical pneumonia, caused by a novel member of Coronaviridae family, namely SARS Coronavirus (CoV), first appeared in Guangdong province of China in November 2002 and soon afterward, within 6 month, spread all over the world, killing more than 700 people. SARS CoV genome is approximately 30 kb + strand ssRNA, that corresponds to polycistronic mRNA. Its genome includes genes encoding two replicate polyproteins and a set of 3` ORFs that code for four structural proteins: surface spike (S) glycoprotein (1256 Amino Acids), envelope, matrix, nucleocapsid, and additional 8-9 predicted ORFs whose protein product function is still under investigation. S protein is of particular interest for mutation analysis being key virulence and host range determinant. Multiple sequence alignment of the S protein in all the 96 SARS-CoV isolates showed that out of 62 SNP sites, 19 are are synonymous, with 58 synonymous SNPs in total, and 43 non-synonymous substitution sites, with 150 non-synonymous SNPs in total. Substitution rate is 1.65% (62/3768) and non-synonymous substitution rate 1.14% (43/3768). Most non-synonymous A. Ac. substitutions are located in external domain; 14 of non-synonymous substitution are in receptor binding domain, 3 of them in the most narrow, intersecting range. As it concerns epitopes, 40 of non-synonymous A. Ac. substitutions are located in overall epitopes domains determined by various authors. Finally, 1 non-synonymous A. Ac. substitution is located in transmembrane domain and 2 in internal domain. Substitution rate in in the S protein was higher than in the whole genome (1.65% to 1.49%) and the ratio Ka/Ks confirmed that the S gene was subjected to Darwinian selection during virus evolution (transmission from animals to humans). The comparative study of SARS-CoV S protein provides essential information for genome polymorphism, indication of strain differences and variants evolution. It may help in development of effective treatment.

Investigation of Process Parameters on Stability of Aluminium Phosphate Gel Suspension

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Aluminium phosphate gel suspension is an active pharmaceutical ingredient with antacid activity in preparations used to prevent hyperacidity.
The gel suspension was chemically amorphous aluminium hydroxyphosphate .
During the process of synthesis and precipitation, the pH value of precipitation directly influences physical and chemical properties of aluminium phosphategel suspnesion and the surface potential of solid phase.
In addition, specific adsorption of various types of ions can be influenced to the position of the point of zero charge.
The purpose of this study was to investigate the influence of process parameters of synthesis and precipitation as well as the effect of adition the selected stabilizers to obtain stable thixotropic suspension of aluminium phosphate meeting the required quality.
The process was investigated with a selected source of ions reacted under constant pH value which was held by fixed hydroxyl to phospahte ration at the time of precipitation. The stirred reactor was the semi-batch type at kilo-lab scale with changed volume and unchanged copmosition of reaction mass.
The stability of the suspension was investigated meeting the ICH guidelines for stability testing of existing active substances and related finished products.
The experimental investigations, based on a matrix with full factorial two-level experimental design, were carried out in the selected range of process variables.
Independent variables were stirring intensity, flow rate and temperature. Selected target functions were rheological characteristics (viscosity and thixotropic value) and chemical quality of the product.
At the fixed Al / P and OH / PO_4 ration, the transfer phenomenon had influenced to the pH value of precipitation and rheological characteristics of suspension. In such a way, at the higher residence time, the higher pH values of precipitation as well as the lower values of dynamic viscosity and thixotropy were achieved by decreasing stirring intensity. The precipitation at higher pH value favored the formation of Al - OH rather than Al - PO_4 bonds and more compact material was formed.
Also, at the final step of the process, the addition of selected stabilizer was contributed to adjustment of the suspension stability characteristics to the approved values.
The presented results will contribute to the engineering research at pilot plant scale and industrial transfer of technology for manufacturing the stabile aluminum phosphate gel suspension.

BIPE P-24 phe

UV-Effects on Flavonoids/Lecithins Formulations with Pharmaceutical Purposes

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UV-radiation effects on antioxidant and protective function of plants pigments, flavonoids (rutin and quercetin), have been studied in this paper. The radiation has been performed both in solution (hexan), and in emulsion systems with lecithins. The latter one serves as a raw base for a numerous pharmaceutical and cosmetics tehnologies. Quercetin and rutin have not been choosen incidently: they behave remarquably different in terms of photostability, overall reactivity and antioxidant capacity permitting well-established gap in their corresponding SAR (Structural Activity Relationship) values. The irradiation was done by UV-A light (350 nm), as well as by UV-B light (300 nm) and UV-C light (254 nm), in a homogeneous solution containing the pigments only (providing an inherent photochemical answer of the involved flavonoids), as well as in the lecithins-containing systems (solution and emulsions). The pigments destruction with an increase of irradiation time has been found in all experiments; however, the photolysis degree was dependent on the particular UV-light involved (UV-A, UV-B or UV-C). The scavenging capacity of flavonoids was determined using 2,2-diphenyl-1-picrylhydryzyl ($DPPH^{\cdot}$) colorimetry test at 515 nm. Antioxidant activity of flavonoids is assessed in a lecithins-containing system where lipid peroxidation is induced by ascorbic acid and $FeSO_4$ (the *blank*). The extent of lipid peroxidation is monitored by thiobarbituric acid (TBA) test. The same system, where lecithins play a target role, has than been studied with the involvement of the corresponding flavonoids.

UV-Effects on Carotenoids/Lecithins Formulations with Pharmaceutical Purposes

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UV-radiation effects on antioxidant and protective function of plants photosynthetic accessory pigments, carotenoids (carotenes and xanthopylls), have been studied in this paper. The radiation has been performed both in solution (hexan), and in emulsion systems with lecithin. The latter one serves as a raw base for a numerous pharmaceutical and cosmetics tehnologies. The pigments destruction with an increase of irradiation time has been found in all experiments; however, the photolysis degree was dependent on on the particular UV-light involved (UV-A, UV-B or UV-C). The irradiation was done by UV-A light (350 nm), as well as by UV-B light (300 nm) and UV-C light (254 nm), in a homogeneous solution containing the pigments only (providing an inherent photochemical answer of the involved carotenoids), as well as in the lecithins-containing systems (solution and emulsions). The scavenging capacity of carotenoids was determined using 2,2-diphenyl-1-picrylhydryzyl ($DPPH^{\cdot}$) colorimetry test at 515 nm. Antioxidant activity of carotenoids is assessed in a lecithins-containing system where lipid peroxidation is induced by ascorbic acid and $FeSO_4$ (the blank). The extent of lipid peroxidation is monitored by thiobarbituric acid (TBA) test. The same system, where lecithins play a target role, has than been studied with the involvement of the corresponding carotenoids.

The Synthesis of Aluminium and Histidine Complexes

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The aim of this work was to investigate the synthesis of aluminium and histidine complexes and amorphous $Al(OH)_3$ powder. To characterize obtained powder it was done many ahalysis such as: powder X-ray diffraction, SEM photographs, IR anaysis, termal and elemental analysis.
The stock solution of Aluminium was prepared by dissolving Al wire 99.9% in HCl 1:1 acid. L-histidine acid p.a. (Sigma) was dissolved in double distilled water.
The aluminium-histidine complex was prepared by reaction of aluminium chloride with histidine at concentration ratio (150:50) mmol at pH value 5.90. The pH was adjusted by addition of NaOH. The reaction temperature was 40° C and it was stirred for 12 hours. The complex was isolated after slow evaporation of water until minimum volume of reacting was obtained and then gentle cooling of the solution until crystallization begun. First, the excess of hystidine crystallized and this precipitate was discarded.After further evaporation of water and cooling the solution the crystal of the complexes were precipitated .The crystal were air-dried .It was done ICP analysis of Al and elemental anlysis of C,H,N. The analysis show that it was $[Al(HHis)His]Cl_2$

Table 1. The Results of elemental analysis of synthetized complex

[%]	N	C	H	Al
Theoretical	20.58	35.29	4.65	6.7
Experimental	21.04	35.89	4.74	6.7

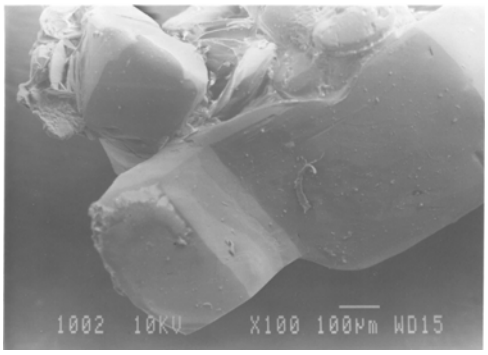


Fig. 1. SEM photograph of the complex

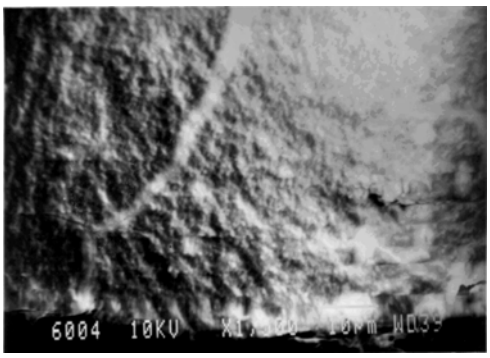


Fig. 2. SEM photograph of $Al(OH)_3$

Aluminium and histidine form the chelate of the composition $[Al(HHis)His]Cl_2$ which belongs to the tetragonal crystal class.Two histidine molecules in the complexes are bond with different binding strength and coordition mode.

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Patent Protection of Product and Process in Chemistry and Pharmacy

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Serbia and Montenegro has harmonized legislation in field industrial property and pharmaceutical industry in particular, with the relevant multilateral agreements. It is important that Serbia and Montenegro harmonizes its regulations in this area with regulations of highly developed countries, in order to join EU. Group of Pharmaceutical Producers of Serbia and Montenegro proclaimed as one of preferred programme of development, more intensive and opportune protection of intellectual property. Three laws have been passed last year in accordance with the WIPO recommendations in the field of industrial property protection: Patent Law, Trademark Law and Law on Industrial Design.

In the new Patent Law is defined that a patent shall mean a right granted for an invention in any field of technology, which is new, involves an inventive step and is susceptible of industrial application. The subject matter of an invention protected by a patent may be a product (ex. a device, substance, composition, biological material) or a process. In order to obtain the adequate protection of an invention from the field of pharmacy and chemistry, it is necessary (in accordance with The Law) that the patent application is composed in acceptable form, i.e. to have description of the invention and to define patent claims, in order to avoid likely consequences due to inadequately presented invention in claims. Patent Law enables protection of inventions in the field of pharmaceutics, chemistry and biotechnology: protection of substances, compositions, microorganisms, plant or animal culture; production procedure and procedure for the application of products, but not the protection of inventions for the surgical or diagnostical procedure or treatment applied directly on human or animal body (in accordance with the European Patent Convention and TRIPS Agreement).

The elaboration of patent applications in the Research and Development Centre in the "Zdravlje–Actavis Company" has been carried out. An analysis of patentability performs examples of patent and published patent applications from the area of technological product derivation methods of organic chemical synthesis and biotechnology. This article included methods of national and international patent protection and showed efficient models of protection to take a decision to grant the patent. This article deals with patent protection of pharmaceutical products and some specific issues that can arise during that procedure.

BIPE P-28 phe

Kinetics of (*E*)-4-(4-Metoxyphenyl)-4-Oxo-2-Butenoic Acid Release from Poly(Acrylic Acid) Hydrogel. Carrier Model for Targeting Drug Delivery

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One of the focal topics of pharmacology is the ability to administer therapeutic moieties so that they selectively reach the desired targets with marginal or no collateral damage. Among of this, polymer therapeutics that includes polymer carriers for the targeted delivery of anticancer (and other) drugs on human accessible surfaces was intensively studied.[1] The one of the major applications of poly(acrylic acid) hydrogels is in sustained gastro-intestinal drug delivery systems.[2,3] Anticancer drugs delivery on human epithelial cancer cells using gel was reported recently.[4] We have previously reported antiproliferative activity of (*E*)-4-aryl-4-oxo-2-butenoic acids toward *human cervix carcinoma* HeLa cells.[5] For this study the (*E*)-4-(4-metoxyphenyl)-4-oxo-2-butenoic acid structurally similar to Cytembena, which have been commercially used as anticancer drug,[6] is chosen.

The aim of present study was formation and examination of the complex of (*E*)-4-(4-metoxyphenyl)-4-oxo-2-butenoic acid as an active compound and poly(acrylic acid) hydrogel, sodium salts, that can be used as carrier model for targeting drug delivery.

Samples of poly(acrylic acid) hydrogel with predefined quantities of (*E*)-4-(4-metoxyphenyl)-4-oxo-2-butenoic acid sodium salt, as active compound, were prepared and the complex existence was confirmed by the IR spectroscopy. The isothermal kinetics of active compound release from hydrogel at 30°, 37° and 42° C in the physiological solution was investigated. The quantities of (*E*)-4-(4-metoxyphenyl)-4-oxo-2-butenoic acid released from hydrogel were determined by the standard UV/VIS spectrophotometrycal method. The constants of release rates were determined, based on kinetics curves. From the rate constants obtained on the different temperatures, kinetic parameters of the investigated process were calculated. The mechanism of active compound release was postulated and discussed.

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Enantioseparation of Racemic Mixtures of Amino Acids Using High Performance Liquid Chromatography

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According to the fact that the need of pure enantiomers in pharmaceutical industry, food industry, cosmetics and agrochemical industry is in tremendous increase, different separation techniques have been under investigation for production of pure enantiomers on a commercial scale.
In the last years attention is focused on the development of new highly selective chiral stationary phases (CSP's) used as packing material in chromatographic columns.
This work, which deals with the separation of racemic mixtures of amino acids using High Performance Liquid Chromatography (HPLC), can be divided in two parts.
The separation of the following α-amino acids: DL-Methionine, DL-Asparagine, DL-Leucine, DL-Serine, DL-Glutamine and DL-Valine was investigated experimentally. Three chiral CSP's were applied: Chirobiotic T (macrocyclic antibiotic-Teicoplanin CSP, Astec, USA) Diaspher-Chirasel-E (macrocyclic antibiotic-scientific sorbent Eremomycin CSP, BioChemMack S&T, Russia) and Chirex (ligand exchange-Cu CSP, Phenomenex, USA). Temperature and flow rate were kept constant, only the composition of the mobile phase was changed.
By taking into consideration the solubility of the amino acids, the cost of the solvent and the time needed for the separation the following systems were chosen for further work:
Chirobiotic T column (DL-Methionine, mobile phase: EtOH:H_2O=40:60v/v and DL-Asparagine, mobile phase: EtOH:H_2O=60:40v/v);
Diaspher-Chirasel-E column (DL-Methionine, mobile phase:
MeOH:H_2O (0,1M NaH_2PO_4)=20:80v/v).
To estimate adsorption equilibria, the ECP method[1] was applied for determination of the single-enantiomer adsorption isotherms. Langmuir and bi-Langmuir isotherm model parameters were estimated. With the determined isotherms, simulation of the elution profiles was performed using the equilibrium-dispersive model[1].
The last goal of this work was the estimation of the production of D and L Methionine enantiomers (purity of 99%) and comparison between Chirobiotic T and Diaspher-Chirasel-E.
Results obtained by this work form a good base for further intentions, like the application of these columns in a Simulated Moving Bed[1] plant.

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BIPE P-30 phe

Investigation of the Possibility of Binding the Anaesthetic on Carboxymethylcellulose

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The preparation of biologically active materials constitutes one of the most interesting trends in the chemical modification of cellulose. To obtain these materials cellulose is subjected to a pretreatment in order to introduce functional groups capable of chemical or physical binding to a suitable active preparation which possess therapeutic activity.
The possibility of obtaining biologically active cellulosic material by sorption of procaine hydrochloride on the samples of carboxymethylcellulose with different degrees of substitution was investigated in this paper. Also the influence of procaine hydrochloride concentration, the sorption duration and the sorption temperature on the amount of bonded and released anaesthetic was examined. Procaine hydrochloride sorption on carboxymethylcellulose samples, with seven different degrees of substitution, was investigated using two different concentration of procaine hydrochloride solutions, $3{,}5\cdot10^{-3}$ mol/dm^3 and $7.0\cdot10^{-3}$ mol/dm^3, during 1, 2 and 3 hours. The desorption of bonded procaine hydrochloride was carried out in 0,95% NaCl solution. The amount of bonded and released anaesthetic was determined by UV-spectrophotometry. It was found that degree of substitution of carboxymethylcellulose and procaine hydrochloride solution concentrations have significant influence on the amount of bonded anaesthetic, while the sorption temperature has no greater influence.

Synthesis of 2,6-Dimethylacetanilide Derivates of Morpholine and Pipiridine

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For morpholine and piperidine substituted derivatives of acetanilide is known to show local anesthetic, antiarrhythmic, antidepressant and potential antibacterial and antiviral activity. Tertiary amines in structure of drug (in aliphatic cyclic form), are appropriate for parenteral application because of its relatively high alkalinity what causes decreasing of salt hydrolysis in water solutions.

The new, simplified and low-cost two step method for the synthesis of two known local anesthetics and antiarrhythmic: N-(2,6-dimethylphenyl)-2-morpholin-4-il-acetamide (Morlincain, ***Mm***), and N-(2,6-dimethylphenyl)-2-piperidin-4-yl-acetamide (***Mp***) are suggested.

All reagents were obtained from commercial sources and freshly distilled immediately before using in synthesis.

In first step, acylation of 2,6-dimethylaniline with chloroacethyl chloride was done during 3 h in ice-water bath, with constant stirring. The reaction is performed in alkaline medium (using solid Na_2CO_3), which prevent anilide acid hydrolysis caused by liberated HCl. Formed ***M*** was recrystallized from acetone, with yield of 79.25%.

In the next step the chlorine radical in ***M*** was nucleophile substituted with morpholine (forming ***Mm***), or with piperidine (giving ***Mp***), in 75% (w/w) ethanol, with mole stoichiometric ratio of reactants (***M*** and morpholine/or piperidine) of 1:2, using aqueous Na_2CO_3 solution (4 g/ 40 ml) as a catalyst, on 80ºC, with constant stirring during 12 h. Ethanol solution was evaporated in vacuum, and products were recrystallized from absolute ethanol with yield of 65.32% (***Mm***) and 87.50% (***Mp***).

The structures of formed compounds (***M***, ***Mm***, ***Mp***) were confirmed on the basis of spectroscopic data (IR, ^{1}H NMR, ^{13}C NMR and APCI LC-MS spectrometry). Elemental analyses were conducted using Elemental Analyser Vario EL III CHNS/O and their results were found to be in good agreement (±0,5%) with the calculated values. The purity of synthesized compounds were confirmed by melting point and TLC separation technique.

The relative lipophilicity (logP) of synthesized products were calculated using *ChemOffice® Ultra 2002, ver.7.0* software: 2.47 (***Mp***), and 1.33 (***Mm***).

Section

Material Science and Engineering
MSEN

MSEN X-NN yyy

X = KN – Keynote lecture
O – Oral presentation
P – Poster presentation

NN = Number

yyy = Topic:
msc - Material Science
nat - Nanotechnology
nma - New Materials
ece - Electrochemical Engineering
mtl - Metallurgy

Design and Performances of 2 and 3 Phase Porous Electrodes for Hydrogen Evolution

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No matter that porous electrodes were known as early as 1880, classical electrochemistry achieved its (technical) progress based on use of planar electrodes, i.e. structures with rather limited surface area. On the other side the highlights of contemporary electrochemistry, achieved e.g. in fuel cells and batteries in general, and were possible only with extensive use of porous electrode structures.

The advantages of porous over planar electrodes are multiple. Increased surface area, due to the existence of a number of fine pores or capillaries is only the less significant factor. Far more important and effective is the phenomenon of thin film electrolyte that exists on the meniscus of the curved pores and minimizes the thickness of the diffusion layer. So, the reacting gas (H_2 and O_2 in most cases) reaches the metal surface after passing the thin film of only 10^{-6} to 10^{-3} mm, compared with 0.1 mm in case of planar electrode. As a result, the limiting current is 10^3 to 10^4 times higher then on planar electrode and similar is the ratio of electrodes power densities.

Unfortunately, pores use to be source of a lot of troubles, especially when three phase electrodes (solid metal, liquid electrolyte and gas reactant/product) are concerned. So, in case of poor gas drainage, the evolved gas accumulates in pores and blocks their surface area. Pores could also diminish the electrical conductivity of both metal structure or electrolyte (saturated with gas bubbles) or evolving gas could eventually destroy the porous metal structure, etc. Thus, dealing with porous electrodes where gas, liquid and solid is supposed to meet under specified conditions is not at al an easy task.

Contemporary electrodes for hydrogen evolution are porous structures and suffer and least some of the troubles attributed to 3-phase electrodes. In order to diminish the list of possible sources of troubles, 2-phase porous electrodes were introduced recently, by use of proton exchange membranes (PEM). These membranes operate, as solid electrolyte and separator, so that liquid phase is not needed any more. Rising the temperature over 100 ^oC one succeeds to have water as reactant in the electrolyses cell, but to avoid the presence of the troublemaking liquid phase.

