

ANNUAL REPORT

2008-2010



Nuclear Chemistry

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Czech Technical University in Prague



DEPARTMENT OF
NUCLEAR CHEMISTRY



CENTRE FOR RADIOCHEMISTRY
AND RADIATION CHEMISTRY

NUCLEAR CHEMISTRY

Annual Report 2008-2010

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Similarly to the 2007 pilot issue of the CTU Nuclear Chemistry Annual Report, this brochure compiles the achievements of two organisation units of the Faculty of Nuclear Sciences and Physical Engineering (FNSPE) of the Czech Technical University in Prague (CTU) – the Department of Nuclear Chemistry (DNC) and the Centre for Radiochemistry and Radiation Chemistry (CRRC). On the top of the list of the main events that happened during the period covered (2008 – 2010), the change of the head of the Department of Nuclear Chemistry should be probably listed; since June 2010, Jan John succeeded Viliam Múčka who had been heading the Department since 2003 and who successfully guided it to a stabilised status following the turbulent period of the transformation of Czech education and science system in 1990s.

Establishment of CRRC back in 2003 and finding a kick-off source of finance for its activities significantly contributed to the fact that today, aside from the current group-leaders and research directors, at both DNC and CRRC there is a strong group of highly competent and motivated young scientists / teachers aged 30–40. This group is getting ready to take over the baton being passed to them from the “fathers-founders” – Academician František Běhounek, a former student of Marie Curie-Skłodowska and Professor Vladimír Majer, author of the first Czech monograph on radiochemistry (1942), Professors Jiří Štáry, Jaroslav Růžička and Adolf Zeman, discoverers and elaborators of the substoichiometric principle (in 1961), Professor Petr Beneš, one of the leading radiochemists in the world in the second half of the last century, and other contributors to the good reputation of the Department of Nuclear Chemistry.

This team, that represents one of the important units of the Czech nuclear community, is well prepared and has an excellent background for entering the (hopefully starting) era of renaissance of nuclear power. The refurbishment and upgrade of the complex of radiochemistry laboratories, announced in the previous report, was further advanced. The laboratories are licensed for work with open sources including the actinides, they are now equipped with a full scale of radiometry instrumentation including gamma and alpha spectrometry, LSC, and radio-TLC imaging scanner. In addition to the external sources, the radiation chemistry research makes use of the in-house medium activity gamma and beta radiation sources. This specialised equipment is backed by a broad analytical background ranging from X-ray fluorescence analyser, HPLC, gas-chromatograph, AAS and a structural X-ray diffractometer to UV-VIS spectrophotometers equipped with external optical probe for in-situ reaction rate measurements. The recently built laser spectrometer for the TRLFS studies of actinides and lanthanides complexation/speciation is now generating the expected outputs.

The current research activities of the DNC and CRRC cover the majority of the fields within the traditional definition of nuclear chemistry – radiochemistry including its separation methods, radioanalytical chemistry, radiotracer techniques and chemistry of the actinides, and radiation chemistry including its applications, e.g., in catalysis, environmental protection, or radiation initiated preparation of solids inclusive nanoparticles – as well as radioecology, radiopharmacy, and labelled compounds. Very recently, radiopharmaceutical chemistry and biomedical applications of radionuclides and ionising radiation are being developed. The CTU has been integrated into several big international EURATOM FP6 or FP7 integrated projects such as ACSEPT, EUROPART, or FUNMIG; thus, the most of the research is performed in close collaboration and co-ordination with the major European Institutes and Universities. The main national collaborations included the Nuclear Research Institute Řež plc., Nuclear Physics Institute of the AS CR, both located in Řež near Prague, Radioactive Waste Repository Authority of the Czech Republic (RAWRA), DIAMO s.p., Stráž pod Ralskem, and many others. The research in nuclear chemistry at the DNC and CRRC continues to be organised in three research groups that, for the purpose of this Report, may be referred to as “Speciation and Migration”, “Separation and Radioanalytics” and „Radiation Chemistry”. Selection of short contributions characterising the research topics in more detail forms the body of this Annual Report.

In the education field, since 2010 CTU became a co-ordinator of the FP7 project CINCH – Cooperation in Education in Nuclear Chemistry (<http://www.cinch-project.eu/>) that aims at coordinating the education in nuclear chemistry, both at Ph.D. and undergraduate levels, within the EU, in collaboration with Russia. A separate part of the project is aiming at preparation of the grounds for a significant improvement of the university – industries collaboration in the training programs.

One of the most important events during the period covered was the leading role of CTU in co-organisation of the international 16th Radiochemical Conference held in 2010 traditionally in the Western Bohemian spa of Mariánské Lázně (<http://www.radchem.cz/>). It was the first time when this conference was organised as a part of the regular bi-annual series of Pan-European nuclear chemistry conferences guaranteed by the Division of Nuclear and Radiochemistry of the EuChemS. Despite the extremely unfavourable circumstances – the infamous Eyjafjallajökull eruption that took place only four days before the start of the conference and the resulting air-traffic havoc – some 200 participants from 28 countries made the conference a clear success. The final programme is available at <http://indico.fifi.cvut.cz/>, RadChem 2010, Timetable. The RadChem Proceedings, compiled from the accepted full papers, have been published in the Journal of Radioanalytical and Nuclear Chemistry (Volume 286, Issues 2 and 3). The Booklet of Abstracts has been published as a special issue of the Czech Chemical Society journal, Chemické Listy, and can be freely accessed at the journal home page at http://www.chemicke-listy.cz/common/content-issue_14-volume_104-year_2010.html/

In 2010, the DNC and CRRC employed 13 research/academic staff as well as 4 part-timers (maternity leave or external staff). At the same time, there were 11 PhD students affiliated with the DNC or CRRC (the total number of PhD students in 2010 being 27, the remaining ones working in various research institutes). Thus, the complex DNC – CRRC resembles rather a small research institute than a typical university department. In 2007, this fact has also motivated our decision to start a series of Annual Reports of Nuclear Chemistry at the CTU. We hope that you will find this report interesting, and that it may help to further promote both our national and namely international collaboration. We hope that all potential new collaborators will find the environment in our research groups as convivial and inspiring as our current colleagues do.



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EDUCATION



Courses Taught



Projects

Courses Taught

List of Courses in the Academic Years 2008/2009, 2009/2010 and 2010/2011

Title, credits (ECTS), semester (W - October to mid-January, S - March to mid-June), lecturer(s)

• Application of large ionizing radiation sources	2		M. Pospíšil
• Applications of radiation chemistry in chemical industry, agriculture and medicine	2		V. Múčka
• Application of radionuclides 1	2	S	J. Mizera*
• Application of radionuclides 2	2	W	J. Mizera*
• Applications of radiation methods	2	S	V. Múčka
• Biosyntheses of labelled compounds	2		S. Smrček*
• Chemical thermodynamics	4	S	V. Múčka
• Chemistry for nuclear engineering	4	S	K. Štamberg, R. Silber
• Chemistry of operation of nuclear power plants	2	W	K. Štamberg
• Chemistry of the Pharmaceuticals	2	W	S. Smrček*
• Chemistry of radioactive elements	2	S	J. John
• Colloid chemistry	3	W	P. Beneš
• Determination of radionuclides in the environment	2	W	M. Němec
• Electrochemistry and theory of solutions 1	3	W	B. Drtinová
• Electrochemistry and theory of solutions 2	2	S	R. Silber
• Environmental chemistry and radiation hygiene	3	S	P. Beneš, L. Hobzová*
• Fundamentals of construction and function of nuclear power plants	3	S	P. Otčenášek*
• Fundamentals of chemistry 1	3	W	A. Motl
• Fundamentals of chemistry 2	3	S	A. Motl
• General chemistry	6	W	A. Motl
• Instrumental radioanalytical methods and their application for the environment monitoring	2		J. Kučera
• Instrumental methods of research 1	5	S	M. Pospíšil
• Instrumental methods of research 2	2	W	M. Pospíšil
• Introduction to Nuclear Chemistry	2	W	P. Beneš
• Introduction to photochemistry and photobiology	2	W	K. Čubová, L. Juha*
• Ionising radiation detection and dosimetry	4	S	J. John, A. Motl
• Isotopes and reaction mechanisms	2		L. Lešetický*
• Kinetic theory of matter	2	S	V. Čuba

* External teacher

• Labelled compounds	2	W	L. Lešetický*
• Laboratory practice in the instrumental methods of research	4	S	M. Pospíšil, R. Silber
• Modelling of the migration processes in the environment	2	S	K. Štamberg
• Measurement and data handling	3	W	A. Vetešník, D. Vopálka
• Nuclear chemistry 1	4	W	P. Beneš
• Nuclear chemistry 2	5	S	J. John
• Nuclear materials technology	2	W	K. Štamberg
• Numerical exercises in physical chemistry 1	2	S	R. Silber
• Numerical exercises in physical chemistry 2	2	W	R. Silber
• Numerical exercises in physical chemistry 3	2	S	B. Drtinová, R. Silber
• Numerical simulation of complex environmental processes	2	W	D. Vopálka
• Practical Exercises in Radiochemistry 1	5	W	M. Němec, V. Čuba
• Practical Exercises in Radiochemistry 2	6	W	M. Němec, V. Čuba
• Production of radionuclides	2	W	O. Lebeda*
• Protection of the environment	2	S	H. Filipská
• Radiation chemistry	3	W	A. Motl
• Radiation methods in biology and medicine	2	W	V. Čuba, V. Múčka
• Radioanalytical methods	3	W	J. John
• Radiopharmaceuticals	2	S	O. Lebeda*
• Radiopharmaceuticals 2	2	W	L. Lešetický*, M. Moša*
• Reaction kinetics	3	S	V. Múčka
• Separation methods in nuclear chemistry 1	3	W	M. Němec
• Separation methods in nuclear chemistry 2	2	W	M. Němec
• Solids	2	W	V. Múčka
• Synthesis of labelled compounds	2	W	L. Lešetický*
• Technology of the fuel cycles of nuclear power plants	2	S	K. Štamberg
• The theory of the electromagnetic field and wave motion	4	S	A. Vetešník
• Trace radiochemistry	3	S	P. Beneš
• Transport processes	2	W	D. Vopálka
• Waste Analysis	2	W	J. Janků*
• Waste Management and Treatment	2	W	M. Kubal*

* External teacher

Projects

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CINCH – COOPERATION IN EDUCATION IN NUCLEAR CHEMISTRY

J. John, V. Čuba, M. Němec, C. Ekberg¹, T. Retegan¹, G. Skarnemark¹, J. Lehto², T. Koivula², S. Kalmykov³, R. A. Aliev³, G. Cote⁴, W. Morscheidt⁴, J. Uhlir⁵, A. Vokál⁵, B. Hanson⁶, J.P. Omtvedt⁷, B. Salbu⁸, L. Skipperud⁸

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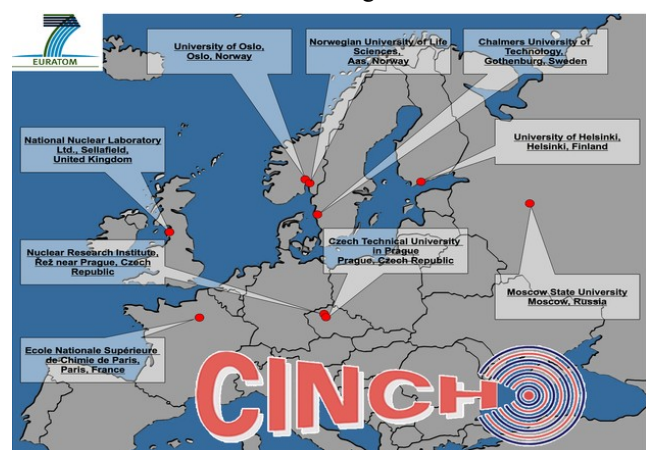
INTRODUCTION

The renaissance of nuclear power, transition to GEN IV reactors or decommissioning of phased-out reactors will require a significant increase of the numbers of the respective specialists, among others also nuclear chemists. The current situation in nuclear chemistry education and training in Europe is quite diverse, ranging from full 3 + 2 + 3 years nuclear chemistry BSc + MSc + PhD study down to teaching the nuclear chemistry at PhD level only.

Therefore, the CINCH project is aiming at coordination of education and training in the field of nuclear chemistry by developing a long-term Euratom Fission Training Scheme (EFTS) providing a common basis to the fragmented activities in this field and thus move the education and training in nuclear chemistry to a qualitatively new level.

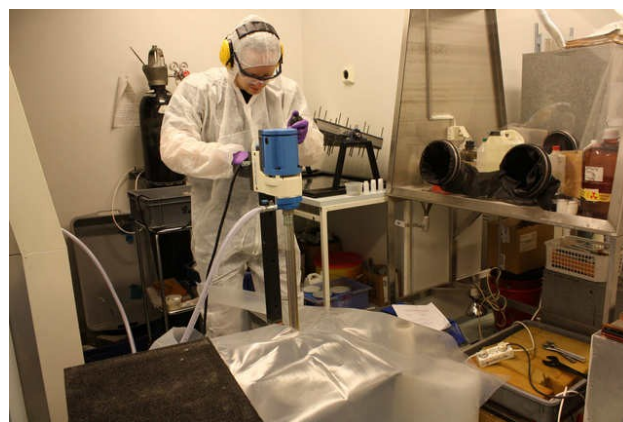
NATURE AND SCOPE OF THE PROJECT

The consortium of the collaborating universities, coordinated by CTU in Prague (Jan John), represents a network of organisations consisting of academia and industrial partners representing some of the key players/countries in the field of delivering and using the education and training in the field of nuclear chemistry, namely that applied to nuclear energy. The universities involved have a long-lasting tradition in delivering the courses in nuclear chemistry; they belong also among the few European universities, where the numbers of students in this field are still significant.



The project aims at coordinating the education in nuclear chemistry, both at Ph.D. and undergraduate levels. A separate part of the project is aiming at the preparation of the grounds for a significant improvement of the university – industries collaboration in the training programmes. The system developed will consist of a mix of collective and individual courses and internships addressing all the levels from senior researchers

and managers, through Ph.D. students down to undergraduate students. Through this partnership, the transfer of higher-level knowledge and technology will be maximised; young students as well as experienced research workers will be addressed. The opportunity to meet with colleagues from the entire Europe during the joint modular courses developed in the project and delivered by the leading experts in the field should increase the attractiveness of careers in nuclear chemistry across the EU.



EXPECTED RESULTS

A system for students and teachers exchange (including internships), based on common compact modular courses, will be developed and grounds for a future "European Master in Nuclear Chemistry" will be prepared. E- and B-learning will belong among the tools used.

Opportunities for students, teachers and scientists will include access to the best educational aids in the area including international joint modular courses, increased competitiveness and mobility of the graduates on the European labour market according to the actual needs of the nuclear industry, promotion of the topic of nuclear chemistry, long-term platform for exchange of experience, ideas, knowledge, and best practices transfer, etc.

Opportunities for employers will include new contacts with training providers from various European countries, improved universities – industries interaction, increased numbers and thus improved availability of qualified specialists in the field of nuclear chemistry, better access to research results, etc.

These results will be clustered round a set of compact joint modular courses in different branches of modern nuclear chemistry, available for both education and training, and a long term sustainable strategy for the nuclear chemistry education including a roadmap for its implementation.

PROJECT INFORMATION

FP7 EFTS Coordination Action No.: 249690.

Website address: www.cinch-project.eu/

Project start date: 01/02/10 (duration 36 months)

OPERATIONAL PROGRAMM PRAGUE ADAPTABILITY - FERMI 2010

Innovation of Nuclear Power Engineering Studies by Intensifying of Co-operation between Prague Universities

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INTRODUCTION

The main goal of the project Fermi 2010 named in the honor of famous Italian physicist Enrico Fermi is to start a major innovation of teaching and co-operation in training of nuclear engineers at selected universities in Prague.

Given the expected re-development of nuclear power and also the safe operation of existing nuclear power plants, in the near future is expected increasing demand for graduates in fields related to nuclear energy. To ensure the quality of education in this field the closer co-operation of universities is needed.

Prague Universities are the traditional pillars of nuclear engineering education in the Czech Republic. The project focuses on nuclear engineering students at **Czech Technical University in Prague** and **Institute of Chemical Technology Prague**.

PARTNERS

Three faculties of the **Czech Technical University in Prague** are involved in the project – Faculty of Nuclear Sciences and Physical Engineering (3 departments including Department of Nuclear Chemistry, and Centre for Radiochemistry and Radiation Chemistry), Faculty of Mechanical Engineering and Faculty of Electrical Engineering. Faculty of Environmental Technology of **Institute of Chemical Technology Prague** is also participating in the project. All above mentioned subjects are members of a voluntary association of academic members **CENEN** (Czech Nuclear Education Network).

OBJECTIVES

Co-operation and improving the quality of teaching are achieved via innovations in curricula of the nuclear engineers. The modifications are accomplished in particular by the introduction of new courses provided by the participating departments; including one voluminous course, in which the students are acquainted with problems of the studied field in all its breadth. The selected subjects of individual departments are incorporated into the curricula of other departments. The aims of the Fermi 2010 are met by providing unique educational facilities, such as the school nuclear reactor VR-1 operated by the CTU in Prague, and by creating a database of e-learning study materials for all participating institutions. Students also gain basic experience and contacts directly in the industry during the excursions, practices and mentorings. The PhD students will be able to form fellowships and scientific publications to engage in cutting-edge of education and research abroad.

Department of Nuclear Chemistry (DNC) and *Centre for Radiochemistry and Radiation Chemistry (CRRC)* participate in the process of innovation of the practical tasks at the school nuclear reactor VR-1 by consultations in the field of radiochemistry and radiation chemistry,

and implement innovative and new tasks into the extended laboratory exercises from nuclear chemistry. The organization of 4 excursions is provided during the project. 60 students are supported to attend industrial companies within the excursions, practices, or mentorings in a field related to the project. Short international fellowships of 4 PhD students are organized.

One of the main output of the Fermi 2010 will be a general optional course *Selected Topics in Nuclear Energy*, which will be lectured by all interested members of the team and their colleagues from the participating departments. Each speaker will lecture on his specialty at a level corresponding to a diverse audience.

DNC and *CRRC* contribute also to the creation of e-learning materials for courses related to the project.



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This project is supported from European Social Fund (ESF), grant No: CZ.2.17/3.1.00/32196.

THE INTER-UNIVERSITY COLLABORATION ON DEVELOPMENT OF THE JOSEF UNDERGROUND FACILITY IN THE FIELD OF DANGEROUS COMPOUNDS DISPOSAL AND GAS STORAGE

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³Technical University of Liberec; ⁴Masaryk University in Brno

INTRODUCTION

Problems related to the construction and operation of underground gas storage tanks, spent nuclear fuel disposal in deep repositories or the potential underground storage of CO₂ are all highly topical issues, both from the ecological and power engineering perspectives. Finding of optimum solutions to such issues requires long-term training of specialists, not only on a theoretical, but also on a practical basis, which should include the option of experimental teaching in an “in situ” environment. Hence, the CTU in Prague, the Institute of Chemical Technology, Prague (ICT), the Technical University of Liberec (TUL) and Masaryk University in Brno (MU), made the decision to combine their scientific expertise and potential in the form of a single inter-university underground laboratory.

The Inter-university Laboratory (InterLab) is located in the SP71 inset in the Mokrsko-West area of the Josef Underground Educational Facility (Josef UEF), in one of a number of recently opened sections of the extensive underground complex, which provided a unique site for the construction of such a laboratory. Josef UEF is located in the Čelina-Mokrsko area of the Příbram region of the Czech Republic. It was constructed in a re-opened section of the abandoned Josef gold exploration gallery and since its opening in 2007 it is operated by the Centre of Experimental Geotechnics, FCE CTU in Prague.

PARTNERS

Two faculties of the **Czech Technical University in Prague** are involved in the project – the Centre of Experimental Geotechnics (CEG) of the Faculty of Civil Engineering (FCE) represented by Prof. J. Pacovský of the CEG as the project's senior coordinator, and the Department of Nuclear Chemistry of the Faculty of Nuclear Sciences and Physical Engineering (FNSPE) represented by Dr. M. Němec. FCE students use a range of the laboratory's facilities as part of the “Laboratory Exercises in Geotechnics and the Experimental Research of Radioactive Waste Disposal” course whilst the Department of Nuclear Chemistry FNSPE use InterLab as an “in situ” laboratory for courses in Practical Exercises in Radiochemistry and Practical Exercises in Instrumental Methods, where they learn the fundamentals of radio-analytical methods and the determination of (radio)nuclides in rock masses directly in the field.

Masaryk University in Brno is represented in the project by the Institute of Geological Sciences, part of the Faculty of Natural Sciences with the responsible researcher Dr. J. Leichmann.

As far as InterLab is concerned, the Institute of Geological Sciences uses the “in situ” geochemistry laboratory for the teaching of the Geochemical and Mine Mapping part of its

master's degree course in geology. The teaching of other courses has been extended to include underground experimentation and several existing courses have been extended by new subjects – the geological and tectonic documentation of mine openings in terms of stability, tectonic failure, hydro-geological characteristics, permeability and other parameters, and the design, implementation and documentation of boreholes etc.

Technical University of Liberec participates in the project through the Institute of New Technologies and Applied Informatics of the Faculty of Mechatronics, Informatics and Interdisciplinary Studies. The researcher responsible for the project is Dr. Milan Hokr.

The Institute's teaching at the facility consists of basic tuition in laboratory experimental methodology as part of the Science Engineering master's degree course and the Modelling and Informatics bachelor degree course. Students are taught the principles and practical applications of various measurement methods and the use of apparatuses for the measurement of physical and chemical variables in underground environments, such as pressure, temperature, pH and Eh. The underground laboratory also serves for the performance of basic experiments in hydrogeology with an emphasis on their significance in gathering data on the characteristics of geological media.

Institute of Chemical Technology Prague is represented in the project by the Institute of Analytical Chemistry which forms part of the Faculty of Chemical Engineering. The Institute is represented by Prof. Ing. Karel Volka, CSc.

A whole series of “Analytical Chemistry and Quality Engineering” courses have been introduced at the facility as part of the “Technical Physical and Analytical Chemistry” master's degree study programme. In addition, “in situ” work will form part of the “Laboratory Exercises in Analytical Chemistry II” bachelor degree course. Teaching is provided either “hands on” in the Josef/InterLab “in situ” analytical and radio analytical laboratory, or indirectly involving the investigation of water media samples and geological materials at the ICT laboratories in Prague aimed at addressing analytical and radio analytical issues related to the inspection and protection of the environment in terms of the disposal of hazardous substances and gases.

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This project has been supported by the Ministry of Education, Youth and Sports of the Czech Republic, grants No: C3/2010 and C14/2011.

UTILIZATION OF THE INTER-UNIVERSITY LABORATORY AT THE DEPARTMENT OF NUCLEAR CHEMISTRY

M. Němec, J. John

INTRODUCTION

The Inter-university Laboratory (InterLab) is a result of collaboration of the CTU in Prague, the Institute of Chemical Technology, Prague (ICT), the Technical University of Liberec (TUL) and Masaryk University in Brno (MU), which made the decision to combine their scientific expertise and potential in the form of a single inter-university underground laboratory. Two parts of the CTU in Prague are involved in the project – the Centre of Experimental Geotechnics (CEG) of the Faculty of Civil Engineering (FCE) represented by prof. Jaroslav Pacovský of the CEG as the project's senior coordinator, and the Department of Nuclear Chemistry of the Faculty of Nuclear Sciences and Physical Engineering (FNSPE) represented by Dr. Mojmir Němec. The laboratory is located in the SP71 inset in the Mokrsko-West area of the Josef Underground Educational Facility (Josef UEF), in one of a number of recently opened sections of the extensive underground complex, which provided a unique site for the construction of such a laboratory. Josef UEF is located in the Čelina-Mokrsko area of the Příbram region of the Czech Republic. It was constructed in a re-opened section of the abandoned Josef gold exploration gallery and since its opening in 2007 it is operated by the Centre of Experimental Geotechnics, FCE CTU in Prague. The laboratory is oriented to the problems related to the construction and operation of underground gas storage tanks and spent nuclear fuel disposal in deep repositories, and mainly long-term education and training of the specialists in such interdisciplinary underground engineering focused on “in situ” experience.

DNC IN THE INTERLAB

The Department of Nuclear Chemistry FNSPE is using the InterLab as an “in situ” laboratory for courses in Practical Exercises in Radiochemistry, where the students are learning the fundamentals of “in situ” radioanalytical methods directly in the field. All partners of the project also collaborate on the multidisciplinary course “Research of engineered and natural barriers”.

PRACTICAL EXERCISES

Radiometric characterisation of a borehole in a rock pillar

For this task special device designed for work in boreholes was constructed. Practically, it is a gamma-ray submersible spectrometer equipped with a LaBr detector – with its outer diameter of 80 mm and water-resistance up to 10 m, it is quite unique device. The task consists of background measurement and borehole and rock characterization with the method of 2 gamma radiation sources in parallel borehole.

Basic principles of rentgenfluorescence analysis

The task is focused on basic understanding and testing of XRF. It uses set of standards and samples prepared directly in the laboratory from basic chemical compounds. Students are testing homogeneity and overall repeatability in preparation of their samples and calibration curves and also precision of the mobile XRF device (NITON GOLDD).

Application of XRF for the prospection of heavy metals including uranium in a rock pillar

This is direct “in situ” task showing the utilization of mobile XRF device for detection and determination of various elements in the rock. Theoretical part includes overview of the basic definitions and terms, mainly about “method of fundamental parameters” for quantitative analysis. The practical part allows students to “prospect” part of the Josef mine for heavier elements and make basic geological/elemental (qualitative) survey.

Determination of gross alpha and beta activities in underground water samples

The exercise uses liquid scintillation counting spectrometry for classification of the underground water from the boreholes. With the evaporation pretreatment, lower limits of detection as low as 30 mBq L⁻¹ for gross alpha and 90 mBq L⁻¹ for gross beta activities could be achieved for a sample produced from 1 L of the underground water.



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This project has been supported by the Ministry of Education, Youth and Sports of the Czech Republic, grants No: C3.2/2010 and C14/2011.

