ANNUAL REPORT

2007

Nuclear Chemistry

Czech Technical University in Prague

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Czech Technical University in Prague

DEPARTMENT OF
NUCLEAR CHEMISTRY

CENTRE FOR RADIOCHEMISTRY
AND RADIATION CHEMISTRY

NUCLEAR CHEMISTRY

Annual Report 2007

Editors: J. John, L. Kraus, V. Múčka, M. Pospíšil, D. Vopálka

EDITORIAL

Since its foundation in 1957, then as part of the Faculty of Technical and Nuclear Physics of the Charles University, the Department of Nuclear Chemistry (DNC) of the Faculty of Nuclear Sciences and Physical Engineering (FNSPE) of the Czech Technical University in Prague (CTU) has been not only the centre of education in nuclear chemistry but also, together with the Nuclear Research Institute in Řež, a leading institution in the research in all the sub-disciplines of this field in the former Czechoslovakia and later in the Czech Republic. This balance was promoted already by the founders of this department – Academician František Běhounek, a former student of Marie Curie-Skłodowska and the most distinguished Czech physicist-radiologist, and Professor Vladimír Majer, author of the first Czech monograph on radiochemistry (1942). Among the most remarkable scientific achievements of the Department, the discovery, in 1961, and elaboration of the substoichiometric principle by Professors Jiří Starý, Jaroslav Růžička and Adolf Zeman should be mentioned. For almost two decades, this discovery paved the way to achieving the utmost limits in trace analysis.

With the decline in the number of "nuclear" students in the 1980s and namely in the 1990s, the balance between education and research slowly became more and more shifted towards research. This trend culminated in 2003 by forming a new daughter unit – the Centre for Radiochemistry and Radiation Chemistry (CRRC) of the CTU. The mission of this research centre has been to fully integrate research in radiochemistry and radiation chemistry at the CTU into the European structures, to procure additional funds crucial for the delayed upgrading of the research infrastructure, and to offer opportunities of professional advancement to a new generation of researchers, all this in close cooperation with the DNC whose premises and equipment it shares.

Most of these ambitious goals were attained and thus nuclear chemistry at the CTU is now well prepared for entering the (hopefully starting) era of renaissance of nuclear power with a new generation of young scientists/teachers working in almost completely refurbished laboratories with modernised instrumentation. The fully upgraded complex of radiochemistry laboratories, licensed for work with open sources including the actinides, is now equipped with a full scale of radiometry instrumentation including gamma and alpha spectrometry, and LSC. 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 HPLC, gas-chromatograph, AAS and a structural X-ray to UV-VIS spectrophotometers equipped with external optical probe for in-situ reaction rate measurements. The very recent, and probably the major acquisition in the history of nuclear chemistry at the CTU, is the newly built laser spectrometer for the TRLFS studies of actinides and lanthanides complexation/speciation. This machine is one of the few machines of this kind that has been placed in the controlled zone and that can be used even for the work with radioactive material.

The current 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 or environmental protection – as well as radioecology. Very recently, radiopharmaceutical chemistry and medical applications of radionuclides and ionising radiation are being developed. At present, the CTU is a member of the ACTINET Network of Excellence, and several research groups became integrated into the 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. Also, the CTU is a well-established member of the IAEA Coordinated Research Programmes; occasionally, some staff members serve as the IAEA experts for various missions or IAEA trainees are hosted in Prague.

The nuclear chemists from the CTU have been active also in organising various seminars and conferences. The most important of these events is the series of the international Radiochemical Conferences held every four years in the Western Bohemian spa of Mariánské Lázně. Since their revival in 1998, the CTU has been – together with the Working Group for Nuclear Chemistry of the Czech Chemical Society – one of the two forces instrumental in their organisation, the other co-operators being the I. M. Marci Spectroscopic Society and the Czech Radioecological Society. Recently, this conference was selected by the Division for Nuclear Chemistry of the EuCheMS to supplement the established NRC series of conferences thus creating a regular bi-annual series of Pan-European nuclear chemistry conferences.

In addition to BSc. course in Nuclear Chemistry, the focal point of postgraduate education is divided approximately equally between the MSc. courses, where the students may opt for majoring in Applied Nuclear Chemistry, (Radio)Chemistry of the Environment, and recently also in Nuclear Chemistry in Biology and Medicine, and the PhD programme that has been focused strongly on research. Recently, with the decreasing numbers of MSc. graduates from the DNC and increasing emphasis on research, also non-nuclear MSc. graduates in chemistry have been admitted to the PhD courses in Nuclear Chemistry. These students then receive intensive training in most of the radiochemistry or radiation chemistry disciplines to reach a standard comparable to the DNC graduates.

In 2007, the DNC and CRRC employed 14 research/academic staff as well as 4 part-timers (maternity leave or external staff). At the same time, there were eight PhD students affiliated with the DNC or CRRC (the total number of PhD students in 2007 being 24, the remaining ones working in various research institutes). The research in nuclear chemistry at the DNC and CRRC was 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". The main research topics of the respective groups were as follows:

Speciation and Migration

- Study of radionuclide release and migration from nuclear facilities into the biogeosphere with an emphasis on physical and chemical forms of existence (speciation) of radionuclides in aqueous parts of the geosphere.
- Development and evaluation of methods of radionuclide speciation analysis, including complexes with humic substances.
- Study of critical radionuclides sorption on materials of repository barriers, on sediments and rock materials.
- Development of advanced migration codes and study of modelling of radionuclide transport in the vicinity of nuclear facilities, especially in the near-field of repositories.

Separation and Radioanalytics

- Development of advanced methods and materials for the Partitioning or for the treatment of operational or decommissioning NPP liquid radioactive waste.
- Development of new materials and separation procedures for the determination of difficult-to-measure radionuclides and for their application in radiochemical NAA and mass-spectrometric analytical techniques (AMS).
- Electrolytic decontamination of soils.
- Study of complexation of lanthanides and actinides with complexants relevant to the Partitioning or treatment of the NPP decontamination solutions using the TRLFS method.