In our research prepared non-platinum electrocatalysts were applied both sides to the PEM, thus forming a solid electrolyte cell, assembly known as catalyst coated membrane (CCM).

By avoiding the liquid phase, a completely new field of electrochemistry is opened, with possibilities that could not be defined in this moment.

Industrial Trails for Production Portland Cement Conformed with EN 197-1

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The results of the investigation if Serbian cement factory maight produce cements conformed with requirements given in standard EN 197-1 are given in this work. Raw materials used for cement production were: Portland cement clinker (K), gypsum, industrial pozzolana (Q), limestone (L) and river sand "Dunavac". With those raw materials four kinds of cements were made on the industrial scale and tested.

The requirements on the composition and properties of Portland cement are stipulated in the EN 197-1:2000 "Composition, specification and conformity criteria for common cements". The most important standardized properties of cement are strength, setting and dimensional stability (soundness), pozzolanicity, and fineness. Depending on the type of cement, limits for the contents of blust-furnace slag, pozzolana, fly ashes, silica fume, burnt oil shale, and filers are established. In addition, the cement standard specifies certain characteristics, such limits for the insoluble residue, pozzolanicity, the loss on ignition, and the contents of carbon dioxide, magnesium oxide, sulfate, and chloride.

In table 1. chemical, physico-chemical and mechanical charcteristics of the four Portland cements produced on industrial scale are given.

Table 1. Chemical, physico-chemical, and mechanical characteristics of the Portland cements

Cement mark	**CEM I**			**CEM II/B-M(L-Q)**			**CEM II/B-M(L-Q)**			**CEM II/B-M(Q-L)**		
Proportions of additions				(L-15%;Q-10 %)			(L-15 %; Q-10 %; sand 5 %)			(Q-15 %; L-10 %; sand 5 %)		
Chemical characteristics (%), Applied methods: JUS EN 196-2 and 196-21												
L.O.I.	1.50			8.06			8.50			6.73		
SiO_2	19.28			22.10			22.80			26.36		
CaO	59.57			56.25			54.42			52.49		
MgO	2.55			1.01			1.78			2.38		
Fe_2O_3	2.93			2.49			2.81			3.10		
Al_2O_3	6.39			6.29			6.50			6.67		
SO_3	1.73			1.85			2.23			1.83		
$Na_2O + K_2O$	1.56			0.63			0.27			0.31		
MnO	0.05			0.05			0.06			0.06		
Physico-chemical characteristics, Applied methods: .JUS EN 196-3 and 196-6												
Fineness, %	3.20			2.60			2.80			5.10		
Initial set, min	180			165			230			210		
Mechanical characteristics, Applied method: .JUS EN 196-1												
	2 d	7 d	28 d	2 d	7 d	28 d	2 d	7 d	28 d	2 d	7 d	28 d
Sstrength, MPa	20.4	35.7	48.2	19.4	33.4	42.5	13.1	24.1	34.9	11.6	23.2	32.5
Soundness, mm	0.5			0.0			0.0			0.0		
Class	**42.5 R**			**42.5 N**			**32.5 R**			**32.5 R**		

It is evident that strength class depends on the quantities and kind of mineral admixture added. Cements prepared with sand has lower standard compressive strength (at 28 days), and consequently, lower strength class.

Generall conclusion which may be stated is that with selected mineral admixtures and technical possibilities of the factory, Portland cements which satisfies requirements given in standard EN 197-1 may be produced.

Optimum Content of SO_3 in Belite Cements

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Introduction

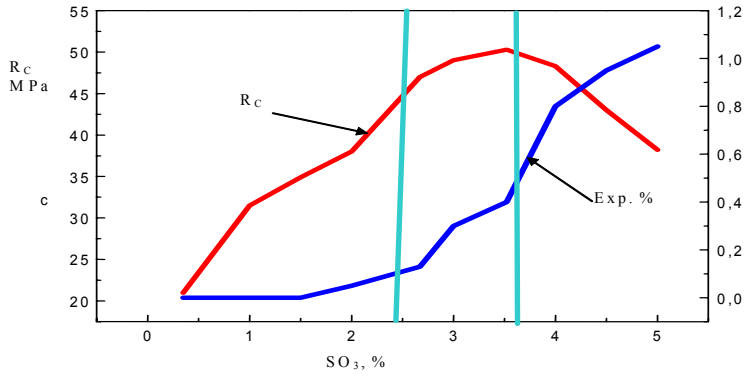
To produce low energy cement with adequate strength development and a lime saturation factor below 85%, as called belite one, is an interesting scope of the cement industry. Using an optimum proportion of gypsum in such cements one can stabilize one of the active forms of C_2S (α and β forms) and in the same time the sulfoaluminate compound can be formed in a convenient quantity, that to obtain cements with good hydraulic activity. The sulfoaluminate belite cements (C_2S, C_4AF, $C_4A_3\check{S}$, and $C_{12}A_7$), obtained from limestone and wastes, can be viewed as ecological cements.

Experimental

The sulphoaluminate belite cement was obtained from limestone (55%) and fly ash (25%), pyrite ash (5%) and gypsum (1-11%). The mixtures were burnt for 45 min./1250 ^oC and than quenched in air. The corresponding cements were obtained by grinding the clinkers to a fineness of 350-360 m^2/kg according to Blaine. Physical-mechanical properties of the cements have been determined according to SR EN 196.

Results

There is a strict correlation between gypsum content, respectively $C_4A_3\check{S}$ and the compressive strengths and the expansions of the hardened structures. An optimum content of SO_3 can be mentioned between 2.5-3.7 % (Fig. 1.).



Compressive strengths and expansion vs. SO_3 content of belite cements

Conclusion

- The sulphoaluminate belite cements have good hydraulic activity, compressive strengths and present good volume constancy if the gypsum content in the clinker is around 7 %, which means 3-4 % SO_3
- The sulfoaluminate belite cements have apparently similar behaviour with that of ordinary Portland cement (see compressive strengths), but, the setting time is shorter and the expansion is higher than those corresponding to the Portland cement.

MSEN O-03 msc

Langmuir and Langmuir-Blodgett Films Composed of Silica Nanoparticles: Preparation and Optical Characterization

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Suitably nanostructured thin films are finding applications in leading new technologies related to optics, electrooptics, membranes, sensors, etc. In this work we report about the preparation and characterization of thin films composed of silica nanoparticles which show advantageous optical (antireflective) properties on solid supports.
Monodisperse silica particle samples have been prepared by the Stöber method in the 50-100 nm particle size range. The particles were spread on the surface of water in a Wilhelmy film balance. Particle structuring during the subsequent film compression (formation of Langmuir film), was followed using Brewster angle microscopy (BAM). The reflectivity of the compressed monoparticulate film was also studied by scanning angle reflectometry (SAR) from wich the effective refractive index and thickness of the films can be assessed. Analyzing the refractive index data in terms of an effective medium approach we could obtain quantitative information about the immersion depth of particles into the water phase.
Mono- and multiparticulate films were prepared by the Langmuir-Blodgett (LB) technique transferring the Langmuir films onto solid supports. The short-range structure of the LB films was studied by scanning electron microscopy (SEM). The optical properties of the LB films on transparent supports were investigated by optical spectroscopy (300-1100 nm). The transmission spectra revealed distinct antireflection properties for all particulate films but the measure of the antireflection was found to be dependent on the size of particles and number of the layers in the films. The effective refractive index, the thickness of the films and porosities were assessed from the spectra by parameter fitting. From the film thickness values obtained for multiparticulate LB films we came to the conclusion that the particles arrange themselves in a close-packed array during the preparation of LB films. The optical properties of LB films, in certain cases, were studied by SAR and the resultant parameters were compared with those obtained from the spectroscopy studies.

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Influence of Precursor on Fullerene Synthesis in RF Thermal Plasma Reactor

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Several graphite powders and mixtures (4827 Asbury Mills, KS4 and KS6 Timcal, flake Alfa Aesar, graphite Aldrich, mixture of iron and KS4 powder) having different mean particle size were processed in RF thermal plasma reactor at atmospheric pressure. It was found that the mean particle size of precursors has an important, but not exclusive effect on the evaporation efficiency. Micro-structural orderliness of precursors which determines their thermal conductivity is another important property that should be considered in the interpretation of observed phenomena.

In this work, mixture of iron and KS4 graphite proved to be the best precursor of fullerene synthesis. The maximum fullerene yield was 18.4 % which was higher compared to pure graphite powder processing in RF reactor without the iron presence.

A previously developed theoretical model of fullerene formation established that the fullerene yield depended on the following parameters: *(i)* concentration of evaporated carbon in the reactor, *(ii)* mean velocity of the plasma gases in the plasma region and *(iii)* the maximum plasma temperature. From plasma parameters affecting fullerene yield, effects of the feed rate of precursors and composition of plasma gas were studied in details. The fullerene yield decreased, while the production rate increased with the feed rate. High helium content of the plasma gas favoured evaporation of graphite particles, and thereby, promoted fullerene formation. It was reasoned by the good thermal conductivity and high ionization potential of helium.

In RF plasma conditions, evaporation of larger graphite particles and formation of carbon cages take place simultaneously. For this reason C_2 radicals just formed can easily get included into defective cages, and higher fullerene cages are produced in significant amount. MS and HPLC analyses of produced fullerene mixtures supported this explanation.

Surface Modification of MWCNTs

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Summary
The most successful route for effective surface modification of multi-wall carbon nanotubes (MWCNTs) was investigated. The present study reveals details of the purification, separation and surface modification of MWCNTs. Encapsulating carbon nanotubes with a polymer, as an alternative approach, can be used to modify the CNT surface, separate CNTs and ultimate are better dispersions. Two different approaches were used to modify MWNTs: in-situ polymerisation of the dissolved CNTs in aniline, and a novel ultrasonically initiated emulsion polymerisation of methylmethacrylate. It was found that this modification results in the purified and separated nanotubes with conserved structural integrity, which can be used for the creation of new nanocomposites.

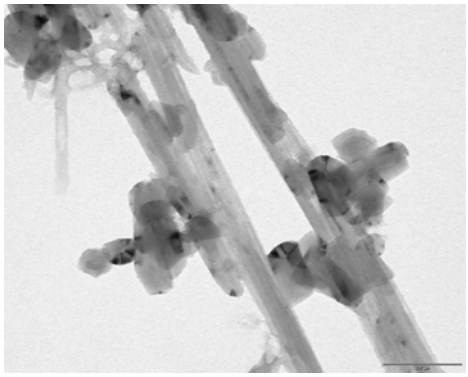
Introduction

Carbon nanotubes (CNTs/polymer) composites have attracted much attention recently. However, the big challenges encountered in making such a composite are:

- Uniform dispersion in polymer matrices without aggregation and/or entanglement
- Improved nanotubes/polymer interface adhesion

Purification and modification of MWCNTs, as a precusors to the coupling, is important. Most approaches to nanotube production lead to materials, which contain either amorphous carbon or metal nanoparticles as impurities. The purification process used today relies largely on oxidation with strong acids. This leads to shortened tubes and increasing number of defects. The purification proposed here is based on thermal treatment and further encapsulation by polyaniline (PAN) and polymethylmethacrylate (PMMA).

Results and Discussion



100nm

Purification and separation of MWCNTs were investigated by Transmission Electron Microscopy (TEM). After the thermal treatment at 590°C impurities such as amorphous carbon were removed living only graphitic onions beside CNTs. CNTs are good electron acceptor, forming a charge-transfer complex at elevated temperatures with aniline as electron donor. However, the presence of graphitic onions is still noticed in that complex (Figure 1).

Encapsulation with PAN and PMMA leads to the deposition of the thin polymer layer on the CNTs surface, further purification and their separation. Surface modified CNTs were subsequently studied by TEM, FTIR, XPS, SANS and Raman.

Formation of Microgel Beads by Electric Dispersion of Polymer Solutions

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Microcapsules are produced by a dropwise addition of one solution into a solidifying bath. By applying an electrostatic potential between the droplet formation device and the collecting solution, it is possible to obtain smaller droplets which are desirable for many applications in biotechnolohy. Droplet formation may be divided into two phases. Under a certain critical value of the electric potential U_c, liquid exits the nozzle as droplets. The surface tension decreases with increasing electric potential resulting in a reduction of droplet diameter to approximately 200 μm. At higher electric potential, liquid exits the nozzle as a jet which subsequently breaks into droplets, which are smaller than 200 μm. In this case, droplet size is mainly determined by the jet instability according to a theory of Rayleigh.

Electroless NiP-TiO_2 Composite Coatings

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CANCELED

Composite are one of the most recently developed types of electroless nickel coatings. These cermet deposits consists of small particles of ceramic, metallic compounds, fluorocarbons, oxides or diamonds dispersed in an electroless nickel-phosphorus matrix. These coatings have a high apparent hardness and superior wear and abrasion resistance.

Composite NiP-TiO_2 layers were prepared by simultaneous electroless deposition of NiP and TiO_2 on brass substrate, from a solution in which TiO_2 particles were kept in suspension by stirring. Following heat treatment in a high vacuum, the plating acquires chromium equivalent hardness. The deposit surfaces were studied by SEM, profilometry and Vickers microhardness and its structure by X-ray diffraction. The fabricated composite materials were tested under corrosion conditions by linear polarization measurements .

Chemical and phase analysis of the produced NiP-TiO_2 coatings confirm the codeposition of nickel and TiO_2 and the formation of a homogeneous material. Electroless deposited composite coatings exhibit an amorphous structure of the nickel matrix in which crystalline titanium oxide is incorporated. Vacuum heat treatment of these layers leads to the formation of a crystalline layer in which the Ni and Ni_3P crystallites appear apart from those of the TiO_2 (anatase). The proposed heating technique is accomplished within less than half an hour and results to a chromium equivalent surface microhardness, which in some cases reaches 1500 HV. Corrosion resistance for both the as-plated and the vacuum heat-treated composite NiP-TiO_2 coatings is excellent and the co-deposition of the TiO_2 particles in the metallic matrix does not seem to effect pore creation in the Ni matrix.

Composite coatings of a nickel matrix with stable inorganic TiO_2 oxide offer the synergistic advantage of the metal matrix which is conductive, corrosion resistant and the oxide which may enhance the corrosion and wear resistance or catalytic properties of the system. These coatings may also be employed on other cheap engineering materials, such as steel, and increase the properties of the system by tailoring the suitability to a new need.

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Hydrogen Glow Discharge Plasma Pretreament for the Conservation of Cu-Based Artefacts

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The plasma reduction of metal artefacts with archaeological and artistic value is a quite novel technique in the fields of restoration and conservation. This work presents the effects and evaluates the efficacy of the application of hydrogen glow discharge plasma of low pressure and temperature on corroded Cu-based alloys as a pre-treatment to remove oxidation chloride products and the final application of a top protective coating**.**

Depending on the environment, copper alloys can exhibit a variety of corrosion products but the most troublesome species are the chlorides because of the instability that their presence imparts to the metallic surface. The process of interaction of chloride-containing species within the bronze patina with moisture and air is a cyclical reaction often referred as bronze-disease, followed by corrosion of the alloy till the complete mineralization of the mass.

Three types of alloys (Cu-Zn-Sn-Pb) were employed in order to study the corrosion resistance and their behaviour during restoration procedures representing a wide range of ancient copper-based objects. The coin resembling samples had a composition similar to the ancient ones and exhibited a structure typical to the one induced by casting. The samples were submitted to soil corrosion (embedded in soil with 3.5% NaCl, acting as the main corrosive agent) and accelerated corrosion (immersion in a $CuCl_2$ aqueous solution, exposure at 100%RH) in order to achieve the most representative corrosion products, with particular interest in the formation of a chloride containing patina.

Different conditions of plasma (temperature, duration) were applied and the effects that plasma imparts on the treated samples were evaluated. The corrosion behavior of the alloys and the extend of the reduction induced by plasma treatment were investigated by means of X-Ray Diffraction, Optical Microscopy, Metallographic observations, Scanning Electron Microscopy with EDS microanalysis, Electrochemical Polarization measurements. The colour alteration of the samples has been monitored at all stages. Soil corroded, accelerated corroded and plasma treated samples were exposed at constant humidity of 94% RH and their weight was monitored, as a stability indicator. A reversible inhibitive topcoat was used and the corrosion behaviour of the system was studied with electrochemical methods.

The results are encouraging but special care should be taken in the case of remaining unreacted cuprous chloride which can lead to new outbreaks of the bronze disease, thus the complementary treatment applied by sealing the surface from moisture and air by a reversible top coat is of paramount importance.

System for Electrochemical Investigations Based on PC and LabVIEW Package

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In the paper a complex system for electrochemical investigations based on PC and LabVIEW software platform is presented. The system is assigned for electrochemical laboratories at faculties and institutes, where it could replace expensive and/or old measurement equipment, rising work comfort and quality of obtained results at a higher level [1].
On the base of our own experience [2,3] and the overview on the needs of other faculties and institutes, we have defined equipment and measurement methods that should be provided, both by hardware and software. Hardware and software have been developed for the next electrochemical methods of investigations:

1. Chronopotentiometry,
2. Chronoamperometry,
3. Galvanostatic Method,
4. Potentiostatic Method,
5. Dirack Voltage Excitation,
6. Dirack Current Excitation,
7. Linear Sweep Voltammetry,
8. Linear Sweep Amperommetry,
9. Cyclic Voltammetry,
10. Electrochemical Impedance Spectroscopy (EIS).

For generation of signals and recording the response of investigated electrochemical system, it was developed a measurement and control system based on PC P4. Beside PC, hardware includes a commercially available AD-DA converter and an interface for analog signals processing, which is the result of our own development.
Platform for software for predicted measurement methods was LabVIEW 6.1 [4], which is regarded as a high standard in the world of measurement techniques and virtual instruments. For the connection with AD-DA converter, i.e. peripheral devices, it was used Master Link collections of drivers, obtained with PCI–2048W converter [5]. Installing those two packages and AD-DA module, one can obtain a very powerful system for measurement, control and processing of signals (virtual instruments).
The developed system was successfully adjusted, tested and compared with other systems. One such system is being used at Technical faculty in Bor for more than one year.

Acknowledgement:
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Electrochemical Behavior of an Ag/TiO_2 Composite Surfaces

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Silver was cathodically deposited on mechanically polished titanium surface from an aqueous $AgNO_3$ solution. The TiO_2 layer formed spontaneously by titanium corrosion templated the deposit morphology, by determining both the placement and the number of silver crystal nuclei. After silver deposition under constant potential, the thickness of TiO_2 was additionally increased by potentiodynamic polarization. Thus formed composite Ag/TiO_2 layer with the silver surface concentration of 0.024 mg cm^{-2}, the SEM photograph of which is presented in Fig.1, was used to study the kinetics of oxygen reduction reaction (ORR) in alkaline solution. Likely to a compact polycrystalline silver electrode, composite electrode was also a good catalyst for ORR in alkaline solutions .

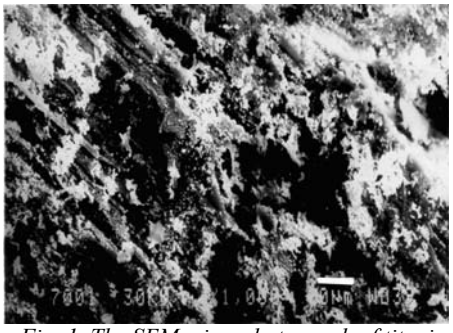


Fig. 1. The SEM microphotograph of titanium surface with cathodically deposited silver. The lenght of the white mark is 10 μm.

By comparing the cyclic voltammograms of composite Ag/TiO_2 electrode to a compact Ag electrode in a 0.1 M NaOH solution, both recorded in a wide potential range, - 1.6 to + 0.9 V vs SCE, it was concluded that the amount of electroactive silver taking part in silver oxide formation on Ag/TiO_2 surface was about 5 times lower than the one characteristic of compact silver electrode.

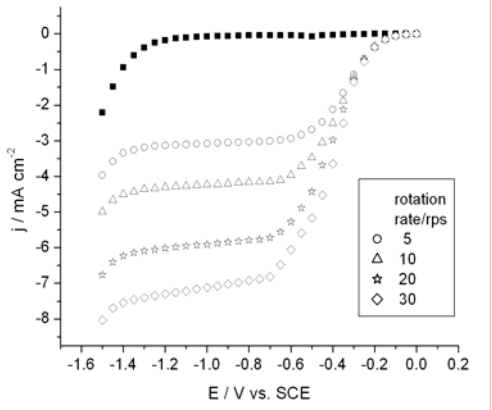


Fig. 2. The voltammograms of oxygen reduction on Ag/TiO_2 rotating disc electrode in oxygen saturated solution 0.02 M NaOH + 0.1 M $KClO_4$ for various rotation rates. Full squares present the baseline voltammogram recorded in an oxygen-free solution.