RESEARCH REPORTS



Speciation and Migration



Separation and Radioanalytics



Radiation Chemistry



Speciation and Migration

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THE EXPERIMENTAL STUDY OF FUCOID SANDSTONES CONTAMINATED DURING URANIUM MINING

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INTRODUCTION

The Stráž pod Ralskem area is significantly marked with the acid in-situ uranium mining (5.7 km²). The geological sequence of interest consists of the Cenomanian and Turonian formations. The Cenomanian sequence is formed by the upper layer of low permeable fucoid sandstone and by the lower layer of crumbly sandstones containing uranium bearing mineralization. The uranium leaching in the past was realized by injecting acid technological solutions which brought about 4 million tons of H₂SO₄ into the deep layers of the Cenomanian aquifer. The scope of this work was to continue in the experimental study needed for the detailed description of interactions between the fucoid sandstones and selected liquid phases.

EXPERIMENTAL

Batch leaching experiments were proceeded with uncontaminated Cenomanian groundwater (CG) and samples of fucoid sandstone from the contaminated area. The liquid-to-solid ratio of 5mL.mg⁻¹ was selected for all these experiments. Diffusion experiments were carried out with CG and acid technological solution (ATS) in which concentrations of dissolved SO₄²⁻, Fe²⁺ + Fe³⁺ and Al³⁺ were 25200, 923 and 4560 mg.L⁻¹, respectively. The solution in the input cells was spiked with SO₄²⁻, labeled with ³⁵S. Considering the heterogeneity of geological environment, diffusion was measured in both vertical and horizontal directions. A supplementary set of batch experiments using labeling with ³⁵S was performed with the aim to determine *K_d* values for sulfates. The exchangeable amount of sulfur initially present in the solid phase was determined as follows:

$$S_{ex} = \frac{C(V - K_d \cdot m) - C_0 \cdot V}{m}$$

Here *C*₀ and *C* are the initial and equilibrium concentrations in the liquid phase, *V* - volume of the liquid phase and *m* - weight of the fucoid sample [2].

RESULTS

Iron sulfides proved to be the most remarkable mineral phases influencing the behavior and balance of sulfur in the studied system. Pyrite is lightly dispersed in the fucoid structure supporting the assumption that its oxidation causes the rapid decrease of pH value (down to 2.7) and the increase of SO₄²⁻ concentration in the liquid phase during leaching experiments. The measured values of *K_d* for all contaminated samples were relatively low (Tab. 1). The results showed that sulfates are released into the liquid phase (CG) considerably. Moreover, the amount of sulphur in sulphates *S*(SO₄²⁻) quantitatively corresponds to the total sulfur concentration *S*_{total} in the leachate (Tab. 1).

Tab. 1. The results of the batch experiments

sample No.	pH	depth m	<i>S</i> _{total} mg g ⁻¹	<i>S</i> (SO ₄ ²⁻) mg g ⁻¹	<i>K_d</i> mL g ⁻¹	<i>S</i> _{ex} mg g ⁻¹
48541	2.74	142	1.40	1.17	0.19	1.21
48544	2.91	143	1.10	1.10	0.18	1.14
48547	3.11	144	1.10	1.08	0.21	1.13
48550	2.85	145	1.45	1.42	0.21	1.48
48555	2.94	148	1.10	1.12	0.29	1.18
48567	2.64	153	1.80	1.67	0.36	1.79

The transport within contaminated fucoid samples is driven by diffusion in contact with both liquid phases (CG, ATS). The faster ³⁵S movement was observed using the labeled ATS (Fig. 1). This implies that ATS dissolved specific Fe/Al minerals or intergranular cements (kaolinite, illite), and thus opened new preferential flow pathways causing more intensive tracer breakthrough.

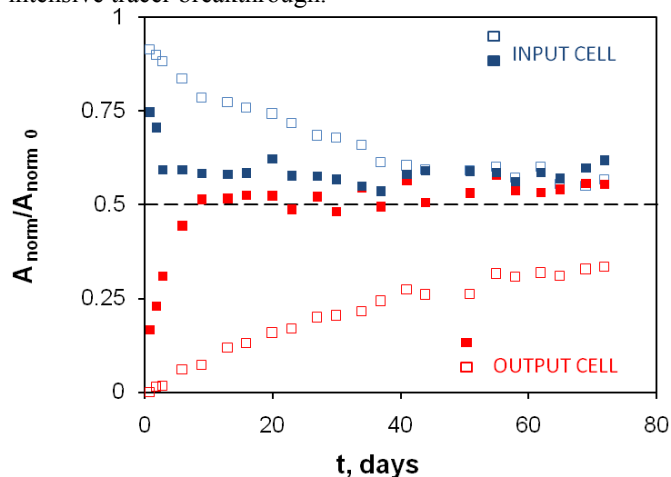


Fig. 1. The diffusion of liquid phases (open symbols – CG, closed symbols – ATS) through the rock sample demonstrated by the relative time change of the spike (³⁵S) activity in both input and output containers.

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STUDY OF IRON OXIDE COATING EFFECTS ON Cs, Pu AND Am SORPTION TO CLAYS

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INTRODUCTION

Understanding of radionuclides transport in porous media is necessary for safety assessment of radioactive waste repositories. One of the most important issues in this respect is their sorption on clays which are often used as engineered barriers. The sorption can be strongly affected by admixtures present in the clays, particularly by their iron oxide coatings; therefore, this effect has been studied by several methods [1]. Here, only some preliminary results of the sorption of several radionuclides on clays containing different amounts of iron oxides are described with the aim to test model methods to be used in the analysis of the effect of the clay composition.

EXPERIMENTAL

Three samples of Triassic clay from the Šaltišiai quarry (Lithuania) with different iron concentration and iron oxides composition, denoted as S, 6 and 7, were used for laboratory experiments. The sorption was studied using a radiotracer method from NaNO_3 solution or two different samples of groundwater, denoted as GW4 and GW6.

RESULTS

In order to examine the effect of pH on cesium sorption on clays, laboratory study of this effect was undertaken with clay S and solution of 0.1M NaNO_3 . The results obtained are shown in Fig. 1. They were fitted using surface complexation model [2] assuming ion exchange of Cs^+ on the so called layer sites and its bonding on dissociated edge sites $-\text{SO}^-$ according to simple reaction $-\text{SO}^- + \text{Cs}^+ = -\text{SOCs}$. From the results of modeling shown in Fig. 1 it is obvious that the goodness-of-fit of the modeling is very good and that the sorption of Cs^+ takes place practically only on the layer sites, which agrees with conclusions published in literature [3].

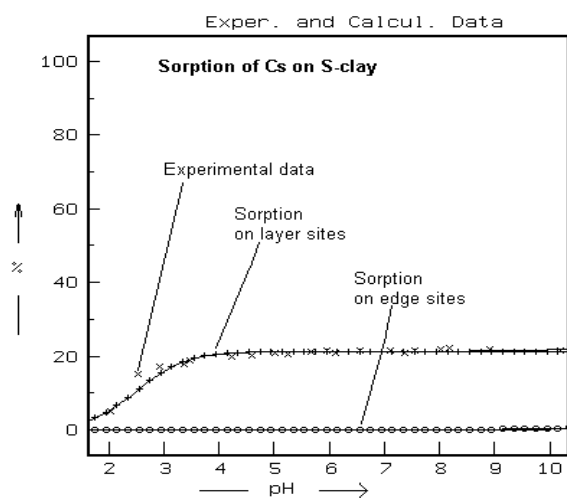


Fig. 1. Sorption of $6.8 \times 10^{-5}\text{M}$ Cs on S-clay as a function of pH.

Experimental kinetic data characterizing the sorption of Cs, Pu and Am on clays 6, 7 and S under variable conditions were fitted using six kinetic differential equations describing six different types of control processes (kinetic sorption mechanisms): so called mass transfer or double film model (DM), film diffusion (FD), inert layer diffusion (ID), reacted layer diffusion (RLD), chemical reaction (CR) and gel diffusion (GD) [4]. In principle, the results point to the diffusion (mass transfer) character of the sorption process; the sorption of Cs^+ is controlled by DM, sorption of Pu and Am by ID. The values of corresponding kinetic coefficients and distribution coefficients K_d , characterizing the rate of sorption and sorption properties of the clays, are given in Tab. 1.

Tab. 1. Results of modeling of sorption kinetics of Cs, Pu and Am on clays 6, 7 and S from GW4 and GW6.

Exper. No.	Starting concentr. [M]	Control process	Kinetic coefficient [min^{-1}]	K_d [mL/g]	WSOS_DF
Cs 6-4	6.8×10^{-5}	DM	4.55×10^{-3}	6.35×10^2	16.50
Cs 6-6	6.8×10^{-5}	DM	4.71×10^{-3}	5.4×10^2	22.31
Cs 7-4	6.8×10^{-5}	DM	5.74×10^{-3}	5.67×10^2	12.10
Cs 7-6	6.8×10^{-5}	DM	5.4×10^{-3}	5.27×10^2	11.60
Pu 6-4	1.10×10^{-9}	ID	6.96×10^{-3}	9.40×10^4	34.40
Pu 7-4	1.10×10^{-9}	ID	3.94×10^{-2}	1.62×10^4	5.14
Pu S-4	1.10×10^{-9}	ID	9.63×10^{-3}	2.86×10^4	15.70
Am 6-4	3.20×10^{-11}	ID	3.29×10^{-3}	4.38×10^4	41.30
Am 7-4	3.20×10^{-11}	ID	2.14×10^{-2}	2.04×10^4	18.20
Am S-4	3.20×10^{-11}	ID	1.42×10^{-2}	1.88×10^4	51.30

The values of WSOS_DF shown in Tab. 1 characterize goodness-of-fit of experimental data by the given kinetic model. If WSOS_DF is equal to or smaller than approximately 20, the agreement between the experimental and calculated data is good. This condition is fulfilled for all the samples tested except for three cases with Pu or Am where the reason of WSOS_DF value deviation from 20 can be a large scatter of experimental data due to the very low metal ion concentrations used. Thus the data given in Tab. 1 can be useful in modeling of migration of the studied elements through engineered barriers made of the clays.

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MODELING OF Pu AND Am SORPTION ON CLAY AND IRON OXIDE MINERALS

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INTRODUCTION

Natural clays can play an important role in retardation of transport of radionuclides from waste repositories. The retardation depends on many factors such as the type of clay, pH, and redox potential. In order to contribute to understanding of such effects, the sorption of Pu and Am has been studied on natural clay and three ferric oxide minerals. Iron oxides are common components of coatings on natural clays and can also be formed by corrosion of waste containers. Am(III) can serve as a model for Pu(III). The results are interpreted using surface complexation modeling (SCM).

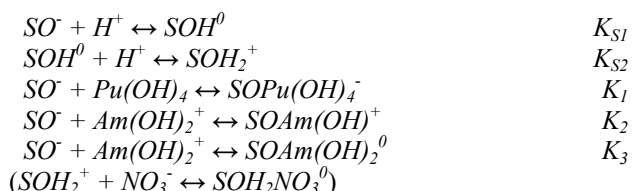
EXPERIMENTAL

Natural Triassic clay from the Šaltiškiai quarry (Lithuania), hematite, goethite, and magnetite were used for laboratory experiments. The sorption was studied by use of radiotracer method from 0.1 mol.L⁻¹ NaNO₃ solution [1].

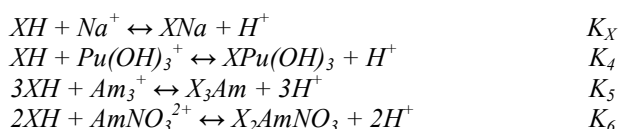
RESULTS

The surface complexation model [2] assuming reactions on the so-called “edge sites” and ion exchange model (IExM) for ion exchange on the so called “layer sites” was used. The choice of sorption reactions for the models was based on the calculated speciation of Pu(IV) and Am(III) in sorption solutions [1]. The following reactions were supposed:

- reactions on edge sites (SOH^0 , SO^- , SOH_2^+)



- reactions on layer sites (XH or XNa)



Three types of the models, namely, two electrostatic, i.e. constant capacitance (CCM) and diffuse double layer (DLM) model, and one chemical equilibrium, non-electrostatic model (CEM), were employed to simulate at first the amphoteric and then sorption properties of the minerals. From the evaluation of acid base titration curves the protonation constants (K_{S1} , K_{S2} - characterizing “edge sites”), ion-exchange constant (K_X - characterizing the “layer sites”) and the total concentrations of both, edge and layer, sites (ΣSOH , ΣXH) were obtained. Then, the values of equilibrium constants (K_1 - K_6) were sought by means of the Newton-Raphson multidimensional nonlinear regression method. The best fit was found when the experimental data obtained were fitted with the non-electrostatic model (CEM). As a fitting criterion, reflecting the agreement between calculated and experimental

values, the $WSOS/DF$ quantity was used [3]. Generally, the agreement is acceptable if $0.1 \leq WSOS/DF \leq 20$.

The resulting values of equilibrium constants and of $WSOS/DF$ parameter are summarized in Table 1. According to the $WSOS/DF$ values obtained, the modelling results can be considered reliable and thus indicative of the sorption mechanism, which can be judged from the comparison of the corresponding reaction constants.

Tab 1. Results of modeling of Pu and Am sorption

Parameter	Clay 0.01M NaNO ₃	Clay 0.1M NaNO ₃	Hematite 0.1M NaNO ₃	Goethite 0.1M NaNO ₃	Magnetite 0.1M NaNO ₃
K_1 [L.mol ⁻¹]	7.00E+4	2.61E+4	1.89E+7 pH 7-9	6.82E+1 pH>8	6.43E+6 pH>5.5
K_2 [L.mol ⁻¹]	4.03E+11 pH>7.5	1.48E+11	1.32E+13 pH>7	2.57E+3	3.18E+5 pH>4
K_3 [L.mol ⁻¹]	1.51E+14 pH>7	6.02E+13	5.69E+12 pH>7	9.44E+5	4.68E+8
K_4 [-]	4.40E+1 pH 4-8	8.76E+1 pH 4-8	6.02E+0 pH 4-7	7.97E-1 pH 4-8	3.69E+1 pH 4-6
K_5 [kg.L ⁻²]	2.33E-8 pH>5	4.44E-6 pH>3.5	6.18E-5 pH<8	1.50E-7 pH 4-10	1.73E-4 pH<6
K_6 [kg.L ⁻¹]	2.05E-1 pH<8	1.11E-1 pH<6	1.83E-1 pH<6	4.77E-3 pH 4-10	3.88E-2
WSOS/DF	0.50	1.35	1.40	18.06	0.03

Only some of the assumed reactions play an important role in sorption of radionuclides and have to be taken into account. For these reactions their pH region of importance is given together with their constant. The constants found indicate higher sorption of Pu(IV) to clay than to iron oxides, while the sorption affinities of these minerals for Am are mutually comparable. Comparison of the constants for Pu(IV) (K_4) and Am(III) ($K_5,6$) exchange on the layer sites presented in Table 1 indicates that Pu(IV) is much more selectively (i.e. strongly) bound by this mechanism than Am(III) on all the minerals studied. This effect is most pronounced for the clay and magnetite and can explain higher Am(III) mobility in the environment. The comparison of constants K_5 and K_6 is very interesting because it points to the great difference between the affinity of layer sites for Am^{3+} and $AmNO_3^{2+}$, which is much higher for $AmNO_3^{2+}$.

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SIMPLIFIED METHOD SUITABLE FOR THE MODELLING OF TRANSPORT OF RADIONUCLIDES IN BED OF GRANULATED SOIL AND ROCK UNDER ELUTION CHROMATOGRAPHY AND NON-EQUILIBRIUM ISOTHERM CONDITIONS

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INTRODUCTION

Transport of i -th component through granulated bed is usually described by 1D partial differential equation of parabolic type (1) comprising four terms on the right-hand side; namely, the dispersion, advection, interaction, and radioactive decay terms. If an equilibrium dynamic sorption/desorption process is assumed, eqs. (1) and (2) can be derived:

$$\frac{\partial C}{\partial t} = \frac{D_i}{R_i} \frac{\partial^2 C_i}{\partial x^2} - \frac{u}{R_i} \frac{\partial C}{\partial x} - \frac{\lambda_i}{R_i} \left(C_i + \frac{\xi}{\varepsilon} f(C_i) \right) \quad (1)$$

$$R_i = 1 + \frac{\xi}{\varepsilon} f'(C_i) \quad f'(C_i) = \frac{\partial q_i}{\partial C_i} \quad (2)$$

The symbols used in eq. (1) and (2) denote: C_i - i -th component concentration in liquid phase, q_i - i -th component concentration in solid phase, D_i - dispersion coefficient of the i -th component, R_i - retardation coefficient of the i -th component, u - axial linear flow rate of liquid phase (i.e., volume flow rate related to free surface of radial cut of given bed), λ_i - decay constant of the i -th component, ξ - bulk density of the granulated bed, ε - porosity of the bed, t - time, x - length parameter, $f'(C_i)$ - first-order derivative of the equilibrium sorption/desorption isotherm, i.e. of the function $q_i = f(C_i)$, describing the interaction of the i -th component with solid phase. In the case of the linear equilibrium isotherm, it holds: $q_i = (K_d)_i \cdot C_i$, $dq_i / dC_i = (K_d)_i$ and $R_i = \text{const.}$ On the other hand, if the equilibrium isotherm, characterizing the system studied, is non-linear (see eq. (2)), then $R_i \neq \text{const.}$

Numerical methods, as a general rule, are used to the solution of eq. (1), but an analytical solution can be found in literature as well - e.g., Račinskij [1]. After its modification, we have obtained the eq. (3), parameters of which can be obtained experimentally:

$$A_{cal} = \frac{k \cdot d_p}{L} \exp \left[- \frac{(R - n_{PV})^2}{(4 \cdot R \cdot n_{PV} / Pe)} \right] \left(\frac{4 \cdot \pi \cdot R \cdot n_{PV}}{Pe} \right)^{0.5} \quad (3)$$

The meanings of the symbols of the eq. (3) are the following: $A_{cal} = C/C_0$, k - empirical constant, L - height of bed, n_{PV} - volume rate of flow expressed as number of pore volumes, Pe - Péclet number ($= u \cdot L / D$). This approach assumes the validity of linear sorption isotherm, i.e. $R = \text{const.}$ and thus it is limited, strictly speaking, to the case of isotope exchange systems and of some systems having very low concentrations of components.

Such limitation can be avoided using our simplified method based, in principle, on the following procedure: the experimental data are fitted by means of Newton-Raphson multidimensional nonlinear regression method [2], the regression function of which consists of eq. (3) and (4). The method uses Freundlich isotherm (eq. (5) and (6)) for the simulation of non-linear equilibrium isotherm assumed to be valid in the described system. Values of four parameters, namely, nF , kF , Pe , and $FitConst$ ($= k \cdot d_p / L$), are sought in the regression procedure.

$$R_{cal} = \left(1 + \frac{\xi}{\varepsilon} \cdot (nF \cdot kF \cdot (A_{cal} \cdot C_0)^{(nF-1)}) \right) \quad (4)$$

$$q = kF \cdot C^{nF}$$

$$(5) \quad f(C) = nF \cdot kF \cdot (A_{cal} \cdot C_0)^{nF-1} \quad (6)$$

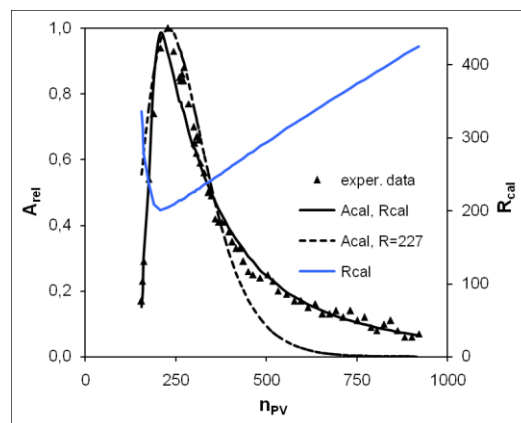
The code, PNLRPall1.fm (Program Package Stamb-2008), was constructed in software product FAMULUS [3].

EXPERIMENTAL

Experiments were performed applying the column technique ($L=7.2$ cm, radius = 2.1 cm, $u=0.18$ cm min⁻¹, $\xi=1.28$ g cm⁻³, $\varepsilon=0.504$ cm³ cm⁻³) with the bed of crushed diorite (0.25 - 0.80 mm). A synthetic ground water spiked with ¹³⁷Cs was used. The outflow from column was sampled and analyzed and the values of A_{exp} as a function of n_{PV} were obtained.

RESULTS

Experimental data obtained, $A_{exp} = f(n_{PV})$, and dependences, $A_{cal} = f(n_{PV})$ and $R_{cal} = f(n_{PV})$, calculated under both assumptions, i.e. $R \neq \text{const.}$ ($= R_{cal}$, eq. (4)) and $R = \text{const.}$ ($= 227$), are shown in the figure below. It is evident that very important differences were found between the assumptions and that the "simplified method" reflecting the non-linear type of equilibrium isotherms can be regarded as useful for the description of real systems.



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MODELING OF TRANSPORT OF ^{137}Cs AND ^{85}Sr IN FUCOIDIC SANDSTONE COLUMNS AND GROUNDWATER SYSTEM USING THE MODEL EQUATIONS BASED ON ERFC FUNCTION (INCLUDING LINEAR AND NON-LINEAR SORPTION/DESORPTION ISOTHERM APPROACH)

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INTRODUCTION

In this work, the models of equilibrium sorption and desorption dynamics based on the erfc-functions with incorporated non-linear equilibrium isotherms were used for fitting experimental data by means of Newton-Raphson non-linear regression method. The description of this work in detail can be found in [1].

EXPERIMENTAL

The sorption experiments with the undisturbed borehole samples (Nos 48118 and 48562) of fucoidic sandstones (5cm in diameter, 10 cm in height) were carried out separately for ^{137}Cs or ^{85}Sr . The spiked cenomanian background groundwater (CBW with concentration C_0) from a suitable large beaker (of several litres) was introduced at the bottom of columns (against gravity), by the use of multi-head peristaltic pump, with flow-rate of $4.4 \pm 0.2 \text{ mL h}^{-1}$ ($0.78 \pm 0.01 \text{ cm h}^{-1}$ water seepage velocity). After the input activity at the column outlet had been obtained, the beaker was filled with original CBW, which was used for desorption of a given cation at the same flow-rate. During each experiment, 5 mL aliquots were taken from the column effluent at certain time intervals and its activity was measured by a gamma counter (1480 Automatic Gamma Counter WIZARD 3 Perkin Elmer Precision) equipped with a NaI/Tl detector.

RESULTS

Theoretical sorption and desorption breakthrough curves, (BTC_S) and (BTC_D) , respectively, expressed as a dependance of relative output activity, $(A_{relS})_{\text{theor}}$ and $(A_{relD})_{\text{theor}}$, on the number of pore volumes, (n_{PVS}) and (n_{PVD}) , were fitted by equations (1a), (1b) and (2a), (2b), respectively. The equations of Freundlich type, (3a) and (3b), or their first derivatives, (5a) and (5b), were used for the calculation of retardation coefficients by Eqs (4a) and (4b), respectively. It is evident, that if exponent n_S or n_D converges to 1, then it deals with linear isotherm and as a result, the value of retardation coefficient is constant.

Eq. (1a) can be used directly until $(A_{relS})_{\text{theor}} \leq 0.5$, but for the calculation of $(A_{relS})_{\text{theor}} > 0.5$ the Eq. (1b) should be used. By analogy, Eqs (2a) and (2b) hold if $(A_{relD})_{\text{theor}} \geq 0.5$ and $(A_{relD})_{\text{theor}} < 0.5$, respectively.

$$(A_{relS})_{\text{theor}} = (A_{IS})_{\text{theor}}/A_0 = 0.5 \cdot \text{erfc}[(R_S)_{\text{theor}} \cdot n_{PVS} / (2 \cdot ((R_S)_{\text{theor}} \cdot n_{PVS} / Pe)^{0.5})] \quad (1a)$$

$$(A_{relS})_{\text{theor}} = (A_{IS})_{\text{theor}}/A_0 = 1 - \{0.5 \cdot \text{erfc}[-((R_S)_{\text{theor}} - n_{PVS}) / (2 \cdot ((R_S)_{\text{theor}} \cdot n_{PVS} / Pe)^{0.5})]\} \quad (1b)$$

$$(A_{relD})_{\text{theor}} = (A_{ID})_{\text{theor}}/A_0 = 1 - \{0.5 \cdot \text{erfc}[(R_D)_{\text{theor}} - n_{PVD}] / (2 \cdot ((R_D)_{\text{theor}} \cdot n_{PVD} / Pe)^{0.5})\} \quad (2a)$$

$$(A_{relD})_{\text{theor}} = (A_{ID})_{\text{theor}}/A_0 = 1 - \{1 - \{0.5 \cdot \text{erfc}[-((R_D)_{\text{theor}} - n_{PVD}) / (2 \cdot ((R_D)_{\text{theor}} \cdot n_{PVD} / Pe)^{0.5})]\} \} \quad (2b)$$

$$q = k_S \cdot C^{n_S} \quad (\text{for sorption}) \quad (3a)$$

$$q = k_D \cdot C^{n_D} \quad (\text{for desorption}) \quad (3b)$$

$$(R_S)_{\text{theor}} = 1 + (\rho/\theta) \cdot f'(C)_S \quad (4a)$$

$$(R_D)_{\text{theor}} = 1 + (\rho/\theta) \cdot f'(C)_D \quad (4b)$$

$$f'(C)_S = dq/dC = (n_S \cdot k_S \cdot ((A_{relS})_{\text{theor}} \cdot C_0)^{(n_S-1)}) \quad (5a)$$

$$f'(C)_D = dq/dC = (n_D \cdot k_D \cdot ((A_{relD})_{\text{theor}} \cdot C_0)^{(n_D-1)}) \quad (5b)$$

Symbols used in the equations denotes:

$(A_{relS})_{\text{theor}}$ – theoretical value of relative output activity of given component from the column; A_0 – experimental value of input activity of liquid phase, in cpm; $(A_{IS})_{\text{theor}}$ – theoretical value of output activity of liquid phase leaving the column in the course of sorption at time tS , in cpm; n_{PVS} ($= u \cdot tS/L$) – experimental value of number of bed pore volumes in the case of sorption at time tS ; tS – time of sorption experiment, in hours; $(R_S)_{\text{theor}}$ – theoretical sorption retardation coefficient; Pe – Péclet number ($= u \cdot L/D_d$) of the column (from the point of view of experimental conditions, it is supposed that the value of Péclet number is the same for both sorption and desorption); u – water seepage velocity, in cm h^{-1} ; L – length of the bed in the column, in cm; D_d – hydrodynamic dispersion coefficient, in $\text{cm}^2 \text{h}^{-1}$; q and C – total concentration of given component (CsNO_3 or $\text{Sr}(\text{NO}_3)_2$) in solid, in mmol g^{-1} , and in liquid, in mmol mL^{-1} , phase, respectively; C_0 – starting concentration, in mmol mL^{-1} ; ρ – bulk density, in g cm^{-3} ; θ – porosity, in $\text{cm}^3 \text{cm}^{-3}$. Index S denotes sorption and index D denotes desorption.