Radiation Chemistry

- Environmental protection – development of radiation methods for degradation of chlorinated hydrocarbons and removal of heavy metals from groundwater and wastewater.
- Radiation catalysis – development of new catalysts, study of their properties, application of ionizing radiation and ion implantation in the various steps of their preparation.

- Radiation corrosion – study of corrosive processes of steel in the field of ionizing radiation, aimed at corrosion of containers with spent nuclear fuel.
- Preparation of nanoparticles – preparation of solid nanoparticles of metals and metal oxides from colloidal dispersions using UV and ionizing radiation.

Most of the international collaborations in this field were based on the links established and maintained within EU FP6 integrated projects EUROPART and FUNMIG or network of Excellence ACTINET (namely Research Centre Jülich, Research Centre Rossendorf, Johannes Guttenberg University, Mainz, or GRS Braunschweig, all Germany; University of Reading, U.K., ANSTO, Australia, or Chalmers University of Technology, Gothenburg, Sweden), IAEA Co-ordinated Research Projects (University of Helsinki, Finland, or RADON, Russia), or earlier collaborations (INEEL, USA). The main national collaborations included the Nuclear Research Institute Řež plc., Nuclear Physics Institute of the AS CR, or Institute of Inorganic Chemistry of the AS CR, all located in Řež near Prague, Radioactive Waste Repository Authority of the Czech Republic (RAWRA); DIAMO s.p., Stráž pod Ralskem, Institute of Chemical Technology, Prague, VŠB – Technical University of Ostrava, or a SME ALLDECO.CZ, Temelín.

The first of the two most important events in 2007 that influenced the present and the future of nuclear chemistry at the CTU was the termination of the extra-budgetary support of the CTU headquarters to the Centre for Radiochemistry and Radiation Chemistry. To simplify the operation of this small research unit, starting from the end of the fiscal year the CRRC was "downgraded" from its status of the independent CTU Research Centre to a Research Centre parallel to the Department of Nuclear Chemistry, both within the structure of the Faculty of Nuclear Sciences and Physical Engineering. This change even strengthened the very close links between the DNC and the CRRC and further facilitated their co-existence.

The other important event that further enhanced the research character of both the DNC and CRRC was the final setting in full operation of the new TRLFS laboratory. This achievement markedly consolidated their research potential, and the new laboratory is expected to contribute significantly to research findings in the near future.

As a result of the development described above, the complex DNC – CRRC resembles today rather a small research institute than a typical university department. This fact has also motivated our decision to try to pilot this version of the Annual Report of Nuclear Chemistry at the CTU – a miniature version of the annual reports we regularly receive from our colleagues from big research institutes worldwide. 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.

Since this Annual Report is a pilot version only, we would very much appreciate any comments and suggestions, namely on whether or not to invest the non-negligible amount of work into compiling such report even in the years to come. The authors of this preface would also like to extend their thanks to the editors of this Report, namely Dr. Vopálka for his constant interest and support, and L. Kraus for the technical and graphic editorial work, without whose effort this report would have never seen the light of the day.

Jan John   Viliam Múčka

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TEACHING

List of Courses in the Academic Year 2007-2008 (in Czech)

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
- 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 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 I 3 W A. Motl
- Fundamentals of chemistry II 3 S A. Motl
- General chemistry 7 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, J. John
- Ionising radiation detection and dosimetry 4 S J. John, A. Motl

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* External teacher

• Isotopes and reaction mechanisms	2		L. Lešetický*
• Kinetic theory of matter	2	S	V. Čuba
• Laboratory practice in radiochemistry 1	5	W	V. Čuba, M. Němec
• Laboratory practice in radiochemistry 2	6	W	V. Čuba, M. Němec
• Laboratory practice in the instrumental methods of research	4	S	M. Pospíšil, R. Silber
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• Nuclear materials technology	2	W	K. Štamberg
• Numerical exercises in physical chemistry 1	2	S	R. Silber
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• Numerical exercises in physical chemistry 3	2	S	R. Silber, B. Drtinová
• Numerical simulation of complex environmental processes	2	W	D. Vopálka
• Production of radionuclides	2	S	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
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• Radiopharmaceuticals 2	2		L. Lešetický*, M. Moša*
• Reaction kinetics	3	S	V. Múčka
• Separation methods in nuclear chemistry 1	3	S	M. Němec
• Separation methods in nuclear chemistry 2	2	W	M. Němec
• Solids	2	W	V. Múčka
• Synthesis of labelled compounds	2		L. Lešetický*
• Technology of the fuel cycles of nuclear power plants	2	W	K. Štamberg
• Trace radiochemistry	3	S	P. Beneš
• Transport processes	2	W	D. Vopálka

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* External teacher

RESEARCH REPORTS

■ Speciation and Migration

■ Separation and Radioanalytics

■ Radiation Chemistry

RADIOTRACER ANALYSIS OF THORIUM COMPLEXATION WITH HUMIC ACID USING FREE-LIQUID ELECTROPHORESIS

P. Beneš, O. Múčková

INTRODUCTION

Complexation of natural radionuclides with humic substances present in surface and ground waters can strongly affect their speciation and migration. Although the strong interaction of humic substances with thorium in natural waters has been well documented, formation and properties of humic complexes of thorium are not well known [1]. Therefore thorium complexation with Aldrich humic acid (HA) was studied in a broad range of experimental conditions using free-liquid electrophoresis. This method can be applied for very low concentrations of thorium and thus precipitation of thorium hydroxide can be avoided. Electrophoretic mobilities of thorium obtained characterize the formation and charge of its humate complexes [2,3].

EXPERIMENTAL

Electrophoretic mobility of thorium labelled with ^{234}Th towards cathode $_{+}u$ and anode $_{-}u$ was measured at its low concentrations ($\leq 10^{-9}$–10^{-5}M) in aqueous solutions of 0.01 M ($HClO_4$ + $NaClO_4$), pH 2-11, variable concentration of Aldrich humic acid (HA, 0 – 10 mg/L), 0 – 0.01 M NaF and 0 – 0.001 M $NaHCO_3$ using a three compartments cell [2]. At least 1 day old solutions were analyzed at 22 ± 3 °C.