In Fig 2 a set of voltammograms of ORR on rotating Ag/TiO_2 composite electrode in oxygen saturated aqueous alkaline solution was presented, for various rotation rates. The voltammogram indicate that ORR takes place easily on the surface under investigation, and shows a large voltage interval of diffusion limitation. It was already published that ORR proceeds on anodic TiO_2 alone too, however, much higher overvoltage is needed to run ORR on TiO_2 than on Ag/TiO_2. It is thus obvious that the main role in the acceleration of this reaction in the case of Ag/TiO_2 plays silver. The catalytic activity on the composite surface studied here is quite comparable with the one of platinum electrode. The comparation with the results for compact silver electrode, in a form of Levich-Koutecki plot, evidenced that ORR on the Ag/TiO_2 composite surface follows a $4e^-$ reaction path in a whole region of overvoltages.

MSEN P-03 ece

Ellipsometric Investigation of Anodic ZrO_2 Films Formed in H_3PO_4 Solutions

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By ellipsometric method the optical parameters and thickness of oxide films formed anodically on the Zr metal surface were investigated. The oxides were grown on the mechanically polished zirconium electrodes under potentiostatic conditions in 1 M H_3PO_4 for the potential range between 0 and 60 V. From measured ellipsometric parameters Δ and Ψ, at in-situ and ex-situ conditions, the complex refractive indices for both, metal substrate and oxide films were calculated. The reflectivities of the electrode surfaces were calculated too. The results shown in table 1 are in good agreement with those obtained by E.M. Patrito and V.A. Macagno [1].

Table 1 Complex refractive index and reflectivity for the substrate and oxide film

in-situ	ex-situ
$\tilde{n}_s = 2{,}54 - i2{,}93$	$\tilde{n}_s = 2{,}368 - i2{,}642$
$\tilde{n}_f = 2{,}09 - i0{,}0418$	$\tilde{n}_f = 1{,}97 - i0{,}0788$
$Ro_s = 0{,}424$	$Ro_s = 0{,}483$
$Ro_f = 0{,}718$	$Ro_f = 0{,}538$

On Fig.1 the thickness-potential profiles at in-situ and ex-situ measurements are shown. The curves on fig.1 indicate linear d-E dependences with change in slopes over the 10 V. The coefficient of anodization below 10 V is approximately 2 nm/V, and then decreases to 1,3 nm/V.

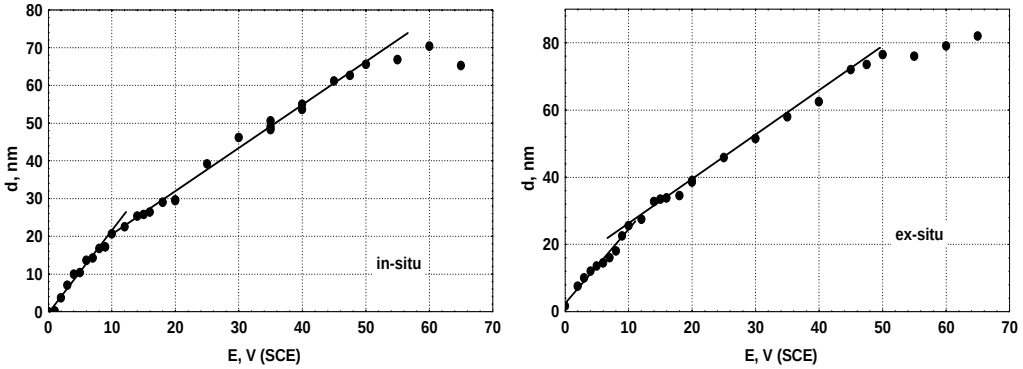


Fig.1. Thickness-potential curves for oxide grown in H_3PO_4

The anodic films formed at the potentials below 10 V are compact. Oxide films formed at the potentials above 10 V are porous.

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Ni/WC Composite Coatings as an Active Cathode Material for Hydrogen Evolution

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Hydrogen evolution reaction (h.e.r.) was investigated on Ni/WC composite coatings obtained by the two ways. The first one is the electochemical deposition on the RDE by a pulsating current from an electrolyte containing both Ni^{2+}ions and WC particles and the second one is the new way of depositing the WC from the aqueous suspension onto the substrate prior to electrochemical deposition of Ni.Activity of the supstrate, Ni/WC composite coating, for hydrogen evolution reaction both in alkaline an acid solutions was investigated.
Linear Tafel lines were obtained at all the investigated substrates. Results are compared with those obtained on pure Ni. Considering that no increase in the true surface area in the case of the composite is observed by the cyclic voltammetry, it appears that the true activity of Ni for the h.e.r. is increased by the presence of the WC particles.That activity is larger the larger the WC content in the coating and, in the pulsating current regime, the higher the frequency of pulsation. Also, the coatings with smaller particles built-in exibit higher activity than those with larger particles. An order of magnitude larger current densities at constant potential are obtained in some cases.

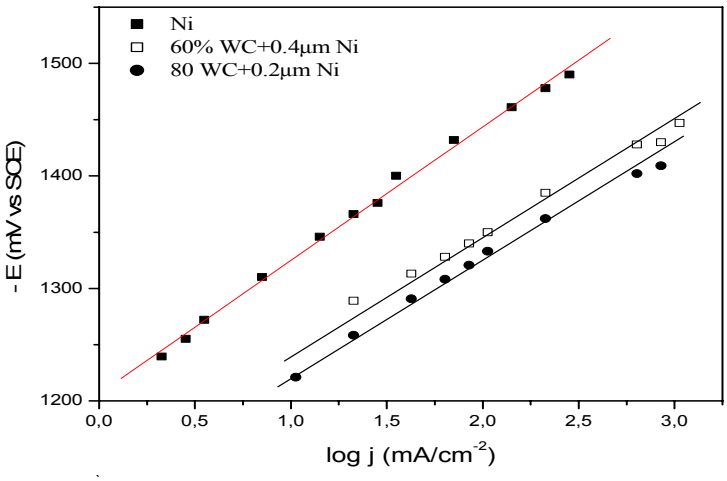


Fig. 1 Tafel functions for h.e.r. on pure Ni and on Ni/WC electrodes obtained by the new way, containing 60 and 80 mass% of WC of particle size of 0.4 μm

Barrier Properties of Anodically Formed Nb_2O_5

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By cyclic voltammetry and ellipsometry the barrier properties of Nb_2O_5, anodically formed on Nb electrode, in various concentrations of acid and alkaline solutions, have been investigated. The cyclic voltammetry I-E profiles reveal to the active/passive transition, i.e. metal dissolution and then, formation of thin passive film. Upon reversing the potential scan, the current decreases abruptly until it reaches almost of constant value that is several orders of magnitude lower than the first forward scan. This behavior can be considered to be the result of high current efficiency under oxide growth. In active region metal dissolution occurs by reaction

$$Nb \rightarrow Nb^{5+} + 5e^-$$

while in the passive region the large current plateau, (Fig.1), is provoked by film thickness grows following the reaction.

$$2Nb + 5H_2O \rightarrow Nb_2O_5 + 10H^+ + e^-$$

The barrier properties of anodically formed Nb_2O_5 in the passive region can most easily interrelated by performing of sequence of cyclic voltammetry measurements in which the final potential is gradually enlarged in each next cycle, Fig.2

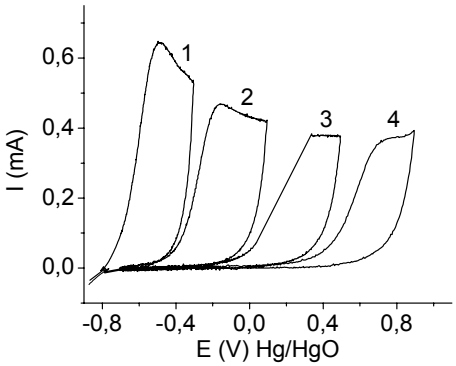


Fig 1. Voltammograms of Nb electrode recorded in 1 M KOH: 1 – first cycle, 2 – second cycle(v = 50 mV/s)

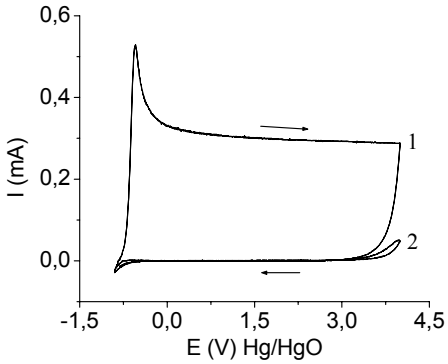


Fig. 2. Voltammograms of Nb electrode recorded in 1 M KOH: 1, 2, 3 and 4 are number of cycles (v = 50 mV/s)

In fig.2, the anodic oxidation may take place only if the actual potential exceeds the maximum value attained in the previous cycle. The large current plateau almost parallel with E axis indicates linear grows of film thickness with applied potential.

The ellipsometric measurements have shown the linear film thickness grows with applied voltage, even at 100 V, indicating barrier properties not only for thin, but also and for thick film. The coefficient of film thickness growth is approximately 2.3 nm/V

Oxygen Reduction Reaction on Anodically Formed TiO_2 and Ta_2O_5

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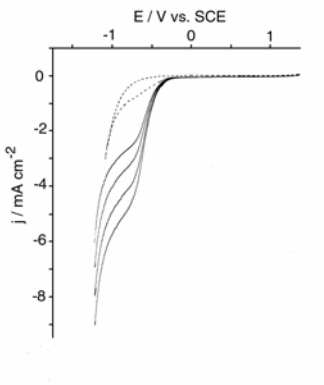


Fig. 1. Voltammograms of O_2 reduction on TiO_2 in 0.1 M $HClO_4$ a rotation rates 5, 10, 20 and 30 rps. Dotted line is the baseline of hydrogen evolution in an deaerated solution

Oxygen reduction reaction (ORR) is a very sluggish electrochemical reaction, characteristic of several different reaction paths, directed primarily by the catalytic action of metal support. Nowadays this reaction is especially interesting as being a main cathodic reaction in fuel cells. Platinum is the best electrocatalyst for this reaction, however, platinum is expensive, and thus much effort was invested to enhance its catalytic effectiveness, for instance by formation of composite Pt/TiO_2 electrodes.

It is known that ORR takes place on pure anodically formed TiO_2. In this work, using rotating disk technique, it was shown that ORR takes place on anodically formed Ta_2O_5 too, without any catalyst addition, and its kinetics was compared to the one taking place on TiO_2.

To prepare the working electrode for electrochemical investigations, the exposed, disk-shaped Ti and Ta surfaces were dry-cleaned by emery paper, and oxidized immediately upon immersion into 0.2 M $KClO_4$ aqueous solution by a potentiodynamic cycle from -1 up to 1.4 V vs. (SCE). After this procedure the surface was covered by an approx. 3 nm thick oxide film. Further potentiodynamic cycles within the same potential limits did not enlarge the film thickness.

Fig.'s 1 and 2 show that TiO_2 and Ta_2O_5 formed potentiodynamically, without any particular activation, permit the reduction of oxygen in acidic O_2-saturated solutions. In accordance to the nernstian dependence of the electrode potentials, ORR precedes the hydrogen evolution. The experiments with various pH's evidenced that the potential at which oxygen reduction onsets, shifts towards more negative values with the increase in pH.

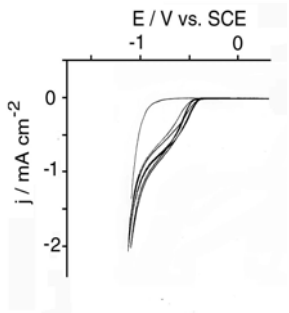


Fig. 2. Voltammograms (direct and reverse curves) of O_2 reduction on Ta_2O_5 in 0.1 M $HClO_4$ at a rotation rates 5, 10 and 20 rps. The single line presents the baseline of hydrogen evolution in deaerated solution.

Most probably, O_2 reduction proceeds through the interaction of oxygen with the ions of lower oxidation states, namely Ti^{3+} and Ta^{4+} ions, which become sufficiently numerous at a sufficiently large cathodic potentials. Namely, within a Ti^{4+} and Ta^{5+} matrix of TiO_2 and Ta_2O_5, respectively, lower oxidation states act as the electron excess sites.

On TiO_2, ORR may become diffusion limited at sufficiently high cathodic polarizations (Fig. 1). Ta_2O_5 is obviously poorer electrocatalyst, since on it (Fig. 2), ORR does not reach diffusion limitation. This may be due to the more expressed dielectric character of Ta_2O_5, and stronger requirements to achieve the flat-band potential, otherwise required to enable to oxide electrode to act like to a metal one.

Investigation of Activated Carbon Cloth for Organic and Unorganic Vapor Adsorption

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Activated carbon cloth of different characteristics was tested as a potential adsorption media for organic and unorganic vapors such as benzene and ammonia. The efficiency of the carbon fibrous adsorbents, which remove contaminants, depends on their pore structure, including internal surface area, shape and pore size distribution and surface chemistry. Activated carbon cloth can be succesfuly applied in the field of ammonia or benzene vapor pollution control and protection. Activated carbon cloth with high surface area and micropore volume and low content of surface groups or without them was a good adsorbent for benzene vapor. Low adsorption capacity for low ammonia concentrations were improved by activated cloth impregnation with suitable additives.

Damage Detection in Laminar Thermoplastic Composite Materials by Means of Embedded Optical Fibers

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This article investigates the possibility of applying optical fibers as sensors for investigation of low energy impact damage in laminar thermoplastic composite materials, in real time. Impact toughness testing by Charpy impact pendulum with different loads was conducted in order to determine method for comparative measurement of resulting damage in material. For that purpose intensity based optical fibers were built in specimens of composite materials with Kevlar 129 (DuPont's registered trade-mark for poly(p-phenylene terephthalamide)) woven fabric as reinforcement, and thermoplastic PVB (poly(vinyl butyral)) as matrix. In some specimens part of layers of Kevlar was replaced with metal mesh (50% or 33% of layers). Also some specimens had more (or less) layers of Kevlar and matrix. Main advantages of fiber optic sensors are their shape and structure which result in easy embedding while preserving mechanical properties of composite material, which make them a reliable automatic system for structure health monitoring.
Experimental testing was conducted in order to observe and analyze response of material under multiple low-energy impacts. Light from the light emitting diode (LED) was launched to the embedded optical fiber and was propagated to the phototransistor based photo detector. During each impact, level of signal, which is proportional to light intensity in optical fiber, drops, and then slowly recovers. Obtained signals were analyzed to find appropriate method for real time damage monitoring. Major part of damage occurs during the impact. Damage reflects in local, temporary release of strain in optical fiber, and raise of signal level. Mathematical method was developed and applied on signals to monitor development of damage in material and for analyzing quality of material.

Results and Conclusions

Obtained results show that intensity based optical fibers could be used for measuring damage in laminar thermoplastic composite materials. Acquired optical fiber signals depend on type of material, but same set of rules (relatively different, depending on type of material) could be specified. Using real time measurement of signal during impact and appropriate analysis enables quantitative evaluation of impact damage in material. Existing methods in most cases uses just intensity of signal before and after the impact, as measure of damage. This method could be used to monitor damage in real time, giving warnings before the fatal damage occurs. Results also show that specimens taken from border parts of material have lower toughness. This results could be used for determining which part of composite material taken from mold could be effectively used, and eventualy for improving manifacturing process of material.

Modeling of the Resin Cure in Unidirectional Composite Rods

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Fiber reinforced polymer composite rods have been increasingly used as cable strength members in telecommunications, railway insulating rods and in maritime structures because of their desirable mechanical properties and resistance to various environmental influences. In order to produce composite with appropriate properties and dimensions, it is necessary to establish a process which enables uniform resin curing and avoids run-away exotherm that could induce matrix burning or cracks. Setting the optimal die temperature regime requires information about the curing reactions taking place inside the die.

A mathematical model has been developed to simulate the vacuum molding process, namely, the profiles of temperature and the degree of cure in a die of cylindrical shape. The kinetic parameters of the epoxy resin were obtained from the differential scanning calorimeter (DSC) scans. Additionally, the shrinkage of the resin is taken into consideration in which way the process parameters could be more precisely determined and the final dimensions of the rod could be accurately predicted.

Results obtained on the basis of mathematical modeling show in depth view on behaviour of composite bulk during resin cure reaction that takes place in the pultrusion die in terms of change in temperature and degree of cure across cross-section of the composite rod and gives insight in effects of change of process parameters (composite rod radius, pulling speed, matrix resin formulation) on temperature and degree of cure profiles. These results can be used in determining optimal processing conditions for the pultrusion process.

Mechanical Properties of Glass Reinforced HDPE and LDPE Tubes

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Composite tubes are increasingly used in various industries such as automotive, aerospace, construction and in materials handling due to their high strength to weight ratio, good insulating properties, toughness and environmental resistance.
Composite tubes were produced by using on-line consolidation process of high-density polyethylene HIPLEX® TR-144 and low density polyethylene HIPTEN® 22003, both produced in HIP-"Petrohemija" a.d. Pančevo, while reinforcement was glass mat from company "Izolma" Raca. Polyethylene film was used in a tape form with 300mm in width and 40μm in thickness. Glass fibers of type E were cut from a chopped strand mat impregnated with urea-formaldehyde polymer, with a diameter of 13 μm and a length of 12 mm.
The on-line consolidation machine included fixed pressure cylinder and steel compaction mandrel. Hot air guns were used as heating sources in the on-line consolidation process.
Composite tubes with 25 laminated layers were produced by varying the processing temperature in the range of 320–330 °C and the winding speed was set to 0,060–0,076 m/min.
The processing conditions, such as temperature, winding speed, compaction pressure and glass fiber fraction were set in such a manner to achieve desired mechanical properties. Tensile tests were performed and results were compared showing that HDPE composite tubes exhibited higher tensile strength. CCD analysis showed the uniformity of wounded reinforcements and critical fracture sites in tested composites. Higher tensile strengths of tubes were achieved by using higher pressure, lower winding speed and higher glass fiber volume fractions.

MSEN P-11 msc

ArF Laser Photolytic Deposition of Nano-Sized Tin Sulfides Incorporated in Polymer Network

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There is enormous interest in synthesis of nanosized metal chalcogenides at room temperature and ongoing attention paid to fabrication of semiconductor nanocomposites in polymeric networks.

In this work we extend our previous research on laser-induced polymerization of CS_2 (ref. 1) and examine the final products chemical-vapour-deposited from the ArF laser photolysis at 193 nm of gaseous CS_2 (10-20 Torr) - $(CH_3)_4Sn$ (10-20 Torr) mixtures in He (total pressure 760 Torr) by X-ray photoelectron spectroscopy, Raman spectroscopy, infrared spectroscopy and electron microscopy and give the first (although indirect) evidence on the gas-phase reaction between Sn and S clusters yielding SnS and SnS_2 at room temperature of the gas phase (ref. 2).

The photolysis results in depletion of both educts, the formation of volatile hydrocarbons and deposition of a yellowish solid coating all the bottom of the reactor. No volatile tin- and sulfur-containing products were observed, which is in agreement with a complete use of CS_2 for the formation of solid deposit.

The Raman spectra of the solids show peaks at 1430-1470 cm^{-1} and 1197-1203 cm^{-1} (respectively assignable to ν(C=C) and ν(C=S) in $(S_2)C=C(S_2)$ configurations), a peak at 517-525 cm^{-1} (corresponding to ν_s(Sn-C) mode in organotin moieties and peaks at 307 and 340-360 cm^{-1} that are respectively attributable to the A_{1g} and A_{2u} (TO, LO) modes in SnS_2.

The FTIR spectra show several structures observed in polythiene films (ν_s(C=S), ν(C=C)S_n) and H_nC-Sn structures. They also indicate Sn=S bonds in SnS and/or SnS_2 tin sulfides and S-S bonds in C-SS-C structures.

TEM images show nano-chain-like agglomerates whose size is smaller with higher laser fluence: 10-20 nm and ca. 100 nm large particles are seen at fluence 340 and 140 mJ cm^{-2}, respectively. Another evidence on the presence of a tin sulfide is provided by the electron diffraction patterns of the selected samples that reveal the presence of the crystalline SnS phase.

The complementary Raman spectral and ED analyses are in keeping with SnS_2 being (at least mostly) in amorphous state and SnS being present in the crystalline state and not being so abundant.