$WSOS/DF$ quantity was used as a fitting criterion [1]; the agreement is acceptable if $0.1 \leq WSOS/DF \leq 20$. The values of parameters obtained in the course of regression procedure are summarized in the table below. According to values of $WSOS/DF$, a fairly good agreement has been found between experimental and theoretical sorption/desorption BTCs data. It is evident that if only the sorption part should be described, the linear isotherm approach (see n_S values) can be found as the best solution.

Parameters	^{137}Cs 48118	^{137}Cs 48562	^{85}Sr 48118	^{85}Sr 48562
$k_S [\text{mL g}^{-1}]$	5.24	1.72	1.80	0.78
n_S	0.99	1.00	1.00	1.02
$(R_S)_{\text{thero}}$	42-44	12-13	14	4-5
$k_D [\text{mL g}^{-1}]$	0.17	0.13	0.14	0.10
n_D	0.75	0.80	0.81	0.84
$(R_D)_{\text{theor}}$	28 - 49	12 - 21	12 - 25	5 - 11
Pe	16.10	7.94	13.50	11.40
$WSOS/DF$	2.16	0.97	1.67	1.34

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URANIUM (VI) SULFATE COMPLEXATION AS A FUNCTION OF TEMPERATURE STUDIED BY TRLFS

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INTRODUCTION

Time-resolved laser-induced fluorescence spectroscopy (TRLFS) has become widely used to direct studies of uranium (VI) complexation. To optimize the resolving capabilities of our TRLFS setup, a speciation study was performed on the system of $\text{H}_2\text{O}-\text{UO}_2^{2+}-\text{SO}_4^{2-}-\text{NaClO}_4$, namely, by varying sulphate concentration ($c = 4 \times 10^{-4} - 7.5 \times 10^{-1} \text{ M}$) at fixed pH ($\text{pH} = 2$), uranium concentration ($c = 1 \times 10^{-5} \text{ M}$), ionic strength ($I = 1$), and at two temperatures ($T = 293.15$ and 298.15 K). The complexation reactions taking place in our system can be generally formulated as follows: $\text{UO}_2^{2+} + n\text{SO}_4^{2-} \leftrightarrow \text{UO}_2(\text{SO}_4)_n^{(n-2n)+}$ ($n = 1, 2, 3$). An estimate of corresponding stability constants from the measured species distribution is the goal of this study.

EXPERIMENTAL

The TRLFS measurements were carried out in 3.5 mL quartz cell under constant temperature maintained with a precision of $\pm 0.05^\circ \text{C}$. With the repetition rate of 10 Hz, the sample was excited by 4 ns laser pulses of the wavelength 266 nm and of the energy 12.5 mJ (VIBRANT™ Tunable Laser System). The laser output energy was monitored by a laser energy meter (FieldMaxII-P™). Fluorescence emission, perpendicular to the laser beam, was focused by two lenses on the entrance slit of a monochromator (MS257™). The emission spectra were recorded in the 438 – 609 nm (600 lines mm^{-1} grating) range using the ICCD camera (Andor iStar), whose logic circuits were synchronized with the laser pulses. For each sample, the time delay was varied in the time interval of 0.18 – 124.68 μs in 0.5 μs steps; the whole system was controlled by a PC.

RESULTS

As for the TRLFS measurements, we were able to identify, together with the free uranyl UO_2^{2+} , all relevant uranium-sulphate complexes, namely, UO_2SO_4 , $\text{UO}_2(\text{SO}_4)_2^{2-}$, $\text{UO}_2(\text{SO}_4)_3^{4-}$. Because the main emission wavelengths of these uranium-sulphate complexes are very similar, it was possible to identify fluorescing species only by their lifetimes. The measured lifetimes of UO_2^{2+} and $\text{UO}_2(\text{SO}_4)_2^{2-}$ fall into the confidence intervals of the respective lifetimes published in [1]. On the other hand, the lifetime confidence intervals of $\text{UO}_2(\text{SO}_4)_2^{2-}$ and $\text{UO}_2(\text{SO}_4)_3^{4-}$ do not overlap with published data [1], they are shifted down by about 0.5 μs . This can be attributed to a possible lifetimes sensitivity to experimental conditions used rather than to any measurement error. The uncertainties in the measured fluorescence intensities of the species are relatively high, up to 20% in the sulfate concentration range of $10^{-2} - 10^{-1} \text{ M SO}_4^{2-}$ (Fig. 1A). As for the calculation of stability constants, namely, $\beta_1 = [\text{UO}_2\text{SO}_4]/([\text{UO}_2^{2+}][\text{SO}_4^{2-}])$, $\beta_2 = [\text{UO}_2(\text{SO}_4)_2^{2-}]/([\text{UO}_2^{2+}][\text{SO}_4^{2-}]^2)$, and $\beta_3 = [\text{UO}_2(\text{SO}_4)_3^{4-}]/([\text{UO}_2^{2+}][\text{SO}_4^{2-}]^3)$, the Newton-Raphson regression procedure was used for fitting the concentrations of U(VI) species determined experimentally (see Figs 1B and 1C). The goodness-of-fit was evaluated by criterion

$WSOS/DF$ [2]; it holds: if $WSOS/DF \leq 20$, then there is a good agreement between experimental and calculated data.

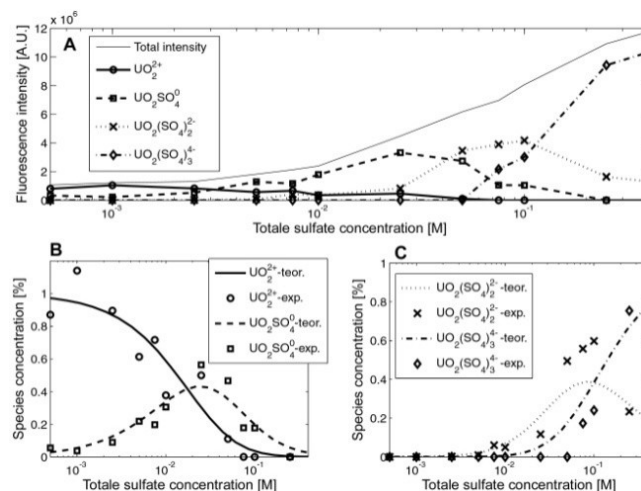


Fig. 1. Distribution of uranium species as a function of the total sulphate concentration. **A:** measured fluorescence intensities; **B** and **C:** experimental and calculated species concentrations.

Tab. 1. Logarithmic values of stability constants, β_1 , β_2 , and β_3 , at two different temperatures and ionic strengths, $I = 1$ (experimentally determined) and $I = 0$.

Stability constants	$\log \beta_1^0(T)$	$\log \beta_2^0(T)$	$\log \beta_3^0(T)$	$\log \beta_1^0(T)$	$\log \beta_2^0(T)$	$\log \beta_3^0(T)$
$T [^\circ \text{C}]$	20			25		
$I = 1$	1.90	3.33	4.47	2.32	3.75	4.11
$I = 0$	3.18 ^{ex}	4.61 ^{ex}	4.13 ^{ex}	3.61 ^{ex}	5.04 ^{ex}	3.77 ^{ex}
$I = 0$	3.08 ^{ab}	4.03 ^{ab}	2.86 ^{ab}	3.14 ^a	4.14 ^a	3.02 ^a
WSOS/DF	30.50			23.60		

^{ex} values obtained from experimental data using SIT method; ^a taken from TDB NEA; ^{ab} TDB NEA values converted by means of Van't Hoff equation

The values of quantities mentioned above are summarized in Table 1 – it is evident, that the uncertainties not only in the fluorescence intensities, but also in stability constants calculations (see WSOS/DF) are relatively high. From the comparison of individual β_i -values it can be concluded as follows: (i) β_1 and β_2 values increase with increasing temperature in all cases, which holds also for DTB NEA β_3 , (ii) experimental and SIT values of β_3 have the opposite trend, (iii) the SIT (i.e. experimental at $I = 0$) values are greater than DBT NEA values by 20% in average.

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THE FACTOR ANALYSIS (COUPLED WITH SPECIATION COMPUTATION) OF TIME SERIES AS A TOOL FOR THE ANALYSIS OF SPECTRA FROM THE TIME-RESOLVED LASER FLUORESCENCE SPECTROSCOPY

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INTRODUCTION

The aim of this work was to design an optimal method for emission spectrochemical analysis of time resolved spectra. The method was supposed to fulfil the following requirements: 1. to be based on the factor analysis; 2. to be applicable for the system composed of two, three or four components; 3. to provide as the output: (i) the spectra of individual species (Z_{lm}), (ii) the fluorescence lifetimes (τ_{km}), and (iii) stability constants (β_m) of individual species.

EXPERIMENTAL

The following four methods were considered: 1. factor analysis of the time series (FATS); 2. factor analysis coupled with speciation computation (FACSC); 3. the FACSC-method alternate for „long columns“ (FACSCCL); 4. factor analysis of time series coupled with the speciation computation (FATSCSC).

The analysed fluorescence data can be ordered into a multidimensional array which is known as a rank 3 tensor $T(l,i,k)$, (Fig.1). The indexes l , i , k denote emission wavelength λ_l , delay between the excitation pulse and the beginning of signal accumulation t_i , and the total sulfate concentration $c_{S,k}$, respectively. The methods FATS and FACSC analyse tensor $T(l,i,k)$ for one fixed index. The method FATS fixes the concentration index k , $Y(l,i) \equiv T(l,i,k)$, and the method FACSC fixes the time delay index i (usually $i = 1$), $Y(l,k) \equiv T(l,i,k)$. The methods FATSCSC and FACSCCL re-order $T(l,i,k)$ into a matrix Y . The FATSCSC method re-orders the kinetic series one-after-another $Y(l,n(i,k)) \equiv T(l,i,k)$, and the FACSCCL method analyses the matrix, columns of which are formed by time-resolved spectra (instead of spectra for fixed delay as in the other methods, $Y(n(l,i),k) \equiv T(l,i,k)$). All methods mentioned normalize and subsequently decompose the matrix Y by means of the singular value decomposition ((Nm)SVD). Several significant components of (Nm)SVD are subsequently fitted to the model of the fluorescence signal ($Y^{(sig)}$) providing the requested outputs, Z_{lm} , τ_{km} , β_m . The method FATS gives only Z_{lm} , τ_{km} , and FACSC gives only Z_{lm} , β_m . The other two methods provide all outputs. The method FATSCSC shall be used if the fluorescence life-times of individual species varies with $c_{S,k}$, but the fluorescence spectra of individual species are constant with respect to both t_i and $c_{S,k}$. In this case, the decay of the fluorescence signal is either exponential or is described by a known model. On the other hand, the FACSCCL method is designed for the situation when parameters of the time-dependence of the decay of fluorescence signal of individual species are constant with respect to $c_{S,k}$, but there is not a known model of the time dependence, and the fluorescence spectra of individual species can vary with t_i . The uncertainties of fitted parameters were determined by means of the support plane analysis method.

RESULTS

The methods used were tested both on the simulated data generated using a mathematical model of the fluorescence data and on real data measured in our laboratory. The uranyl-sulfate-aquatic system (UO_2^{2+} - SO_4^{2-} - H_2O) was chosen for both data categories.

The validation of the methods was executed using the simulated data. The method FATSCSC is very robust and trustful method up to the noise level observed in the experimental data ($a \in (10; 30)$). The method FACSCCL is relatively robust as well ($a_{crit} > 30$), a critical value a_{crit} for the FATS method was estimated to be $a_{crit} \approx 10$. The validation of the FACSC has not been finished yet.

The real data (series of 35 solutions, $\text{pH} = 2$, $I = 0.3$, $T = 18^\circ\text{C}$, $c_S \in (10^{-5}, 10^{-1}) \text{ mol dm}^{-3}$) were analyzed with the following results:

1. All methods give results qualitatively consistent both among each other and with literature
2. While the fluorescence lifetimes τ_{km} acquired by individual methods are in good agreement both among each other and with the literature data, the differences among values of common logarithms of the stability constants ($\log \beta_1$, $\log \beta_2$) obtained by methods used are significant ($\log \beta_1 \in (1.1; 2.5)$; $\log \beta_2 \in (2.1; 3.9)$). The discussion of the latter results, including the comparison with the literature data, is being prepared.

$$Y(l,i) = \sum_{j=1}^b W_j V_{ij} U_{ij} + \sum_{j=b+1}^{\min(l,i)} W_j V_{ij} U_{ij}$$

signal noise

model generality ↑

$T(l,i,k)$ → $Y(l,i)$ (k = fix) → FATS

$T(l,i,k)$ → $Y(l,k)$ (i = fix) → FACSC

$T(l,i,k)$ → $Y(l, n(i, k))$ → FATSCSC

$T(l,i,k)$ → $Y(n(l, i), k)$ → FACSCCL

$$\chi^2_{MLE} \equiv \sum_{i=1}^s \sum_{j=1}^b \frac{\left(\sum_{m=1}^b C_{im}^{(mod)} R_{mj} - V_{ij} W_j \right)^2}{\sigma_{ij}^2} + \sum_{i=1}^s \sum_{j=1}^b \ln(\sigma_{ij}^2)$$

$$C_{im}^{(mod)} = C_m^{(mod)}(c_{S,i}, \zeta_m, \tau_{m(k)}, \beta_m)$$

Fig. 1. Diagram of the methods used. U is a matrix of subspectra of the same size as Y , V is an orthogonal matrix of loadings, and W_j are non-negative numbers ordered by decreasing values. The b denotes number of supposed individual independent species in $T(l,i,k)$. The χ^2_{MLE} criterion is minimized with respect to the parameters R_{mj} , μ_m or ζ_m , τ_m or $\tau_{m,k}$, β_m .

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DETERMINATION OF $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$ COMPLEX CHARACTERISTICS BASED ON THE EVALUATION OF FLUORESCENCE SPECTRA OBTAINED BY TRLFS

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INTRODUCTION

In studying the migration of uranium in localities where increased incidence is observed, it is important to monitor the forms of its existence - speciation. The methodology of differentiated time resolved laser fluorescence spectroscopy (TRLFS) allows to study the forms of uranium. Here we focused on the study of molecular forms of $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$, which are significantly present in natural waters with a pH range from 7 to 8. The impulse for this work was interest in studying the uranium migration in the Ruprechtov area, which is taken as a natural analogue of a permanent deposition of highly radioactive waste in sedimentary rocks.

EXPERIMENTAL

Tunable laser system based on flash lamp pumped Q-switched Nd:YAG laser was used as the fluorescence excitation source (repetition rate 10 Hz, pulse length < 2 ns). The fourth harmonic generation (wavelength of 266 nm) of the basic laser wavelength (1064 nm) was used for sample excitation. Measurements were performed at the temperature in the range of 13–20°C of the studied solution. Emitted fluorescence was detected using monochromator and imaging spectrograph. The focus of the work consisted of evaluating total intensities of fluorescent signal corresponding to the observed form for sets of solutions, whose composition differed mainly in the calcium concentration.

RESULTS

Total intensities of fluorescent signals corresponding to the reference form for sets of solutions, whose composition differed mainly in the calcium concentration, were evaluated. The time evolution of $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$ fluorescence spectral characteristic is illustrated in Fig. 1. The dependence of fluorescence intensity on the solution temperature for concentration $c(\text{Ca}^{2+}) = 1 \times 10^{-3} \text{ mol L}^{-1}$ is presented in Fig. 2. Fluorescence intensity dependence on temperature for different concentrations is shown in Fig. 3.

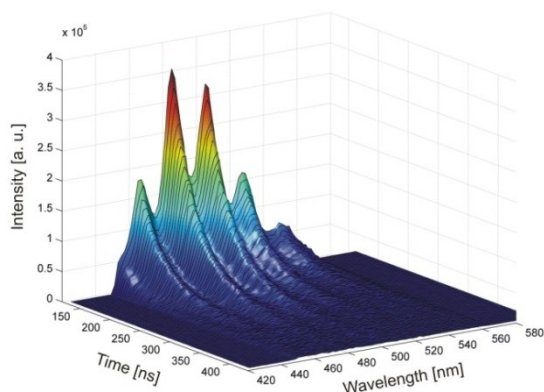


Fig. 1. Time evolution of $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$ fluorescence spectral characteristic.

The equilibrium reaction constant was determined for two temperatures relative to the zero ionic strength. Results were obtained by evaluating ratios of fluorescent signals corresponding to the solutions of different Ca^{2+} concentration by method based on speciation calculations in PHREEQC program; HATCHES database was used. The value of the logarithm of $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$ stability constant was determined as 30.65 ± 0.45 for 20°C and 31.43 ± 0.25 for 13°C. As well the complex stability constant for temperature of 25°C was determined ($\log K_0 = 30.1 \pm 0.3$, what is in agreement with literature data [1]) and standard reaction enthalpy ($\Delta H^\circ = 179.3 \text{ kJ mol}^{-1}$).

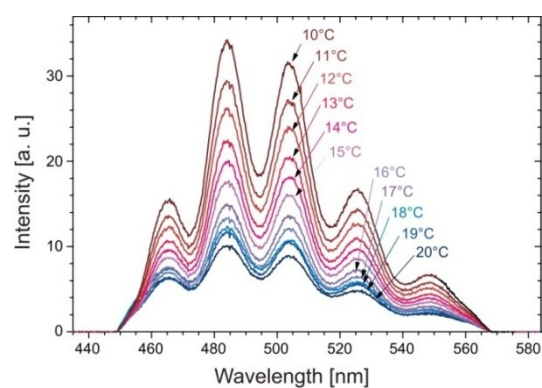


Fig. 2. Dependence of fluorescence intensity decrease of $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$ on the solution temperature, $c(\text{Ca}^{2+}) = 1 \times 10^{-3} \text{ mol L}^{-1}$

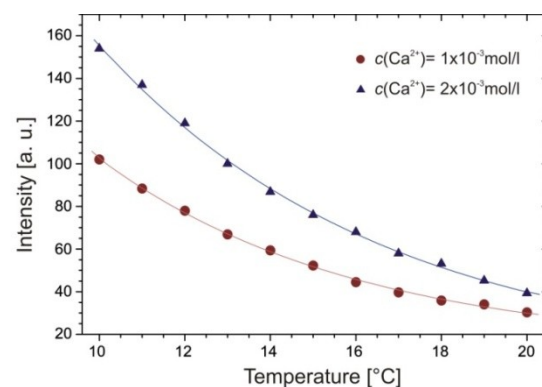


Fig. 3. The comparison of dependences of $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$ fluorescence intensity decrease on the temperature for solutions with concentration $c(\text{Ca}^{2+})$ equal to 1×10^{-3} and $2 \times 10^{-3} \text{ mol L}^{-1}$.

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SPECIATION OF URANYL-SULFATE COMPLEXES STUDIED BY UV-VIS ABSORPTION SPECTRA DECOMPOSITION

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INTRODUCTION

Considerably broad attention has been paid to the use of UV-VIS absorption spectrometry for study of complexes formation and stability constants determination during last years. Especially in a case of U(VI), where Hennig et al. [1] used UV-VIS spectroscopy for the study of U(VI)–SO₄²⁻ system at constant total uranium concentration [UO₂²⁺] = 50 mM and gradually increasing ratio [SO₄²⁻]/[UO₂²⁺] from 0 up to 59. Similar system was studied by Meinrath et al. [2] at pH interval 3.12 – 3.78. The subject of our work [3] was to extend the study of UV-VIS absorption spectra of a system similar to that one studied by Hennig et al. [1] with following aims: (i) To specify the speciation modelling of systems characterized by high values of ionic strength using the SIT theory. (ii) To develop an evaluation method enabling to perform the deconvolution of absorption experimental spectra onto the spectra of individual species and the determination of thermodynamic stability constants (valid for zero ionic strength).

EXPERIMENTAL

A series of UO₂(NO₃)₂·6H₂O and Na₂SO₄ solutions in distilled water was prepared for U(VI) - SO₄²⁻ - NO₃⁻ species absorption spectra determination (RS solutions, further called sulphate-nitrate system). Total uranium concentration [U(VI)] = 5·10⁻² mol·L⁻¹ and pH value pH = 2 were constant in these solutions. Twenty five solutions of different Φ_S = [SO₄²⁻]/[U(VI)] within the range from Φ_S = 0 up to Φ_S = 17.6 were prepared. Due to the additions of HNO₃ used for pH correction, the ratio Φ_N = [NO₃⁻]/[U(VI)] varied from 2.20 up to 3.04 in RS solutions. To estimate the influence of nitrate U(VI) complexes on RS solutions spectra another series of sulphate-free eight RN solutions containing UO₂(NO₃)₂·6H₂O and NaNO₃ was prepared for spectrophotometric measurements, in which pH and [U(VI)] were the same as in RS samples and Φ_N was varying from Φ_N = 2.18 up to 60.20.

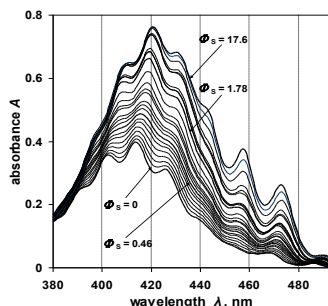


Fig. 1. Absorption spectra of RS solutions (sulphate-nitrate system) for different Φ_S = [SO₄²⁻]/[U(VI)] values.

Absorption spectra were recorded using UV/VIS spectrophotometer CARY 100 within the wavelength range of 190 – 900 nm at scan rate 500 nm·min⁻¹ and plastic cuvettes of 1 cm path-length were used. The parts of RS spectra selected for calculations are given in Fig. 1.

RESULTS

The speciation of U(VI) in RN solutions and RS solutions was calculated. Stability constants at zero ionic strength $\beta_{i,I=0}$ available in literature were recalculated to $\beta_{i,I}$ values at actual ionic strength I according to the equation (1), that follows from the Special Ion Interaction Theory (SIT).

$$\log \beta_{i,I} = \log \beta_{i,I=0} + \Delta z^2 \cdot D - \Delta \epsilon \cdot I \quad (1)$$

There, $D = 0.5091 \sqrt{I} / (1 + 1.5 \sqrt{I})$ stands for the so called Debye-Hückel term, Δz^2 is the sum of squares of charges of individual components in the respective complexation reaction, and $\Delta \epsilon$ is the sum of coefficients reflecting the mutual interaction of respective ions. The method of decomposition of overall spectra is based upon the assumption of Lambert – Beer's law applicability for each uranyl species present in the solution. In the way of evaluation of a system of m absorption spectra of solutions with the constant value of the uranium concentration, the total absorbance $A_{\text{exp},\lambda,j}$ at the wavelength λ corresponding to the total uranium concentration C_U in the j -th solution can be expressed as the sum of contributions corresponding to the all uranium species present in the solution according to the equation (2).

$$A_{\text{exp},\lambda,j} = \sum_{i=1}^n x_{ji} a_{\lambda i} \quad \text{for } j = 1, 2, \dots, m \quad (2)$$

Here x_{ji} represents the molar fraction of the i -th uranium species in the j -th solution and $a_{\lambda i}$ the absorbance of pure species i for the concentration C_U at the wavelength λ . As values x_{ji} can be determined by a speciation calculation and $A_{\text{exp},\lambda,j}$ is measured absorbance, the determination of values $a_{\lambda i}$ from the system of linear equations (2) represents a basic step to the deconvolution of measured spectrum onto the spectra of individual species. System of equations (2) for $m > n$ was solved by means of a least square method using simple matrix algorithms. This way the deconvolution of spectra was performed. The fitting of original experimental spectra by modelled overall absorbance spectra computed backward from partial spectra of individual species enabled to discuss values of stability constants $\beta_{i,I=0}$ used for the determination of speciation in studied solutions. Determined stability constants of UO₂SO₄, UO₂(SO₄)₂²⁻, UO₂NO₃⁺ and UO₂(NO₃)₂ coincided well with published data, but those for UO₂(SO₄)₃⁴⁻ and UO₂(NO₃)₃⁻ were significantly lower.

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DIFFUSION OF CESIUM THROUGH THE COMPACTED BENTONITE

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INTRODUCTION

A safety analysis of the disposal system requires the values of the migration parameters of radionuclides in the clay and compacted bentonite. Several types of migration experiments are used to determine these parameters, the through-diffusion being the dominated type of them [1]. The usual ways of determination of diffusion coefficients of radionuclides in the plug of a barrier material are based on analytical solutions of the diffusion equation for specific boundary conditions. The use of small volumes of inlet and/or outlet reservoirs, which seems to be convenient from a practical point of view, requires either a demanding laboratory procedure keeping as close as possible the ideal shapes of boundary conditions or a numerical solution of transport of the studied nuclide in the system. The numerical solution including balancing in all parts of the system (plug of compacted bentonite, filters, and reservoirs) can respect the real shape of boundary conditions and extends then the possibilities of experiment evaluation. Such approach was used in our work [2], in which the diffusion of non-reacting species (HTO and Cl⁻) through the layer of compacted bentonite was successfully evaluated using own code prepared with the use of the GoldSim Contaminant Transport Module.

EXPERIMENTAL

A set of long-term diffusion experiments was finished in our laboratory this year. Study of diffusion of cesium through the block of compacted Ca/Mg bentonite of the Czech origin (site Rokle) was focused on the influence of (i) bentonite compaction and (ii) cesium concentration in the input reservoir. The results of the study of bentonite compaction are presented here. Diffusion cells, in which relatively high thickness of ceramic filters (5 mm) comparing with thickness of the bentonite plug (15 mm) was used, were directly connected to both input and output reservoirs. The volumes of liquid phases in reservoirs were 140 mL for experiment C (dry density of bentonite $\rho = 1.6 \text{ g mL}^{-1}$) and 185 mL for experiment D ($\rho = 1.2 \text{ g mL}^{-1}$), volume of the bentonite plug was 10.7 mL in both diffusion cells used. The 0.1 M calcium nitrate solution of pH 7.5 adjusted with NaOH was prepared as a basic solution for all containers. The initial 0.01 molar concentration of CsCl, spiked with ¹³⁷Cs, was used in input containers. Time change of cesium concentration in all four containers was measured radiometrically. The concentration profile of cesium in the bentonite layer at the end of the experiments was determined by measurement of ¹³⁷Cs activity in thin bentonite slices of weight about 0.2 g.