RESULTS

It was found that addition of HA to the solution caused decrease in $_{+}u$ and increase in $_{-}u$ due to the formation of negatively charged humate complexes (ThHA). The changes were used for calculation of the abundance (*%ThHA*) and the mean mobility ($_{-}u_{ThHA}$) of the complexes. In the absence of added fluorides and carbonates, *%ThHA* approached 100 in the solutions containing $\leq 10^{-9}$ M Th and 0.1 – 10 mg/L HA, indicating predominance of ThHA complexes. An increase in the concentration of Th brought about a decrease in the abundance of ThHA at pH 2 and 3, when the ratio [Th]/[HA] exceeded 10^{-7} mol/mg. At the ratio equal to 10^{-6} mol/mg thorium bonding by HA significantly exceeded proton exchange capacity of dissociated carboxyl groups of the HA [3]. This suggests that the complexation proceeds at least partially by displacement of hydrogen ions from the nondissociated groups.
An attempt to calculate stability constant (in L/eq)

$$\beta_1 = [ThHA^{3+}] \cdot [Th^{4+}]^{-1} \cdot [HA^{-}]_{free}^{-1}$$

for pH 2 – 4 was complicated by the large value of *%ThHA* and its uncertainty so that only the minimum possible value of log β_1 = 9.59 could be determined, which is lower than that published for pH 4. Therefore *%ThHA* was suppressed by the addition of NaF to the solution and β_1 was recalculated. However, the value of β_1 thus obtained strongly depended on the concentration of NaF, which indicated formation of mixed complexes $ThF_{2-4}HA^{-x}$.

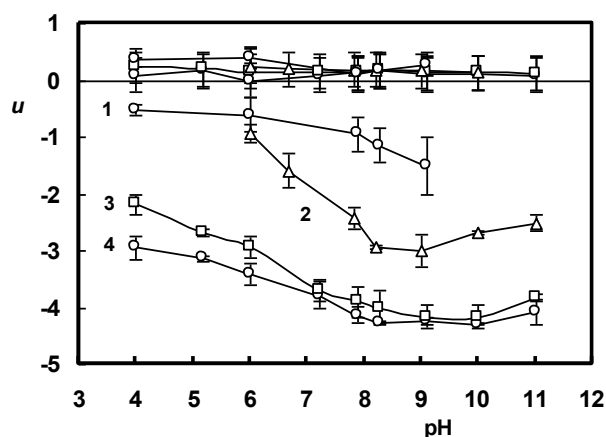**Fig. 1.** The mean electrophoretic mobility of Th (in 10^{-4} $cm^2 s^{-1} V^{-1}$, at [Th] $\leq 10^{-9}$ M) as a function of pH and composition of solution: **1** – 0.01 M ($NaClO_4$ + NaOH), **2** – as in **1** + 0.001 M $NaHCO_3$, **3** – as in **1** + 1 mg/L humic acid, **4** – as in **1** + 10 mg/L humic acid.

The mean electrophoretic mobility of the complexes formed at [Th] $\leq 10^{-9}$ M and absence of fluorides and carbonates (Fig. 1 and [3]) was found to increase with [HA] (0.1 – 10 mg/L) and with pH up to pH 7. The first effect must be due to the association of HA molecules. The complexes formed at the higher [HA] are larger and have higher negative charge, also due to the relatively lower neutralisation of the charge of HA by cationic forms of thorium. The increase in $_{-}u_{ThHA}$ with increasing pH can be explained by the increasing dissociation of carboxyl groups of HA and by the decreasing neutralisation of the charge of HA molecules with the increasing hydrolysis of thorium.
Both this and the previous effects cease above pH 8 where inorganic thorium exists in solution predominantly as $Th(OH)_4$. The practically constant value of $_{-}u_{ThHA}$ found at pH 8 – 11 and [HA] = 1 – 10 mg/L can therefore be most easily explained by the formation of $Th(OH)_4HA^{-}$ complex. The stability constant of this complex

$$\beta_{1,4,1} = [Th(OH)_4HA^{-}] \cdot [Th^{4+}]^{-1} \cdot [OH^{-}]^{-4} \cdot [HA^{-}]_{free}^{-1}$$

calculated from the mobilities $_{-}u$ of thorium in solutions containing carbonates and HA, considering the known stability constants of thorium carbonates, is log $\beta_{1,4,1}$ = 45.13 (for I = 0).

REFERENCES

[1] P. Reiller (2005) Radiochim. Acta 93, 43-55.
[2] P. Beneš et al. (1980) Trace Chemistry of Aqueous Solutions, Elsevier, Amsterdam, p. 43
[3] P. Beneš (2006) Uranium in the Environment, Springer, Berlin, 79-86

TRLFS STUDY OF URANYL INTERACTION WITH HUMIC ACID

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INTRODUCTION

Study of uranyl speciation in the presence of humic acid (HA) by TRLFS has been based on extremely short fluorescence lifetime (fs) of uranyl-HA complex, which cannot be observed by ordinary (ns) TRLFS systems. However, also ns TRLFS enables to determine the degree of complexation of U(VI) with apparently nonluminescent ligand using the static quenching effect, as the formation of the UO_2-HA complex causes a decrease in the fluorescence emission signal without changes in its lifetime [1,2].

EXPERIMENTAL

Using TRLFS, U(VI) fluorescence in slightly acidic solution in the presence of HA Aldrich was measured in the dependence on uranium concentration. For the experiment evaluation, a calibration curve constructed from the dependence of UO_2^{2+} fluorescence intensity on its concentration in solution without HA was used similarly to Czerwinski et al. [2]. The extent of interaction of U(VI) with HA was determined from the emission signal of uncomplexed UO_2^{2+} in the dependence on the total uranium concentration (10^{-6} - 10^{-5} mol.l^{-1}) at a constant HA concentration (20 mg.l^{-1}) and pH 3.2 ± 0.15.