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The Compression Strenght of Composite Polyethylene-Short Glas Fiber

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A composite is a synergistic combination of two or more physically distinct materials. The properties of the composite material are superior, and possibly unique in some respects, to those of the individual constituents. Thermoplastic composites possess the same fiber dominated properties as conventional composites but with the following benefits: greater variety of matrix/fiber combinations and fiber volume fractions available to give profile the exact physical and mechanical properties for application requires, thermoplastics are tough and can be remelted, use of recycled/reclaim components, without use of solvents and they are recyclable.
Processing of thermoplastic composites has a great influence on the properties of composites. The shaping process of thermoplastic composites is influenced by the orientation and geometry (aspect ratio- length divided by effective diameter, L/D) of the fibers within the composites.
In this paper, the investigation of processing of the composite material high density polyethylene- short glass fiber was reported. The started material for reinforcement- short fibers was a wasted glass mat – a felt made of randomly oriented short fibers cuts to shape called preforms, which are impregnate with urea-formaldehyde. Glass mat was chopped to obtain short glass fibers. The particles selected by dimension and then mixed with bonding polymer. The samples were processed by hot isostatic compression (pressure 41.38 MPa, temperature 160-170ºC, time 26 min).
The referent sample from pure polyethylene and nine Series of composite samples (three in respect of L/D ratio and three in respect of fiber contents: 30% mass., 40 % mass., 50 % mass.) were processed. The aspect ratio L/D for the series was obtained by image analyzing of glass fibers. The compression strength tests of samples normal to direction of processing compression were performed.
The effect of the fiber content and L/D ratio on the compression strength of composites was investigated. From the experimental investigations it is obvious that glass fibers reinforce polymer, and as aspect ratio L/D was raised, the values of compression strength was raised too. The best results were obtained for samples with fiber contents of 30% mass, and for the highest value of L/D ratio. The falling of compression strength values with increasing of fiber content was pointed out to limitation of preparing the starting composite mixture-the premix for higher fiber contents for this process of hot isostatic compression was needed.

MSEN P-13 msc

Structural Study of Multi Component Glass Coatings Obtained from Nigerian Raw Materials

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CANCELED

Field emission Scanning Electron Microscopy is used to show evidence of direct uniform coating obtained on the application of glass coating on steel substrates.
Structures and compositions of Nigerian raw materials were investigated using X-ray diffractometer and classical wet method of chemical analysis.
Different ratios of the mineral samples and other chemical substances were liquefied to obtain glass coatings, which were applied on steel samples.
A correlation is established between the various ratios of the raw materials mixtures and the properties of the coatings obtained.
The topography and morphology of the coated samples are evaluated. This paper presents a comparison of the structural features.

Influence of Mechanical Activation on Decomposition of $LiYO_2$ Phase

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This paper deals with $LiYO_2$ phase, which was synthesized by mixing as-received Y_2O_3 and Li_2CO_3 powders and calcining the mixture at 1400°C. The XRD pattern revealed the monophase composition with well developed tetragonal crystal habitus (SEM). This powder was mechanically activated in vibratory mill for 5, 15, 30, 45, 60, 120 and 240 min. X-ray analysis was used to follow structural changes. The results showed that the $LiYO_2$ phase total decomposed into Li_2O and Y_2O_3, respectively, after 60 min of treatment. Further mechanical activation of powders lead to grain size reduction. Williamson-Hall plots were used to separate the effects of size and strain in the nanocrystals powder.

Porous Ceramic Material from Wastes

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Chemiceram, Sfantu Gheorgh, Romania
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Introduction

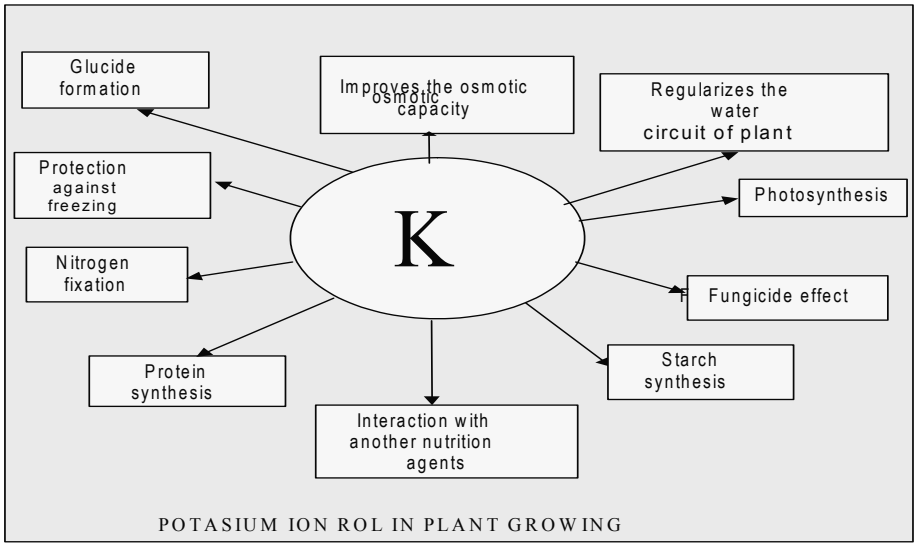
Porous ceramic materials have many applications in: industrials fields, in agriculture (especially in horticulture) or in household. They can be classified according to porosity and field of utilization: to filter drinking or residual water, filter warm gases or gases with impurities; sterilize milk etc.or to fertilize the soil and to provide nutrition to plants

Experimental

Ceramic matrix has been obtained using basic ceramic raw materials (clay), pore forming (celulozic waste with high potasium content) and organic adittive (good paste plasticity). Traditional ceramic processing was used to obtain different type of porous ceramic.

Results

On the sintered samples was determined the potassium effect upon the growing and nutrition plant processes (in horticulture).



POTASIUM ION ROL IN PLANT GROWING

Conclusions

The celulosic waste in ceramic matrix improved the plant growing and nutrition by the potassium content.

Alternative Methods to Complex Evolutions Mathematical Description

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CANCELED

Although issues related to the extent of which mechanistic approaches should be used for a mathematical understanding (and, therefore control) of every natural process are not of recent days, a series of complex evolutions [...] benefit from other means of mathematical treatment. This statement could hold for several reasons, the most important being that deterministic methods are difficult or even impossible to be used to model systems characterized by many parameters involved, being interconnected in a complex manner. On the other way, handy procedures such as statistical models do not offer sufficient information or even fail, sometimes, to provide accurate results, depending on the quality and quantity of the data they were fed with.

As an alternative method, in the paper it is used a stochastic approach. The option is supported by its low implementation costs (both from the knowledge and time involved perspective – take for example the average time expenditure for dealing with CFD applications!). To fully benefit from the advantages of the concept, several applications (identified by A, B and C) were made, referring to a wide range of problems encountered in the oxide materials industry. In order to validate the method, results were compared with the ones coming from experimental works available.

A. A first application will refer to solid phase transport and transformation model within clinkering installations. Clinkering installations represent systems that have not been well described, yet, by an overall, analytical mathematical model. The investigation method makes use of stochastic modeling, for which, on the basis of a set of testing values the trajectory of the granular material and the consecutive changes of its states were simulated. The application requires the prior definition of the stochastic transition matrices.
B. Diffusion modeling in disordered media: diffusion is treated as being a step-by-step perturbation propagation, strongly related with the inner morphology of the system. The method needs to represent the structure of the system by overlapping directed (oriented) graphs, one for the solid phase and the other for the void space. Graph nodes will become computation cells of the studied parameter (concentration, temperature etc.). By properly adjusting the computation cells' density (an iterative procedure is required), and by making use of interpolation methods one can characterize the corresponding field in any point of the subsequent structure.
C. Crack propagation as well as other natural phenomena showing a stochastic evolution can be modeled in a deterministic manner only at a microscopic scale. When shifting at a larger scale (macroscopic), it could be of interest to know whether if the process can be modeled as a Markov chain or it shows a wider dependency, i.e. on preceding steps. The aim was to simulate and analyze crack propagation in clay made, thin plates (68/36/6mm), subjected to a single fracture by applying flexural tension. Two methods will be compared, i.e. Monte Carlo and a modified Pattern Classification Method as concerning their effectiveness (52% and 66%, respectively, as success rates).

The aim of the paper is, therefore, to provide a useful and easy-to-use method to deal with challenging-to-be-modeled processes.

Elaboration of a Rapid Method for Determining the Early Heat of Hydration of Cement to be Used in Strength Prediction

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Introduction

The heat flow released at cement hydration has a major importance in investigating the hydration mechanism and kinetics, which are referred to in selecting and prescribing the operational parameters of the cement manufacturing process. The aim of investigation was to obtain a rapid method for determination of the heat of hydration released in the early hydration stages of CEM I cement type. An experimental model for predicting the cement standard strength can be conceived based on the heat of hydration.

Experiments

Preliminary experimental determinations were carried out in order to: (i) set an optimal dosage cement/sand/water; (ii) establish the optimal accelerator type and ratio; (iii) establish the temperature recording frequency; (iv) obtain a rapid method for determining and calculating the early heat of hydration; and (v) obtain a correspondence relation between cement standard strength and early heat of hydration

Results and Discussion

The experiments were carried out so as to diminish the time necessary to reach the upper temperature recorded at cement (CEM I) mortar hydration from 11–13 hours down to just 2.5–3 hours depending on the cement quality (Fig. 1). A correspondence relation of type $y = ax + b$ was established using the heat of hydration released within above time interval with the help of an accelerator (Fig. 2).

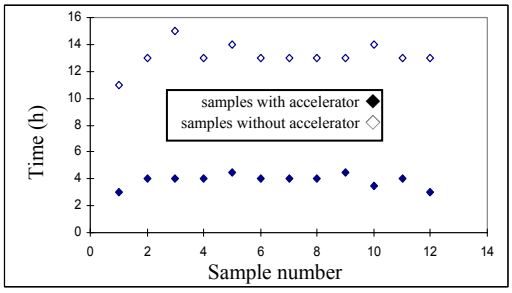


Fig. 1 Time for obtaining maximum temperature

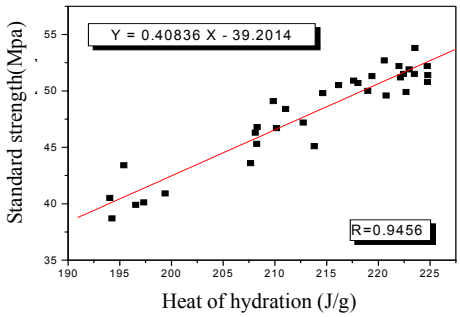


Fig. 2 Variation pattern of standard strength depending on hydration heat flow rapid obtained

Conclusions

The method is reliable, rapid and new. It allows determination of early heat of hydration of CEM I cement in just 2.5 hours using a semi-adiabatic method. Moreover, the established regression equation provides a rapid solution for calculation of cement compressive strength in approximately 3 hours from the cement manufacture. The precision of predicted value for compressive strength is ± 2.5 MPa. The method for prediction of 28 days compressive strength can be applied in the manufacturer laboratory in two cases: (i) modifications of the raw mixture composition and (ii) changes in cement type.

Waste Storage Containing Heavy Metals in Ceramic Matrix

Adina Mihail, Daniela Alina Muntean*, Marcela Muntean

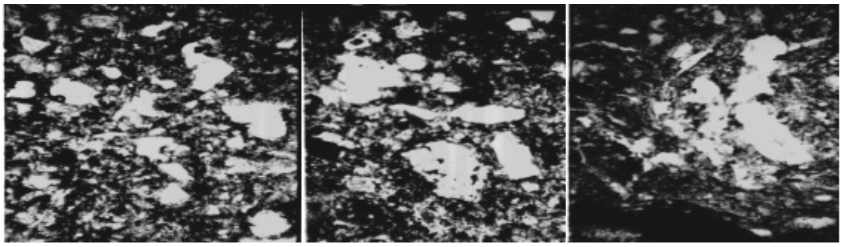
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Introduction

The rational waste utilization can partially remedy the situation created by the price raising up of the energy or the penury of some raw materials, contributing so to the environment protection. The brick technology development trends the high product quality and concomitantly, the use a waste and recycled materials as raw mixtures. In order to obtain the ceramic matrix a wide range of raw materials can be used beginning with the finest and the most pretentious ones (Al_2O_3, ZrO_2, high purity kaolin, etc.) ending with the most common ones (clays, diatomite) and including also various type of wastes (fly ash, municipal solid waste, different slurries).

Experimental

Ceramic matrix has been obtained using as raw materials local clay, fly ash (FA) and municipal solid waste (MSW). The particle size distribution of the Romanian fly ash is 60-80 % less than 63 μm. It containes aprox. 3.62% combustion components giving caloric value of 627kJ/kg. The MSW has a small content, 4-5.5 % of lead, zinc and chromium oxides. The wastes were used as alumina-siliceous components, partially substituting the clay (25-50%).



Reference 35% FA 35% MSW

Results

Brick samples with clay and those with clay and 35 % of FA, MSW or its mixture show some differences from structural point of view: pores distribution and sturcture uniformity. The samples with FA have a bigger density in comparison with reference sample and that with MSW, at the same burning temperature and the water absorption is direct correlated with sample compactity. For all samples the compressive strength are situated between 15-24 MPa.
The samples with wastes have a good stability at the leaching test. Basically, the above mentioned cations have been immobilised in the ceramic matrix sintered at 1000 ^{o}C.

Conclusions

The flay ash and municipal solid waste wastes can be use in ceramic matrix as reciclyed materials, substituted up to 50% the clay with good consecences.

MSEN P-19 msc

Comparative Study About Hydrogen Sorption in Sponge and Powder Titanium

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Currently, hydrogen may be stored as a compressed gas or a cryogenic liquid. Neither method appears to be practical for many applications in which hydrogen use would otherwise be attractive. For example, gaseous storage of stationary fuel is not feasible because of the large volume or weight of the storage vessels. Liquid hydrogen could be use extensively but the liquefaction process is relatively expensive.
The hydrogen can be stored for a long term with a high separation factor, like solid metal hydride. Using hydride-forming metals and intermetallic compounds, for example, recovery, purification and storage of heavy isotopes in tritium containing system, can solve many problems arising in the nuclear-fuel cycle.
The paper presents a comparative study about hydrogen sorption on two titanium structures: powder and sponge. Also, is presented the characterization, by X-Ray diffraction, of two structures, before and after sorption process.
From results, it is obtain that sorption method is efficient for both samples. Kinetic curves indicating that sorption rate for titanium powder is grater than sponge titanium. This is the effect of reaction surface, which is grate for powder titanium.
Sorption capacity for hydrogen is lower for powder titanium for identical experimental conditions. The difference between storage capacities could be explained by activation temperature, which it was lower for powder titanium comparatively with sponge. In table, one is presented the results of XRD analysis for both samples, sponge and powder titanium, after sorption process.

Table 1

Sample	Cristalografic phase	Weight (%)	Vol. (%)
Hydride of sponge titanium	TiH_2 (cI2/1)	100%	100%
Hydride of powder titanium	Ti-α (hP2/1) TiH_2 (cI2/1)	17,5±0,2% 82,5±0,2%	15,0±0,1% 85,0±0,1%

Investigation of Mechanochemically Activated Mixture for Obtaining Low-Melting Glass

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Mechanochemical activation of initial materials used for the obtaining the low-melting glasses of PbO-B_2O_3-SiO_2 system, with following chemical composition: 40 mol% (69,4 wt%) of PbO, 34 % (18,4 wt%) of B_2O_3 and 26 mol % (12,2 wt %) of SiO_2 was studied.
Raw materials that were used in the experimental work were minium (Pb_3O_4), boric acid (H_3BO_3) and quartz sand (SiO_2). Prepared glass mixtures were mechanochemically activated. Mechanochemical activation was performed in high-energy vibro mill with rings. Four time periods of mechanochemical activation were chosen. Activated glass mixtures were investigated by: FTIR spectroscopic analysis and DTA (differential thermal analysis). Applied methods for the quantification of mechanochemical activation effects showed that effects of mechanochemical activation on the properties of glass mixtures for obtaining low-melting glasses are considerable.

MSEN P-21 msc

Mechanochemical Activation of MgO and its Application as a Filler in Polyester Resin

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This paper presents the alternations of physical and chemical properties of MgO, as a result of applied level of mechanochemical activation. The intention was to provide the chemical or physical bonding between filler and polymer by the mechanochemical activation of the filler (MgO) surface.

Non-activated and mechanochemically activated MgO (activation time was 7,15 and 35 minutes) was incorporated into the polyester resin that was reinforced with glass fibers. Dependence of mechanical properties of composite on activation time, as well as on MgO content, was observed.

Characterization of the filler involved methods of structural analysis, thermal analysis as well as determination of specific surface area and particle size. Further characterization of the composite material included determination of mechanical properties: tensile strength, flexural strength and hardness.

Based on the results of IR spectroscopy, it is concluded that there is no sign of any changes in the remained part of spectra, or more precisely the presence of the absorption bands of the new compounds are not observed. According to the DTA, TG and DTG analysis it is also concluded that initial sample contains water in the form of hydroxide and that mechanochemical activation didn't cause the loss of hydroxyl water. This is completely in accordance with the results of X-ray diffraction analysis. Results of X-ray analysis illustrate the intensity changes of the peaks, but without dislocation, indicating the surface characteristic of the alternations, induced by mechanochemical activation. Determination of values of the specific surface pointed out that mechanochemical activation of MgO for the period of 7 minutes leads to the considerable decrease in the values of the specific surface due to particles agglomeration and increase of the particle surface activity. Further activation, for the period of 15 minutes and especially for the period of 35 minutes, value of specific surface increase as a result of agglomerate destruction and the value remains almost the same as initial, non-activated sample. Dependence of mean particle diameter and value of the specific surface in the process of mechanochemical activation is very specific. In case of MgO, mean particle diameter is not significantly changed under the mechanical activation, while value of the specific surface considerably varies, reaching almost tenfold of the initial value determined values of the specific surface for nonactivated sample and sample activated for of 7 minutes were 22.06 and 2.86 m^2/g respectively.

The embedment of the filler into the polyester resin with glass fibers leads towards certain drop in tensile and flexural strength. Application of non-activated as well as mechanochemically activated filler MgO has no influence on mechanical properties of the composite. The increase of mechanochemical activation time of the MgO, affects decrement of the tensile and flexural strength of the composite, obtained by embedment of the filler into the polyester resin with glass fibers, demonstrating that the reduction of particle size and the increase of specific surface do not have positive effects in usage of inorganic fillers in materials with organic component.

The Use of Image Analysis for Interaction of 1,3,5-Trisubstituted Isocyanurates with Oxidiser and Different Binders in Composite Materials

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Composite propellants are nonhomogenous propellants and comprise primarily crystalline oxidizer and metal fuels uniformly suspended in a resin binder. The strength of the bonds between the polymer matrix and the oxidizer are determining the mechanical properties of the composite propellants. In order to achieve the good mechanical properties of the fuel, bonding agents are added to the mixture. The role of the bonding agents is to enable the good interactions (interphase) between the polymer matrix and the oxidizer grains. The level of interconnection between the phases could be measured using the surface obtained by cutting the composite material and observing the resulting surface.

The problem in visualization of such a material is to enable the vision of the polymer matrix and the grains in the image as both phases are white. There are two possible ways to do it: to add the pigment into the matrix polymer so as to make the matrix colored and different from the grain color. Other possibility is to find the solvent for one of the phases and to dissolute one of the phases in appropriate solvent so as the remaining phase could be colored, photographed and analyzed using the image analysis program. The morphological characteristics of the image could be established and analyzed.

The topic of this research is to establish the conditions of preparation of composite propellant containing ammonium-perchlorate and HMX and RDX as oxidizers, and polymer of polybutadien type and 1,3,5-trisubstituted isocyanurates as bonding agent. The bonding phenomenon is investigated by optical microscopy. The established procedure of preparation will enable the visualization of the composite structure and morphological characteristics of the surface will be obtained and discussed. From the morphological properties of the obtained composite we are able to make the decision about the suitable polymer for the preparation of the uniformly distributed composite propellant.

MSEN P-23 msc

Surface Characteristics of Different Carbon Materials

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The application of carbon materials is mainly dependent on its mechanical and surface properties. Elucidation of carbon material's surface structure and chemical properties is important to understand the chemical processes leading to the stabilization or activation of the surface.

In this work surface characteristics of different carbon materials were investigated. The materials under consideration were: activated carbon, carbon monolith, carbon felth and glassy carbon (powder, plate and broken plate). The surface functional groups of the carbon materials studied were determined by Boehm's method and the specific surface area was studied by BET method with N_2 adsorption. Surface morphology was characterized using scanning electron microscopy (SEM).

All carbon materials tested have basic character, and it was found that carbon felth has the highest amount of surface functional groups while activated carbon has the lowest. Comparing the results obtained using BET analysis with Boehm titration results it was found that the number of functional groups does not depend on specific surface area. Also, the number of functional groups on glassy carbon surface, obtained by TPD is twice higher than the number obtained by Boehm titration. From these observations it can be assumed that complete determination of functional groups could not be obtained by Boehm method, probably because used solutions are not able to reach microporous structure.