RESULTS

The results of the diffusion experiments are presented in Figs. 1 and 2. The greater change of cesium concentration in the output container for experiment D corresponds to the lower compaction of the bentonite in this experiment in comparison with experiment C. Both more rapid decrease of activity in the input container and lower activity in the bentonite plug corresponding to experiment C can be

explained by lower volume of containers used in experiment C in comparison to experiment D.

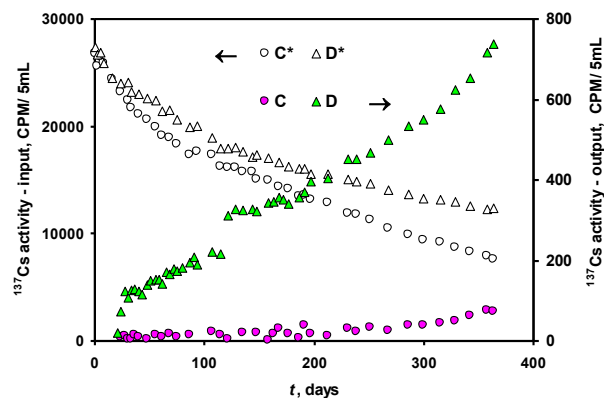


Fig. 1. Change of ¹³⁷Cs activity in input (C*, D*) and output reservoirs (C, D). Experiment C: bentonite dry density $\rho = 1.6 \text{ g mL}^{-1}$; experiment D: $\rho = 1.2 \text{ g mL}^{-1}$.

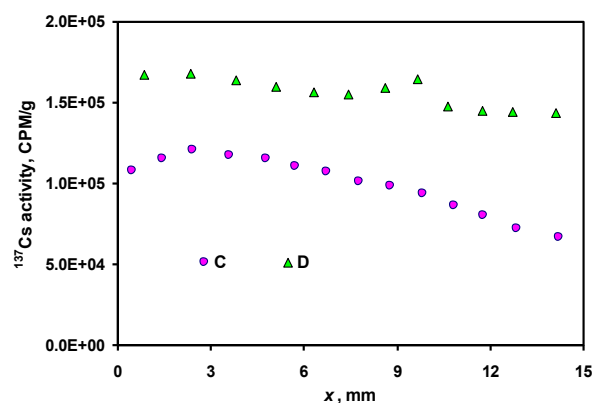


Fig. 2. Measured activity profiles in bentonite plugs at the end of the diffusion experiments.

The unexpectedly low decrease of ¹³⁷Cs activity in the profiles of bentonite plugs can be explained by the strongly non-linear character of the cesium interaction with the bentonite surface that was observed also in our previous work [3], and by the presence of relatively thick filters that influence the diffusion transport. The determination of the diffusion coefficients by the prepared numerical treatment on experimental data obtained was not able as the code does not respect properly the non-linear character of sorption.

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This research has been supported by the Ministry of Education of the Czech Republic under contract No. MSM 6840770020 and by the Ministry of Industry and Trade of the Czech Republic under contract No. 1H-PK/25.

MODELLING OF TROUGH-DIFFUSION EXPERIMENTS USING PHREEQC2: INCLUSION OF THE CHARACTERIZATION OF URANYL SORPTION ON MESOPOROUS SILICA MCM-41 BY A SURFACE COMPLEXATION MODEL

D. Vopálka, K. Štamberg

INTRODUCTION

The diffusion experiments in standard configurations (e.g., through-diffusion and in-diffusion) are used for the determination of parameters necessary for the modelling of diffusion transport in porous media. The methods of evaluation of such experiments are based on analytical solutions of diffusion equation for appropriate initial and boundary conditions (e.g. [1]). As PHREEQC2 enables to model one-dimensional multicomponent transport, we have made an attempt to model the diffusion transport in the configuration of a standardized diffusion experiment with a non-trivial description of interaction. Our previous study of U(VI) interaction with highly sorbing mesoporous silica type of MCM-41 [2] lends to us an instrument for such study.

EVALUATION OF BATCH EXPERIMENTS

The method based on the classical batch technique [2] was used for the determination of the input data needed to the modelling of diffusion through the bed of MCM-41. The non-electrostatic model (CEM) was used for the description of sorption. The surface acidity constants and the total site density (ΣXOH) were obtained by fitting of acid-base titration data. The values of surface complexation constants, for five surface reactions assumed, were determined by fitting of sorption dependences on pH. The specific surface area, SP, was determined by means of BET method.

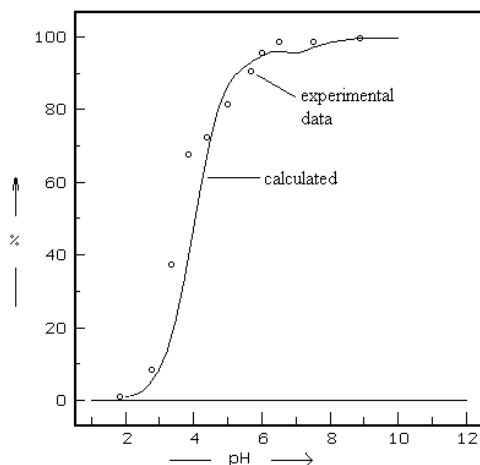


Fig. 1. Percentage sorption of U(VI) on MCM-41 in the absence of carbonates ($I = 0.01$).

From Fig.1 it can be seen that, in the absence of carbonates, sorption of U(VI) strongly increases in the pH interval from 3 to 6 and then remains constant. In the presence of carbonates the sorption decreased at $\text{pH} > 5$.

RESULTS

The evaluation of diffusion experiments in the standard through-diffusion configuration enables to estimate both the basic characteristics of diffusion, namely, the effective diffusion coefficient D_e , and the apparent diffusion

coefficient D_a . We modelled such experiments for the porous layer containing sorbent MCM-41 using the data described above with the aim to analyze the influence of interaction model on the values of D_e and D_a .

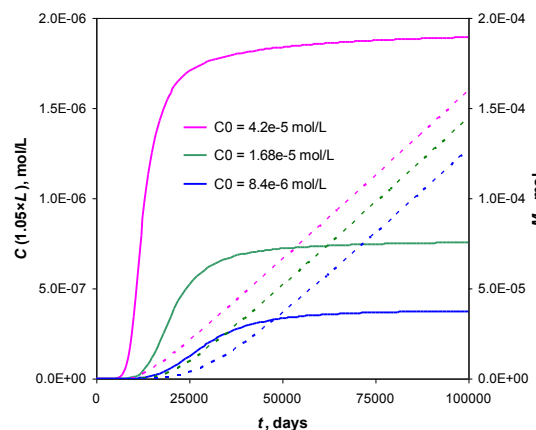


Fig. 2. Modelling of three experiments of uranium through-diffusion in the absence of carbonates at pH 6 in a layer containing MCM-41 sorbent of 10 cm length (L): uranium concentrations (full lines - C) in the output filter and total mass (dotted lines - M_r) diffused through the layer.

The results presented in Fig. 2 demonstrate the behaviour of the model used. The integral value of all U(VI) species in liquid phase (M_r) in the boundary filter gives the total U(VI) diffused through the body. This quantity enables to determine the value of effective diffusion coefficient D_e from the slope of the function $M_r = f(t)$. The transformation of the concentration measured in the boundary filter into quantity M_r further enables to determine the value of apparent diffusion coefficient D_a , which comprises the retardation of the diffusion transport due to the sorption. D_a was determined from the results of modelled experiments of the through-diffusion by means of time-lag method using the relation $D_a = L^2/6T$. Here L is width of the body of the porous material and T is time corresponding to the intersection of t -axis with the asymptote to total mass diffused. From the results presented in Fig. 2 it can be concluded that the D_a value decreases with the fall of the input concentration, as quantity T increases with the decrease of input concentration. The sorption isotherm for the modelled system is consequently non-linear and the K_d values decrease with the increase of equilibrium concentration in the liquid phase.

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This research has been supported by the Ministry of Education of the Czech Republic under contract No. MSM 6840770020 and by RAWRA Czech Republic.

STOCHASTIC MODELLING OF RADIONUCLIDE TRANSPORT IN THE NEAR-FIELD REGION OF A HIGH LEVEL NUCLEAR WASTE REPOSITORY

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INTRODUCTION

A modified model of processes that occur in a deep geological repository was developed using the GoldSim computer code [1]. This model includes radioactive decay and ingrowth in the canister and in the bentonite buffer, solubility limitation of the concentration of studied nuclides in the void volume of the canister with spent nuclear fuel, and diffusive migration of radionuclides through the surrounding bentonite layer controlled by their sorption on bentonite and by the output boundary condition formulated with respect to the rate of the water flow in the rock. Own model of radionuclides release from the fuel matrix, congruently with UO_2 matrix dissolution controlled by diffusion transport and solubility limitation of uranium, was developed. Parametric studies with this model helped to understand the role of selected parameters of the near-field region of the final repository. The probabilistic simulation environment of the GoldSim code [2] enabled to intensify such studies.

EXAMPLES OF PROBABILISTIC SIMULATIONS

The first probabilistic study performed analyzed the influence of the uncertainty of three selected parameters on the time dependent probability distribution functions of the release rates of activities of selected critical radionuclides and of the total activity released from the near-field region into the rock environment. One canister with approx. 1 tU of spent VVER-440 fuel in standard scenario described in [1] was selected as the source term. Results presented here demonstrate the influence of (i) uncertainty in K_d value describing interaction of uranium with bentonite (represented by log-normal distribution; minimum $0.1 \text{ m}^3 \text{ kg}^{-1}$, median $0.2 \text{ m}^3 \text{ kg}^{-1}$, geometric standard deviation equal 40, maximum $10 \text{ m}^3 \text{ kg}^{-1}$) and (ii) uncertainty of time of canister failure t_K (Weibull distribution; minimum 100 years, mean 1100 years, shape factor 1.8). The presentation of results of probabilistic simulations, in which Latin hypercube sampling for about 500 realizations was used, was formalized by plotting the selected percentiles of the set of time histories.

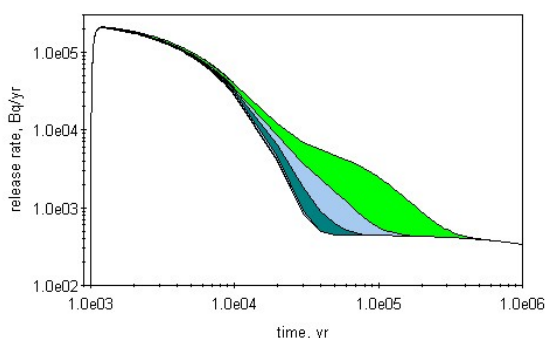


Fig. 1. Influence of uncertainty of uranium K_d on the probability density function of ^{135}Cs activity release, $t_K = 1000$ years.

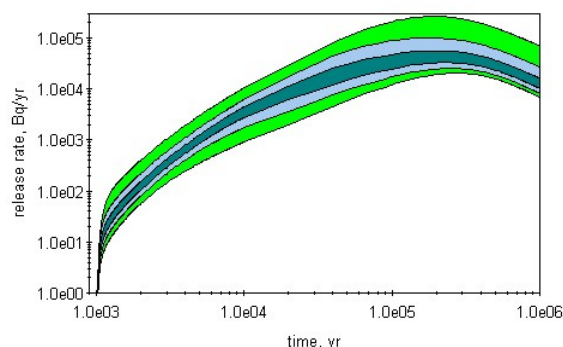


Fig. 2. Influence of uncertainty of uranium K_d on the probability density function of ^{226}Ra activity release, $t_K = 1000$ years.

Percentiles presented in Figs. 1-3 are as follows: $Q_{0.95} - Q_{0.05}$ green areas, $Q_{0.75} - Q_{0.25}$ gray areas, $Q_{0.60} - Q_{0.40}$ dark areas. The probabilistic approach, that we used, confirmed its marked advantage [3], which lies in the explicit representation of parameter uncertainty. Serious problem of this approach, difficult to solve, is the necessity to obtain the appropriate density functions for each parameter prior to the stochastic modelling.

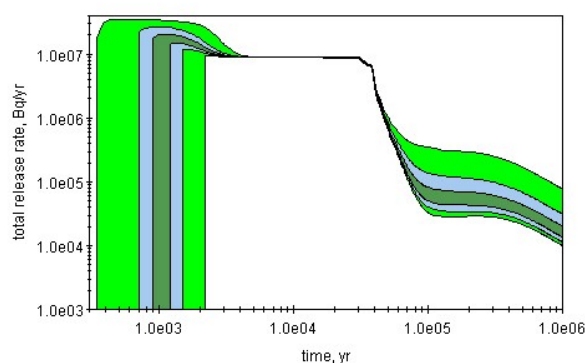


Fig. 3. Influence of uncertainties of uranium K_d and t_K on the probability density function of total activity release on the boundary bentonite buffer – rock.

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THE LIQUID EXTRACTION OF MINOR ACTINIDES WITH CyMe₄-BTBP IN SELECTED DILUENTS

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INTRODUCTION

One of the contemporary issues connected with the spent nuclear fuel is its reprocessing. Partitioning and transmutation (P&T) gives possibilities how to solve this problem and the main goals of P&T are decreasing the time and the volume needed to store HAW, and reduction of a hazard associated with spent fuel [1]. The CyMe₄-BTBP has been demonstrated to be a prospective extractant for the liquid-liquid extraction of minor actinides. This extractant in cyclohexanone has useful values of the distribution ratios and separation factor, and also fast kinetics. However, cyclohexanone is partially miscible with water. The main purpose of this study was to find a better suitable diluent based on cyclohexanone derivatives.

EXPERIMENTAL

As an extractant, CyMe₄-BTBP (6,6'-bis (5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-1,2,4-benzo-tri-azin-3-yl)-2,2'-bipyridine) [2] in different cyclohexanone derivatives was used. Nitric acid of different concentrations was spiked with ¹⁵²Eu and ²⁴¹Am stock solutions. 1 mL of the aqueous phase was contacted with 1 mL of the solvent for 6 hours using an orbital shaker. After the contact, the phases were separated by centrifugation and then samples from each phase were taken for γ -measurement with HPGe detector.

RESULTS

No extraction by any neat alkylated cyclohexanone was observed, although both D(Am) and D(Eu) in neat cyclohexanone are approximately 0.06. No volume changes were seen either.

Solubility of CyMe₄-BTBP in diluents with long alkyl-group in position 2 plus one additional methyl group (for example menthone) was very low.

It was seen that the position of the substituent is more important for the extraction properties than the number of alkyl groups and length of the substituent in the molecule. Extraction properties of the tested diluents are presented in Fig. 1.

The substituents in position 2 seem to be responsible for the bad kinetic properties (regardless of the type of the alkyl group) and the cyclohexanone derivatives with more alkyl chains generally cause rather slow kinetics. Kinetics results are shown in Fig. 2.

CONCLUSIONS

It has been shown that the alkylated cyclohexanones are promising diluents for the partitioning of the minor actinides from lanthanides by CyMe₄-BTBP; 3-methyl-cyclohexanone was found to have the optimum properties compared with the other cyclohexanone derivatives.

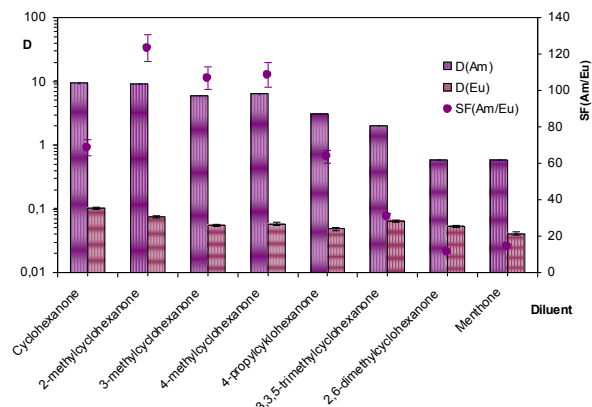


Fig. 1. Influence of the position and number of alkyl group(s) on ¹⁵²Eu and ²⁴¹Am extraction from 4M HNO₃ (organic phase: 5 mM CyMe₄-BTBP in mentioned diluent. Radionuclides: ¹⁵²Eu and ²⁴¹Am. Contact time 6 hrs.

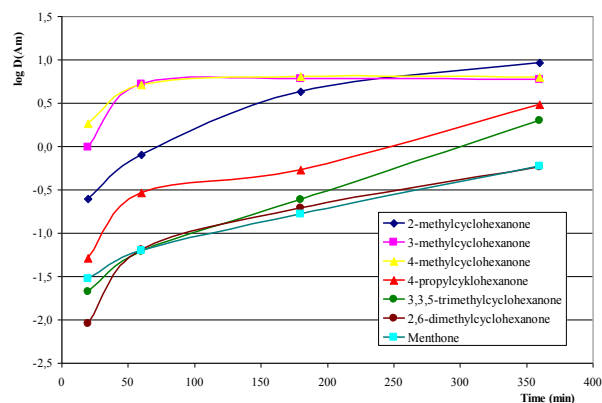


Fig. 2. Kinetic behavior of CyMe₄-BTBP in different diluents; the same conditions as reported in Fig. 1.

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STUDY OF EXTRACTION PROPERTIES OF CyMe₄-BTTP

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INTRODUCTION

The reprocessing of spent nuclear fuel is considered to be the most convenient strategy to the sustainability of nuclear energy. Actinoids and lanthanoids recycling is the most promising way to reduce the radiotoxicity of radioactive waste. Supported by the European Union, the ACSEPT collaborative project (Actinide reCycling by SEparation and Transmutation) was founded. The objective of this project is to develop chemical separations applicable in fuel reprocessing technology. To meet this challenge, new kinds of molecules, which are considered as prospective extracting agents, are synthesized and the experiments are carried out in order to study their extraction properties.

EXPERIMENTAL

Solvent extraction experiments were carried out to test extraction properties of CyMe₄-BTTP (Fig. 1). The solution of this molecule in 1-octanol was used as an organic phase and diluted nitric acid (0.1 – 4 mol L⁻¹) as an aqueous phase. The samples were spiked with ¹⁵²Eu and ²⁴¹Am as the representatives of lanthanoids and actinoids, respectively. For the synergistic experiments the following mixtures were used: 0.01M CyMe₄-BTTP with 0.1M quinoline or with 0.25M DMBDMDMA in 1-octanol. The activity of aqueous and organic phase was measured via gamma spectrometer with HPGe detector.

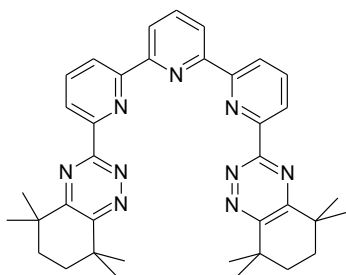


Fig. 1. Structure of the studied molecule CyMe₄-BTTP

RESULTS

To test the extraction properties of CyMe₄-BTTP, the basic experiments were performed. The distribution ratio of americium and europium in relation to HNO₃ concentration for the 0.01M solution of CyMe₄-BTTP in 1-octanol is shown in Figure 2. The values of distribution ratio of americium reach the maximum at 2M nitric acid. On the other hand, the values of distribution ratios of europium lie below the limits of detection over the whole studied range of acidities. Therefore, the values of separation factor cannot be directly evaluated, but they vary from SF_{Am/Eu} > 2 in 0.1M nitric acid to SF_{Am/Eu} > 31 in 2M nitric acid.

The maximum solubility of CyMe₄-BTTP was determined as 20 mmol L⁻¹. Higher concentrations cannot be prepared in 1-octanol because of the suspension creation.

Further experiments focused on determining the binding possibilities of this molecule. Because of the low values of distribution ratio of ¹⁵²Eu only ²⁴¹Am solution was used for spiking the samples.

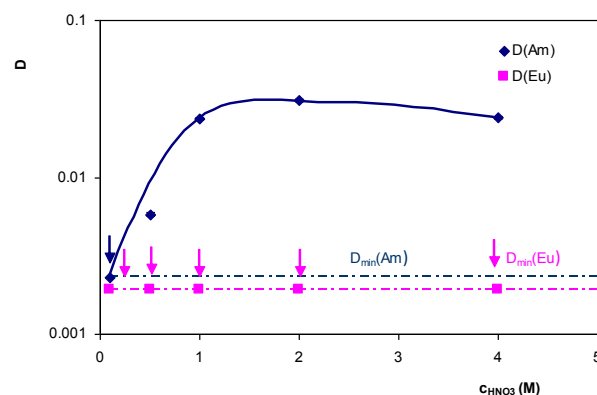


Fig. 2. Distribution of americium and europium between 0.01M CyMe₄-BTTP in 1-octanol and 0.1 - 4M HNO₃ (contact time: 6 hrs)

The values of distribution ratios of Am depending on the concentration of extracting agent are shown in Figure 3. The slope of observed dependence is almost equal to one (0.973) indicating that one molecule of CyMe₄-BTTP binds with one americium atom. When compared with BTBPs, the values of distribution ratios observed for CyMe₄-BTTP are rather low. This may be ascribed to the formation of a less hydrophobic 1:1 complex of CyMe₄-BTTP with americium and europium while the BTBPs form 1:2 complexes [1].

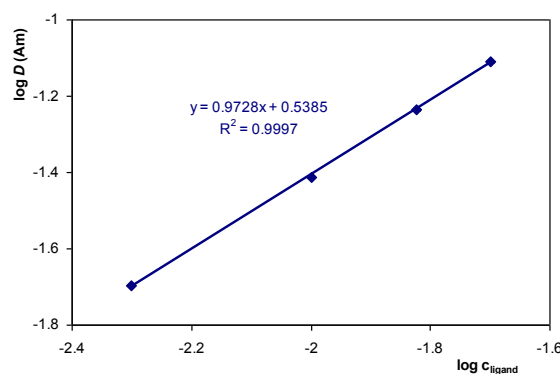


Fig. 3. Distribution of americium between CyMe₄-BTTP in 1-octanol and 2M HNO₃ (contact time: 6 hrs)

CyMe₄-BTTP was also studied in synergistic systems with quinoline and DMBDMDMA as the phase-transfer reagent. However, no synergistic effects were observed in the chosen systems.

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This research has been supported by Euratom FP7 grant ACSEPT (FP7-CP-2007-211 267) and by the Czech grants MSM 6840770020.

THE SEPARATION OF AMERICIUM(III) FROM EUROPIUM(III) BY TWO NEW 6,6'-BISTRIAZINYL-2,2'-BIPYRIDINES DERIVED FROM HETEROCYCLIC α -DIKETONES

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INTRODUCTION

The presence of long-lived radionuclides, where the most important are minor actinides, in the spent nuclear fuel is responsible for the long-term radiotoxicity. Decrease of the long-term radiotoxicity may be achieved by partitioning of minor actinides with their subsequent transmutation. However, the separation of minor actinides from lanthanides (both trivalent) is challenging because of the chemical similarity of these elements.

Two new extractants proposed for partitioning of the minor actinides (Fig. 1) have been studied and compared with the reference molecule CyMe₄-BTBP.

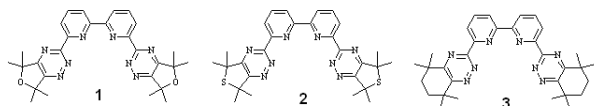


Fig. 1. Structure of Cy₅-O-Me₄-BTBP (1), Cy₅-S-Me₄-BTBP (2), and CyMe₄-BTBP (3).

EXPERIMENTAL

Nitric acid solutions of different concentrations were spiked with ¹⁵²Eu and ²⁴¹Am solutions. 1 mL of the aqueous phase was contacted with 1 mL of the organic phase (Cy₅-S-Me₄-BTBP or Cy₅-O-Me₄-BTBP in different diluents) for 6 hours using an orbital shaker. After the contacting, aliquots of both phases were taken for activity measurement by means of γ -spectrometry with HPGe detector.

RESULTS

The affinity for Am(III) and the selectivity for Am(III) over Eu(III) of Cy₅-S-Me₄-BTBP were generally higher than for Cy₅-O-Me₄-BTBP. For both these ligands, the extraction of Am(III) and Eu(III) from 3 M HNO₃ into organic phase of 3 mM ligands varied in the diluent used (Fig. 2). The highest distribution coefficients D(Am) and separation factors SF(Am/Eu) were observed when cyclohexanone and 2-methylcyclohexanone, respectively, were used as diluents.

For Cy₅-S-Me₄-BTBP, there is a strong correlation between the distribution coefficient for Am(III) and the permittivity of the diluent used.

With 1-octanol as the diluent, low distribution coefficients (D(Am) < 1) were observed for Cy₅-S-Me₄-BTBP although this ligand extracts Am(III) selectively (SF_{Am/Eu} = 16 - 46 in the range of 1 - 4 M HNO₃).

The kinetics of extraction of Am(III) and Eu(III) by Cy₅-S-Me₄-BTBP was faster in the system with cyclohexanone than in that with 1-octanol due to the phase-transfer effect of cyclohexanone.

CONCLUSIONS

It has been shown that the affinities for Am(III) and the selectivities for Am(III) over Eu(III) of both of the ligands studied, Cy₅-O-Me₄-BTBP and Cy₅-S-Me₄-BTBP, are lower than those of CyMe₄-BTBP [1] (Fig. 3) indicating that the design of the aliphatic part of the BTBP molecule is very important in the context of the development of future ligands for the partitioning of actinides from lanthanides.

When comparing Cy₅-O-Me₄-BTBP and Cy₅-S-Me₄-BTBP, Cy₅-S-Me₄-BTBP has not only higher solubility, but also better extraction properties.

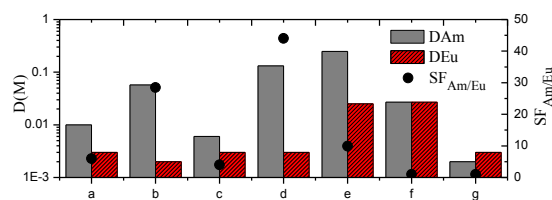


Fig. 2. Extraction of Am(III) and Eu(III) from 3 M HNO₃ by 3 mM Cy₅-S-Me₄-BTBP in various diluents (a = tetrachloroethane, b = dichloroethane, c = nitrobenzene, d = 2-methylcyclohexanone, e = cyclohexanone, f = cyclohexanone without ligand, g = toluene).