RESULTS

The system containing no other complexing agent besides HA is relatively simple. The only luminiscent uranyl forms in the solution are UO_2^{2+} and products of its hydrolysis, restricted to UO_2OH^+ in the sufficiently acidic medium (pH < 4). Evaluation of the uranyl fluorescence decay curves within pH range of about $1 - 4$ revealed two species with significantly different lifetimes of 1.4 μs (UO_2^{2+}) and 66 μs (UO_2OH^+). Deconvolution of the fluorescence spectra provided as well two species with the emission bands at 471, 488, 509, 533, 559 nm (UO_2^{2+}), and 479, 496, 518, 542 nm (UO_2OH^+). Although UO_2OH^+ represents minor species in the slightly acidic solution, its intensive fluorescence is observed from pH > 1, and at pH > 3 it represents a major component in the spectrum.

Fluorescence signals of uncomplexed UO_2^{2+} (calibration dependence without HA), and of UO_2^{2+} and UO_2OH^+ in the presence of HA are illustrated by Fig. 1. Sigmoid curve can be fitted by various functions using nonlinear regression. In the presence of HA, fluorescence signal decreases markedly without changes in the lifetimes and positions of the emission bands reflecting the static quenching due to the uranyl complexation by HA. Evaluation of the degree of complexation has been done using several methods: as the ratio of the measured UO_2^{2+} intensities without and with HA at equal total uranyl concentration (method 1), or using various calibration methods – nonlinear, i.e., sigmoid within the entire calibration range (method 2), linear calibration using three lowest or two highest concentrations (methods 3 and 4, respectively; see Fig. 1). The uranyl-HA abundances calculated using the methods $1 - 4$ are presented in Tab. 1.
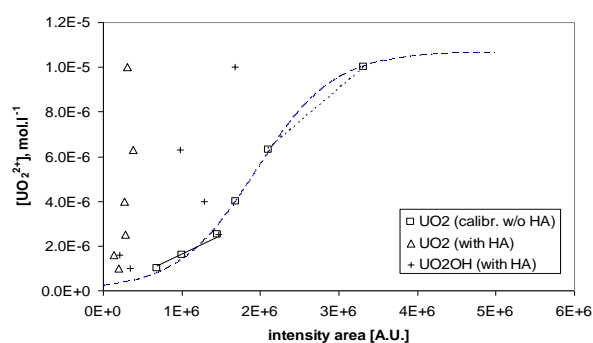

Fig. 1. Fluorescence signals of uncomplexed UO_2^{2+} (calibration dependence without HA), and of UO_2^{2+} and UO_2OH^+ in the presence of HA.

Unexpected increase in the uranyl-HA abundance with increasing uranyl concentration, although subject to fluctuations depending on the evaluation method, has been ascribed to insufficient stability of the solution pH. Fluctuation of pH must have been reflected in high fluctuations of UO_2^{2+} and UO_2OH^+ fluorescence signals as well as in the degree of deprotonation of HA functional (carboxylic) groups, which changes dramatically around pH ~ 3. The uranyl-HA abundance at the highest uranyl concentration is also surprisingly high considering that only about 10 % (~ 1.6×10^{-5} mol.l^{-1}) of HA exchangeable groups is deprotonated at pH ~ 3.2. The experiments will be repeated under strict conditions, particularly pH stabilization. Moreover, calibration range must cover much lower uranyl concentrations allowing determination of the uncomplexed UO_2^{2+} in the solution by interpolation instead of extrapolation.

Tab. 1. Abundance of uranyl-HA complexes in the dependence on uranium concentration calculated from TRLFS data using various calibration methods

Total uranium concentration (mol.l^{-1})	UO₂-HA (%) determined using evaluation method No.:			
	1	2	3	4
1.0×10^{-6}	71.1	70.0	67.7	41.1
1.6×10^{-6}	86.5	83.3	86.0	74.6
2.5×10^{-6}	80.5	85.7	81.2	65.8
4.0×10^{-6}	84.1	91.4	89.0	79.9
6.3×10^{-6}	81.9	93.1	90.0	81.8
1.0×10^{-5}	90.9	96.3	95.0	91.0

REFERENCES

[1] G. Geipel (2006) Coordination Chemistry Reviews 250, 844-854

[2] K. R. Czerwinski et al. (1994) Radiochim Acta 65, 111-119

STUDY OF LEACHING KINETICS OF FUCOID SANDSTONE SAMPLES
FROM THE STRÁŽ POD RALSKEM SITE

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INTRODUCTION

The in-situ leaching of uranium in the Stráž deposit, Northern Bohemia, was characteristic by the use of injection of technological solutions containing sulfuric acid into underground layers of the Cenomanian age [1]. Since 1990 when the leaching was finished, monitoring and remediation of the contaminated area still continue. When aiming to control the spreading of the contamination from the Cenomanian into Turonian aquifer, which serves as the water source for a big populated area, it is necessary to minimize also the transport of contaminants from the layer of fucoid sandstone which forms a part of the Cenomanian aquifer. Preliminary study of the content and transport of contaminants in the fucoid sandstone performed in 2006 [2] enabled to prepare a complex research program that comprised various experimental and modeling approaches. In 2007, experimental study of fucoid sandstone samples, received from the state enterprise DIAMO, included batch and column leaching experiments, squeezing of the pore water from the sandstone material and diffusion of selected radioactive tracers into the compact block of the rock.

EXPERIMENTAL

Leaching of material from six fucoid sandstone samples and modified sequential extraction (modified Tessier scheme) of them were performed applying the batch technique. Samples were chosen from different depths of a fucoid core hole No. VP 8C 7095 (142 – 153 m). Parameters of experimental procedures performed under ambient temperature are summarized in Tab. 1.