As a specific test for the surface activity, cementation of silver from aqueous solution of silver salts was used. The silver deposit on impregnated carbon material was studied as a function of the immersion time from the aqueous $AgNO_3$ solution (concentration 75mg/dm^3), and as a function of the concentration of $AgNO_3$ solution (25, 50, 75, 100 and 125mg/dm^3). The amount of Ag deposited was found to be proportional to the immersion time and to the concentration of $AgNO_3$ solution in contact with carbon materials, as expected. However, specific surface area of the materials is not relevant for silver deposition. The highest amount of silver was deposited at the surface of glassy carbon, sample with the lowest porosity.

Comparative Estimation of Woven Fabrics Bending Ability by the Application of Direct and Indirect Indicators

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Bending ability of woven fabrics under action of their own weight, known as drape, is very important usage characteristic whose studying is necessary for successfully designing of clothing materials of desired aesthetic properties. Because of that, investigation of these properties is one of the most frequent topic in metrology of textile materials.

The experiment was conducted on woven fabrics of different raw material (cotton, wool, viscose, flax) made in variants of plain and twill weave. Drapability of woven fabrics was determined by the application of direct indicators (stiffness, bending modulus) as well as indirect indicators (drape coefficient, ratio C/A, where C is the maximum dimension of projection along the fabric-warp direction and A is the maximum dimension of projection across the fabric-weft direction). Cantilever method, described by Luvishis, was used for determination of direct indicators. Values of indirect indicators were obtained from the device constructed, by the authors, for the purpose of this investigation. The way on which device functions is based on measuring the surface of the shadow of circular fabric's sample, placed on horizontal circular support whose diameter is less than diameter of investigated sample. Structural characteristics as well as direct and indirect indicators of bending ability of investigated woven fabrics are given in the lower Table.

Table. Structural characteristics and indicators of bending ability of investigated woven fabrics

Ordinal number of fabric		1	2	3	4	5	6
Sample		Cotton	Cotton	Flax	Viscose	Wool	Wool
Structural characteristics							
Type of weave		plain	plain	plain	plain	plain	twill 2/2
Fineness, tex	warp	35	12	48	27	27x2	49
	weft	35	12	44	34	23x2	23x2
Density, dm^{-1}	warp	269	597	209	257	170	171
	weft	221	311	188	268	184	181
Crimp, %	warp	7.8	6.5	6.7	9.3	4.6	5.7
	weft	8.6	6.5	3.2	8.1	8.5	5.4
Mass, $g \cdot m^{-2}$		180	122	202	160	193	180
Thickness, mm		0.364	0.222	0.368	0.366	0.522	0.560
Direct indicators of bending ability of investigated woven fabrics							
Stiffness $x10^{-7}$, $N \cdot m^2$	**warp**	6.25	1.66	9.72	0.806	5.02	3.03
	weft	4.11	1.12	12.12	0.750	5.68	3.29
Bending modulus $x10^7$, $N \cdot m^{-2}$	warp	0.517	0.582	0.788	0.066	0.114	0.085
	weft	0.340	0.408	0.970	0.061	0.129	0.092
Indirect indicators of bending ability of investigated woven fabrics							
Drape coefficient, %		64.7	54.2	66.1	23.5	58.8	46.6
Ratio *(C/A)*		1.07	1.03	1.01	0.953	1.06	0.955

On the basis of the results of the imposed investigation it is possible to conclude that the results obtained by the usage of direct and indirect methods are in agreement. Also, the sensitivity of the applied methods concerning the raw material as well as the constructive characteristics of woven fabrics can be noticed.

Characteristics of Vitreous Carbon Manufacturing from Synthetic Resins

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A study is described of the vitreous carbon obtaining from synthetic foundry resins (phenol-formaldehyde and furan resins) and the influence of technological particularities and raw materials chemical characteristics.
Vitreous carbon is related to graphite crystal but with a large disorder and microscopic and submicroscopic voids (depending on nature of raw materials), which explain its low density of 1.5 [g/cm^3] compared with 2.25 [g/cm^3] for theoretical density of graphite crystal. Generally, this material is obtained by pyrogenation and subsequent thermal treatment carbonaceous materials with transversal molecular bonds.
For this experimental study, the vitreous carbon was obtained by pyrogenation of synthetic foundry resins, with modified chemical composition, at different final temperature of heat treatment in two distinct technological conditions: natural circulation of volatile matters and inert medium.
The influence of raw material nature (pH, degree of reticulation, chemical composition) on vitreous carbon characteristics has been studied.
Among other things, was funded that the loss mass is significant smaller for phenol-formaldehyde resins with pH = 2 – 7 and total sulfur content is smaller for vitreous carbons obtaining in inert medium. Also, the complete reticulated resin gave compact carbonaceous material (with apparent density of 1.329 [g/cm^3]) and the resins with small degree of reticulation, carbon foams (with apparent density of 0.2 – 0.5 [g/cm^3]).

Influence of Accompanying Substances of Hemp Fibres on Their Electric Resistance

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Hemp fibres belong to the group of natural, cellulose bast fibres. These fibres have exceptionally properties like: antimicrobe effect, absence of allergy effect, extraordinary sorption properties, good electro-physical properties (small static electricity in regard to the other cellulose fibres) as well as the high value of breaking strength (the highest strength natural fibre). Hemp fibres, in regard to the other fibres, show the best protection from UV rays and fit very well to the ecological trends. Because of the good resistance to static electricity, hemp fibres can be used for production of working and protecting clothes.

However, hemp fibres have some drawback, like: heterogenous chemicaly composition, large quantity of accompanying supstances (lignin, pectins, waxes) and unsatisfied fineness and evenes.

Drawbacks of hemp fibres are possible to eliminate or reduce, in a great extent, by the application of appropriate modification treatment of hemp fibres. Aimed at discovering the appropriate modification treatment of hemp fibres, corelation between chemical composition, fineness and volume electric resistance as well as volume electric resistivity of hemp fibres were presented in this paper.

In experimental part of this paper, by the application of exceptional procedure for determination of chemical composition, accompanying substances of hemp fibres are gradualy removed. After each phase some fibrous substrats were separated. After that fineness and volume electric resistance were determined.

Results of the imposed experiment showed that owing to the removing of the components step by step, hemp fibres became more fineness and their volume electric resistance increased. But, the volume electric resistivity, which is resistive characteristics of hemp fibres, increased only with the removing of substances solubilities in wather as well as removing the fats and waxes. After that, the decrease of the volume electric resistivity of investigated fibres, in the case when pectins and lignin were removed, was noticed. This phenomenon can be explained by the change of chemical composition and structure of hemp fibres after this modification.

MSEN P-27 msc

Use of Embedded Optical Fibers as Intensity-Based Sensors for Damage Detection in Composite Tubes under Internal Pressure

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Filament-wound glass-fiber-reinforced epoxy tubes are being increasingly used for a wide range of applications, such as high-pressure containers in chemical plant, the aerospace and defence industry, gas and liquid transfer pipes in the gas, oil and nuclear industries. Most of the conventional damage assessment methods are time-consuming and are often difficult to implement on hard-to-reach parts of the structure. For these reasons, a built-in assessment system must be developed to constantly monitor the structural integrity of critical components. Optical fiber sensors that can easily be embedded in the structure have shown a potential to provide real-time health monitoring of the structures with a desired sensitivity and the sensor size. In this study, the feasibility of real time monitoring of damage of cross-ply composite tubes under internal pressure using embedded intensity-based optical fiber sensor was evaluated by comparison with surface-mounted extensometer and load data. Experimental results showed that the sensing response of embedded optical fiber was in good agreement with that of the surface-mounted extensometers and load sensors. The proposed system demonstrate good potential to monitor the mechanical behavior of composite tubes under internal pressure loading that is typically encountered in the industry environment.

Computational Simulations of Thermal Phenomena in Fiber-Reinforced Thermoplastic Tape Winding Process

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On-line consolidation process is newly developed technique for manufacturing cylindrical composite parts such as rods, tubes, pipes etc, and this technique is commonly used in processes such as filament winding and tape laying. A focused heat source is aimed at the interface between incoming towpreg and substrate to create a molten zone. Energy from a highly focused heater melts the surfaces of the towpreg and composite substrate while, at the same time, the compacting roller compresses the material and squeezes out excess resin. Continuous operation of the on-line consolidation process is achieved by rotating the mandrel. The speed of on-line consolidation is limited by the time required for intimate contact and diffusion bonding. In this case the matrix was polyethylene film (high and low density) and the reinforcement was glass mat, while the heating was based on hot-air system.

It is well-known that mechanical properties of consolidated parts depend on their thermal history during manufacture, so therefore, a transient heat transfer analysis is needed to investigate this thermal history. The mathematical technique used for calculations is the finite volume method. For computation purposes, the profile is divided into small volume parts - elements. Because of the cylindrical symmetry and the assumption that there is no heat flow in circumferential direction, three-dimensional problem is reduced to two dimensions. During computation, temperatures at all elements are iteratively approximated with heat transfer equations. Results of this calculation were very helpful to set the right temperature of hot-air, and to predict temperature distribution within composite part during on-line consolidation.

MSEN P-29 msc

Damage Detection in Ballistic Composite Laminates by Means of Embedded Optical Fibers

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This article the describes procedure of embedding fiberoptic sensors in laminar thermoplastic composite material, as well as damage investigation after ballistic loading. Thermoplastic reinforced composite materials were made for increased material damage resistance during ballistic loading. Damage inside the composite material was detected by observing intensity drop of the light signal transmitted through the optical fibers. Experimental testing was carried out in order to observe and analyze the response of material under various load conditions. Diferent type of Kevlar® reinforced composite materials (thermoplastic, thermoreactive and thermoplastic with ceramic plate as impact face) was made. Material damage resistance during ballistic loading was investigated and compared. Specimens were tested at multiple load conditions.

The opto-electronic part of measurement system consists of two light emitting diodes as light source for optical fibers, and two photodetectors for light intensity measurement. Output signal was acquired from photo detectors by means of the data acquisition board and personal computer. Measurements have shown intensity drop of transmitted light signal as a result of applied loading on composite structure for all optical fibers. All diagrams show similar behavior of light signal intensity. In fact, all of them can be divided into three zones: zone of penetration of the first composite layer, bullet traveling zone through composite material till its final stopping, and material relaxation zone. The attenuation of the light signal intensity during impact is caused by the influence of the applied dynamic stress on the embedded optical fibers. Applied stress caused microbending of the optical fiber, changing shape of its cross section and the unequally changes of indices of refraction of core and cladding due to stress-optic effect. The main goal of experiment is development of system for thermoplastic composite structure health monitoring during real life exploitation.

Results and Conclusions

Results of experiments confirmed that the optical fibers could be applied as intensity sensors in real-time monitoring of structural changes in thermoplastic laminar composite materials under the ballistic loading. Light signal intensity drops in an optical fiber in response to applied loading on composite material.

Compressional Behavior of Knitted Fabrics Exposed to Repeated Wash and Wear Cycles

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The quality requirements of knitted fabrics nowadays become highly demanding in terms of appearance and comfort properties. It is well known that yarns are subjected to tensile, bending, torsion and compression during wear and care of apparels. For instance, the shrinkage of knitted fabrics significantly increases with the introduction of home laundering.
The appropriate selection of row materials could be the way to reduce the deformation of knits caused by mechanical forces. Keeping in mind the fact that natural fibers and man-made fibers can significantly differ in respect to elastic properties, natural fiber and synthetic fiber knits for the experiment were produced. The single jersey knitted samples were produced on a circular machine (NoE20) by combining two of the hemp and polyacrylonitrile (PAC) yarns. In that way, the experimental material included three different variants of knitted fabrics: 100% hemp knit, 100% PAC knit and hemp 50%/PAC 50% knit. The structure of these yarns were identical (fineness and twist), so the structure of knitted samples were the same, too. An investigation of behavior of knitted fabrics during relaxation of compression was realized. In order to indicate the change of compressional properties of knitted fabrics the same investigation after undergoing repeated wash and wear cycles (during eight weeks) was realized. The knitted fabrics were exposed to compression by the use of apparatus (TexTesT-306) for measuring the thickness of textile surfaces. The samples were composed and relaxed for five cycles progressively increasing the load from 30g (thickness of sample without loading – JUS F.S2.021), through 170g, 420g, 670g and 1170g to approximately tenfold load of 1670g.
Although the structure of tested samples was the same, the differences in compressional behavior of knitted fabrics were shown. It is obvious that the differences in respect to elastic properties of hemp and PAC fibers were projected into knits. It is well known that hemp fibers are characterized by low elasticity, while PAC fibers are considered as soft fibers because of a lower density and satisfied shape retention properties.
The compression curves were drawn in order to obtain an insight into the change of compressional behavior of knitted fabrics during wear. Also, these curves enabled comparative estimation of compressional behavior of knits made of different yarn component. By the aid of the data the surfaces proportional to the work of compression for each of cycles, as well as the hysteresis of compression among the first and the fifth cycles of loading-unloading cycles were calculated. Hysteresis of compression was watched from the aspect of ability of elastic recovery, in order to compare tested knitted fabrics. In that sense, a less surface means better ability of elastic recovery. From the first to the fifth loading-unloading cycles, the surface of hysteresis of compression decreased. The phenomenon described for each of knitted fabrics was shown. The results obtained by investigating compressional behavior of knits exposed to wear and care cycles, confirmed the earlier mentioned trends. Also, the change of compressional behavior of knitted fabrics during wear was confirmed. However, the analysis of comparative compression behavior of knits before and after wear, pointed the differences between tested samples. The worsening of ability of elastic recovery of pure hemp knit is noticed. Hemp/PAC knit showed the same effect, unlike pure PAC knit which showed the better ability of compression recovery after undergoing repeated wear and wash cycles.

The Possibility of Concrete Protection Against Cavitation Erosion by Polyurethane Multilayer Coatings

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Cavitation involves the formation and subsequent collapse of bubbles within the liquid. The pressure waves emitted during bubble collapses, interact with neighboring solid surfaces, leading to material damage. Cavitation damage has been observed on many concrete structures exposed to cavitation. Because cavitation erosion is basically a surface phenomenon, the use of flexible material coatings sometimes improves successfully erosion resistance.
This paper describes cavitation resistance of polyurethane multilayers coatied on the clean cuted concrete samples. These coatings have excellent athesion with concrete and very good abrasive resistance as well as easy deposition on concrete. Phisical properties of all layers are given in Table 1. Samples were tested using the Modified Vibratory Cavitation Test Method.
The first layer was a 2-component, solvent-free, low viskozity, UV stable polyurethane primer. It cures using chemical cross-linking to produce a thin mil primer with excellent abrasion characteristics for long term wear protection.
The second layer was a 2-component, 100% solids polyurethane membranes available in medium and high viscosity. They cure using chemical cross-linking to form a dynamically flexible waterproofing membrane.
The third layer was a 2-component, 100% solids, polyurethane coating and binder. It cures using chemical, cross-linking to form a hard elastic, abrasion-resistant coating and binder.
During our testing, only thickness of the third layer was changeable. Better cavitation resistance obtained by increase of the third layer thickness. Such behaviour is a result of better elasticity of coating.
These preliminary investigations approved the possibility of concrete protection against cavitation erosion by polyurethane multilayer coatings. Because, subsequent investigations ought to be performed by change of membrana thickness in view of best elongation of membrana as well as retrieval of optimal thickness of all layers.

Table 1. *Phisical properties of polyurethane multilayer coating*

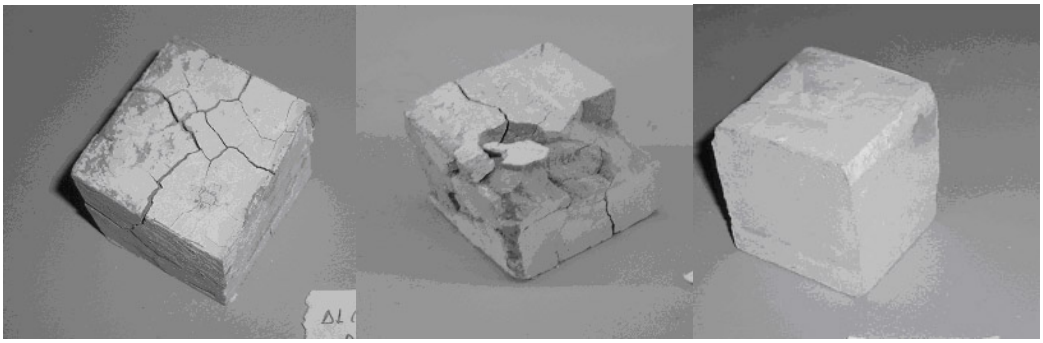
	Primer	*Membrana*	*Coating*
Density, g/cm^3	*1,05*	*1,1*	*1,54*
*Viscosity, mPa*s*	*1200*	*3500*	*2000*
Elongation, %	*25*	*750*	*10*
Hardness	*77 Shore D*	*75 Shore A*	*75 Shore D*
Tensile strenght, N/mm^2	*31*	*10*	*29*
Compresive strenght, N/mm^2	*-*	*-*	*63*

Behaviour of Blended Cement Pastes at Elevated Temperature

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Fire can cause severe damage to building structures. This fact has increased the importance of the fire resistance of concrete. The consideration of the fire resistance of concrete requires the complete knowledge of the behaviour of each concrete component under elevated temperatures.
In the present paper the cohesion of blended cement pastes upon heating, is studied. Natural Pozzolana, fly ash, ground granulated blastfurnace slag, metakaolin and limestone were used as main cement constituents. Blended cements were prepared by replacing a part of Portland Cement (PC) with the above minerals (10% w/w in the case of metakaolin, 20% w/w in the case of the rest materials). The specimens were water cured for 3 months and then they were thermally treated at 200, 400, 600 800 and 1000°C for 1h. Visual inspection, mass measurements and ultrasonic velocity measurements were carried out after each thermal treatment. It is concluded that the cohesion of the pastes is strongly affected by the kind of the main constituent added in Portland cement. The use of pozzolanic materials and especially metakaolin improves the fire resistance of the pastes while the samples with limestone show the worst behaviour (Fig 1.). The damage of the specimens is due mainly to the transformation of free CaO to $Ca(OH)_2$ and tooks place rather during the cooling than the heating.



PC Cement with limestone Cement with metakaolin

Fig. 1. Specimens thermally treated at 800°C for 1h

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Influence of Using Secondary Raw Materials and Alternative Fuels on Cement Manufacturing

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Introduction

The industrial process of heating at high temperature in rotary kilns, which is essential in cement manufacture, creates favorable conditions to use industrial wastes in different ways:

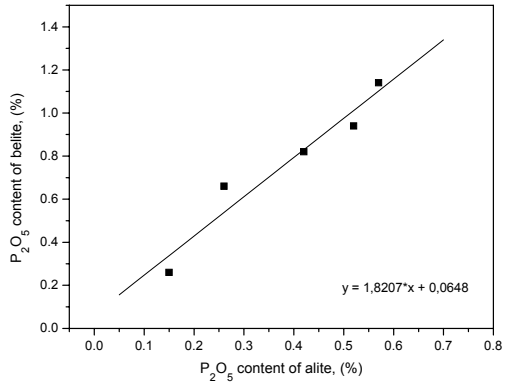
- as alternate and substitute raw materials (slag from iron and steel industries, fly ash from coal based thermal power plants, red mud, lime bearing carbonate sludge from paper etc.),
- as partial replacement of fossil fuels (meat and bone meal, rice husk and straw, sewage sludge, oil shale, rubber and plastic wastes, scrap motor tyres etc.).

This paper deals with potential for use blastfurnace slag as raw material and meat and bone meal (MBM) as alternative fuel on the chemistry of clinker formation and hydration activity.

Materials and Methods

An industrial raw mixture, which consists mainly of crystalline limestone and blastfurnace slag, was used in these tests. Laboratory clinkers were obtained by adding different amounts of MBM at the industrial raw mixture. Three industrial clinkers were studied comparative in order to observe if the burning regime has an influence on the incorporation of phosphorus into clinker minerals. X-ray microanalysis was performed on selected clinker samples in order to assess the phosphorus incorporation level in alite and belite. The hydration activity was evaluated by means of nonevaporable water content and X-ray diffraction.

Results and Discussion



X-ray microanalysis results reveal a large variability of P_2O_5 distribution in alite and belite for clinker samples burned with a high amount of MBM. A drop of phosphorus amount incorporated in calcium silicate phases in the case of industrial clinkers is due to heat treatment. The concentration of P_2O_5 present in belite is almost two times higher than that in the alite.

Fig. 1. P_2O_5 contents of alite and belite, according to X-ray microanalysis

Conclusions

The increasing amount of P_2O_5 decreases the raw mixture burnability by reducing the capacity of CaO to combine with acidic oxides. However, phosphorus present in calcium silicate phases of clinker accelerates the reaction with water due to stabilization of high temperature polymorph form of belite and distortions of the crystalline structure of alite and belite.