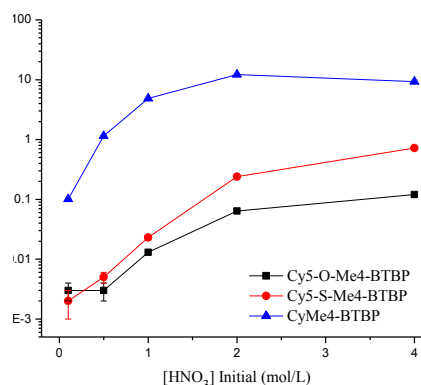


Fig. 3. Comparison of the dependencies of the distribution coefficients for americium(III) on initial nitric acid concentrations for Cy₅-O-Me₄-BTBP (■), Cy₅-S-Me₄-BTBP (●), and CyMe₄-BTBP (▲) in cyclohexanone (concentration of ligands used: 5 mmol L⁻¹).

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This work has been supported by the Czech Ministry of Education, Youth and Sports grant MSM 6840770020 and Euratom FP7 grant ACSEPT (FP7-CP-2007-211 267).

PREPARATION OF SAMPLES FOR ALPHA-SPECTROMETRY BY DIRECT EVAPORATION OF EXTRACTED SPECIES

K. Štastná, V. Fiala, J. John

INTRODUCTION

The aim of the study was to investigate the influence of sample preparation methods of direct evaporation on counting efficiency and energy resolution of alpha-spectrometry in order to select the method suitable for screening tests with trace amounts of radionuclides. Three methods of direct evaporation were tested: simple evaporation, evaporation with volatile organic solvent, and evaporation in the presence of tensioactive agent. The method developed should enable determination of distribution coefficient D in liquid-liquid extraction experiments by direct comparison of the alpha-activities of organic and aqueous phases rather than using the activities of aqueous phases measured prior to and after contacting with an organic phase which deteriorates the upper and lower limits of detection.

EXPERIMENTAL

The samples for alpha-spectrometry were prepared in three different ways as follows: 1. Simple evaporation: 10 μL of ^{241}Am solution was transferred directly onto a stainless steel planchet, 2. Evaporation with acetone: 10 μL of ^{241}Am solution was mixed with 40 μL of acetone and transferred onto the planchet, 3. Evaporation with tetraethylene glycol: 10 μL of ^{241}Am solution was deposited on the planchet, and 4 μL of tetraethylene glycol was added. All samples were evaporated to dryness under infrared lamp and heated in flame until glowed with dull red colour. Samples were measured using ORTEC® OCTETE Plus Integrated Alpha-Spectroscopy System (ORTEC, Advanced Measurement Technology, Inc., USA) with surface barrier silicon detector NUTRONICS ND.200.20.100 (area 200 mm^2), (NUTRONICS, Ltd., UK) at a distance of 16 mm, and the spectra were evaluated by AlphaVision-32 Alpha Analysis Software (ORTEC, Advanced Measurement Technology, Inc., USA). The efficiency of the selected method was tested for the case of americium extraction by $\text{CyMe}_4\text{-BTBP}$ [1] compound in cyclohexanone from nitric acid medium (aqueous phase: 1 mL of 2M HNO_3 spiked with the trace amount of ^{241}Am ; organic phase: 1 mL of 5mM solution of $\text{CyMe}_4\text{-BTBP}$ in cyclohexanone; shaking time: 24 hrs).

RESULTS

Table 1 shows the influence of sample preparation method on overall count-rate and FWHM (full width at half maximum) resolution summarising the values measured, means, theoretical (based on the measured count-rates, only) and/or experimental (calculated from the replicates) standard deviations (σ_t and σ_e , respectively) of total peak areas and FWHMs, the best values achieved being written in bold.

Tab. 1. Comparison of α -sample preparation methods.

Method	Counts per 10 min			FWHM (keV)	
	Mean	σ_e	σ_t	Mean	σ_e
Evaporation:					
simple	895	30	30	41	5
with acetone	853	19	29	50	18
with tetraethylene glycol	829	71	29	40	6

The method of simple evaporation was selected to evaluate the efficiency of extraction experiments. Distribution ratios $D = T_{\text{org}}/T_{\text{aq}}$ and $D' = (T_{\text{st}} - T_{\text{aq}})/T_{\text{aq}}$ were calculated from the total peak areas of aliquots of organic (T_{org}) and aqueous (T_{aq}) phases, or aliquots of standards (T_{st}) and aqueous phases. Within the experimental uncertainty, the values of D_{Am} (11.9 ± 0.2) and D'_{Am} (12.3 ± 0.4) are identical. It can be concluded that, if proper care of sample preparation is taken, the efficiency of extraction may be evaluated by simple comparison of the α -activities of organic and aqueous phases after contacting.

Fig. 1. α -samples prepared by direct evaporation. From left counterclockwise: simple evaporation, evaporation with acetone, and evaporation with tetraethylene glycol.



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Am/Eu CHROMATOGRAPHIC SEPARATION WITH NEW SOLID EXTRACTANTS BASED ON CyMe₄BTBP

K. V. Mareš, J. John

INTRODUCTION

The family of bis-triazinyl-bipyridine (BTBP) extractants was recently demonstrated to separate efficiently minor actinides (MAN) from the reprocessing waste using liquid-liquid extraction. High separation factors between MAN and lanthanides could be achieved in one stage [1].

At the Czech Technical University in Prague, the studies directed towards proposal of a chromatographic process for the partitioning of minor actinides from high active liquid waste are carried on [2]. Selective separation of the actinides from the lanthanides by solid extractants with BTBPs ligands have been considered.

EXPERIMENTAL

The material used was based on extraction agent 6,6'-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo[1,2,4]triazin-3-yl)-[2,2']bipyridine (CyMe₄BTBP) supported on Synchrom E5. The characterisation of extraction properties of the materials studied was carried out through weight distribution ratios determination, kinetics experiments and dynamic extraction capacity determination.

Preparation of the E5-CyMe₄BTBP solid extractant:

The solution of the extractant CyMe₄BTBP in a diluent cyclohexanone was further diluted by tetrahydrofuran and added to the beads of Synchrom E5. After careful mixing, the volatile diluent was evaporated at 25–35 °C under vacuum and under continuous agitation.

Determination of the distribution coefficients:

The suspension of 16 mg of the solid extractant ($V/m = 250 \text{ mL g}^{-1}$) and 4 mL of the HNO₃ solution labelled with ¹⁵²Eu and ²⁴¹Am, pre-saturated by cyclohexanone, was shaken in 50mL PE bottles for the required time using an orbital shaker at 250 rpm.

Column experiments:

The polypropylene cartridge (bed volume, BV = 1.27 mL) was filled with a dry solid extractant that has been wetted prior to the experiment by sucking 1M HNO₃ through the column by means of a syringe. The sorption, washing and elution solutions, pre-saturated with cyclohexanone,

were passed through the column by means of a peristaltic pump.

RESULTS

For E5–CyMe₄BTBP[cyclohexanone] material, the best results were achieved in 1M HNO₃ (D_g observed was about 300 mL g^{-1}). In batch experiments, D_g s were found to suffice for dynamic application and the kinetics was found to be much faster in cyclohexanone than in nitrobenzene or chlorinated diluents (from previous studies). In cyclohexane, the equilibrium was achieved in approximately one hour. In a dynamic experiment with E5–CyMe₄BTBP[cyclohexanone] solid extractants americium was quantitatively retained in the column from ~ 100 BV of simulated waste while europium quantitatively passed. The practically usable flow rates were up to $3 \cdot \text{BV hr}^{-1}$, which suffices for practical applications. The sorbed americium could be efficiently eluted with 0.5M glycolic acid with pH of 4. The results obtained are encouraging, in further studies, solutions with realistic Ln concentrations will be investigated.

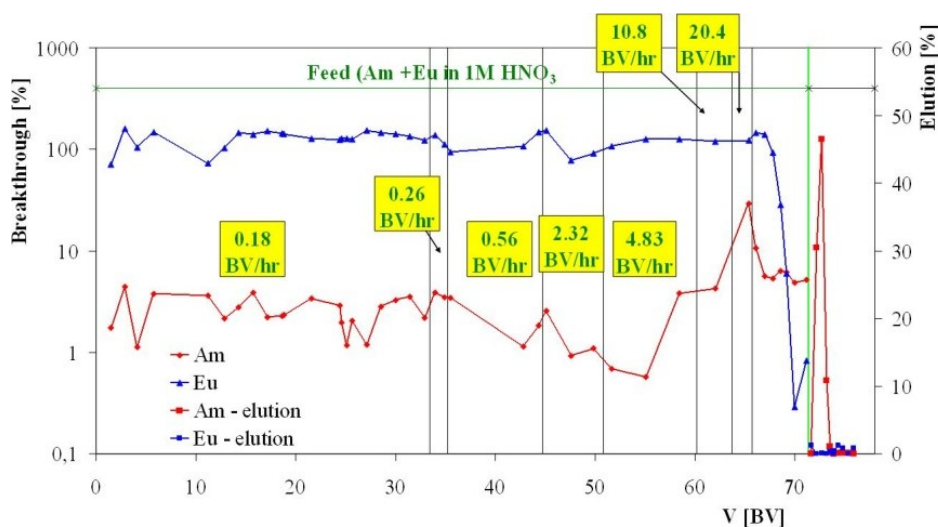
CONCLUSIONS

The resulting D_g s of Am suffice for dynamic application and the kinetics allows for practically applicable flow-rates.

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Feed:

65 BV carrier free Eu + Am
in 1M HNO₃
variable flow rate

Wash:

1M HNO₃,
 $v = 1.7 \text{ BV/hr}$

Am elution:

0.5M HGlyc, pH = 4,
 $v = 1.1 \text{ BV/hr}$

Americium fraction:

- recovery > 98 %
- < 1 % of Eu

Europium fraction:

- recovery > 99 %
- < 2 % of Am

Fig.1. Breakthrough of Eu and Am through a column of E5-CyMe₄BTBP[cyclohexanone] solid extractant.

STUDY OF EXTRACTION PROPERTIES OF THIALICALIX[4]ARENES

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INTRODUCTION

The reprocessing of spent nuclear fuel is a key process in the so called “Closed fuel cycle”. Generally, the research is gathered under the name “Partitioning and Transmutation”, P&T. For the separation process, liquid – liquid extraction is mostly used and thiacalixarenes [1] belong among the potentially prospective extraction agents. The objective of this study was to test the possibilities of lanthanoids and actinoids separation with two representatives of the thiacalixarene family (1), (2).

EXPERIMENTAL

For testing the extraction properties, the liquid-liquid extraction experiments were carried out. The distribution of ^{152}Eu and ^{241}Am between the thiacalixarene solution in nitrobenzene, chlorobenzene or 1,2-dichloroethane and the aqueous phase (from pH = 6 to 0.1M HNO_3 or COSAN in 0.1M HNO_3) was studied. The values of $D(\text{Am})$ and $D(\text{Eu})$ and of $\text{SF}_{\text{Am/Eu}}$ were determined. COSAN molecules (chloro-, resp. bromo-protected bis(1,2-dicarbollide) cobaltic acid or bis(1,2-dicarbollide) cobaltic acid - CCl , resp. CBr or C) were investigated as potential synergistic agents. The activities of aqueous and organic phases were measured via γ spectrometer with HPGe detector.

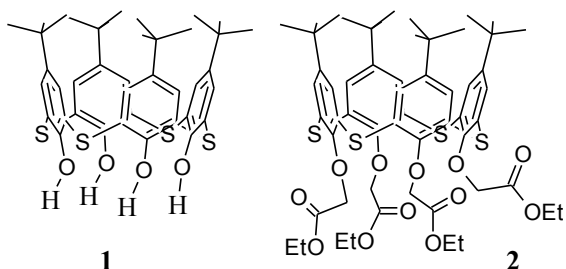


Fig.1. Structures of the studies thiacalixarenes.

RESULTS

The extraction properties of thiacalixarene (1) and (2) were studied in the pH range of 1 - 6. The values of $D(\text{Am})$ and $D(\text{Eu})$ clearly show no extraction at high acidic solutions regardless the used diluent.

On the other hand, Kyrš et al. reported efficient Eu extraction by thiacalixarene (2) from acidic solutions (0.1 M HNO_3) exploiting the synergistic effect with COSAN compound [2]. In order to get a broader idea of the co-extractants behaviour, the synergistic curve was investigated. The results, shown in Fig. 2, confirmed the previously published data [2]. Further experiments focused on the determination of the extracted species stoichiometry with thiacalixarene (2) dissolved in 1,2-dichloroethane. The results obtained indicate that the extracted complex has the following composition: $\text{MeH}(\text{thiacalixarene}(\mathbf{2}))_2(\text{CCl})_4$.

Three COSAN molecules were chosen to investigate more closely the synergistic effect with the thiacalixarenes. Although the synergistic curves of each extraction system were not studied, based on the previous experiments with thiacalixarene

(2) / CCl system, all experiments were performed with 1:1 molar ratio of both extractants.

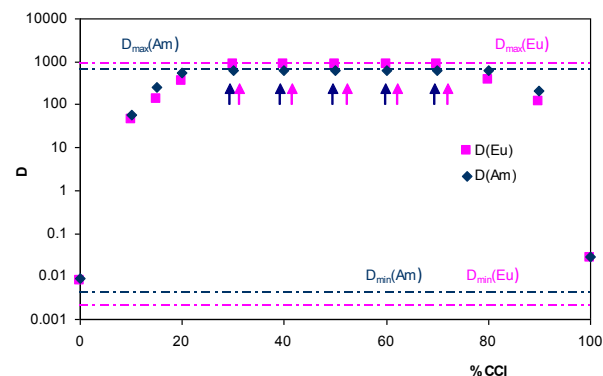


Fig. 2. Synergistic extraction of Am and Eu in isomolar series (total concentration of extractants: 33 mM; org. phase: thiacalixarene (2) in chlorobenzene; aq. phase: CCl in 0.1 M HNO_3 spiked with ^{152}Eu and ^{241}Am ; contact time: 20 hours).

The observed synergistic effect depended dramatically on the used thiacalixarene. The values of $D(\text{Am})$ and $D(\text{Eu})$ in thiacalixarene (1) systems are below 1 and those measured in the thiacalixarene (2) systems lie above the upper detection limits. The effect of used diluent is also noticeable. The nitrobenzene synergistic systems provide lower values of D s than the chlorobenzene or 1,2-dichloroethane systems. Moreover, the values of $D(\text{Am})$ and $D(\text{Eu})$ are very similar for each extraction system regardless of the used COSAN. Regarding the separation of Am/Eu in the synergistic systems, the values of $\text{SF}_{\text{Am/Eu}}$ are always close to 1 and therefore, no separation was observed.

CONCLUSIONS

The synergistic systems containing one of the COSAN molecules and thiacalixarene (1) or (2) dissolved in the organic diluent were closely investigated. The probable composition of extracted species is $\text{MeH}(\text{thiacalixarene}(\mathbf{2}))_2(\text{CCl})_4$. The results showed that the synergistic effect depends significantly on the type of the used thiacalixarene and diluent and it is not strongly influenced by the type of the used COSAN molecule used.

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INTRODUCTION

The efficient separation of lanthanoids and actinoids from the high active wastes is a key problem in the reprocessing of spent nuclear fuel. Thiocalixarenes [1] belong to the family of extracting agents prospective for the Partitioning processes. Besides the generally used liquid-liquid extraction, extraction chromatography with the newly developed thiocalixarenes-based composite materials may be performed. The main purpose of this study was to test a new composite material based on thiocalix[4]arene incorporated into styrene-divinylbenzene copolymer support (Synachrom E5).

EXPERIMENTAL

The composite materials were prepared by impregnation of the commercial Synachrom E5 beads (styrene-divinylbenzene copolymer, grain size 0.3–0.5 mm, Lachema) with thiocalix[4]arene (Fig. 1) solutions.

The values of weight distribution ratios D_g of ^{152}Eu and ^{241}Am and the values of the mutual separation factors were determined.

As aqueous phase, 1×10^{-5} – 1M nitric acid or acetate buffer of pH ranging from 1 to 6 was used. 0.01M thiocalixarene solution in nitrobenzene or 1,1,2,2-tetrachloroethane, or saturated solution ($\leq 0.05\text{M}$) of thiocalixarene in 1,1,2,2-tetrachloroethane was embedded into the beads. The testing was carried out with $V/m = 250 \text{ mL g}^{-1}$.

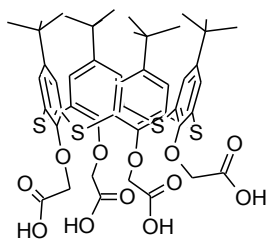


Fig. 1 Structure of the studied thiocalix[4]arene ligand

RESULTS AND DISCUSSION

At first, the extraction ability of thiocalix[4]arene in nitrobenzene was studied in liquid-liquid extraction experiments with aqueous phase in the range of 0.001 - 3M nitric acid. However, at low acidities of the aqueous phase, the third phase formation was observed. It was found that this third phase retained almost all the activity ($\sim 87\%$) in the batch experiment. Therefore, it was decided to test the thiocalixarene behaviour in the extraction chromatography experiments.

Both of the prepared materials extracted europium and americium most efficiently at pH range of 4 – 6.

As an example, the results obtained with the composite material containing saturated solution of thiocalixarene in 1,1,2,2-tetrachloroethane are shown in Figure 2. It can be seen that the highest sorption occurred at pH = 6 ($D_g(\text{Am}) = 48550 \text{ mL g}^{-1}$, $D_g(\text{Eu}) = 18408 \text{ mL g}^{-1}$).

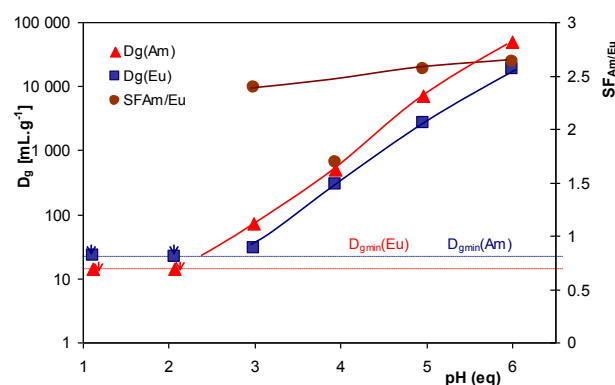


Fig. 2 Distribution of americium and europium between 0.1M acetate buffer with 0.1M NO_3^- and solid extractant containing saturated solution ($\leq 0.05\text{M}$) of the thiocalixarene embedded in 1,1,2,2 tetrachloroethane embedded into Synachrom E5 (0.014 g thiocalixarene per 1 g Synachrom E5) and the respective separation factors $\text{SF}_{\text{Am/Eu}}$ ($V/m = 250 \text{ mL g}^{-1}$; contact time: 20 hrs)

The most important findings that result from the study of these materials may be summarised as follows:

- composite materials with nitrobenzene used as a diluent ($D_g(\text{Am}) = 1903 \text{ mg L}^{-1}$) are significantly more efficient than the materials with 1,1,2,2-tetrachloroethane diluent ($D_g(\text{Am}) = 118 \text{ mg L}^{-1}$),
- increase in the thiocalixarene concentration by 5 times caused increase in the value of D_g almost by two orders of magnitude,
- buffering of the aqueous phase or the addition of nitrates negatively influenced the americium and europium sorption (3–4 times decrease of the values of weight distribution ratios D_g).

REFERENCES

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This research has been supported by Czech Science Foundation grant GA 104-07-1242.

INTRODUCTION

This study focused on studying properties of extraction-chromatographic material prepared by immobilization of tributylphosphate (TBP) into the matrix of polyacrylonitrile (PAN). These materials have been developed at the Department of Nuclear Chemistry at the CTU in Prague. For preliminary characterization of the material, uranium was used. The kinetics of uranium extraction, the influence of nitrates and nitric acid concentration on the values of weight distribution coefficient D_g as well as extraction isotherm were determined.

EXPERIMENTAL

The material studied was prepared in two different ways:

1) by coagulation of dispersed mixture of TBP added to a solution of the PAN dissolved in nitric acid or dimethylsulfoxide (DMSO) into water bath [1,2] – TBP-PAN(DMSO) and TBP-PAN(HNO_3),
2) by impregnation of ready-made PAN beads with TBP solution [1,2] – PAN-TBP.

In experiments for evaluation of extraction abilities of the material studied, 100 mg of the solid extractant and 5 mL ($V/m = 50 \text{ mL g}^{-1}$) of appropriate uranium solutions spiked with ^{233}U were contacted for required time using an orbital shaker. Liquid scintillation spectrometry was used for uranium activity measurement.

RESULTS

Characterisations of the prepared materials are given in table 1. It shows that during preparation of the beads by coagulation, losses of TBP occurred. Therefore, material prepared by impregnation of PAN beads was chosen for further testing.

Tab.1. Characterisations of the prepared materials

	TBP content (% w/w)		Bulk density (g mL^{-1})	Grain size (mm)
	Theoretical	Determined		
TBP-PAN(DMSO)	40	0	0.08	0.3-0.8
TBP-PAN(HNO_3)	40	9.2	0.13	0.3-0.8
PAN-TBP	33.3	34.3	0.35	0.3-0.8

Study of the kinetics of U sorption revealed that two hours are needed to reach equilibrium in the system of TBP-PAN/ $\text{UO}_2^{2+}/3\text{M HNO}_3$. Figure 1 shows increasing extraction ability of the solid extractant towards uranium with increasing acidity of solution.

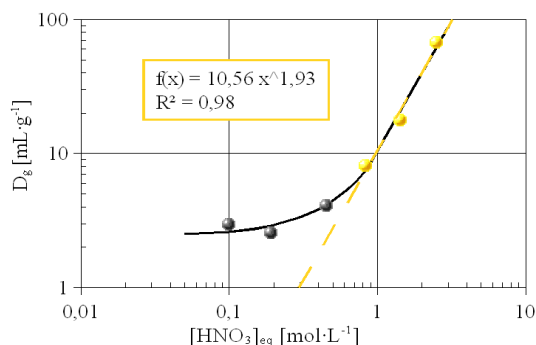


Fig.1 Dependence of D_g of uranium on equilibrium concentration of HNO_3 ($V/m = 50 \text{ mL g}^{-1}$; contact time 2 hrs).

Slope analysis of this dependence at higher HNO_3 concentrations, after correction for HNO_3 extraction by TBP, refer to extraction of $\text{UO}_2(\text{NO}_3)_2$ species into organic phase. This fact is supported by results observed from slope analysis of D_g values depending on increasing counter ion concentration in aqueous phase (Figure 2)

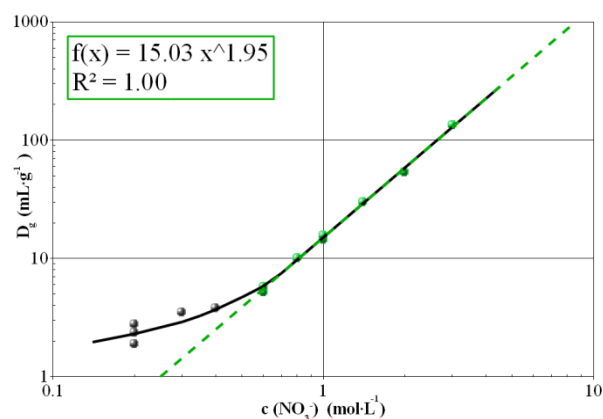


Fig. 2 Dependence of uranium D_g values on total nitrate concentration (PAN-TBP, $V/m = 50 \text{ mL g}^{-1}$, $c(\text{HNO}_3) = 0.2 \text{ mol L}^{-1}$, 2 hrs of contact time).

Figure 3 shows extraction isotherm for uranium performed in 3M HNO_3 . The results obtained agree well with solvent extraction data observed earlier in the work [2].

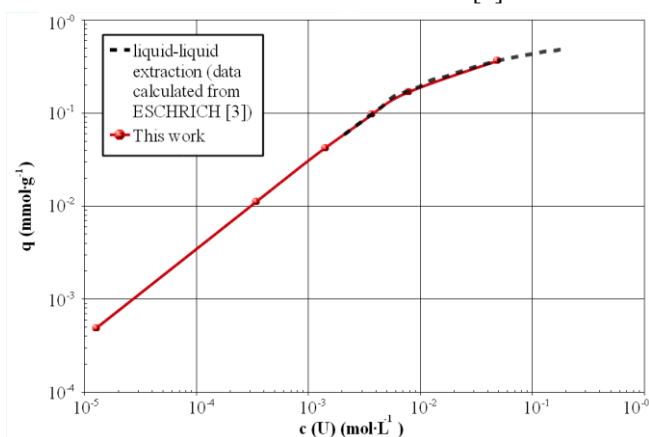


Fig.3 Uranium extraction isotherm for PAN-TBP material (PAN-TBP, $V/m = 50 \text{ mL g}^{-1}$, $3 \text{ mol L}^{-1} \text{ HNO}_3$, 2 hrs contact time).

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This work has been supported by the Ministry of Education Youth and Sports of Czech Republic under contract No. MSM6840770020 and EU FP7 grant ACSEPT (FP7-CP-2007-211 267).

INTRODUCTION

Europium is often used as a model of fission products from the lanthanides group and of minor actinides Am and Cm. Glycolic acid (HOCH_2COOH), contained in current decontamination solutions, is suggested to be used as a complexing agent in reprocessing of spent nuclear fuel. Because the complexes of Eu with glycolic acid show good fluorescent properties, the method of TRLFS was chosen for their speciation studies. For the determination of stability constants, TRLFS method was complemented by liquid-liquid extraction.

EXPERIMENTAL

For calculation of dissociation constants of glycolic acid K_1 and K_2 , determined by means of titration with sodium hydroxide, program FAMULUS was used.

The TRLFS experiments were performed at excitation wavelength of 395 nm. The formation and stability of carbonate and hydroxo (under N_2 atmosphere) complexes of europium were examined to determine their influence on stability constants determination. Next, the effect of pH on formation of europium complexes with glycolic acid was investigated in sodium perchlorate solutions.