	Leaching	Sequential extraction		
		step 1	step 2	step 3
Reagent	cenomanian H_2O	distilled H_2O	1M $MgCl_2$	1M CH_3COONa
Contact time	1-5-24-120 hrs	1 hr	1 hr	5 hrs
Phase ratio V/m	5 ml/g	20 ml/g		

Tab. 1. Conditions of the leaching experiments with the fucoid sandstone samples.

Concentrations of constituent cations and anions in leachates were measured with the aim to assess dominant geochemical processes that could take place during leaching in situ. Measured concentrations of many minor contaminants (e.g., V, U, Be, Cr) were near to detection limits of used analytical methods. The main part of the study dealt with the study of behaviour of dominant contaminants, like SO_4^{2-}, Cl^-, Al, Fe.

RESULTS

Differences among results of the sequential extraction obtained for different samples studied were not significant. On the contrary the set of samples could be divided into two parts with respect to the rate of leaching of dominant

cations and change in pH. From the time dependence of Fe leaching and change of pH with time, which are exemplified in Fig. 1, a region corresponding to depths between 143-145 m can be observed that seems to be homogenous with respect to the leaching procedure used. The smaller total amount of Al and Fe sequentially extracted than that leached with cenomanian water in longer time indicated the dissolution of some characteristic minerals containing Al and Fe (e.g. jarosite, alunite). Significant changes in behaviour of all fucoid materials were observed with respect to the change of pH value. This could imply the rinse of deposit of the technological solution used by in-situ uranium leaching from the fucoid sandstone, and transformation of HSO_4^- to SO_4^{2-}.
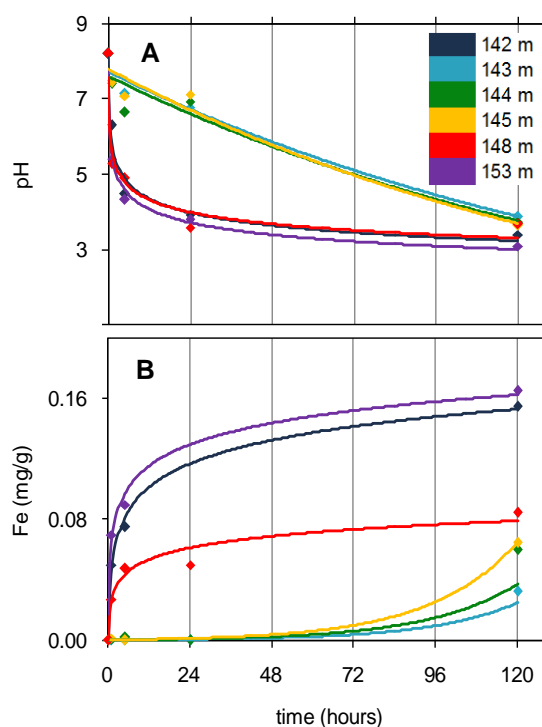

Fig. 1. Dependence of pH (A) and Fe concentration (B) on the leaching time for samples from various depths of the fucoid core.

REFERENCES

[1] M. Balatka et. al (2006) Uranium in the Environment Springer, Berlin, 437-447
[2] D. Vopálka et al. (2007) Proceedings of Workshop, CTU in Prague, 462-463

STUDY OF DECONTAMINATION OF MINE WATERS FROM URANIUM

K. Štamberg, P. Beneš, D. Vopálka, O. Múčková

INTRODUCTION

The mining of uranium ores is known to have adverse effects on the environment. One of these effects, necessary to be monitored and controlled, is the contamination from mining waters discharged to surface waters. Important sources of this contamination can be uranium and its daughter radionuclides. Traditionally, [226]Ra has received great attention because of its long half-life and the harmful effects of its alpha radiation on human health after ingestion. But, depending on the mineralogic composition of uranium ore and hydrogeological and chemical conditions in mining site, uranium content in the mining waters can be most important. It is the case of mining site Příbram, characterized by the carbonate type of uranium ore and by the hydrogen carbonate type of mining water. Even if the mining era was closed already 20 years ago, the mine water is still discharged and decontamined using the ion exchange technology. As the composition of discharged water has continued to change, it is necessary to correspondingly adjust parameters of the technology. Therefore we investigated two basic technological ion exchange processes, i.e. sorption and elution of uranium, with the aim to optimize their conditions.

EXPERIMENTAL

Sorption and elution experiments were performed applying the batch technique. The samples of strongly basic anion exchanger AMP (made in Ukraine) and of mining water were supplied by DIAMO s.e., Příbram. Experimental data were obtained on: (i) the uranium sorption kinetics, (ii) the uranium sorption equilibrium isotherms, (iii) the influence of the composition of elution solution consisting of NaCl (0.85-1.90M) + Na_2CO_3 (0-0.17M), at the temperature of 40^0C, on the elution efficiency of uranium. In conclusion, the parametric study of the sorption process, taking place in plant continuous counter-current column, was carried out using the code KOLONA (D. Vopálka).

RESULTS

(i) The experimental sorption kinetic data and the kinetic curve, calculated from them using the so called Gel Diffusion Model (MGD) [1], are presented in Fig. 1. As can be seen, the goodness-of-fit is very good (WSOS/DF=4.27 [2]) and thus the MGD kinetic model suits well for the description of the kinetics.

(ii) Fig. 2 shows an example of sorption isotherm (sorption capacity, q, as a function of concentration in solution, C). Both the experimental data and the curve calculated by means of Langmuir equation [1,2] (regression coefficient=0.92) are presented. It is evident that the sorption selectivity is relatively high especially at the low concentration of uranium.

(iii) In the elution of uranium from the ion exchanger, the concentration of both components of the elution solution, NaCl and Na_2CO_3, play the important role: in principle, the higher concentrations, the higher efficiency. As expected, no direct proportion could be found but the composition in the range 1.35-1.90M NaCl + 0.17M Na_2CO_3 can be regarded as optimum from the economic point of view.