Determination of the Hydrogen Diffusion Coefficient in Metal Hydrides by Constant Current Discharge Technique

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Different approaches have been proposed for evaluation of hydrogen diffusion coefficient (D_H) in metal hydride (MH) alloy electrodes [1]. Zheng et al. estimated D_H for $LaNi_{4.25}Al_{0.75}$ electrode using a constant current discharge technique and reported the value 3.3 10^{-11} cm^2 s^{-1}. In this work we are used the same galvanostatic technique to determine the hydrogen diffusion coefficient through a $LmNi_{3.55}Co_{0.75}Mn_{0.4}Al_{0.3}$ electrode in 1M KOH aqueous solution. The construction of the electrochemical cell used was described previously [2]. The working electrode firstly was charged with 60 mA g^{-1} for 3 hours. After that, circuit was kept open for a 30 min to let electrode potential to be equilibrated, according which was possible to calculate the corresponding equilibrium hydrogen pressure. The applied discharge current density was 60 mA g^{-1}. From the obtained discharge curve it was possible to determine the transition time corresponding to the total time taken for the electrode potential to reach cutoff potential of - 0.6 V with respect to the Hg/HgO1 M KOH at the given discharge rate. The average particle size of MH alloy electrode was determined by scanning electron microscopy analysis. The obtained D_H value was 3.5 10^{-11} cm^2 s^{-1}. This is in good agreement with previously reported D_H values regarding to the amount of the absorbed hydrogen in MH electrodes having a similar composition [1-3].

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Effect of Mineral Admixtures Addition on the Durability of Limestone Cement Paste under Sulfate Attack

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It is generally accepted that conventional sulfate attack of cementitious materials involves the formation and the expansive properties of ettringite. However, another kind of sulfate attack, concerning cements and concretes containing limestone and attributed to the formation of thaumasite ($CaSiO_3 \cdot CaCO_3 \cdot CaSO_4 \cdot 15H_2O$), has been widely discussed during the last years. Thaumasite form of sulphate attack (TSA) requires a source of calcium silicate, sulfate and carbonate ions, excess humidity and low temperature. During the last 10 years, the TSA has been found in field structures and buildings in many countries worldwide.

In the present paper the effect of mineral admixtures on the durability of limestone cement paste under sulfate attack at low temperatures (5°C) is studied. Natural Pozzolana (P), fly ash (F.A.), ground granulated blastfurnace slag (GGBS), metakaolin (M) and a limestone cement (PLC) containing 15% w/w limestone were used. Cement paste specimens were prepared by replacing a varying part of the limestone cement with the above minerals. The specimens were immersed in a 1.8% $MgSO_4$ solution and cured at 5°C. Visual inspection, mass measurements and ultrasonic pulse velocity measurements were carried out at regular intervals for one year. It is confirmed that Portland limestone cements are susceptible to the TSA at low temperatures (fig. 1). The use of fly ash and metakaolin improves the resistance of limestone cements against sulfate attack at low temperatures (fig. 1).

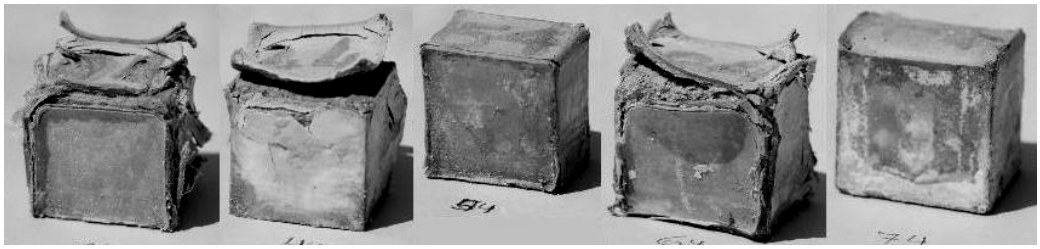


Fig. 1 Specimens cured for 8 months in a 1.8% $MgSO_4$ solution at 5°C

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Chloride Diffusion into Portland Limestone Cement Concrete

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The use of Portland limestone cements seems to have many benefits, both technical and economical [1,2]. The new European Standard EN 197-1 identifies 4 types of Portland limestone cement containing 6-20% limestone (II/A-L, II/A-LL) and 21-35% limestone (II/B-L, II/B-LL), respectively [3]. It is expected that the future world production of Portland limestone cement will be continuously increased. The wide use of limestone cement requires a thorough knowledge of the cement and concrete properties.

In this paper the diffusion of chloride ions through limestone cement concrete is studied. Portland limestone cements of different fineness and limestone content (0-35% w/w) have been produced by intergrinding clinker, gypsum and limestone (table 1). In order to have compatible results, the produced cements were designed to have the same level of strength. Six concrete mixtures were prepared (table 1) and the Nordtest Method [4] was applied for the determination of the chloride penetration parameters. The diffusion equation of Fick's second low was used for the determination of the diffusion coefficient D (table 1). It is concluded that Portland limestone cement concrete indicates competitive behavior with the Portland cement concrete. Furthermore, a limestone addition up to 15% has a positive effect on the resistance against chloride penetration of the concrete.

Table 1: Materials and results

Code	L (%)	Specific surface (cm^2/g)	Concrete composition			28 d. concrete compr. strength (MPa)	Diffusion coefficient D (m^2/s) x 10^{-11}
			W/C	Cement (kg/m^3)	Aggregates (kg/m^3)		
1	0	2600	0.70	270	1940	31.85	10.6
2	10	3400	0.70	270	1935	27.40	8.7
3	15	3660	0.70	270	1935	27.30	7.6
4	20	4700	0.70	270	1930	28.00	12.0
5	25	3800	0.62	320	1904	26.50	16.0
6	35	5300	0.62	320	1900	26.55	6.9

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Quantitative Microstructure Analysis on the Example of $AlCu_5Mg_3$ and $AlCu_5Mg_5$ Alloys

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In this paper, by using automatic device QUANTIMET 500 MC, for the quantitative picture analysis and applying linear method of measurement through the example of $AlCu_5Mg_3$ and $AlCu_5Mg_5$ alloys, we have determined grain size (min, max and medium values), as well as relative standard measuring errors (RSE), dendrite arm spacing (DAS) and length eutectic (Le) and also distribution by size (histogram) and volume participation of α-hard solution and eutectic.

We have also studied the influence of grain-refining additives $AlTi_5B1$ for the same chemical composition of the aluminium-copper-magnesium alloy. It has been concluded that with the increase of titanium content, the mean value of grain size decreases. Titanium is added as grain refiner and it is very effective in reducing the grain size. If this results in a better dispersion of insoluble constituents, porosity and nonmetallic inclusions, a significant improvement in mechanical properties results. Grain size controls the distribution[1] of porosity and constituents, and for this reason the properties of the high-copper alloys are very sensitive to grain size.

In alloys containing high magnesium the average values of the DAS and grain size were found to decrease and we obtain a fine, uniform grain structure. Grain size and structure of dendrite and eutecticum depend on processing parameters[2], first of all on melt temperature and the solidification rate. Also, in alloys containing high magnesium the average values of the eutectic cell length and volume fractions of the eutectic were found to increase. Magnesium increases[3] the strength and hardness of the alloys, especially in castings, a decrease ductility and impact resistance.

Testing of properties of these materials included also measuring of hardness and determination of pressure strength. Hardness was measured by the Brinell method. Pressure strength of the samples was tested on an electronic cutter of 10 t. The changes in chemical composition of the alloy causes changes in the structure and these are reflected in the Brinell hardness and the compression strength. The hardness of the modified alloy is higher than the hardness of the alloy without any modification treatment. By increasing the content of magnesium the hardness and compression strength also increase.

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Synthesis of Calcium Aluminates through the Polymeric Precursor Route

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Calcium aluminates are of the main constituents of cement materials and have been widely used in the steel industry. Recently, they have been used in advanced applications in optical and structural ceramics. The Pechini technique is a polymeric precursor route for the synthesis of polycrystalline ceramics, which is based on the ability of certain alpha-hydroxycarboxyl acids, such as citric acid, to form polybasic acid chelates with certain metallic ions. The citric solution, when heated with a polyhydroxilic alcohol, undergoes a polyesterification reaction. The combustion of the resulting polymer produces oxides of high purity at much lower temperature than the conventional solid synthesis.

In the present work, the polymeric precursor route was applied for the synthesis of pure calcium aluminate compounds, such as $CaO{\cdot}Al_2O_3$ (CA) and $3CaO{\cdot}Al_2O_3$ (C_3A). The polyesterification reaction was monitored through continuous conductivity measurements, while XRD and FTIR experiments were used to identify the intermediate and final products during sintering. Determination of uncombined CaO, after thermal treatment at various temperatures, was used in order to evaluate the reactivity of the precursor powders. Finally, CA and C_3A were also prepared through solid state synthesis. As it is concluded, the Pechini technique can be successfully applied for the preparation of high purity CA and C_3A (Fig. 1,2 II). The formation of C_3A and CA requires a three-hour sintering at 1000°C and 900°C, respectively. The main intermediate product, in the case of C_3A, is $5CaO{\cdot}3Al_2O_3$, while in CA there are not any other crystalline intermediate products. Secondary phases were identified in samples prepared by solid state synthesis, even after sintering at 1400°C for 15 hours and at 1350°C for 20h, for CA and C_3A respectively (Fig. 1,2 III).

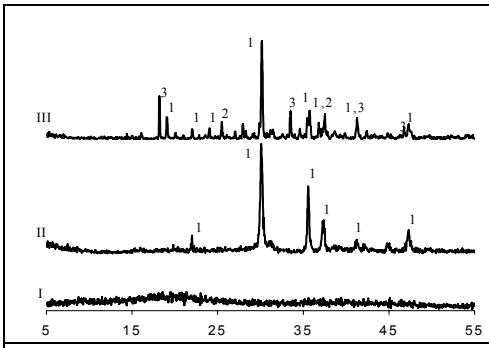


Figure 1: XRD patterns of $CaO{\cdot}Al_2O_3$ dried gel (I), sintered at 900°C for 3h (II), and solid state synthesis (15h at 1400°C) (III). 1:$CaO{\cdot}Al_2O_3$, 2: $CaO{\cdot}2Al_2O_3$, 3: $12CaO{\cdot}7Al_2O_3$

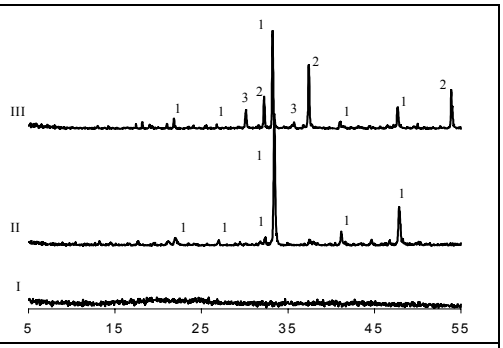


Figure 2: XRD patterns of $3CaO{\cdot}Al_2O_3$ dried gel (I), sintered at 1000°C for 3h (II), and solid state synthesis (20h at 1350°C) (III). 1: $3CaO{\cdot}Al_2O_3$, 2: CaO, 3: $CaO{\cdot}Al_2O_3$

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Microstructural Evolution of Ni_3Al Precipitates under Applied Uniaxial Tensile Stress

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Aircraft turbine engines need materials with strength at high temperatures. The present day materials for this application are Ni-based superalloys which have evolved trough small incremental changes. These alloy are composed of Ni_3Al (γ') intermetallic precipitates in a Ni-Al (γ) matrix with admixtures of 10-12 other elements dissolved in one or both of the major phases. The precipitates impart strength to the alloy by impeding dislocation movements. The objective of the present work is to evaluate the kinetics of coarsening and the morphological evolution of the precipitates under an externally applied tensile stress. In previous work[1], it has been demonstrated that a compressive stress tends to slow down the growth rate of the precipitates, and a model, based on diffusion in the fcc lattice when the unit cell is slightly tetragonally distorted, was developed[2]. It predicts how the coefficient of diffusion changes under an applied stress and accounts semi-quantitatively for the experimentally observed retardation of coarsening kinetics under compressive stress. One of the implications of the model is that the application of a tensile stress should produce an enhancement of the coefficient of diffusion and a corresponding acceleration of the coarsening kinetics.

The experiments were performed on a Ni-Al (13.4 at. % Al) single crystal oriented precisely by means of X-ray diffraction with Laue back reflection method. Cylindrical and conical specimens were threaded at both ends, solution treated at 1200 °C for 2 hours, quenched in refrigerated brine and then aged in a protective argon atmosphere at 640 ± 2 °C with the axis of the applied tensile stress parallel to [100]. The variables were stress and aging time. The microstructures of all the specimens were evaluated using transmission electron microscopy (TEM). Thin foils were prepared by slicing the samples in a direction perpendicular to the axis of the applied stress then dimpled and thinned electrochemically. Dark-field images of the precipitates were taken using a {100} superlattice reflection from the ordered γ' phase. The radius of an individual particle was calculated from the formula $r = r_{min}(A + 1)/2$, where r_{min} is the radius of the smallest circle inscribed in the image of the particle and A is the aspect ratio of the particle.

The research is currently in progress, but we have obtained enough data to show that for tensile stresses up to about 45 MPa there is an increase in the kinetics of coarsening. The decrease at larger stresses is not understood, and we are running experiments at 37.5 and 52.5 MPa to clarify the behavior in the region of 45 MPa.

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Ab initio Total Energy Calculations of Copper Nitride: The Effect of Lattice Parameters and Cu Content in the Electronic Properties

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We have studied the structural and electronic properties of bulk copper nitride by performing first principles total energy calculations using the full-potential linearized augmented plane wave (FP-LAPW) method. In our study we have considered two types of cells: the ideal cubic anti-ReO_3 structure corresponding to Cu_3N (Fig. 1), and a unit cell with an extra Cu atom at the center of the cube. In the first case, our calculated lattice parameter a = 3.82 Å is in excellent agreement with the experimental value a = 3.807 Å. The structure is semiconductor with a small indirect band-gap. The increasing of the lattice parameter results in larger band-gaps. An addition of an extra Cu atom at the center of the cell results in a slightly larger lattice parameter a = 3.88 Å, and the structure becomes fully metallic. Our calculated value is similar to the experimental lattice parameter corresponding to a metallic copper nitride film.

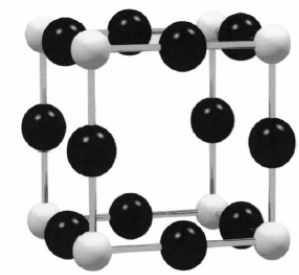


Fig. 1. Unit cell of Cu_3N. Black and gray circles represent copper and nitrogen atoms, respectively.

Acknowledgements:
We acknowledge support from CONACyT, Projects #33587-E, #I39171-E and DGAPA-UNAM Projects #IN111600, #IN104803. This work was supported by the Supercomputer CenterDGSCA-UNAM. We thank Dr. W. DelaCruz for suggesting this problem to us, Carlos Gonzalez and Juan Peralta for technical support.

Influence of Chemical Composition on Relative Degree of Recovery in Heat-Resistant Al Alloys

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Results of the influence of zirconium and lanthanides on structure and properties of aluminum alloys used at elevated working temperatures are presented in this work. The relative degree of recovery was determined by monitoring the change in the micro-hardness with time and temperature, as well as different zirconium and lanthanides contents. It was used for evaluation of creep-resistance of the alloys. On the basis of the relative degree of recovery it is possible to predict the optimal chemical composition of alloy that provides good mechanical properties when operating at elevated temperatures.

Experimental

Six aluminum alloys were prepared by melting RR 58 (AA 2618) alloy, Al-Zr5 master alloy and misch metal (50 % Ce and 50 % other elements) in a resistance-heated furnace with the graphite crucible. The RR 58 alloy was produced by standard melting procedure. Pre-alloy AlZr5 was added to melts in order to achieve the certain zirconium content.The cast specimens with thickness of 9-10 mm were subjected to the homogenizing heat treatment for 22 hours at the temperature of 510-515 ^{o}C and cooled together with the furnace. The homogenized specimens were hot forged and then cold rolled resulting in a final thickness of 0.5-0.6 mm. The recovery process was performed on the all alloys at five selected temperatures, in the range 150 to 350 ^{o}C, and for nine different time periods (1-320 min).

During the recovery process, the annihilation of vacancies is a dominant process at low temperatures, but the movement of dislocations without activation of climb process is operative at moderate temperatures. At the higher temperatures the dislocation climb is a dominant process. So, it could be supposed that lanthanides obstructed the dislocation climb more efficient than zirconium. Therefore, the alloys containing lanthanides have higher values for the relative degree of recovery i.e. higher recovery resistance at high temperature compared to alloys with zirconium.

Conclusions

- Zirconium increases the relative degree of recovery of produced alloys.
- Lanthanides increase also the relative degree of recovery according to their contents in the alloy.
- At low temperatures (150 – 250 ^{o}C), zirconium exhibited stronger effects on the recovery process than lanthanides.
- At higher temperatures (300 – 350 ^{o}C) the alloys containing the lanthanides possess greater relative degree of recovery. Hence, these alloys are exhibited greater recovery resistance at higher temperatures than alloys with zirconium.
- The heat-resistant aluminum alloys RR58 additionally alloyed with zirconium and lanthanides would have good mechanical properties.

Analysis of Low-Alloy Steel Decarburization During Heating Prior to Hot Rolling

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Process of steel heating, prior to rolling, is carried out in different flame furnaces in oxidative atmosphere, i.e. under conditions of fuel combustion. During heating, besides heat transfer, other different processes take place, such as reactions between metal and the oxidising furnace atmosphere. In that case, at high temeprature, an oxide layer is formed on the surface of steel billet. This process can be followed by decarburization of surface under the oxide layer, as a result of carbon oxidation. The depth of a decarburized layer usually exeedes the values which are determined by actual technical demands. The sensitivity to surface decarburization is especially characteristic for low-alloy bearing steel. The phenomenon of steel decarburization in context of heating conditions was presented in this work. In addition, heating conditions effect of different protective coatings, regarding minimization of the decarburization rate, were analyzed. Investigation were carried out in a walking beam furnace, fired by heavy fuel oil, with air excess value of 14 %, during heating of low-alloy chromium steel billets with a high carbon content.

Methods

The investigations presented in this paper are based on experimental (temperature measurement and metalographic method) methods. The first part of the experimental work was carried out in order to analyze the influence of different protective coatings application on the decarburization rate. The second part was done to define optimal heating conditions regarding a minimum of decarburization.

Results and Conclusions

By using three types of protective coatings during steel heating, the depth of a decarburized layer was decreased, and no layer with the total decarburization was found at the treated speciments. The depth of that layer over the billet edge is more uniform than in case of heating without coating, but the efficiancy of coating application depends on its type.

The results obtained by metalographic method, as a referent way for identification of decarburized layer, show that it is possible to eliminate decarburization. For that it is necessary to optimize billet heating process and use a water glass as a protective coating. An optimized heating process consists in the following: heating temperature less than 1100 ^{o}C, heating time at the temperature above 700 ^{o}C less than 30 minutes, equalized heat flow along the furnace width, heating in oxidative atmosphere.

Decarburized layers are characterized by reduced and nonuniform hardness. An additional control of decarburization in a surface layer of a rolled billet, by using chemical method of microhardness measuring, shows a certain decreasing of carbon content in surface layer during steel heating (8 mm diameter profile). It means that it is not posssible to speak about an absolute elimination of decarburization in real industrial conditions. It is possible to speak only about a reliable hot rolled profile production with carbon content in the surface layer which is higher than the minimum allowed (eutectoid) content on the maximum of decarburization depth.

MSEN P-43 mtl

Characterization of Ternaty Alloys in Ag–In–Sn System

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Introduction

Lead – free soldering became very popular in the whole world, because of high ecological demands in industry. Most of alternative alloys have high content of tin, and some of them are already used in electronic industry. One of them is Ag-Sn. In order to decrease melting point of alloy, addition of indium is used and it is expected that Ag-In-Sn alloy will be suitable for replace Sn-Pb standard solder alloy.

Experimental and results

Ag –In, In-Sn and Ag-Sn binary systems have been determined by many researchers, but the ternary system from these elements is still unknown. From that reasons, the results of characterization of Ag-In-Sn alloys are presented in this paper. The investigated samples are chosen from two sections A and B, with molar ratio of In : Sn (1:4; 1:2). DTA, XRD analysis and optic microscopy were used as methods for characterization of Ag-In-Sn ternary alloys.

Table 1. Characteristic temperatures on DTA curves for investigated Ag-In-Sn alloys

SECTION	X_{Ag}	TEMPERATURE ON DTA CURVE, °C						
		THE FIRST PEAK			THE SECOND PEAK			The end of phase transformation
		Start	maximum	End	Start	maximum	End	
In:Sn=1:4	0,1				185	219	270	384
	0,2				190	229	282	410
	0,3				190	220	261	427
	0,4				190	215	259	465
	0,5				191	215	264	514
In:Sn=1:2	0,1	155	168	184	184	213	261	383
	0,2				184	219	282	408
	0,3				190	224	266	386
	0,4				196	219	265	378
	0,5				200	221	264	422

The microstructures of each alloy were determined by optic microscopy and XRD analysis. It is an eutectic structure with Sn matrix and Ag_3Sn intermetalic compound in it (dark phase), and the light phase (Ag with In). With the increasement of In content in alloy, the dark phase contains In-Sn compounds, and that is confirmed by the first peak on the DTA curve (alloy B1).