To determine stability constants, aqueous solution of europium complexes with glycolic acid at pH 2.7 was contacted with di-(2-ethylhexyl) phosphoric acid in toluene. Based on the results of extraction, the stability constants of complexes were calculated using the graphic and FAMULUS model methods.

RESULTS

Dissociation constants determined by titration of HOCH_2COOH with NaOH were of values: $\log K_1 = 3.32$ and $\log K_2 = 11.12$.

Fig. 1 and Fig. 2 show TRLFS normalized spectra of carbonate and hydroxo complexes.

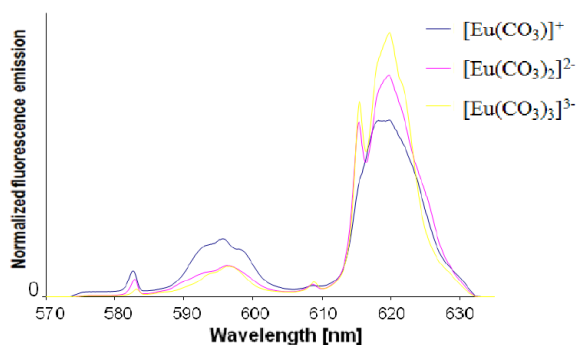


Fig. 1. Normalized spectra of carbonate complexes

Hydroxo complexes observed demonstrated expressively lower values of lifetime of fluorescence than carbonate complexes. All solutions prepared under N_2 atmosphere were carbonate complexes free.

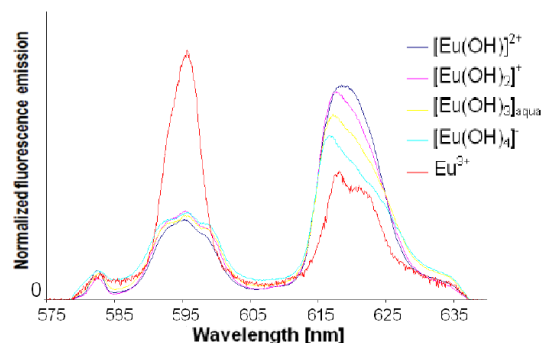


Fig. 2. Normalized spectra of hydroxo complexes

From Fig. 3 it can be seen that only two different complexes are present in the studied systems. This result is in good agreement with the data of Stumpf et al. [1].

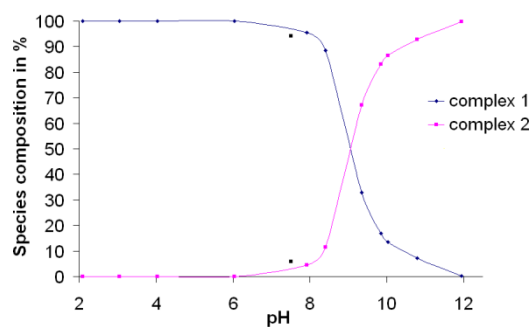


Fig. 3. Species composition (complex 1 $[\text{Eu}(\text{HOCH}_2\text{CO}_2)_4(\text{OH})]^{2-}$ and complex 2 $[\text{Eu}(\text{HOCH}_2\text{CO}_2)_3(\text{OCH}_2\text{CO}_2)(\text{OH})]^{3-}$)

The lifetimes of fluorescence of complex 1 and complex 2 were calculated as following: $306 \pm 8 \mu\text{s}$ and $523 \pm 33 \mu\text{s}$, respectively. Stability constants of these complexes 1 and 2 determined (ionic strength $I = 3.5 \text{ mol L}^{-1}$) using the FAMULUS program were: $\log \beta_1 = 17.64$ and $\log \beta_2 = 19.04$.

Stability constants of $[\text{Eu}(\text{HOCH}_2\text{COO}^-)_x]^{3-x}$ were determined by liquid-liquid extraction as follows: $\log K_1 = 3.09$ and $\log K_2 = 1.78$. The smaller number of complexes formed in the system than expected has been most probably caused by the incomplete dissociation of glycolic acid at pH 2.7. This issue could be solved by extraction performed at higher pH ($\text{pH} \approx 5$), where complete dissociation to the first degree is accomplished.

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DESTRUCTION OF RADIOACTIVE ORGANIC WASTE USING MOLTEN SALT OXIDATION

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INTRODUCTION

Within Molten Salt Oxidation (MSO processing), solid or liquid waste is injected with air under the surface of the molten salt, usually Na_2CO_3 , at temperatures between 750 and 900°C. Flameless oxidation takes place within the salt bath in the chemical reactor converting the organic components of the waste into carbon dioxide and water. The product offgas leaving the processor is treated to remove any entrained salt particulate and essentially all water vapor before being discharged to the facility offgas system. Reactive species such as fluorine, chlorine, bromine, iodine, sulfur, phosphorous, and arsenic in the organic waste react with the molten salt to form the corresponding neutralized salts. Radioactive metals react with the molten salt and air to form metal salts or oxides.

The Nuclear Research Institute Řež, plc., Czech Technical University in Prague, Czech Republic, and Hazen Research, Inc. in Colorado, USA are interested in developing MSO for the destruction of organic radioactive waste (contaminated ion exchangers and contaminated oil). MSO, which is a thermal flameless treatment technology, is now a viable technology for the treatment of organic materials, i.e. contaminated ion exchangers. The general advantages of the MSO process are complete destruction of organic material at the end of the process (even complex poly-aromatic compounds that are difficult to destroy with other methods), operation at lower temperatures than vitrification is performed, and the radioactive species capture in the salt bath, which also scrubs acid gases from the offgas.

DESCRIPTION OF THE EQUIPMENT

A laboratory MSO system similar to those used in previous studies [1] was set up in a laboratory of the Center of Radioactive Waste Management in the Nuclear Research Institute in Řež. A Clare 4.0 electric furnace, supplied by Clasic (150-mm internal diameter and 150-mm height) was used. The maximum operational temperature was 1000°C. The heating elements are made from KANTHAL A1. A microprocessor with supporting circuits handles all of the functions of the entire system. This unit works with a real time clock in manual or automatic mode.

The furnace is protected by a stainless steel containment vessel with a removable lid containing an Inconel 550 thermocouple holder, Inconel 550 downcomer with concentric tubes for air and feed injection, and a separate exhaust gas pipe. A 0.7-L silicon carbide crucible (110-mm outside diameter and 270-mm height with a 1-cm thick wall) is placed inside the stainless steel containment vessel.

RESULTS

The experiments were focused on the destruction of ion exchangers and contaminated oils. Preliminary experiments involved selecting a salt mixture, testing one particular mixture of salt that is envisaged to be useful at the nuclear power plant radioactive waste management, and testing the downcomer's ability to introduce the oil.

Some salt mixtures were tested and it was found that the experimental values of melting temperatures correspond very closely to the theoretical values of melting temperatures. However, it was necessary to set the furnace temperature a little higher than is the theoretical value; as expected, the higher temperature was applied, the faster salt was melted. In preliminary tests, a mixture of gear oils (used at most of the nuclear power plants in the Czech Republic) containing 80:20 of TB32:TB46 ratio was charred at below 200°C. A mixture of anion (Purolite 400 MB in BO_3^{3-} form) and cation (Purolite C100H mixed K^+ and Na^+ forms) ion exchangers in a ratio of 1:2, respectively, charred well below 550°C. Therefore, it was decided to use the mixture of salts $\text{Na}_2\text{CO}_3/\text{K}_2\text{CO}_3/\text{KCl}$ (0.414:0.359:0.227) which melting temperature (m.t.) is 580°C. While the downcomer for liquid pumping was easy to construct and validate, the downcomer for solid particle introduction was harder to develop and therefore it was decided to use in further experiments the solid downcomer developed at Hazen which runs based on the principle of the screw tube conveyor.

CONCLUSIONS

The preliminary experiments with MSO in the small scale demonstrated that it can be used efficiently for organic mixed waste destruction. The testing of an appropriate salt (mixture) that will be useful for complete destruction of organic matter while having as low temperature as possible was successful and the mixture of salts $\text{Na}_2\text{CO}_3/\text{K}_2\text{CO}_3/\text{KCl}$ was finally selected. For solid particle introduction the downcomer that was developed in Hazen Research, Inc. in USA will be used for the destruction of radioactive ion exchangers at Řež.

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SELECTIVELY LABELED BETULININES IN CANCER RESEARCH

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INTRODUCTION

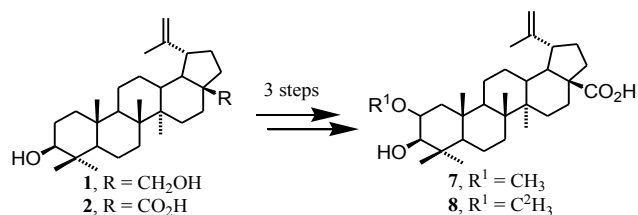
The pentacyclic triterpenoids have played a unique role among natural products from the beginning of the 21st century, mainly for their various biological activities [1]. The derivatives of betulin (1) and betulinic acid (2) have been tested on various tumor cell lines for their activity [2]. That heterogeneous family of triterpenoids, including highly oxidized lupane, des-E-lupane, oleanane, taraxastene and others derivatives, possesses a significant cytotoxic and antiviral activity and was named Betulinines [2]. Betulinines have proved multispectral cytotoxic activity on the panel of 10 tumor cell lines of different histogenetical origin [1, 2]. For the investigation of mechanism of action, selectively labeled molecules of the most active compounds are synthesized.

EXPERIMENTAL

Spectral data were recorded in cooperation with IOCB AS CR and Betulinines Chemical Group. Detection of Radio - TLC plates was carried out by means of AR – 2000 Imaging Scanner. The activity of labeled compounds was measured on LSC. Cytotoxic activities of all mentioned compounds were tested at LEM FH in Olomouc on the panel of T-lymphoblastic leukemia (CEM).

RESULTS

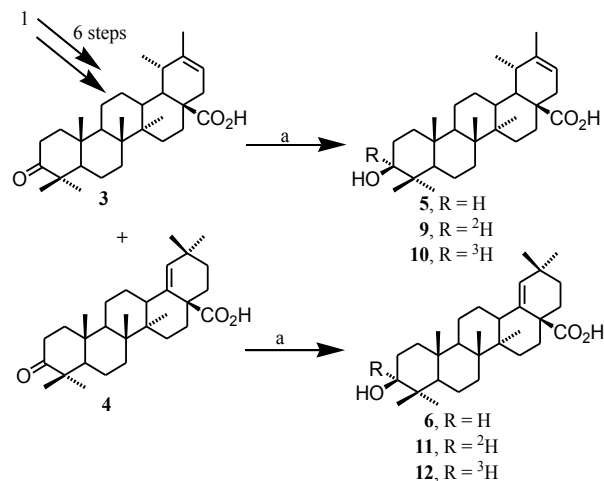
Betulin (1) was extracted from the outer layers of birch bark, *Betula pendula*. Acid 2 was extracted from the bark of plane tree, *Platanus hispanica*. Heterobetulonic (3) and moronic (4) acids were synthesized from betulin (1) in six steps. (Scheme 2)



Sch. 1. Synthesis of methoxy ethers 7 and 8

Oxidation of benzylated 1 with subsequent alkylation with CH₃I or C[²H]₃I followed by debenzylation and hydrogenation of double bond 1(2) afforded acids 7 and 8. (Scheme 1)

The purpose of this work was to synthesize series of deuterated derivatives as summarized in Schemes 1 and 2. Reaction of ketoacids 3 and 4 with sodium borohydride afforded hydroxyacids 5 and 6. Analogous procedure was employed to prepare 9 and 11 using NaB[²H]₄, 10 and 12 using NaB[³H]₄.



Sch. 2. Reduction of keto acids. Reagents and conditions: (a) NaB[³H]₄, MeOH, THF, 0 °C

Figure 1 shows the radiochromatogram of compound 10, where the peak with R_f 0.11 was isolated in a yield of 14%.

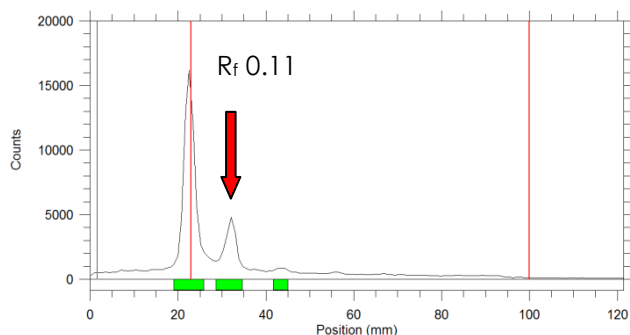


Fig. 1. Chromatogram of compound 10

CONCLUSIONS

Several labeled analogues of the most active betulines were synthesized. The cytotoxicity of the derivatives was studied in CEM lines and childhood cancer lines. It has been found that acids 5, 6 and methoxy ether 11 show interesting anti-cancer activity *in vitro*. Compound 11 just entered *in vivo* experiments on mice model.

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STUDY OF HDEHP-PAN SOLID EXTRACTANTS FOR THE DETERMINATION OF ^{90}Sr

F. Kužel, P. Staffová, I. Špendlíková, J. John, and F. Šebesta

INTRODUCTION

One of the advantageous methods for the radionuclide separation is the method using solid extractants. A procedure similar to that developed by Burnett et al. [1] for the determination of ^{228}Ra by measurement of the equilibrium activity of its daughter, ^{228}Ac , separated by Ln Resin was proposed for the determination of ^{90}Sr by means of measuring the activity of its daughter, ^{90}Y , separated onto one of the new solid extractants developed at the Czech Technical University (CTU) in Prague. The solid extractants studied contained di-(2-ethylhexyl)phosphoric acid (HDEHP) in the support based on modified polyacrylonitrile (PAN). The particular objective of this study was to study the uptake of Ba^{2+} and Eu^{3+} , as models for Sr^{2+} and Y^{3+} , by the solid extractants containing HDEHP inside of PAN matrix. Throughout this study, the performance of these materials was compared with the behaviour of commercial Ln ResinTM produced by Eichrom Technologies LLC (USA) and characterised in detail in the work of Horwitz et al. [2].

EXPERIMENTAL

In the experiments, all the chemicals used were of p.a. purity. The HDEHP-PAN materials were prepared at the CTU in Prague, at the Department of Nuclear Chemistry except for Ln Resin, which was purchased at Triskem International (France).

The batch experiments were carried out as follows:

6 mL of appropriate aqueous solution was spiked with 5 μL of $^{152+154}\text{Eu}$ solution and 10 μL of ^{133}Ba solution. After mixing, 2 mL were taken as standards and 4 mL were contacted with 16 mg of the solid extractant for 20 hours. Activities of standards and samples were measured by means of a γ spectrometer with HPGe detector.

RESULTS

The effect of increasing nitric acid concentration ($10^{-3} - 3 \text{ M}$) on extraction ability of the solid extractants prepared was studied for four types of these extractants which differ in the preparation and composition and compared with the commercial Ln Resin. The results observed for all the studied solid extractants were similar to those published by Horwitz et al. [2]. Since our study was focused on determination of ^{90}Sr in environment, the mosses were chosen as testing matrix. In further experiments we focused on study of influence of other ions that may be present in the target system. First, the effect of the nitrate concentration on the D_g values was chosen as a model example of the total salinity influence. The results observed showed that with increasing total salinity of the aqueous phase, the Ba^{2+} and Eu^{3+} D_g values are rapidly decreasing.

Afterwards, the effect of Ca^{2+} ions, as the most common homologue of Sr^{2+} , was studied. The results obtained confirmed the expectation that europium uptake is not significantly influenced even by relatively high Ca^{2+} concentrations. The main interfering ion in the strontium determination in vegetation samples is expected to be Fe^{3+} ion. The results of the study of its influence on europium uptake showed its strong dependence on the Fe^{3+} concentration present.

Based on the previous results, the possibility of masking Fe^{3+} ions by ascorbic acid was studied. The introduction of the ascorbic acid to the hydrochloric acid system led to the significant suppression of the negative influence of Fe^{3+} ions on Eu^{3+} sorption. As expected, the ascorbic acid was not suitable masking agent in the system with HNO_3 due to its oxidizative properties.

After the basic characterization of the solid extractant, it was decided to study uptake of europium from a simulated solution of a leachate of ashed green plant sample. The composition of the simulated solution was based on the average mineral composition of green plants as given by Epstein [3].

In applying the solid extractant to simulate solution in the system of 0.1 M hydrochloric acid, the results revealed a dramatic drop of the europium mass distribution coefficients in both absence and presence of ascorbic acid. This effect was ascribed to the high salinity of the solution ($>3.5 \text{ mol L}^{-1}$).

To find compromise between the simulated solution relative concentration and the value of the europium mass distribution coefficient, detailed study of the dependence of $D_g(\text{Eu})$ on the relative concentration of the simulated solution (from 0 (without simulated solution) to 1 (pure simulated solution)) was performed. Based on the results obtained, the optimum dilution of the simulated solution was established as approximately 10 times. Such dilution allows to transfer 40 g of green plants into 100 mL of solution while still maintaining high values of $D_g(\text{Eu})$.

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²³⁶U IN WELL WATER – A TOOL FOR URANIUM PROSPECTION?

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INTRODUCTION

The radionuclides ²³⁶U and ²³⁹Pu are produced via neutron capture on ²³⁵U and ²³⁸U, respectively. Both are now widely dispersed in the environment as a result of atmospheric weapons testing and reprocessing operations of spent nuclear fuel. Although the main sources of ²³⁶U and ²³⁹Pu in present day environments are anthropogenic, small amounts are also produced naturally in uranium ores via the same neutron capture reactions as in nuclear weapons and reactors. In a natural ore or mineral, neutrons are produced from e.g. the spontaneous fission of ²³⁸U and ²³⁵U, neutron fission of ²³⁵U, or (α, n) reactions with lighter elements in the mineral matrix.

Natural ²³⁶U/²³⁸U ratios on the order of 10⁻¹⁰ have been reported in a variety of uranium containing ores and minerals, but no widespread survey has been completed to date because levels are too low for routine detection by techniques other than AMS. These studies indicate that if the ²³⁶U/²³⁸U ratio is greater than 10⁻⁹ (²³⁶U/²³⁴U > 2x10⁻⁵), the sample has seen a significant neutron flux.

EXPLANATION

Natural ²³⁶U/²³⁸U ratios have been usually measured by conventional (mass) spectroscopic methods. However, detection limits with conventional mass spectroscopy for ²³⁶U/²³⁸U are ~10⁻¹⁰, leading to errors larger than 50% for uranium ore samples. In alpha spectroscopy, detection efficiency is ultimately determined by the ability to retain uranium during the chemical separation and the detector geometry. The chemical form of the uranium on the planchette is not that important as long as the sample is plated thinly; the sensitivity is often limited by counting time and half-life of the radionuclide.

Therefore the satisfactory measurement of natural ²³⁶U is difficult or even impossible without AMS. However, even with AMS, measurements of natural ²³⁶U/²³⁸U are challenging because of the device interferences from the abundant isotopes ²³⁵U and ²³⁸U. In mass spectrometry, ion source efficiency is generally the limiting factor. Sample matrix and chemical form can dramatically affect ionization efficiency and the formation of various molecular ions, which can cause interferences with other isotopes, e.g. ²³⁵UH⁺ and ²³⁶U⁺ or ²³⁶U¹⁶O⁻, ²³⁵U¹⁶OH⁻ and ²³⁵U¹⁷O⁻. The VERA facility at the University of Vienna is at present the only one with an additional high energy filter before the detector to remove rare scattered ions masquerading as ²³⁶U. This shows crucial role of the chemistry used for sample preparation, storing and manipulating conditions of the uranium target.

PROJECT PLAN

Generally, the equilibrium ratio of ²³⁶U/U in natural ore is proportional to the thermal neutron flux, which is expected to be proportional to the uranium concentration in the first approximation. Since this fingerprint of high grade ore should stay unaltered in weathering and dissolution, it should still be detectable in well water which was in subsurface contact with the ore; thus, such wells should be usable as natural probes for uranium prospection. We expect this signature to be more unambiguous than the uranium concentration in water.

This project is dedicated to finding the dependency of ²³⁶U/U ratio on the ore presence and its grade from the samples of underground or well water. The aims combine practical application of such dependency with the development of chemical and measurement procedures and can be summarized as follows:

- Development of sample preparation procedure for uranium separation from underground water, which will repeatably provide the lowest contamination and isotopic changes possible, and which will be suitable for AMS measurement from the point of view of uranium chemical form and sample purity.
- Measurement of samples from several localities of the former and present uranium mines in the Czech Republic, and other possible sources of well/underground water containing uranium, prepared with the developed method.
- Proposal of the ²³⁶U production mechanism and its variations depending on the geological conditions, neutron poisons and water presence.

We will discuss the feasibility of uranium prospection by using natural ²³⁶U in well and underground water, and summarize the existing measurements. Uranium ores show up to ²³⁶U/U=10⁻¹⁰, but measurements of uranium from low-concentration rocks or deep well water are sparse or unavailable. The connection between uranium concentration and the ²³⁶U/U ratio will be discussed, since matrix nuclides (serving as (α, n) targets or "neutron poisons") and water content of the rock can alter the ²³⁶U production significantly.

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(RADIO)CHEMISTRY IN AMS – A SERVANT OR A PARTNER?

M. Němec, J. John

INTRODUCTION

The world demand for ultratrace analyses of radionuclides with long half-lives has been increasing not only in dating, material, environmental, geo- and cosmochemical studies, but also recently in the pharmaceutical and pharmacological applications. The most sensitive tool for such analyses is the dynamically advancing method of Accelerator Mass Spectrometry (AMS) which enables the determination of long-lived radionuclides in concentrations or amounts lower by up to 6 orders of magnitude than those measured by radiometric methods.

REASON

AMS is a very powerful but technologically challenging analytical method that is, at present, mainly a domain of physicists. The sample preparation is often carried out by physicists without wider background in chemistry and its procedures or, in a better case, by chemists without practice in the work with radionuclides and/or sufficient knowledge of AMS needs. Moreover, the collaboration between chemists and physicists in AMS, similarly to some other ultratrace analytical methods, seems to be rather insufficient. However, making full use of the sensitivity of AMS is possible only if precise, reproducible, and well defined methods for sample preparation are used.

SUGGESTION

We suggest that here is the place where radiochemistry, after more than 100 years of its development, can help with its powerful toolbox of micropreparations, carrier and tracing methods, tracking of contamination sources, numerous separation procedures optimised for radiometric determinations and, in some cases, even with chemical suppression of isobars interferences. Full integration of radiochemistry separation and preparation methods into AMS sample preparation could create a synergy resulting in quality samples/methods well suited for high precision AMS measurements at further decreased background and improved sensitivity.

Thus, this is an appeal on a closer collaboration between (radio)chemists and physicists in the field of Accelerator Mass Spectrometry, thus contributing to a better use of its potential.

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Half-life 10-100 million years																Source: Lawrence Livermore National Laboratory and Google	
H	He																
Li	Be	Xx															
Na	Mg	Xx															
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

¹⁰Be Half-life: 1.36x10⁶ years
Applications: geo- and glacial-chronology, climate studies, weathering and landscape evolution together with ²⁶Al
Measurement and preparation: BeO mixed Cu, Ag, Nb powders or Be co-precipitated their salts and baked to oxides; BeF₂ and BeBaF₂ precipitated from hydroxides
Interferences: ¹⁰B, improved chemical separation, additional magnet and filter setup

¹⁴C Half-life: 5760 years
Applications: dating in archeology, climate research, dendrochronology, biomedical and pharmaceutical research
Measurement and preparation: CO₂ from combusted samples, amorphous carbon - CO₂ reduction in Fe, Co, TiH, Zn systems
Interferences: ¹³CH, ¹²CH, molecular ions at lower acceleration energies, suppression by sample preparation and device settings

²³⁶U Half-life: 2.3x10⁷ years
Applications: environmental safeguards systems, mining and reprocessing monitor, geology and prospection of U ores?
Measurement and preparation: matrix dependent; dissolution in HNO₃/HF or leaching with NaOH and HF digestion, ion-exchange chromatography methods
Interferences: machine dependent, other U and actinide isotopes and their molecular ions, special device setup needed (e.g. TOF)

Pu Half-life: 24119 years (²³⁹Pu), 3.733x10⁵ years (²⁴²Pu), 8.26x10⁷ years (²⁴⁴Pu)
Applications: anthropogenic influences in nature, erosion and sediment studies, supernova explosions,
Measurement and preparation: matrix dependent; dissolution in aqua regia, coprecipitation and ion exchange purification
Interferences: similar to other actinides, high mass resolution needed, suppression of other actinides possible by improved chemistry



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EFFECT OF DOSE AND DOSE RATE OF GAMMA RADIATION ON CATALYTIC ACTIVITY OF CATALASE*

V. Čuba, T. Pavelková, V. Múčka

INTRODUCTION

Tetrameric ferriheme catalase has significant catalytic and peroxidatic activity. The presence of catalase decreases lethality of ionizing radiation (IR) on cells [1] mainly because it catalyses the decomposition of hydrogen peroxide produced during irradiation [2]. The most significant mechanism of catalase decomposition in diluted aqueous solution will be its reaction with reactive intermediates produced during radiolysis of water.

The aim of presented work was (a) to study the kinetics of hydrogen peroxide decomposition at various temperatures by bovine catalase irradiated with gamma rays in diluted aqueous solution and (b) to determine the influence of dose and dose rate on rate constants and activation energy of the reaction.

EXPERIMENTAL

Diluted aqueous solutions with enzyme concentrations of 10^{-3} g mL⁻¹ and 10^{-5} g mL⁻¹ in 0.01 mol dm⁻³ phosphate buffer (pH = 7.1) were used for the study. Samples were irradiated in closed 50 mL polypropylene test tubes at ambient temperature of 25°C, using ⁶⁰Co source Gammacell 220 with two dose rates 5.5 and 70 Gy h⁻¹. Solutions containing 1×10^{-5} g mL⁻¹ catalase were irradiated with doses up to 100 Gy; samples containing 1×10^{-3} g mL⁻¹ catalase were irradiated with doses up to 1000 Gy.

Catalytic activity of catalase was measured immediately after stopping the irradiation of samples. The catalytic decomposition of hydrogen peroxide at constant pressure and constant temperatures of 27, 32, 37, 42 and 47°C was used for the measurements [3].