The parametric study was focused on the simulation of influence of the main technological sorption parameters on the breakthrough of uranium concentration (C_b in effluent from sorption column), namely of flow rates of both mining water (V) and anion exchanger (M), and of residual uranium capacity after elution (q_r). The quantity q_r can be designated as the key parameter, the influence of which is demonstrated in Fig. 3.
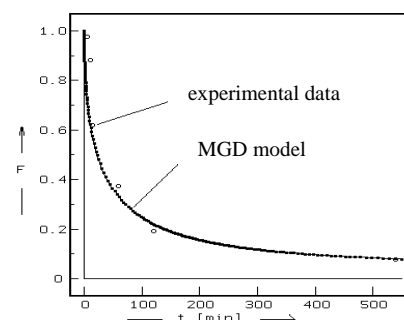

Fig. 1. Experimental and modelled uranium sorption kinetics (F - relative uranium concentration in the liquid phase).
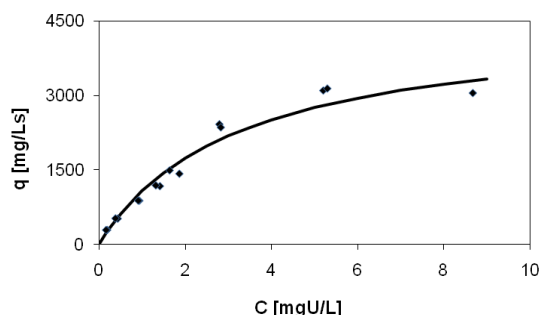

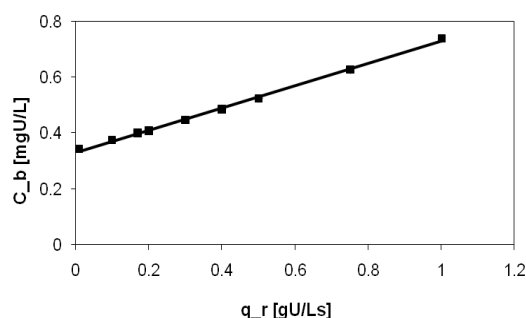**Fig. 2.** Uranium sorption equilibrium isotherm - AMP.

Fig. 3. Simulation of residual capacity (q_r) on breakthrough uranium concentration (C_b) (V = 94 m^3/hr; M = 0.3 m^3/hr).

REFERENCES

[1] P. Beneš et al. (1994) Radiochimica Acta 66/67, 315-321

[2] H. Filipská et al. (2005) Acta Polytechnica 45(5), 11-18

CESIUM UPTAKE BY Ca/Mg BENTONITE - EVALUATION BY A MULTICOMPONENT TWO-SITE ION-EXCHANGE MODEL

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INTRODUCTION

Understanding of contaminant migration processes at the basic level in a laboratory study can help to develop models, which may be used in transport codes to predict the fate of pollutants on the field scale. Our work performed with Ca/Mg bentonite of the Czech origin (deposit Rokle, NW Bohemia) was aimed at better understanding of cesium uptake processes. This type of bentonite, which is proposed to be used in the Czech project of deep underground repository, has two main features different from worldwide studied Na bentonites [1]: (i) the great influence of phase ratio m/V on the shape of Cs sorption isotherm in the range of higher Cs concentration, and (ii) a substantial content of micas and mica-type clay minerals (about 19 wt. %) that are believed to cause the specific Cs sorption in the lower concentration range due to the presence of the Frayed Edge Sites (FES). Experimental and modelling studies (mainly using geochemical code PHREEQC) presented here aim to obtain suitable input data for modelling of cesium migration in the compacted bentonite Rokle.

EXPERIMENTS

Sorption equilibrium

Cesium sorption was studied using batch technique for wide ranges of both bentonite-to-water ratio (m/V) and initial concentration of CsCl (10^{-7} – 10^{-1} mol/L). Radioactive tracer ^{137}Cs was used preferably in the range of lower Cs concentrations; comparison with results obtained without tracer (AAS and/or ICP-AES techniques) was very good. The non-linear shape of sorption isotherms and the influence of m/V value was observed in the whole concentration range studied (Fig.1). The shape of isotherms indicated the possibility to describe them by a two-site model.
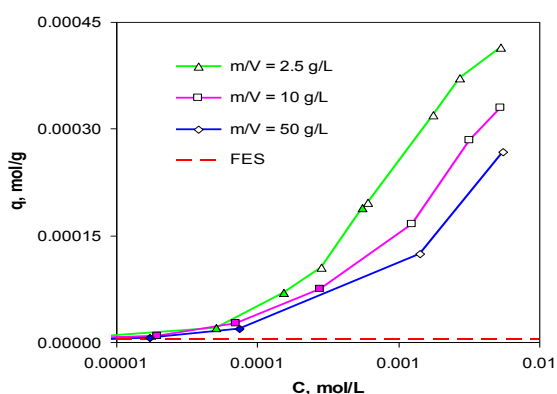

Fig. 1. Cesium sorption isotherms for three values of V/m; capacity corresponding to FES is indicated.

Determination of FES capacity

The standard silver-thiourea method [2] using 0.015 M AgTU solution for both pretreatment of bentonite samples and as the background solution in experiments with Cs was used for the characterization of frayed edge sites of bentonite. The elimination of the real competition of Cs^+ and $AgTU^+$ cations on the planar sites (RES) by our own original evaluation procedure enabled to determine the Cs-AgTU selectivity coefficient for the RES. The obtained value (0.041) well agreed with the value determined by evaluation from a set of equilibrium sorption experiments in which the initial concentrations of both Cs and AgTU were changed.

DATA EVALUATION

The data obtained by evaluation of the experiments are summarized in Tab. 1. For the determination of $\log_{10}K_0$ corresponding to interaction of individual cations with ion exchange sites was used an optimization method based on the speciation computation by PHREEQC, the value of CEC equal to 0.50 equiv·kg^{-1} for used bentonite sample was determined in the previous work [1].