Conclusion

The In content in alloy have crucial influence on the beginning and the end of phase transformation. Appearance of the first peak in alloys with %In > 29% indicates In-Sn low temperature area which is not suitable for solders in electronic industry. Because of that, the most appropriate alloys which might be an alternative for the common Pb-Sn solders are Ag-In-Sn alloys with high percent of tin, small percent of silver and with less than 29% of indium.

Biocompatible Metallic materials for Osteosynthesis Made by ICEM-SA, Romania

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Biomedical materials are a section of materials science what deals with the design, synthesis and use of materials for surgical implants in the human body in order to re-establish the function and/or the structure of degraded human structures. The large range of applications of metallic materials may be due to the multiple combinations of chemical, physical and mechanical properties making them compatible with the biological environment.

The orthopaedic implant is a mechanical device which replaces or supports parts of the human skeleton structure, being exposed to a variety of biological and mechanical stress. The implant must perform requirements without causing any adverse effects on the human body.

The paper presents the applied research developed by ICEM - SA for the manufacturing and validation of bars and wires from austenitic stainless steel for the production of accessories for osteosynthesis medical kits and of temporary orthopaedic implants.

The quality requirements for this austenitic stainless steel are:

- fine grain structure;
- reduced content of non-metallic inclusions and solid phase (i.e. carbide of chrome and molybdenum);
- absence of delta ferrite;
- absence of segregation of alloying elements;
- surface quality of semi-finished products with influence on mechanical properties and corrosion resistance;
- high tensile strehgth (over 800 N/mm^2).

All metallic materials was tested for evaluation of biocompatibility , tests necessary for using this products as implants in human body.

Researches Concerning the Manufacturing of Spectral Standard Samples Made of Steel and Special Alloys

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In the past decades, the iron and steel development, in production and research clamed development of new, quick and precise analyses procedures, used in steelmaking and final characterization processes of final product.
Spectral standard samples can be reference materials (RM), certified reference material (CRM) or setting-up samples.
In the last ten years, in ICEM-SA has been a permanent preoccupation in research and achievement of spectral standard samples for medium alloy steels, tool steels and Ni alloys, materialized in certified reference materials witch represents the object of contract with MBH – Great Britain, active since 1996. In order to extent the steel classes to be introduced in this catalog; it has been created a research and experimental program at laboratory and semi-industrial scale.
The laboratory experiments made at ICEM SA, which establish the future semi-industrial experiments, lead to new technological models of obtaining and control of binary samples like FeXi, CoXi (Xi = C, Mn, Si, Cr, Ni, Mo etc.) and representative standard samples for medium alloy steels with residuary elements, stainless steels (especially for the austenitic stainless steels used for medical application) and cobalt alloy like CoCrMo.
Spectral standard samples (RM and CRM) has to achieve some requirements in order to be utilized in the analytic processes of chemical characterization of materials, . i.e:

- to be representative for analysed materials;
- chemical and structural (micro- and macrostructure)homogeneity;

Spectral analysis of the ferrous and non ferrous alloys is based on the dependence of the intensity of spectral line by the concentration of the analysed element, i.e. **I = f(C).**
Over the analysed element is being exerted the influence of other elements in this way leading the spectrometrical determination to be dependent of the following factors:

- the presence of the nonmetallic inclusions;
- formation of some compounds with hydrogen;
- changing the vaporization temperature;
- changing the thermal conductivity;
- the influence of alloying elements over the alteration of the spectral nature.

Spectral standard binary samples are made from binary alloys in which the alloy element change in concentrations range as close as possible to the values in witch the mentioned element is present in different ferrous and non-ferrous alloys.
Representative standard samples have in their chemical composition definite chemical elements, in concentration range approximate with those in current production.
Through achievement of certificated spectral standard samples is intended to create an national system of spectral standard samples with metrological performances at the European level imposed by European and international standards.
The research and practical accomplishment of binary and representative spectral standard samples in ICEM SA lead to the establishment of concentration range and technological models for industrial manufacturing of spectral standard samples from medium alloy steels, austenitic stainless steels and cobalt alloys.

Comparison Between Strustures, Mechanical Characteristics and Corrosion Resistance of Ni-Based Alloys Obtained through Different Methods

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The specific technological feature of Ni-based alloys which have the nickel contents about 60% and chromium about 10% alloyed with refractory elements, improved researches and development of some specifically powder metallurgy technologies.
The technological flows which were established by classic metallurgy technologies or by powder metallurgy allowed achievement of NiCrFeTiAl alloys which have a homogeneous structure with a great dispersion of the hardness precipitations like nitride γ' type $Ni_3(Ti,Al)$ and carbides type Cr_{23} C_6, high mechanical characteristics at temperature and good corrosion resistance .
Because the technologic specific properties obtained of alloys Ni-based through classic technologies (**CT**) require many mechanical processing and remeltings that have as a result great materials and power consumptions and the yield is of approximate 60%.The powder metallurgy technologies (**PM**) permitted to obtain the products with different geometry and alloyed with many elements which have different physicals-chemicals properties and the yield is of 92%. The mechanical properties of bars from alloys which are obtained through **CT** and **PM** are presented in Table 1 **.The difference among values between alloys can be explain by the residual porosity which is present in products obtained by PM, although the values of density 8,22 g/cm^3 is near of theoretical density 8,47 g/cm^3.**
The rate of corrosion **K < 0,1 g/m^{2}h** for NiCrFeTiAl alloy obtained by **CT** indicated a maximum corrosion resistance at general corrosion in comparison with NiCrFeTiAl alloy obtained by **PM** which have the rate of corrosion **0,1< K<1 g/m^{2}h** indicated a medium corrosion resistance at general corrosion .

Table 1

TECHNOLOGIY USED	TEMPERATURE ° C	MECHANICAL CHARACTERISTICS			
		R_m, N/mm ^{2}	$R_{p0,2}$, N/mm ^{2}	A_5, %	HV
CT	20	680	460	48	310
	550	528	308	50	-
PM	20	589	225	40	289
	550	470	198	44	-

The distribution phases like carbides type Cr_{23} C_6 and nitride γ' type $Ni_3(Ti,Al)$, into the matrix (solid solution austenitic γ on the Ni-based) is the same for both alloys**, with a little exceptions when the distribution of carbides into alloy obtained by PM are deposited on the grain boundary, which explain a great rate of corrosion** .
The fracture aspects at 20°C and at 550°C are different, respectively for the alloy which was obtain by CT is a ductility fracture aspect at both temperatures ; the alloy which was obtain by PM at 20°C is a ductility fracture aspect and at 550°C is a mixed fracture, respectively intergranular fracture aspect and transgranular fracture aspect.
This difference between the fracture aspects can be explain through **the residual porosity which is present in products and by the distribution of carbides which are deposited on the grain boundary, obtained by PM .**

Pipe Formation in Ingot Casting

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The influence of various parameters on the pipe formation in ingot casting is studied. A numerical simulation of the shrinkage during steel ingot solidification is developed and compared with experimental results. The main factor influencing the yield in ingot casting is the shrinkage pipe formation. During solidification and cooling most metals decrease in volume and pores are consequently formed. The liquid in the hot –top will serve as a reservoir for compensating the pore formation in the ingot. As is well known, most alloys solidify over a certain temperature interval. The total volume change can be estimated using a material balance equation:

$$\frac{dV}{dt} = \frac{dV_s}{dt}\beta + \frac{dV_c^s}{dt} + \frac{dV_c^l}{dt}$$

The first term on the right hand side describes the volume change caused by solidification shrinkage, the second term the volume change caused by thermal contraction in the solidified shell and the third by thermal contraction of the liquid, when the superheat disappears. Using a two-dimensional numerical model the temperature changes was determined. The obtained temperature curves, for a total shrinkage calculation, are used. For a experimental investigations, the alloy steels with different carbon content, (steel 1: 0.12 %C, steel 2: 0.16%C, steel 3: 0.41%C and steel 4: 0.73%C) are used. The measured data agree well with the numerically determined results. In Fig.1, the experimentally and theoretically determined shrinkage values are presented as a function of carbon content.
The shrinkage at 0.12 and 0.16% C is higher than in steel 3 and 4, because δ/γ transformation. With increasing carbon content, the shrinkage decrease.

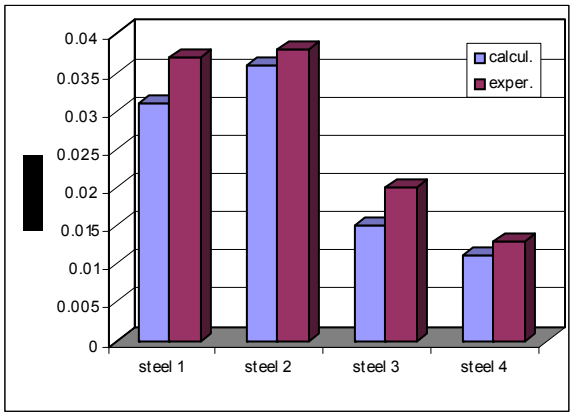


Fig.1 Comparison between measured and calculated shrinkage values

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Thermal Treatment Influence on Al-Alloy Behavior in NaCl Solutions

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Aluminum alloys perform different corrosion stability. The aim of this paper is to predict alloy content by making a combination of alloying elements (Mg and others) to obtain corrosive stable alloys in chloride solutions.
Thermal regime was performed as follows: heating to 520 ± 5^0C by 6 hours, quenching in hot water and subsequent aging on 205^0C by 7 hours followed by air cooling.
Experimental part includes: chemical examination as well as examination of mechanical properties of thermal treated alloys. Some of the alloys (5 and 8) were chosen for the examination of corrosion resistance in NaCl solutions (0,51M, 0,051M and 0,0051M). Micro structural analysis includes thermal treated alloys. Some of the alloying elements (Mg, Zn, and Cu) were used as pure ones and others (Mn and Ti) in the prealloy form.
Experimental part was performed in the Laboratory of Faculty of Metallurgy and Technology Podgorica. Diagrams of corrosion stability are obtained:

- corrosion potential versus time, $e_{corr}=f(\tau)$
- polarization resistance method, Rp
- potentiodynamic method

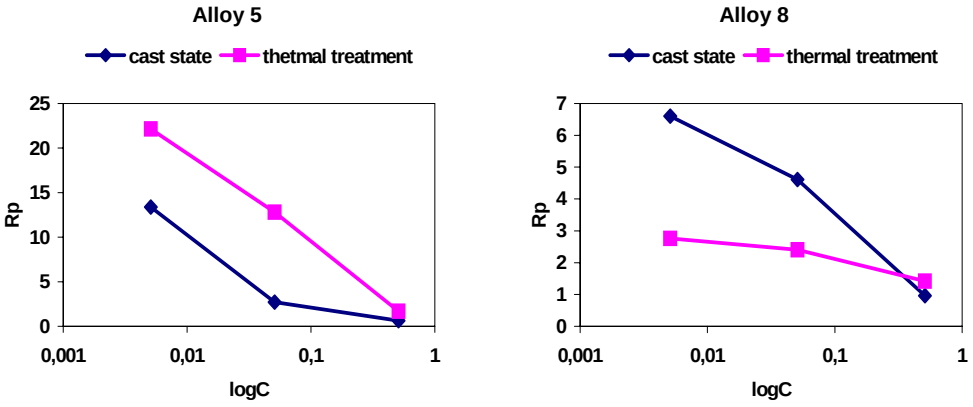


Fig 1.Comparative values of polarization resistance Al alloys 5 and 8 in solutions of NaCl

Values of Rp are lower in thermal treatment state for alloy 5 in every solution of NaCl. Alloy 8 show lower values of Rp in thermally treated state in solutions of 0,0051M and 0,051M NaCl.

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MSEN P-49 mtl

Separation of Palladium from Rhodium

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During elaboration of a technological procedure of palladium separation from rhodium – The semi-plant for noble metals processing, DP Azotara Pančevo – appeared materials of final palladium with ingredients of rhodium which content ranged at first within approximately 10% by weight, reducing later on to approximately 3% by weight. First separations of palladium by dimethylglyoksim during the analysis of those materials were followed by lagging of a precipitate into filtrate. It was clear that the problem of in-quantitative precipitation arose due to exceeding of the highest concentration of palladium in solution. From the other side during the analysis of other materials containing noble metals such as platinum, palladium and rhodium, during the phase of palladium separation by dimethylglyoksim, the green colored precipitate was obtained, what pointed out to the appearance of co-precipitated platinum.

In order to solve these problems following data had to be obtained:

1. Maximum concentration of palladium during precipitation
2. Precipitation conditions which prevent co-precipitation of platinum.

By the review of literature it was found out that such data was recorded by G.H. Ayers and E.W. Berg studying precipitation of palladium in the presence of platinum, rhodium and iridium. Within their work following precipitation procedure is recorded: Solutions containing the several platinum metal chlorides, in different proportions, were made approximately 3% by volume in concentrated hydrochloric acid; the palladium concentration was taken so as not to exceed 0,1 gram of palladium per 250 ml. of solution. Each series of tests containing a given amount of palladium was run quadruplicate. A calculated 10% excess of 1% dimethylglyoksim in 95% ethyl alcohol was added at room temperature, the mixture was stirred well and allowed to stand for exactly 1 hour. The precipitate was collected on a medium-porosity sintered glass filter by suction, and washed four times with cold 3% hydrochloric acid.

In order to check the mentioned procedure from a point of view of establishing maximum concentration of palladium in solution during precipitation by dimethylglyoksim in our laboratory following modular systems was tested:

1. Palladium in a form of solid phase – mono-component system with 0.1g of palladium in 250 ml of solution.
2. Mixture of palladium and rhodium in a form of solid phase of a content similar to the content of material sample of final palladium: 0.1 g of palladium and 0.01 g of rhodium in 250 ml of solution.

The tests shown that by application of the mentioned conditions on these systems a quantitative palladium precipitation is obtained in the mono-component as well as in two-component system. Palladium quantitative precipitation for the mono-component system is 99.88% and for two-component system is 100.42%. In two-component system a larger weight is a consequence of contamination with ions of Na^+ and SO_4^{2-} originated from sodium pirosulphates, and because of that washing with hot water is to be introduced.

From the other side, by application of this precipitation procedure on a real system – samples of material with noble metals (platinum, palladium and rhodium) the problem of platinum co-precipitation was solved by correction of precipitation temperature from water bath temperature to a room temperature. In a such way pure yellow palladium dimethylglyoximate is obtained without contamination with platinum.

Mechanical Behavior and Corrosion Properties of Some AA6xxx Aluminum Alloys in T5 Temper

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Paper describes the mechanical behavior and corrosion properties of three heat treatable extruded Al-Mg-Si aluminum alloys. The alloys were tested in final T5 temper (air-quenched directly on the press and artificially aged) after processing by extrusion of semi-continuous cast and homogenized billets. The Al-Mg-Si materials have a broad application range in transportation, architecture and engineering due to its favorable combination of strength, plasticity, toughness, weldability and corrosion properties. The behavior of extruded profiles was also compared to aluminum of commercial purity in terms of its corrosion properties in sea and natural water.

Results

The AlMgSi1 is the typical 6082 alloy and other two are AlMgSi0.7 containing a small excess of silicon in relation to the magnesium. The chemical composition of AlMgSi0.7Zr alloy was planned to provide higher strength in as T5 tempered condition (quenching in blown air and artificial aging).

Hence, the effects of small addition zirconium and manganese on mechanical properties and corrosion behavior in fresh water and 0.51 mol Na-chloride solution were investigated. The AlMgSi0.7(Zr) alloy is the most sensitive to the billet temperature since the achieved values of tensile strength increase reaches 310 MPa. The other two alloys are less sensitive to quenching temperature and show similar levels of strength. The AlMgSi1 alloy shows the lowest strength after T5 tempering due to small quenching effects connected with the relatively slow cooling rates for air quenching compared to the water quenching which is recommended for the combination of main alloying elements. This explains also the highest level of total elongation for AlMgSi1 profiles.

The addition of Zr to the base AlMgSi0.7 alloy increases the corrosion rate in both corrosion mediums. The difference between Al-Mg-Si alloys and CP aluminum is significant in natural water, but in chloride solution the corrosion rates are similar. CP aluminum shows also significantly higher polarization resistance in natural water but CP Al and Al-Mg-Si alloys show similar R_{pol} values in chloride solution.

Conclusion

The addition of Zr and Mn significantly increases the strength, reaching 310 MPa of tensile strength. The corrosion behavior of investigated Al-Mg-Si alloys in fresh water and 0.51 mol NaCl solution is satisfactory even though the increasing of alloying elements content caused a small deterioration. The AlMgSi0.7(Zr) alloy has the most favorable combination of strength, ductility and corrosion properties. The alloys AlMgSi0.7 and AlMgSi0.7(Zr) offer the wide range of combinations of good mechanical and corrosion properties suitable for a wide range of profile application.

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Influence of Tartaric Acid on the Crystallization of $Al(OH)_3$

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Crystallization of $Al(OH)_3$ from caustic soda solution is the most important part of Bayer process for alumina production. Several phenomena occur during this process and there are, nucleation, aglomeration and growth of $Al(OH)_3$ crystal growth, and all of them influence on the physico- chemical characteristics of precipitated $Al(OH)_3$. There are a lot parametres that have influence on the mentioned phnomena and there are temeperature, caustic soda concentration, caustic ratio, seed ratio as well as the presence of impurities. In the caustic soda solution exist mostly inorganic impurities, but there is the certain concentration of organic impurities.

In this paper we have investigated the influene of tartaric acid on the phenomena that occur during the crystallization of $Al(OH)_3$ caustic soda solution and on the physco-chemical charcteristics of precipitated $Al(OH)_3$ at the different temperature and caustic soda concentration.

Obtained results have shown that in the presence of tartaric acid the change of nucleation, agglomeration and crystal growth of $Al(OH)_3$ particles have the same character as in the case of crystallization from pure solution, but the tartaric acid show inhibitory influence on the mentioned phenomena. In accordinance to the change of this processes, the total soda content in the precipitated $Al(OH)_3$ is changed.

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Obtaining Selenium from Anode Slime in Controlled Gas Atmosphere

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Recent years, in many companies for anode slime treatment there is a trend of use the new roasting method (deselenization) from copper anode slime, in the controlled gas atmosphere, instead of the existing sulphuric acid roasting method. The main advantages of the new deselenization method are as follow: sulphuric acid elimination, improved operation conditions, shorter process time and high deselenizaton degree (over 99%).

The aim of this work was to consider a possibility of complete selenium removal from anode slime by the use of new deselenization method, and obtaining selenium powder of commercial quality.

Decopperized anode slime from the Anode Slime Treatment Plant in Bor was used for all laboratory experiments.

Characteristics of THE new investigated deselenization method (based on laboratory analyses) are AS follow:

- Roasting is carried out with introduction of SO_2 and O_2 gases
- Optimum ratio of gases flow: $SO_2 : O_2 = 1 : 10$
- Roasting temperature: max 600^OC
- Gases flow at furnace outlet is controlled by gradual temperature increase during roasting process

The results of experimental investigations in laboratory scale defined the optimum parameters of analyzed deselenization method. Selenium dioxide gas is emitted during roasting process and absorbed into sulphuric acid solution, and reduced into elementary selenium in presence of liberated SO_2. The obtained selenium has a form of technical quality powder (min 99.5 % Se), used in metallurgy.

MSEN P-53 mtl

Efficiency Increase of the Existing Process for Selenium Recovery in RTB Bor

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Selenium is recovered from anode slime, obtained as secondary product in electrolytical copper refining. Low grade copper ores with increased content of selenium and tellurium are in exploitation in the world as well as in our country. The existing method for selenium recovery in RTB Bor consists of sulphating roasting. The equipment was designed for maximum selenium content of 30% in decopperized anode slime. Averaged selenium content is 50 – 60% for the last five years what has an important influence on decreased recovery of selenium and environment endangerous.

For the aim of efficiency increase the deselenization process of anode slime with increased selenium content, an analysis of the existing deselenization process was carried out and technological solution was proposed for improvement.

Qualitative and quantitative estimation of the content of gases made.

Table 1. Characteristics and content of gases from deselenization process gasova iz procesa deselenizacije

Components of gases	Measuring point			
	Outlet from local ventilation system		Outlet from settling tank	
	min	max	min	max
a)selenium dioxide, mg/m^3	0	118000	/	/
b)sulphur dioxide, mg/m^3	1120	3542	580	5170
c)selenic acid, mg/m^3	/	/	0	48390
d)solid particles, mg/m^3	0.059	58	0	90
CHEMICAL CONTENT	SeO_2, H_2SeO_3, SO_2, Se, CO_2			

Analysis of sulphur dioxide and selenium oxide content was carried out during process as well as content of selenium ions in absorbing solution.