RESULTS

It was observed that catalytic decomposition of hydrogen peroxide under given conditions using non-irradiated catalase is the first order reaction in the whole measured interval at all temperatures. There are only minor differences in kinetic curves at various temperatures, as the catalase kinetics is known to have very small temperature dependence due to the low energy of activation [4]. With non-irradiated catalase, we found that in studied interval, the degree of hydrogen peroxide decomposition does not depend on the reaction temperature. Even after irradiation, the decomposition still proceeds as the first order reaction. We may assume that the mechanism of hydrogen peroxide decomposition does not change significantly in the first order interval, despite the irradiation or change of temperature.

Non-exponential decrease of catalase activity with the dose at both dose rates is in agreement with findings of other authors [5] who observed similar behavior in irradiated air saturated solutions, albeit at much higher enzyme concentrations and higher dose rate. This agreement indicates that the mechanism of radiation induced inactivation of catalase, i.e. the type of radiation induced damage, does not change in wide range of concentrations and dose rates.

The data displayed in Arrhenius coordinates indicate that the activation energy of hydrogen peroxide decomposition is roughly independent of the applied dose. The similar results were obtained for higher dose rate of 70 Gy h⁻¹. The average obtained value of activation energy is 9.8 kJ mol⁻¹, which is in good agreement with values of other authors [4, 6].

Figure 1 illustrates that irradiation of more concentrated, 10^{-3} g mL⁻¹, catalase solution at higher doses has a lower effect than irradiation of more dilute 10^{-5} g mL⁻¹ solution at lower doses. Kinetic curves indicate that gamma irradiation affects the reaction more significantly at a higher dose rate.

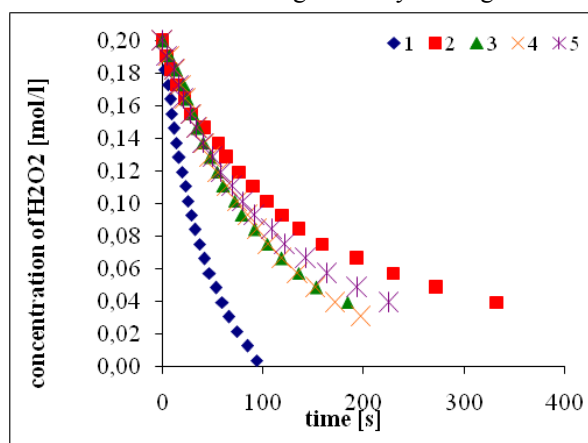


Fig. 1. Effect of catalase concentration on radiation inactivation, catalytic activity measured at 37°C;

1: 0 Gy;

2: 50 Gy, concentration of irradiated catalase 10^{-5} mg L⁻¹;

3: 250 Gy, concentration of irradiated catalase 10^{-3} mg L⁻¹;

4: 500 Gy, concentration of irradiated catalase 10^{-3} mg L⁻¹;

5: 1000 Gy, concentration of irradiated catalase 10^{-3} mg L⁻¹

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BEHAVIOR OF CADMIUM(II) IN IRRADIATED AQUEOUS SOLUTIONS

B. Drtinová, M. Pospíšil

INTRODUCTION

- heavy metals contained predominantly in industrial wastewater = dangerous contaminants
- their removal before the recycling or releasing of wastewater into the environment
- utilization of ionizing radiation as an alternative process to the conventional chemical methods

EXPERIMENTAL

- starting solutions of Cd^{II} (in form of nitrate or chloride) with initial concentration of 27 or 100 mg L^{-1}
- added complexants - $3 \times 10^{-4} \text{ mol L}^{-1}$ EDTA and 2.5×10^{-4} , 5×10^{-4} or $1 \times 10^{-3} \text{ mol L}^{-1}$ citric acid (HCit)
- OH radical scavengers - HCOOK , CO_3^{2-} , HCO_3^{2-} , and 10% methanol
- irradiated by accelerated electrons (4.5 MeV) from linear accelerator (dose rates of 1.5 kGy s^{-1}) determined by alanine dosimeter
- changes in metal concentration determined by atomic absorption spectroscopy with flame atomization
- normalized concentration $N_C = [\text{Cd}^{\text{II}}]/[\text{Cd}^{\text{II}}]_0$, where $[\text{Cd}^{\text{II}}]_0$ is the initial and $[\text{Cd}^{\text{II}}]$ the actual concentration of soluble cadmium species
- speciation modelling of cadmium in solution before irradiation - PHREEQC program with MINTEQA database

RESULTS

The radiation behavior of cadmium present in initial solution as an uncomplexed species:

- In the absence of OH radical scavengers the radiation reduction of cadmium does not occur.
- Cadmium (100 mg L^{-1}) can be completely removed from aqueous solutions (pH ~5 – 6) containing $1 \times 10^{-2} \text{ mol L}^{-1}$ of HCOOK at the dose of 15 kGy (Fig. 1).
- HCOOK behaves like a weak complexant and the species $\text{Cd}(\text{Formate})^+$ is formed.
- Product of irradiation of the solutions containing $\text{Cd}(\text{NO}_3)_2$ and HCOOK is CdCO_3 .
- The radiation product in the system containing chloride is metallic cadmium.
- The positive effect of deaeration with N_2O or N_2 was observed in the range of lower doses.
- The addition of solid promoters (bentonite, active carbon, zeolite, Cu_2O , NiO , TiO_2 , and CuO) reduced the efficiency of radiation removal of cadmium.

The radiation behavior of cadmium present in initial solution as a complexed species:

- The efficient degradation of cadmium complexed with EDTA proceeds up to 90% at the dose of 45 kGy with addition of $5 \times 10^{-3} \text{ mol L}^{-1} \text{ CO}_3^{2-}$ as pH buffer (pH of 10.5) (Fig. 2).
- The product of irradiation is CdCO_3 .

- The presence of $1 \times 10^{-2} \text{ mol L}^{-1}$ of HCOOK in the solution is necessary for the radiation removal of cadmium complexed with citric acid ($1 \times 10^{-3} \text{ mol L}^{-1}$) at pH = 8.
- With increasing concentration of HCOOK decreases the pH value necessary for radiation removal of cadmium.
- The efficiency of removal of cadmium could be enhanced by adding zeolite as a solid promoter in the irradiated system.

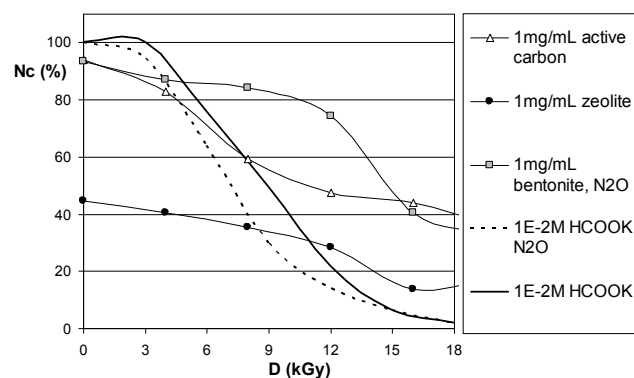


Fig. 1. Dependence of normalized concentration N_C of Cd^{II} ions on the dose of irradiation D for the sample with an addition of $1 \times 10^{-2} \text{ mol L}^{-1} \text{ HCOOK}$ and modifiers

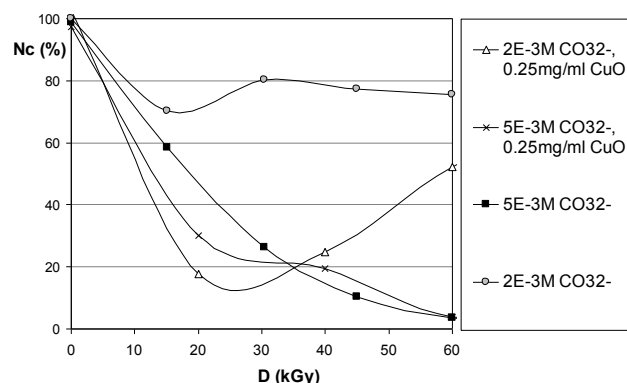


Fig. 2. Dependence of normalized concentration N_C of Cd^{II} species on the dose of irradiation D (100 mg L^{-1} of Cd^{II} , $3 \times 10^{-4} \text{ mol L}^{-1}$ EDTA, and with addition of solid modifiers in systems containing CO_3^{2-})

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PRODUCTS OF RADIATION REMOVAL OF LEAD FROM AQUEOUS SOLUTIONS

B. Drtinová, M. Pospíšil, V. Čuba

INTRODUCTION

- heavy metals contained predominantly in industrial wastewater = dangerous contaminants
- their removal before the recycling or releasing of wastewater into the environment
- utilization of ionizing radiation as an alternative process to the conventional chemical methods

EXPERIMENTAL

- starting solutions of Pb^{II} (in form of nitrate) with initial concentration of 100 mg L^{-1}
- OH radical scavengers - HCOOK, isopropanol
- irradiated by accelerated electrons (4.5 MeV) from linear accelerator (dose rates of $0.5 - 1 \text{ kGy s}^{-1}$) determined by alanine dosimeter
- changes in metal concentration determined by atomic absorption spectroscopy with flame atomization
- normalized concentration $N_C = [Pb^{II}]/[Pb^{II}]_0$, where $[Pb^{II}]_0$ is the initial and $[Pb^{II}]$ the actual concentration of soluble lead species
- thermogravimetric analysis - Netzsch STA 409 with quadrupole mass-spectrometer Balzers QMG 420
- speciation modelling of lead in solution before irradiation - PHREEQC program with MINTEQ database

RESULTS

- Lead (100 mg L^{-1}) can be completely removed from aqueous solutions ($\text{pH} \sim 5 - 6$) containing $1 \times 10^{-2} \text{ mol L}^{-1}$ of HCOOK already at the dose of 2.5 kGy (Fig. 1).
- HCOOK behaves like a weak complexant and the species $Pb(\text{Formate})^+$ is formed ($\leq 3\%$ of HCOOK present).
- With increasing concentration of HCOOK in the solution, species $Pb(\text{Formate})^+$ is present up to 50% (Fig. 2).
- In the system with lead in the 10-times excess over HCOOK the product is metallic lead - HCOOK works as an OH radical scavenger; species $Pb(\text{Formate})^+$ is not present in solution.
- In the system containing half the amount of lead in comparison to concentration of HCOOK, surprisingly, product of radiation removal is mix of metallic lead and precipitate of $PbCO_3$.
- In the system with 50-times excess of HCOOK over lead, the product is $PbCO_3$, with traces of metallic lead and probably precipitate of $Pb(\text{COO})_2$.
- The carbonate precipitation takes place when CO_2 formed by radiolytic degradation of HCOOK reacts and precipitates with Pb^{2+} , forming $PbCO_3$.

$$Pb^{2+} + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{PbCO}_3 + 2\text{H}^+$$

- The presence of nitrate ion is very important for the radiation process because it scavenges solvated electron with a relatively high yield; hence, it significantly contributes to generation of an oxidative environment which converts the formate ion to CO_2 .
- Under the slightly acidic conditions, at $\text{pH} < 5.75$, in the system with isopropanol before irradiation, Pb^{2+} is the major species and represents 98% of lead.
- In the system with 10% isopropanol, as an OH radical scavenger, radiation reduction of lead occurs and the product is metallic lead.

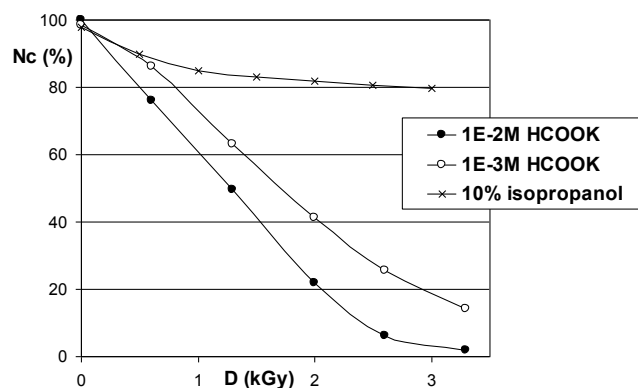


Fig. 1. Dependence of normalized concentration N_C of Pb^{II} on the dose of irradiation D for the sample with an addition of $1 \times 10^{-2} \text{ mol L}^{-1}$ HCOOK, for the sample with the addition of $1 \times 10^{-3} \text{ mol L}^{-1}$ HCOOK or for the sample with addition of 10% isopropanol

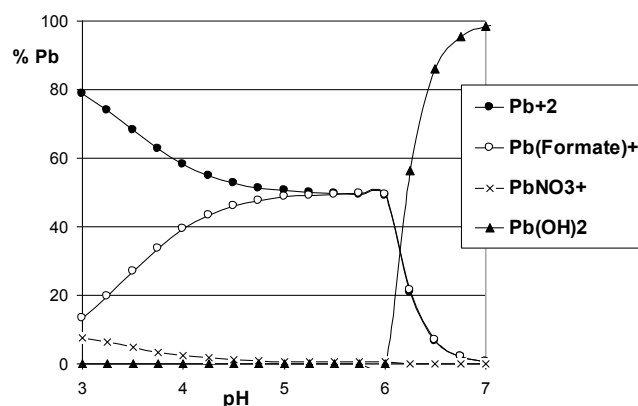


Fig. 2. Speciation of HCOOH in the system containing 100 mg L^{-1} Pb ($Pb(\text{NO}_3)_2$) and $1 \times 10^{-2} \text{ mol L}^{-1}$ HCOOK

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MEASUREMENT OF GROWTH AND SURVIVAL CURVES OF MICROORGANISMS INFLUENCED BY RADIATION

V. Múčka, P. Bláha, V. Čuba

INTRODUCTION

One important part of radiation chemistry is [1, 2] its application to radiation biology of microorganisms. The aim of this paper was to find and verify convenient methods and conditions for objective and quantitative comparison of growth and survival curves for gamma or UV irradiated cells using earlier experiences [3, 4]. The yeasts *Saccharomyces cerevisiae* were chosen for this purpose.

EXPERIMENTAL

The aqueous suspension of the cells was irradiated with gamma ^{60}Co or with germicidal medium pressure mercury UVH 1016-6 lamp or low pressure mercury lamp. The cell suspension was intensively agitated during UV irradiation so that the light energy was absorbed by a whole mass of irradiated sample. Hence, it was possible to express the dose rate in Gy h^{-1} (instead of fluence rate or exposure rate in W m^{-2}). Therefore, both types of irradiation (gamma and UV) could be directly compared. After irradiation, 4 mL of sample were transferred into 15 mL of the liquid substrate and the turbidity of suspension was measured during cultivation of culture at 30 °C. Another aliquot part of irradiated suspension was, after dilution, plated on the complete nutrient agar for cultivation of colonies.

RESULTS

Using the special method for evaluation of growth curves in semilog plots it was found that the slope k of the straight line constructed in this way describes objectively the growth of microbial culture. Following qualitative conclusions can be drawn from the growth curves constructed in this way: First, the slopes of straight lines decrease monotonously with increasing doses of gamma and UV irradiation. Secondly, the effect of UV radiation is much more significant than the effect of gamma irradiation. Thirdly, gamma and UV irradiation cause the stable changes in reproductive abilities of cells transferred to the daughter generations as the irradiation of inoculum leads to increase in the characteristic doubling time of microbial culture (not only to a prolongation of the lag phase). Following statements can be drawn from the dependences of Δk and Δk_r values (absolute and relative differences in the slopes of growth straight lines prior and after irradiation, respectively) on the dose of irradiation (Fig. 1): First, the dependences in Fig. 1 confirm that the doubling time of microorganisms increases with increasing doses of both kinds of irradiation. Secondly, the doses of gamma irradiation ranged from 1 to 2 kGy do not cause a higher damage of the culture than about 30 %. On the other hand, the UV doses above 300 Gy cause a total inhibition of the cell proliferation ($\Delta k_r = 100$ %). This great difference in the effect of both kinds of irradiation may be due to very different time of exposure and the difference in applied dose rates of both kinds of irradiation (the dose rate of UV irradiation was about thousand times higher than

the dose rate in the case of gamma irradiation). A dramatic difference in action of gamma and UV radiation can be demonstrated also by means of surviving curves: With increase in dose rate of gamma radiation by the factor of 12, the slope of straight line $\ln [\text{percent survival}] = f(D)$ decreases by the factor of 1.7. Practically the same decrease in the slope (by the factor of 1.6) needs the increase in dose rate of UV irradiation by the factor of 3.3 only.

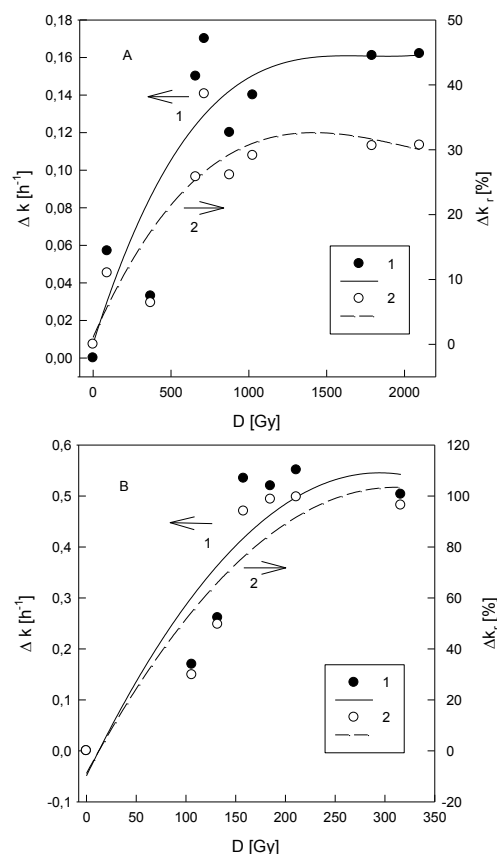


Fig. 1. Dependence of absolute (Δk) or relative (Δk_r) differences in the slopes of growth curves in semilog plot prior and after (A) γ and (B) UV irradiation on the applied dose

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PHOTO - AND RADIATION INDUCED PREPARATION OF ALUMINIUM OXIDE

J. Bárta, M. Pospíšil, V. Čuba, V. Múčka

INTRODUCTION

In addition to general use of alumina in different industrial applications such as e.g. protective coatings, soft abrasives, refractories, membranes, ceramic material, imitation of jewel and etc. in recent decades the substantial attention has been devoted to the study of nano-sized particles, especially organized nanoporous alumina owing to its thermal and chemical stability, adsorption ability and catalytic activity [1]. Moreover, the metastable forms of aluminium oxide, so called transition alumina, have extensive potential for being used in other special applications such as thermometric gas sensors, dosimeters or precursors for oxide composites, possessing promising luminescent, thermoluminescent and scintillation properties [2, 3]. Major part of conventional procedures leads to the formation of various precursors. During the course of their calcination, the different intermediate phases of Al_2O_3 or their mixtures up to stable $\alpha\text{-Al}_2\text{O}_3$ are created dependent predominantly on the temperature. Therefore, the synthesis of alumina with tunable properties appears to be complicated and new methods solving this problem are intensively explored. One of the promising methods may be radiation- or photo- induced preparation from aqueous solutions of aluminium salts with suitable admixtures.

The aim of this work was to explore the fundamental possibilities of radiation and photolytic preparation of Al_2O_3 from aqueous solutions, inclusive of experimental conditions leading to this material and to perform its basic characterization.

EXPERIMENTAL

The aqueous solutions of aluminium chloride or nitrate (10^{-2} and $2.5 \times 10^{-2} \text{ mol dm}^{-3}$) containing alkaline formate as scavenger for OH radicals and H_2O_2 were irradiated by accelerated 4.5 MeV electrons by doses ranging from 0 to 80 kGy and by medium pressure mercury lamp with maximum power input of 400 W. Separation of formed finely dispersed solid phase was performed using microfiltration cell and Millipore 0.45 μm filter. After washing and drying at 40 $^\circ\text{C}$, the samples were thermally treated at various temperatures under vacuum or in air. The solid products of radiation or photolytic treatment were investigated by means of X-Ray Powder Diffraction and by thermoanalyzer connected with quadrupole mass spectrometer. Their textural parameters such as specific surface area, determination of pore volumes and sizes were performed using ASAP 2010 apparatus.

RESULTS

Crystalline aluminium oxide was successfully prepared by radiolysis or photolysis of aqueous solutions of aluminium salt (chloride or nitrate) containing alkaline formate and hydrogen peroxide, all in suitable concentration ratio.

During irradiation the pH value of solutions increases and predominantly amorphous solid phase consisting of hydrated aluminium oxide, hydrated $\text{Al}(\text{OH})_3$ or their mixture, as well as $\text{AlO}(\text{OH})$ – boehmite, differing in their stability in time is formed. Analogously to classical chemical procedures, the subsequent thermal treatment of these precursors in air or under vacuum led, depending on the temperature, to the various crystalline modifications (Fig. 1) of alumina with different textural and structural parameters.

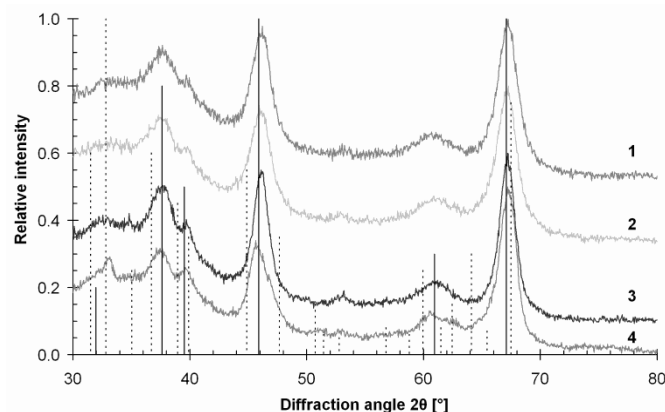


Fig. 1. Diffractograms of solid phase separated from UV- or accelerated electrons irradiated solution of $2.5 \times 10^{-2} \text{ mol dm}^{-3} \text{ AlCl}_3$ with $10^{-1} \text{ mol dm}^{-3} \text{ HCOOK}$ and $1 \text{ mol dm}^{-3} \text{ H}_2\text{O}_2$ after thermal treatment under vacuum or in air; UV-irradiated and treated at 800 $^\circ\text{C}$ in air (1), electron beam irradiated and treated at 800 $^\circ\text{C}$ under vacuum (2), UV-irradiated and treated at 1000 $^\circ\text{C}$ under vacuum (3), electron beam irradiated and treated at 1000 $^\circ\text{C}$ in air (4). Solid line - $\gamma\text{-Al}_2\text{O}_3$, dashed line - $\theta\text{-Al}_2\text{O}_3$.

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EFFECT OF RADIATION ON METALLIC COMPOUNDS IN AQUEOUS SOLUTIONS

J. Bárta, M. Pospíšil, V. Čuba

INTRODUCTION

For several decades, the effects of radiation on various solutions containing metal ions have been studied. Radiation-induced reduction can be used for preparation of metallic nanoparticles (colloidal metals) [1]. Metal ions are reduced by $\text{H}\cdot$ radicals and e_{aq}^- (which are produced by the radiolysis of water), they aggregate and form bigger particles. To prevent or hinder the aggregation, a stabilizing agent must be present in the solution, e.g. gelatine, polyvinyl alcohol or polyacrylate [1, 2]. Preparation of colloidal metal strongly depends on pH of the solution [3], which can even affect the composition of the final product.

EXPERIMENTAL

We have studied the influence of γ -radiation, accelerated electrons and UV light on the aqueous solutions of 10^{-3} to 10^{-2} mol dm $^{-3}$ copper sulphate (CuSO_4) at natural pH in the presence of various stabilizing agents (ethylenediaminetetraacetic acid EDTA, polyvinyl alcohol PVA, sodium hexametaphosphate SHMP) and/or $\cdot\text{OH}$ scavenger (propan-2-ol). To prevent reactions of dissolved oxygen with unstable products of radiolysis, yielding various strong oxidizing species, all solutions had been deaerated by nitrogen prior to irradiation. Three radiation sources were used for experiments: radionuclide source Gammacell 220 (^{60}Co , dose rate of 8 Gy h $^{-1}$), pulse linear electron accelerator LINAC 4-1200 (mean electron energy of 4.5 MeV) and medium-pressure mercury lamp.

RESULTS

AAS analysis clearly showed that with the increasing dose, the concentration of copper ions in γ -irradiated solutions decreased only in the presence of $\cdot\text{OH}$ scavenger. At the absorbed dose of 10 kGy, the decrease to circa 10 % of initial concentration of copper ions was observed. The pH changed during irradiation process from circa 5.6 (natural pH) to 3.3 (at 10 kGy) and absorption peak at 750 nm (caused by presence of $[\text{Cu}(\text{EDTA})]^{2-}$ complex) diminished, which corresponds to supposed reduction of copper ions. During irradiation with accelerated electrons, dark pink colloid was formed in studied solutions containing PVA, whereas, in other solutions, black-coloured precipitate was formed. Both precipitate and colloid were found to be extremely sensitive to oxygen and rapidly dissolved when brought into the contact with air. X-Ray Powder Diffraction analysis of the precipitate proved the presence of crystalline copper Cu and cuprous oxide Cu_2O , which could be formed during the irradiation (Fig. 1, [3]).

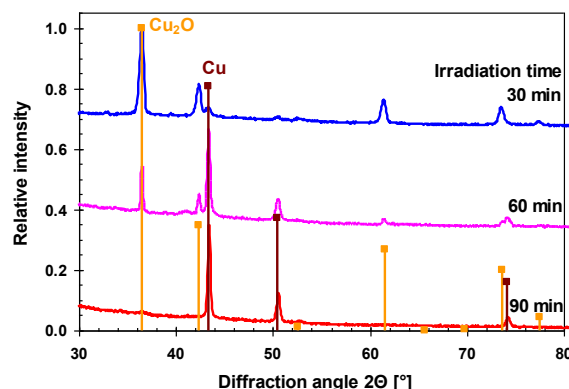


Fig. 1. Diffractogram of the precipitate formed during UV-light irradiation (1.3 mol dm^{-3} propan-2-ol, $10^{-2} \text{ mol dm}^{-3}$ CuSO_4 , $<10^{-5} \text{ mol dm}^{-3}$ PVA)

According to the Mie Scattering theory, nanometre-sized copper particles exhibit absorption peak at around 580 nm (surface plasmon peak) and a weak, broad absorption band between 300 and 500 nm. After irradiation, both these features have been observed in the optical absorption spectra of studied solutions, in which both OH scavenger and stabilizing agent were present (Fig. 2).