Tab. 1. Determined surface chemical parameters of the Czech Ca/Mg bentonite.

Initial occupation of planar sites			
Ca^{2+}	34.6 %	Na^+	10.2 %
Mg^{2+}	40.4 %	K^+	14.4 %
Surface chemical parameters (planar sites)			
Species	$\log_{10} K_0$		
ZNa	20	by definition	
ZCs	20.85		
ZK	20.35		
Z$_2$Ca	40.30	Gaines-Thomas	
Z$_2$Mg	39.30	convention	
Z(AgTU)	22.24		
Frayed edge sites			
FES capacity	0.0034	equiv·kg^{-1}	

The non-linear shape of equilibrium isotherm indicated applicability of the ion exchange model, and resulted in a remarkable inverse influence of the value of equilibrium Cs concentration on the K_d values. This result implies that in experiments with compacted bentonite, which is supposed to be used as the buffer layer in the final disposal of radioactive waste, the rate of the diffusion flow through the plug of compacted bentonite should follow the change of Cs input concentration.

REFERENCES

[1] Z. Klika et al. (2007) Langmuir 23, p. 1227
[2] A. de Koning et al. (2007) Appl. Geochem. 22, p. 219

AN IMPROVEMENT OF THE MODEL OF RADIONUCLIDE TRANSPORT IN THE NEAR-FIELD REGION OF THE HIGH LEVEL NUCLEAR WASTE REPOSITORY

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INTRODUCTION

New modules for modelling processes that occur in a deep geological repository were developed using the GoldSim computer code [1]. These modules help to understand the role of selected parameters of the near-field region of the final repository and to prepare an own complex model of the repository behaviour. The source term module 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. The model of the source term needs further improvement in order to obtain a more realistic description of the behaviour or radionuclides in the near-field region.

MODEL MODIFICATION

The modifications of the source term model performed in the last year included mainly linking of the dissolution rate of basic matrix (pellet of UO_2) with the decrement of uranium in container due to the diffusion flow of uranium from engineered barriers, and model preparation for application of the concentration-dependent (nonlinear) interaction isotherm. The second task was made only with a model of a laboratory diffusion cell; results obtained will be discussed later.
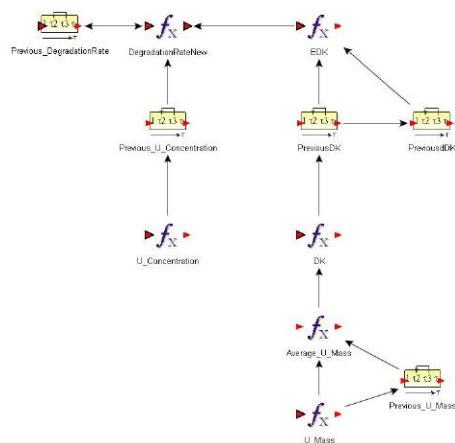

Fig. 1. Block diagram of the calculation of the fuel matrix dissolution rate.

Dissolution of fuel matrix will be in reality limited by at least two factors: (i) solubility limitation of uranium in the void volume of the container with the spent nuclear fuel, and (ii) by the uranium flow through the bentonite layer into the rock environment, which is controlled by uranium sorption in the bentonite layer and by uranium concentration at the boundary between bentonite and rock. These effects that in reality should diminish the release of nuclides trapped in the fuel matrix were not yet considered in the current code [2], in which the constant rate of matrix degradation was assumed for all elements. The scheme of the main part of the model improvement is presented on Fig. 1.

RESULTS

The comparison of results of computations performed with the old model (DEG0 – without calculation of the time change of matrix degradation rate) and the improved model (DEG2) showed the great influence of the change of the used matrix degradation rate. The use of the constant rate for nuclides that are bound in the fuel matrix gives the rapidly greater release rates of appropriate activities in the initial time period. In Fig. 2 and 3 is demonstrated character of the differences in simulation computations. E.g., for Cs-135 model DEG2 calculates activity fluxes about three orders of magnitude lower and establishment of a steady flux of Cs-135 activity, which reflects a steady flow of fuel degradation products after reaching of a stationary state after „saturation" of bentonite in respect to uranium.
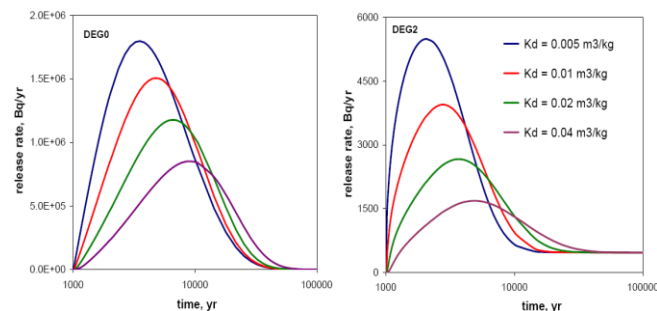

Fig. 2. Dependence of the flux of Cs-135 activity from near-field to the rock environment on the value of distribution coefficient Kd in bentonite for the two model approaches (DEG0 left, DEG2 right).
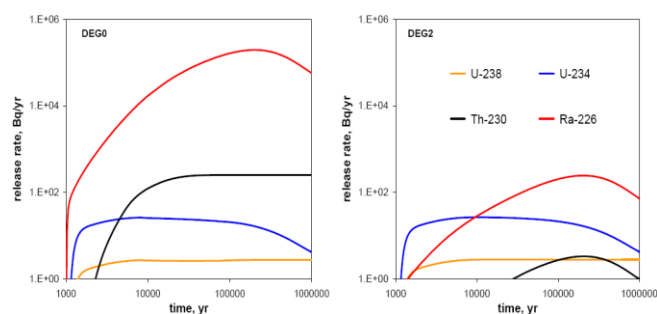

Fig. 3. Modelling of the activity fluxes corresponding to four nuclides from the uranium chain performed by the two model approaches.