By analyzing sulphur dioxide content, it was found out that the quantity of sulphur dioxide at the end of deselenization process is not enough for total selenium reduction. By correction of concentrated H_2SO_4 : anode slime ration, an optimum content of sulphur dioxide in absorbing liquid was found out what has caused total selenium reduction both with higher recovery of selenium.

An addiotional system for gas absorbtion was proposed that would include venturi scruber and absorbing column, designed for fullfilment the existing ecological criteria regarding to MDK for present pollutants in deselenization process.

Mechanical Properties of CuFe1 Wire *vs.* Range of Cold Deformation and Annealing Temperature

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Objectives

This paper considers production of CuFe1 wire regarding optimal mechanical properties required for electronic tubes manufacturing.

Applied Methods

Tests were performed by combination of range of deformation within two successive annealing treatments, changing of intermediate annealing temperature i.e. final annealing temperature. Cold deformation was performed by drawing and annealing in protective atmosphere. Mechanical properties were tested by destructive test instrument (R_m, $R_{p0,2}$, A_{200}).

Results and Discussion

Test results indicate that range of cold deformation above 90% tends to decrease parameters R_m, $R_{p0.2}$ and A_{200} at final annealing temperature increase from 650°C to 800°C. Also, mechanical properties of hard drawn wire continually decrease as annealing temperature increase i.e. from R_m=480 Mpa at $T_{annealing}$=320°C (duration of three hours) to R_m=270 Mpa at $T_{annealing}$=800°C (duration 30 s). On the other hand elongation A_{200}, as relevant mechanical property required for electronic tube manufacturing, differs from 2% for cold drawn wire up to 5% for annealed wire at 320°C (3 h). Further increasing annealing temperature to 650°C (duration 0.5 h) elongation A_{200} increases towards its maximum of 30% i.e. at annealing temperature of 800°C (duration 50 s) elongation slightly drops to 26%, having overall range of deformation of 90% between two successive annealing treatments. However when the overall range of deformation was less than 90% elongation figures were higher i.e. some 30% but R_m parameter was lower amounted 290 MPa. By final annealing treatment at 650°C, R_m showed some 310 MPa e.i. elongation was some 29% what could be accepted for specific purposes.

MSEN P-55 mtl

Oxinitriding and Oxidation of Nitrided Layer

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Oxinitriding and oxidation of nitrided layer belong to case carburising processes. In oxi-nitriding, the diffusion of ions of two elements (oxygen and nitrogen) is carried out simultaneously. The oxidation of nitrided layer is process which is carried step-by-step: treated part first is nitrided and that the oxidation of nitrided layer takes a place.

Either the terms oxinitriding and oxidation (i.e. postoxdation) of chemical treatment seem to be the same, there are some differences in the way they are provided, also in the obtained properties. Oxinitriding represents one diffusion process in which saturation of N_2 and O_2 have occurred. But, when it's talking about oxinitriding, it almost means on gas nitriding. Gas nitriding or oxinitriding is performed in cracked amonia or in mixtures of amonia cracked products with other gases (N_2, CH_4, O_2, etc.), but sometimes in pyrolitic triethanolamine.

Nitriding in fused salts (also called: salt bath) is performed during blowing the air or pure oxygen through the bath. So, for calculation for an optimum air flow rate there is avalilable a specialy derived formulae. Although in nitriding into the fused salts, when cyanides and cyanates are used, the main process is of course the diffusion of nitrogen, but the diffusion of C or O_2 are not neglected but rather less discused. The practical role of C and O_2 are in obtaining a combine effect on wear properties of such treated part. The presence of carbon in salt bath atmosphere is great, so that this process is realy a carbonitriding or nitrocarburizing process.

Oxinitriding of nitrided layer can be considering as a post-oxidation process.

The oxinitriding of steel in industrial practice is done both in gaseous or in fused salts (like bath cyaniding) media but not yet in pulsed plasma. Main reason for absence of oxygen in plasma state lies in fact that in plasma the oxygen is always an extremly active component, and overheating of working part easily will be achieved, even uncontroled. Further, when the oxygen is present in plasma frunace, the corrosion of chamber will be happened, even a destroying and damaging the chamber. From that point of view, the oxidation of previously nitrided layer has greater advantage.

Here are described some effects of using oxinitriding for common used steels and oxidation of previously nitrided steels.

Decopperization of Deselenized Anode Slime

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Anode slime treatment for the aim of precious metals recovery means copper removal in the first technological stage of trteatment. The existing technological line in RTB Bor consists of anode slime leaching with diluted sulphuric acid at presence of air. Due to heterougenous characteristics of processed copper ores, sulphide copper appears in anode slime, droppped back in decopperized anode slime in unchanged form by the use of existing technology.
In the following stage of anode slime treatment – deselenization process, copper concentration appears in deselenized anode slime. Increased copper content is unfavourable for pyrometallurgical or hydrometallurgical method of precious metals recovery.
The aim of this work is removal of copper from deselenized anode slime for precious metals recovery by the use of hydrometallurgical method. Chemical and physical characterization of starting raw material was carried out. Chemical content of deselenized anode slime is preseneted in Table 1.

Table1. Chemical content of deselenized anode slime

Element	Au	Ag	Pt	Pd	Se	Te	Fe	Zn	Si	Pb	**Cu**	S
Content, %	1.68	16.55	0.009	0.08	2.71	2.07	2.15	0.15	6.20	8.26	**21.11**	8.82

Investigationws of copper removal by leaching of deselenized anodeslime were carried out with the following reagents: diluted sulphuric acid, ammonium hydroxide, hydrochloric acid at presence of chlorine.
The best results were realized by leaching with hydrochloric acid apresence of chlorine. Kinetics of leaching process was carried out where optimum temperature of 95 ^{o}C and time of 2 h were established.
Over 99% of copper were leached at optimum process conditions.
Optimum conditions of selective copper leaching were realized by control of redox potential where silver was transformed into chloride form suitable for further hydrometallurgical treatment.

Continous Casting Process Development for Production of Low Cu Alloy with Mg for Trolley Wire

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Low alloyed copper with magnesium is used in production of contact conductor for drawn power cable. It replaces the low alloyed copper with cadmium where poisonous cadmium oxide is formed in production, so the additional investments are required for human and environment protection. Copper magnesium has better wear resistance than CuCd and does not pollute the environment. This material replaces more and more copper cadmium on the European fast railway lines.

Developed technology for continuous upward casting for production of oxygenless copper wire, developed in Copper Institute Bor, is used as a base for this technology development.

Conception of this new technological line consists of continuous casting upward the round profile of unlimited length and further cold deformation. Its importance is in elimination of pressing from production process, i.e. hot treatment, what reduces and makes cheaper the production process with a tendency of improvement the product quality.

Namely, classic technology for low alloyed copper production consists of: block casting, hot pressing and cold deformation. Regarding to energetic efficiency, the all modern requirements on human environment protection is satisfied by the use of this technology.

Table 1. Results of mechanical characteristics the cold drawn CuMg wire

Size Ø mm	Tensile strength Rm (MPa)	Elongation A_{200} %	HB N/mm^2	Reduction %
20	223,59	45,83	57,9	-
18,5	238,74	8,72		14,43
16,8	253,48	6,66	107	17,53
15,2	293,31	7,00	107	18,49
13,5	432,30	2,66	118	20,76
12,6	434,08	2,66	128	12,88
Trolley	454,86	5,35		

At total deformation degree of $\varepsilon = 75\%$ the obtained mechanical and electrical characteristics corresponds to the Standard for this content of Mg bronze. Namely, the obtained average tensile strength of 454.86 MPa and high electrical conductivity of 43 $m/\Omega mm^2$.

More uniform and small grain-size structure could be noticed in comparison with cast pure copper with equal section and increased strength and tensile strength at macrostructure of longitudinal, and cross-section, the cast CuMg wire Ø20 mm.

Bioleaching of Copper Smelter Slag

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The sulphyric acid and mesophilic leaching of a copper concentrate of smelter slag using microbial mixed culture (30 ^{0}C) were carried out in a laboratory unit using separation funnel of 0.5 l in volume, termostated in ... acid and mesophilic leaching with efficiacy of copper recovery were examined. The sample of copper smelter slag concentrate from RTB Bor, containing 4.2% Cu, 34.5% Fe(II), 30.9% SiO_2, has been used in this study.
The leaching tests have been carried out on ground slag samples 90 % less than 44 μm. The mineralogical study showed that this slag has a fayalite structure, where 60% is in the form of fayalyte, and 10% in the form of copper sulfides.
Experiments were performed under operation conditions such as: solids' concentration 4% (w/w), air flow 20 Nl/h (21% v/v O_2, and 0.03% v/v CO_2), and residence time of 10 days. In the case of bioleaching, existence of free bacteria in leach solution was detected using sample of bioleach medium as innoculum in 9K solution.

Sulphuric acid leaching test was carried out at pH 1 - 1.5, by adjusting the pH of the slurry with 10N sulphuric acid at the temperature of 30 ^{0}C. Table 1 shows the copper, iron and silica content at the end of the acid-lech test.

Table 1. Chemical composition of the acidleach solution sample

Constituent	Cu^{2+}	Σ Fe	Fe^{2+}	Fe^{3+}	Si
Content (g/l)	1.31	23.41	11.17	12.24	2.91

Due to its amorphous structure, smelter slag cannot efficiently be leached with sulphuric acid; the formation of silica gel induces an increase of leach liquor viscosity and difficult pulp filtration. The copper recovery of 82 % and copper leach rate of 5.5 mg/l/h. were attained durung the test work.

Mesophilic leaching test was carried out at pH 1.8-2.5, at the temperature of 30 ^{0}C. Table 2 shows the copper, iron and silica content at the end of the bioleaching test.

Table 2. Chemical composition of the bioleach solution sample

Constituent	Cu^{2+}	Σ Fe	Fe^{2+}	Fe^{3+}	Si
Content (g/l)	1.6	4.09	0.03	4.09	1.68

By the bioleaching test was performed simultaneous iron oxidation and removal. In this test work was produced leach solution containing copper with lower iron and silica gel. The copper recovery of 99 % and copper leach rate of 6.7 mg/l/h. were attained durung the test work..
Leaching with microbial mixed culture at 30 ^{0}C, can effectively be used to extract copper from amorphous copper smelter slag after grinding 90% < 44 μm. By using this method, both silica gel formation and iron coextraction can be avoided. Recovered solution could be further treated by solvent extraction and electrowinning or salt precipitation.

MSEN P-59 nma

Investigation of Interfacial Bonding in HMX/AP Model Propellant Composite

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Composite propellants are nonhomogenous propellants and comprise primarely crystalline oxidizer and metal fuels uniformly suspended in a resin binder. The strenght of the bonds between the polymer matrix and the oxidizer are determining the mechanical properties of the composite propellants. One way of improving mechanical properties of solid propellants is to add suitable bonding agents. For ammonium-perchlorate (AP) there are many effective bonding agents. But for nitramine fillers, for example cyclotetramethyltetramine (HMX) there are still few suitable bonding agents but thier effect in HMX/AP system was not reported.

In this work, a series of novel compounds which comprise the structural features of hydantoin and isocyanurate derivatives, developed by ourselves, have been used as bonding agents in HMX/AP system. The mechanical properties of model propellant composite containing these novel bonding agents were determined. Tensile test parameters used for characterization mechanical properties are: stress at maximum strain (σ_m), strain at maximum stress (ε_m) and strain at break (ε_b). The parameters selected for characterization of bonding effect are $\varepsilon_m/\varepsilon_b$, $\Delta \varepsilon_{mx}$ and $\Delta \sigma_{mx}$. The addition of the bonding agent increases ε_m value, decreses $\varepsilon_m/\varepsilon_b$, so that means that interfacial adhesion between AP and HTPB (hydroxy terminated polybutadiene) and HMX and HTPB, has been improved. Poor adhesion between AP and HTPB and HMX and HTPB in the propellant in the absence of bonding agent results in low values of stress and modulus.

Mechanical properties of investigated propellant shown that hydantion and isocyanurate bonding agents have a large effect on strain at maximum stress which is the critical property for composite propellant. Significant improvement in strain at maximum stress and decreasing values of stress show that hydantoin is specially useful for propellant uses at -40 ^oC. Content of 0.10 % hydantoin inreases stress and strain 32 % and 44 % respectively at 25 ^oC. This means that adhesion is better and dewetting is ocured at higher applied stress and polymer matrix is more extended. The consequence is higher elongation at maximum stress. The greater content of hydantoin (0.20 %) in propellant gives greater increment for stress, but smaller extension. This means that strain at break is not improved. It can be supposed that hydantoin can effects binder cross link density because of the presence of the same –OH groups as HTPB polymer. On the other hand, because of hydantoin is a highly polar organic molecule it can be probably bonded ionic to the AP crystal. It is shown that interaction between AP and polymer with hydantoin is good and therefore the bonding agent is useful for AP/HTPB propellant systems.

Composite solid propellant with hydantoin and isocyanurate bonding agents provides stronger interfacial bonds between AP/HTPB system and HMX/HTPB system causing better values of stress and strain at each temperature. Combined tensile test parameters with the results obtained from FTIR analysis, the interfacial bonding of these novel bonding agents with HMX was evaluated.

Optical Fiber with Composite Magnetic Coatings as the Base of Magnetic Sensor Element

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Multi mode optical fiber with composite polymer magnetic coating was investigated as an optical fiber magnetic sensor element (OFMSE) for detecting external magnetic field. OFMSE can be used in areas that are too harsh to measure with conventional sensor system, since the optical fiber is usually made of dielectric material that have high resistance to vibration, electromagnetic interference, thermal shock and corrosion. Also, it is very interesting as a component of ″smart materials″- composite materials sensitive on the magnetic field.

The composite coating was formed by dispersing of magnetic powder of Nd-Fe-B in poly-(ethylene-co-vinyl acetate) – EVA solution in toluene. Sensing element constructed in this paper consists of two optical fiber held in close proximity to each other, and are based on the principle of intensity modulation. One of them is coated with composite polymer – magnetic coating is cantilevered on the plastic plate. The cantilevered section moves in the opposite direction to the rest of the sensor in response to an applied magnetic field and the amount of light coupled between two fibers is modulated.

The influences of the applied external magnetic field and oscillating magnetic field in the change of intensity of light signal propagated trough constructed OFMSE was investigated. In this paper, the influence of the content of magnetic powder in the composite coating on optical propagation characteristics of OFMSE was investigated. Measurements were done both in slowly applied and oscillating magnetic field. If the amount of magnetic powder in composite coating is decreased signal attenuation decreased in both of fields.

Comparative Study about Obtaining and HPCL, UV-VIS and IR Characteristics of Some *meso*-Tetraphenylporphyrine Monomeric and Dimeric Complexes with Zr(IV)

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Introduction

The purpose of the present study is concerned about the versatile chemistry of Zr (IV) complexes with *meso*-tetraphenylporphyrin both regarding the monomer and the sandwich type dimmer with a single metallic centre. The synthesis of both compounds, IR spectra, UV-vis behavior of the two metalloporphyrins with Zr (IV) and the HPLC spectra registered on polar and nonpolar column are comparatively discussed.

Results and Discussions

The mixture of the reaction compounds, which was obtained by using the third method of synthesis, implying as reagents the complexe between tetrahydrofurane (THF) and $ZrCl_4$, gave after HPLC analysis on Kromasil polar column a ratio between monomer/dimmer compound=2,78/ 1 (retention times for monomer and dimmer are given: $t_R$monomer=4,49 min; $t_R$dimmer=3,47 min).
By comparison of UV-vis spectra of *meso*-tetraphenylporphyrin with UV-vis spectra of monomer and dimmer complexes, it was put into evidence that Soret band from monomeric compound is hypsochromic shifted and the Soret band from dimmeric compound (Figure 1) is divided in to components, both of the peaks suffering a hypochromic effect.

*Figure 1. Comparative presentation of the UV-vis spectra of bis [5,10,15,20-tetraphenyl-21H,23H-porphirinate-N21,N22,N23,N24] zirconium(IV) (1.496*10^{-6} M) and H_2TPP (2.084*10^{-6} M) superposed*

MSEN P-62 nma

Crystal Growth Kinetics of Leucite in Glass

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Leucite is a potassium aluminosilicate ($KAlSi_2O_6$). Its presence enables good mechanical, chemical and other properties suitable for applications as biomaterials. The amount, crystal size and structure directly affect on properties of final composite material. Due to that, kinetics and mechanism of its crystallization are the subject of constant interest.

In this work the results of investigation of the crystal growth kinetics of leucite in glass were presented. Investigation was performed on the bulk samples of multicomponent glass with composition of :$50SiO_2 19Al_2O_3 5CaF_2 13$ MgO13 K_2O (wet %). The experiments were carried out by isothermal heating of glass samples in the temperatures range of T=850-1100^oC. XRD of fully crystallized sample shows that the leucite (72vol %) was formed as primary phase, and phlogopite (24vol%) and diopside (4 zap.%) were formed as the secondary ones. SEM analyses showed that leucite crystals started to grow in the form of equiaxial dendrites with pronounced anisotropy. Such morphology of crystals shows that process of their growth evolved at faceted crystal/glass interface. By measuring of dimension of the largest crystals with different times at same temperature, a linear relationship was obtained . From the slope of the line so plotted, the crystal growth rate at fixed temperture was calculated. The temperature dependence of the rate of leucite crystal growth is shown at Fig.1.

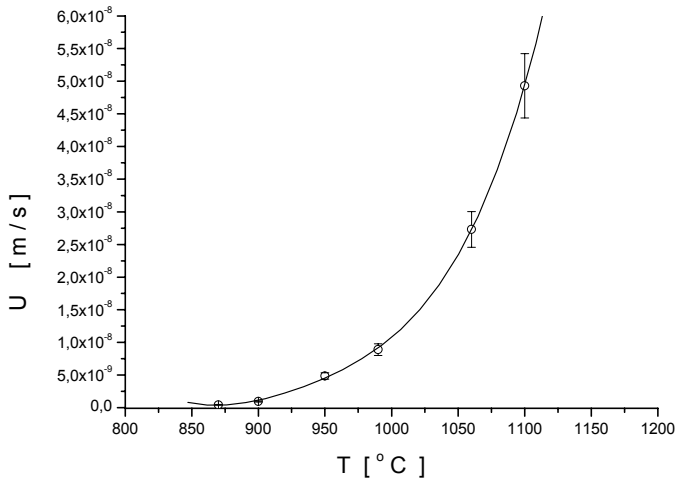


Fig 1. The growth rate U as a function of temperature

From the relationship of ln ($U/\Delta T^2$) vs 1/T, the value of activation energy of the leucite crystal growth E_a=293.5±15 kJ/mol was calculated. Here is $\Delta T=T_l-T$ and T_l is liquidus temperature of glass.

MSEN P-63 nat

Preparation and Studies of Nickel Carbonate Nanoparticles in Microemulsion System and Some Aspects of Their Application

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CANCELED

The preparation of nanoparticles in microemulsion systems and their application in modern chemical technology has drawn the attention of a num ber of scientists. The ultrafine particles of nickel carbonate have specific characteristics. They have important applications in catalysts and conducting and magnetic materials. This study is therefore aimed at the preparation of nano-sized particles of nickel carbonate in microemulsion conditions, by chemical reaction and their possible application as nanocatalysts. The shape and size of particles are determinated by electronic microscopy. The obtained ultrafine particles are spherical whit size to 50 nm. The quantity of NiO in nanostructure catalysts are determinated by atomic absorption analysis. Their morphology and structure are determinated by scaning electronic microscopy.

Heat Insulating Properties of the Upper Shoe Materials

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Heat transfer is a very important characteristic of each material. In this research heat transfer is charcterised by heat resistance and consequently by heat conductivity.
The ability of foot heat protection is significant at shoes. The most shoes are produced from natural or artificial leather, synthetic materials and textile. To learn more about the heat conductivity values of the upper shoe materials and for material comparision heat resistance of samples was measured by an unsteady method. For these measurements a machine constructed according to Fitch was used. Two heated baords represent a part of the measuring device. They touch the measured sample and give or take heat during the process of unsteady heat transfer through the measured sample. Thus the heat resistance evaluation in the range of the early temperatures of measuring boards is reached.
The samples were made from materials of various origin and thickness used for shoe uppers production. Dependance of heat conductivity value on the type of material (and on the way of dressing at leather) was observed.
The results show that heat conductivity differences among various types of leather and other shoe upper materials are significant and of a big importance while choosing appropriate materials for different utility of shoes and for various heat - moisture conditions.
The heat conductivity differences among various types of dressing do not show considerable variations. Way of dressing does not seem to be critical criterion while choosing the appropriate material

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