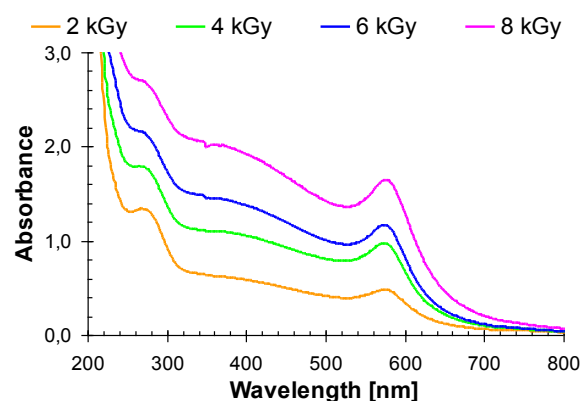


Fig. 2. Evolution of optical absorption spectra with increasing dose (1.3 mol dm^{-3} propan-2-ol, $10^{-2} \text{ mol dm}^{-3}$ CuSO_4 , $<10^{-5} \text{ mol dm}^{-3}$ PVA)

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REMOVAL OF NICKEL AND COBALT IONS FROM AQUEOUS SOLUTIONS USING ELECTRON-BEAM TREATMENT

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INTRODUCTION

Irradiation of the aqueous solutions containing various concentration levels of heavy toxic metals such as Hg, Pb, Cd was successfully applied as a method for effective removal of these hazardous contaminants. In the presence of substances scavenging hydroxyl radicals produced through water radiolysis, the metal ions may be gradually reduced to their lower oxidation states or up to insoluble metallic form. While radiation reduction (with gamma rays or accelerated electrons) of solutions containing divalent ions of above mentioned metals was thoroughly studied by means of pulse radiolysis, and mechanism of the whole process was sufficiently clarified, the similar data concerning reduction of ions of the less toxic metal ions such as Ni^{2+} and Co^{2+} , especially reactions leading to the final precipitated product are poor or contradictory [1,2].

The aim of this work was to investigate the possibilities of removal of Ni^{2+} and Co^{2+} ions from aqueous solution using accelerated 4.5 MeV electrons under different conditions.

EXPERIMENTAL

The aqueous solutions of Ni^{2+} or Co^{2+} ions, in form of nitrate, of different concentration and various OH radical scavengers were irradiated in glass ampoules by accelerated electrons with doses ranging from 0 to 120 kGy with a dose rate of 1.5 kGy s^{-1} . Products of irradiation – finely dispersed metallic particles or precipitated compounds were separated by centrifugation. The changes of metal ions concentration in solution were determined using AAS with flame atomization. Several sets of solutions were saturated with oxygen, nitrogen or nitrous oxide prior irradiation. The solid products of radiation treatment were further investigated by X-ray diffraction analysis and by thermal analysis connected with quadrupole mass spectrometry. The process of radiation removal may be characterized by relative concentration $C_N = [\text{Me}^{2+}] / [\text{Me}^{2+}]_0$ where $[\text{Me}^{2+}]_0$ is the initial and $[\text{Me}^{2+}]$ the actual concentration of the metal ion, or by radiation chemical yield $G(-\text{Me}^{2+})$, in $\mu\text{mol J}^{-1}$.

RESULTS

The high degree of removal of metal ions (more than 90%) requires different doses applied for Ni^{2+} or Co^{2+} ions depended also on their initial concentration and concentration of HCOOK scavenger. The optimum value of pH lies in the range of 6 - 8. Different courses of dependence of radiation chemical yields $G(-\text{Me}^{2+})$ on the dose of radiation for both metal ions give evidence for different and complicated mechanism of the radiation process. It was found that, in the solutions containing formate scavenger, the precipitate does not correspond to the colloidal metals. The results of thermoanalyse showed that the majority part of product is formed by basic carbonate of variable stoichiometry. Therefore, the radiation reduction is not the only process leading to the removal

of metal ions from the solution. The proportion between solid product of reduction and precipitation may be different for Co or Ni as it follows from Fig. 1 representing the effect of different gases on relative concentration, C_N , which were applied before the irradiation.

In contrast to the systems containing formate as scavenger for OH radicals, in solutions with aliphatic alcohols as scavengers (methanol, ethanol, and 2-propanol) the radiation reduction takes place as predominant process due to reduction of Me^+ intermediate by corresponding alcohol radicals. However, their reducing power is different.

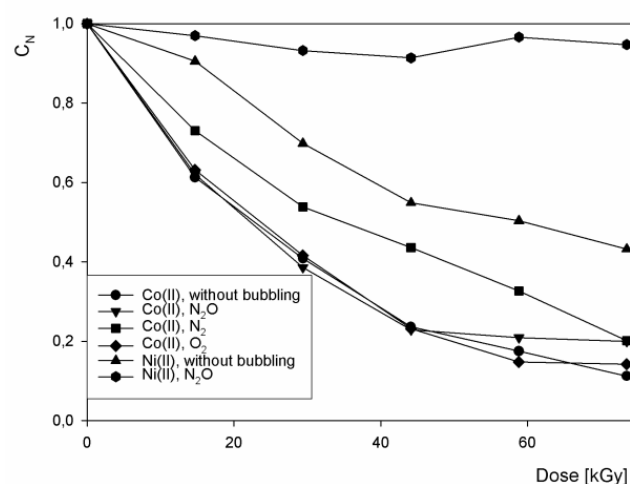


Fig. 1. Dependence of relative concentration C_N of Co^{2+} and Ni^{2+} ions on the dose of irradiation for the standard solutions nondeaerated and deaerated by bubbling with N_2O , N_2 , and O_2 .

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REACTION ORDERS OF RADIATION DECHLORINATIONS OF CHLORINATED HYDROCARBONS

V. Múčka, V. Čuba, R. Silber, M. Pospíšil

INTRODUCTION

The irradiation of aqueous solutions of chlorinated hydrocarbons with ionizing radiation represents alternative method used for remediation of the waste or groundwater [1]. According to some papers [2], radiation induced dechlorination is rather complicated process involving hundreds of elemental reactions. Therefore, the investigation of influence of various conditions on the reaction order of dechlorination of four early studied hydrocarbons (PCE -tetrachloroethene [3], TCE – trichloroethene [4], CHCl_3 – chloroform [5], and CCl_4 – tetrachloromethane [6]) was performed.

EXPERIMENTAL

Following approximate description of dechlorination kinetics may be proposed under the condition of steady state concentration of hydrated electrons:

$$k \times t \times b^m = [1/(n-1)] \times [1/c^{n-1} - 1/c_0^{n-1}] \quad (1)$$

$$k \times t \times b^m = \ln(c_0/c) \quad (2)$$

for $n \neq 1$ and for $n = 1$, respectively, where k is the rate constant, t is the time (or, at the constant dose rate, the dose D), b is the steady state concentration of the hydrated electrons, m and n are the partial reaction orders related to the electrons and chlorinated hydrocarbons, respectively, and c_0 and c are initial and actual concentrations of chlorinated hydrocarbon, respectively. The n -value at which the function $1/c^{n-1} = f(D)$ (for $n \neq 1$) or $\ln c = f(D)$ (for $n = 1$) will be linear determines reaction order related to chlorinated hydrocarbons. In other words, n possessing the highest regression factor of linear fit will determine reaction order.

RESULTS

The regression factors depend non-monotonously on the values of n (supposed reaction order). The X-coordinate of the pronounced maximum on these dependences determines the order of reaction. The maxima shift to higher values when broader dose ranges are considered for evaluation of reaction order. That means that the reaction order increases with the dose (Fig. 1). This dependence and relatively high values of the reaction orders in some systems indicates complexity of the processes occurring in irradiated solutions. The linear rise of the reaction order indicates increasing sensitivity of reaction rate to the change of chlorinated hydrocarbons concentration. It may be due to the fact that the concentrations of chlorinated hydrocarbons, unlike the e_{aq}^- or OH^\cdot reactants, decrease in the course of irradiation. In the same way, it was found that the reaction orders decrease with increasing initial concentrations of chlorinated hydrocarbons, namely at very low initial concentrations. The high values of the reaction orders at low initial concentrations may be explained similarly as it was done above in the case of dose dependences. The reaction

order of PCE dechlorination may be significantly reduced by ozone introduction, namely at low initial concentration of hydrocarbon. Besides, the order of dechlorination of tetrachloromethane was found to be higher at higher concentration of NO_3^- ions because of high efficiency of scavenging of electrons by these ions.

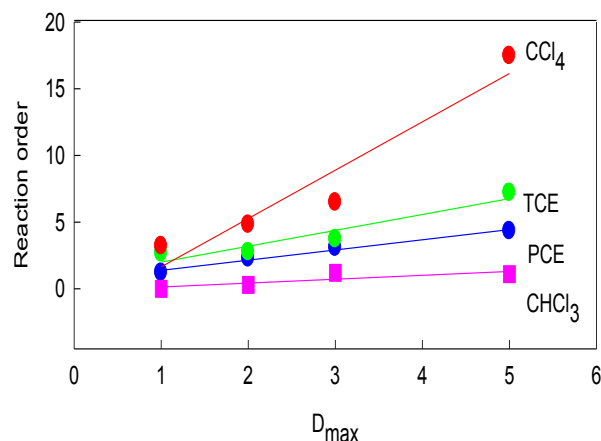


Fig. 1. Dependence of reaction order on the maximum absorbed dose D_{\max} for dechlorination of PCE, TCE, CHCl_3 , and CCl_4 .

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CATALYTIC ACTIVITY OF RADIATION INDUCED SILVER NANOPARTICLES IN HYDROGEN PEROXIDE DECOMPOSITION

R. Silber

INTRODUCTION

Most of the radiation-assisted methods is the photoreduction of AgNO_3 aqueous solution upon exposure to UV light. Some reports refer to the reduction of noble metals in aqueous solutions by gamma radiation, too. However, application of electron beam irradiation to the nanoparticles preparation is rare. Reducing effect of Triton X-100 and subsequent stabilizing effect on the nanoparticles are also well known. The present contribution deals with the effect of fast electrons irradiation conditions on the catalytic activity of silver nanoparticles prepared by reduction of AgNO_3 in Triton X-100 aqueous solutions.

EXPERIMENTAL

Influence of various molar ratios of non-ionic surfactant Triton X-100 (polyoxyethylene-t-octylphenyl ether) and AgNO_3 in water on the radiolysis efficiency was studied. Concentration of Triton X-100 varied from 0.01 to 2 of weight % at constant concentration of AgNO_3 (0.1 mol L^{-1}). Some reduction sensibilizers were used. Irradiation was realized in glass ampoules (20 mL volume) with fast 4 MeV electrons from linear accelerator LINAC; current of electrons, which influences resulting dose, may be controlled up to 0.35 mA.

Irradiation experiments were performed above critical micelle concentration and the temperature was below the cloud point.

RESULTS

Depending on applied dose (from 0 to 32 kGy), formations of yellow, brown and black coloured colloid systems were observed. Formation of well-dispersed silver nanoparticles was confirmed by means of electron microscopy, X-rays diffraction patterns and UV-visible spectroscopy. Radiation yield (expressed as a number of species per 100 eV of absorbed energy) of silver was measured by argentometric titration with potentiometric detection. Catalytic activity of prepared systems was tested via the reaction of hydrogen peroxide decomposition. Some amount of colloid solution was injected into stirred H_2O_2 solution and rate of released oxygen was measured by recording of system pressure increase. Experiments were performed at constant temperature and constant system volume. Catalytic activity was characterized through the hydrogen peroxide decomposition rate constant.

CONCLUSIONS

The most interesting result of this study is the proportionality of silver nanoparticles catalytic activity, represented by rate constant, to the concentration of Ag nanoparticles characterised by the value of UV absorbance, and to the applied dose of ionising radiation, which is the main factor for determination of these species formation. So, rate constant of hydrogen peroxide decomposition may be used as a characteristic factor for preparation of nano-system.

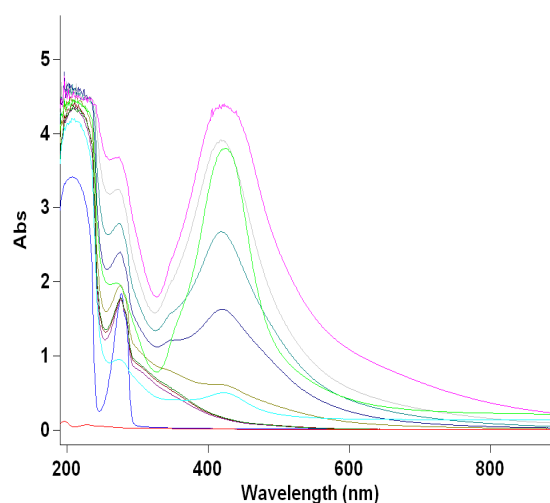


Fig. 1. Irradiation effect characterised by the values of UV absorbance arises with the applied dose of ionising radiation

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INTRODUCTION

Thiacalixarenes [1] are members of calixarene family that belongs among prospective extractants for the Partitioning process. Thiacalixarenes contain sulphur atoms instead of CH₂ group bridges in a calixarene structure. Although the calixarene family is known for a long time, the radiation stability of thiacalixarenes has not been extensively studied, yet.

EXPERIMENTAL

Radiation stability of thiacalixarenes (**1**) and (**2**) (Fig. 1) was assessed as the change in the distribution ratios of ²⁴¹Am and ¹⁵²Eu in synergistic systems. The aqueous phase consisted of a solution of COSAN (chloro-protected bis(1,2-dicarbolide) cobaltic acid) in 0.1M nitric acid; solutions of thiacalixarenes in nitrobenzene or 1,2-dichloroethane were used as the organic phase. Distribution ratios *D* for ¹⁵²Eu and ²⁴¹Am and their mutual separation factors were evaluated. The concentration of thiacalixarene in the irradiated samples was measured using HPLC and the activity of aqueous and organic phase was measured via gamma spectrometer with HPGe detector. The samples (solvent, solvent + water) were irradiated up to 100 kGy either by a pulse linear electron accelerator LINAC-4-1200 (Tesla V.T. Mikroel) or by a ⁶⁰Co source (Gammacell 220, AEC Ltd.). After the irradiation, the samples were processed for solvent extraction experiments as mentioned above.

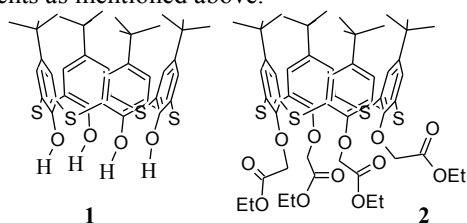


Fig. 1. Structures of studied thiacalixarenes.

RESULTS

In previous studies [2], it was found out that the extraction properties of thiacalixarenes increased dramatically in the presence of COSAN compounds. These studies showed that the synergistic effect depends significantly on the used thiacalixarene and diluent. However, it was found that the effect is independent on the type of COSAN compound used in experiments. The experiments performed in this work revealed that the radiation stability of studied systems is rather low.

It can be seen from Fig. 2 that in the case of the 1,2-dichloroethane solution, no ageing effect was observed during 10 weeks and no hydrolysis occurred in the contact with water during the same time in the blank samples. Fast decrease of the distribution ratio of americium with increasing dose was observed. In the solvent irradiated with a dose of 100 kGy, the distribution ratio of Am is 1/10 of the blank value.

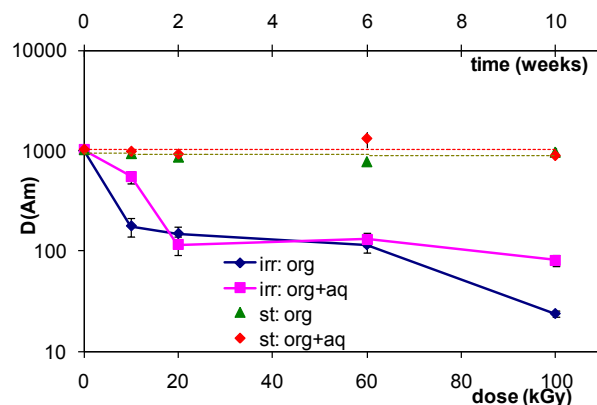


Fig. 2. Change in *D*(Am) for the irradiated (irr) and blank (st) samples with and without added water (Gammacell; org. phase: thiacalixarene (**2**) in 1,2-dichloroethane; aq. phase: 16.5mM COSAN in 0.1M HNO₃; contact time: 20 hrs).

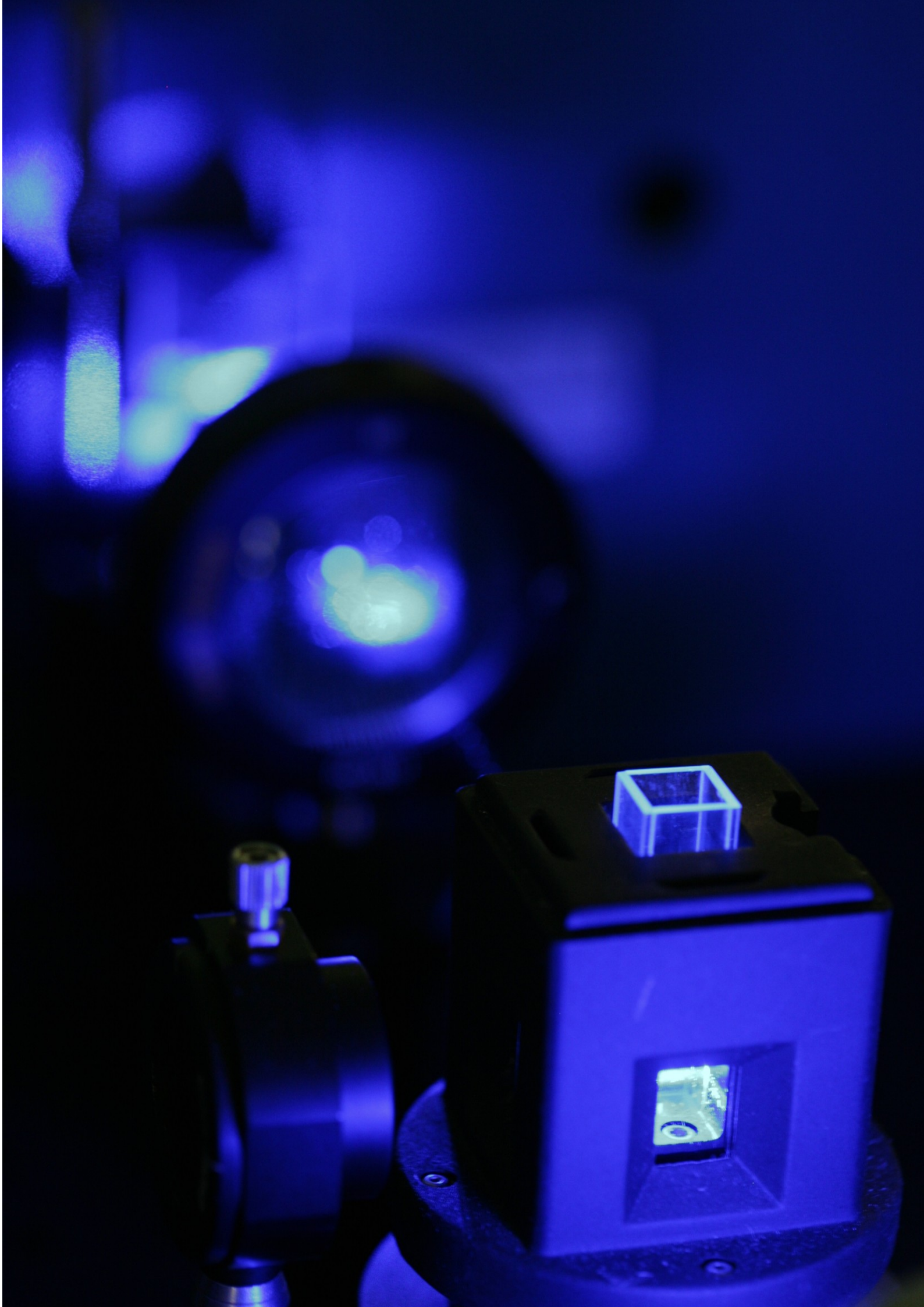
The nitrobenzene system seems to be somewhat less stable in time and less resistant towards hydrolysis since a slight decrease in the values of *D*(Am) in blank samples can be seen. Contrary to the results obtained in the 1,2-dichloroethane system, the values of *D*(Am) are very similar for the irradiated samples and blanks. It may indicate that the solvent is resistant towards the irradiation and what is observed is only the ageing effect.

Also, it seems that the presence of water during the irradiation does not influence significantly the radiation stability of thiacalixarene (**2**) and the solvents irradiated on LINAC (electrons) seem to be less degraded than those irradiated with Gammacell (γ radiation).

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Author, **Title**, Supervisor, Year

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K. Eigner Henke

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V. Kleinová

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M. Němec

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J. Pejchal

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M. Semelová

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R. Silber, 2010

PROJECTS AND GRANTS

Title, Code, Donator/Contractor; Chief Scientific Investigator(s)

Application of Radionuclides and Ionising Radiation, MSM6840770040, Ministry of Education, Youth and Sports, Czech Republic; J. John and M. Pospíšil

Safety of Nuclear Installations, MSM6840770020, Ministry of Education, Youth and Sports, Czech Republic; J. John, F. Šebesta and D. Vopálka

ACSEPT - Actinide reCYcling by SEparation and Transmutation, EC FP7 CP 211267, Euratom FP7, J. John and F. Šebesta

CINCH - Coordination of Education In Nuclear Chemistry, CA 249690, Euratom FP7, J. John

Extraction Properties and Radiation Stability of Thiocalixarene Derivatives, GA104/07/1242, Czech Science Foundation; V. Čuba

Use of Nuclear Analytical Techniques for Studying the Interaction of Tc-99 and Re in the Environment, GA 203/08/1276, Czech Science Foundation, F. Šebesta

Nanocomposite, Ceramic and Thin-layer Scintillators, KAN300100802, Grant Agency of the Academy of Sciences of the Czech Republic, V. Múčka

Research into the Properties of Materials for Safe Disposal of Radioactive Waste and the Development of Evaluation Procedures, FR-TI1/362, Ministry of Industry and Trade, D. Vopálka

Research of Barriers for Repositories of Radioactive Wastes, 1H-PK/25, Ministry of Industry and Trade, Czech Republic; D. Vopálka

Technology of the Electrochemical Decontamination of Soils, FI-IM4/0353, Ministry of Industry and Trade, Czech Republic; M. Němec

Utilisation of Innovative Remediation Technologies and Processes in the Removing of Uranium Chemical Mining Effects, FT-TA3/070, Ministry of Industry and Trade, Czech Republic; D. Vopálka

11th NEUDOS: Dosimetry in C 290 MeV/n ion Beam with Different Passive and Active Detectors, CTU 0916614, CTU Prague, K. Brabcová

Modern Trends in Radiation Chemistry-preparation of Oxide Catalysts, SGS10/095/OHK4/1T/14, CTU Prague, V. Čuba

Nuclear Energetics, Utilization of Radionuclides and Ionizing Radiation, SGS10/212/OHK4/2T/14, CTU Prague, M. Němec

Study of Release/Uptake Behavior of Natural Rock Samples from Ruprechtov Site, FJFI 43-100005, Nuclear Research Institute Řež plc, B. Drtinová

Determination of the Activities of Natural Radionuclides and Fission Products in the Samples Originating from Decontamination Processes, FJFI 49-08030, ALLDECO.CZ Temelín, J. John

Development of Advanced Methods of Actinides Speciation Study and Description of their Sorption on Mineral Surfaces, FJFI 40-07016; RAWRA Czech Republic, D. Vopálka

Fermi 2010 – Innovation of Education of the Nuclear Power Engineering by Cooperation of Prague's Universities' Departments, CZ.2.17/3.1.00/32196, EU Structural Funds / OPFA, B.Drtinová

The Inter-university Collaboration on Development of the Josef Underground Facility on the Field of Deposition of Dangerous Compounds and Gates, CTU 05-100321, Ministry of Education, Youth and Sports, M. Němec

Modernisation of the Instrumental Background for Education at FNSPE – Harmonisation of the Conditions for Handling of Ionising Radiation Sources for the Education and Research Needs with the Valid Legislation, CTU 05-047001, CTU Prague, M. Němec

Meeting the Legislative Requirements in the FNSPE Laboratories, CTU 4/31, CTU Prague, M. Němec

Innovation of the Instrumentation of the Laboratory for Practical Training in Nuclear Chemistry, CTU 05-14500, CTU Prague, J. John

RESEARCH FELLOWSHIPS / VISITING SCIENTISTS

OUTGOING:

B. Drtinová

The Effect of Gamma-Irradiation on the Extraction of Actinides by EiTDPa

Oregon State University, Radiation Center, Corvallis, U.S.A., April - June 2008

M. Němec

Accelerator Mass Spectrometry: Sample preparation for radiocarbon measurements

University of Bern and ETH Zürich, Switzerland, February 2008 - July 2009

J. Šuláková

Novel extractants for liquid-liquid extraction or extraction chromatographic separation of actinides and lanthanides

Washington State University, Radiochemistry, Pullman, WA, U.S.A, February 2008 - December 2010

INCOMING:

G. Modolo

Separation of minor actinides from high active liquid waste

Forschungszentrum Jülich, Jülich, Germany, January 2008

H. Gaggeler

Chemistry with single atoms of superheavy elements

Bern University, Department of Radiochemistry and Paul Scherrer Institute, Villigen, Switzerland, March 2008

L. Malinen

Influence of organic matter photodegradation on the separation of radiocobalt from liquid radioactive waste

University of Helsinki, Laboratory of Radiochemistry, Helsinki, Finland, April 2008

G. Geipel

Fluorescence in uranium(VI) systems - new insights from interactions in biosystems

Forschungszentrum Dresden, Rossendorf, Germany, May 2008

K. Viehweger

Synthetic and natural flavanoid metal interactions - possible importance to metal homoestasis of plants cells

Forschungszentrum Dresden, Rossendorf, Germany, May 2008

Baohua Gu

Biological Remediation of Uranium-Contaminated Groundwater and Soil

Oak Ridge National Laboratory, Environmental Sciences Division, U.S.A., August 2008

J.D. Navratil

Advances in the chemistry of actinoids / Molten salt oxidation of organic radioactive waste

Clemson University, Department of the Environmental Engineering and Earth Sciences, Clemson, SC, U.S.A., March – April 2009

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