REFERENCES

[1] D. Vopálka et al. (2006) Czechoslovak Journal of Physics 56, 623-628
[2] D. Lukin et al. (2004) NRI Report No. ÚJV-12137 CH, p. 36

ON THE WAY TO A CHROMATOGRAPHIC PROCESS FOR MINOR ACTINIDES PARTITIONING FROM HIGH LEVEL LIQUID WASTES

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INTRODUCTION

The final aim of this study was the proposal of a two-stage chromatographic process for partitioning of minor actinides from high level liquid waste: in the first stage, the lanthanides and actinides should be separated jointly from HLLW; in the second stage, selective separation of the actinides from the lanthanides should follow. Composite materials based on the prospective extraction agents incorporated in the support based on polyacrylonitrile (PAN) were used. The selection of the materials was based on the results of testing of properties of a broad scale of materials carried out within the EUROPART project [1].

EXPERIMENTAL

The materials used were based on the following extraction agents: octyl(phenyl)-N,N'-diisobutylcarbamoylmethyl-phosphine oxide (CMPO), N,N,N',N'-tetraoctyl-3-oxa-pentanediamide (TODGA), bis(2,4,4-trimethylpentyl) dithiophosphinic acid, and 6,6'-Bis-(5,6-dipentyl-[1,2,4]tri-azin-3-yl-[2,2']bipyridine (C_5BTBP). The characterisation of extraction properties of the materials studied was carried out through weight distribution ratios determination, kinetics experiments, dynamic extraction capacity determination, and extraction isotherm determination.

RESULTS

Prospective results for the co-separation of lanthanides and actinides from acidic high level waste were obtained with both the TODGA–PAN and CMPO–PAN materials. The behaviour of the TODGA–PAN material was similar to that of the recently commercialised material DGA Resin™; the behaviour of the CMPO–PAN material was similar to that of the commercial TRUEX Resin™ (both commercial materials produced by Eichrom Industries, USA, for analytical applications; both use Amberchrom® GC 71C as a support). However, higher D_g values were obtained with the materials with PAN binding matrix.

For the mutual separation of lanthanides and actinides both the materials based on C_5BTBP and dithiophosphinic acid showed prospective. Acceptable extraction properties of C5BTBP–PAN material were reached only after dissolving the solid C_5BTBP in a suitable diluent, the best results were achieved for the PAN–C5BTBP[nitrobenzene], PAN–C5BTBP[cyclohexanone], and PAN–C5BTBP[tetra-chloroethane] materials. An attempt to overcome the problems with the poor chemical stability of dithiophosphinic acid was performed; good stability of its ammonium salt, used as an intermediate for the long-term storage of the purified extractant, was demonstrated.

An attempt was performed to propose a two-stage process for the partitioning of minor actinides from HLLW. Lanthanides and minor actinides co-separation from 3M HNO_3 solution was successfully performed in the first step on the columns loaded with either TODGA–PAN or CMPO–PAN materials. An example of the Eu elution profile is shown in Fig. 1.
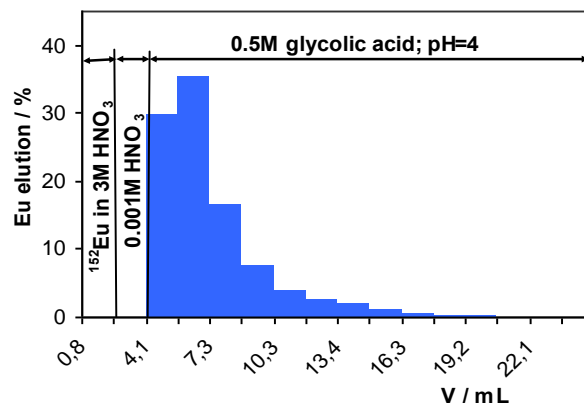

Fig. 1. Elution diagram of europium from TODGA–PAN column (column loaded to 10 % of its capacity, flow rate 2.3 BV.hr^{-1}, BV=1.27 mL)

During the preliminary testing of the second step – MAn and Ln mutual separation – the behaviour of the C_5BTBP-based solid extractants in packed beds did not exactly follow their behaviour in batch experiments. On the contrary, successful and efficient Eu / Am separation was achieved with the dithiophosphinic acid containing material (see Fig. 2).
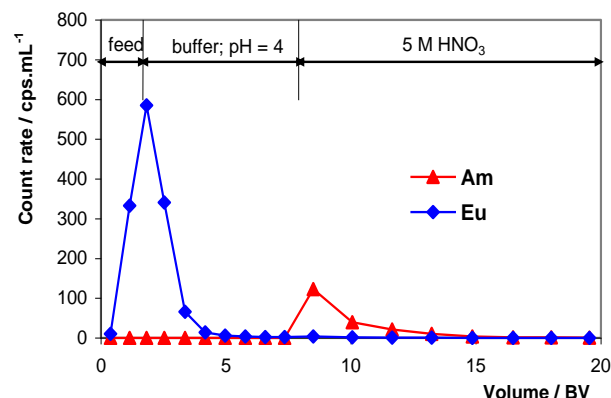

Fig. 2. Separation of macroamount of Eu from micro-amount of Am using E5–(C301+TBP+dodecane) material (feed: acetate buffer pH=4, 0.1M NaNO$_3$, 10^{-3}M Eu; flow rate 3.1 BV.hr^{-1}; BV=0.6 mL).

REFERENCES

[1] C. Hill et al. (2007) EUROPART (Contract No: FI6W-CT-2003-508 854), Final Activity Report, CEA France

RHENIUM SEPARATION USING NEW EXTRACTION CHROMATOGRAPHIC MATERIAL

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INTRODUCTION

Rhenium is one of the least abundant elements in the earth crust (0.4 ng.g^{-1}) and its concentration in environment is not well known. Its determination with various modes of AAS, ICP-MS or RNAA requires separation and/or preconcentration. For separation of Re as ReO$_4^-$ anion, ion exchange chromatography is commonly used with strongly basic anion exchangers or extraction chromatographic material TEVA Resin (Eichrom Technologies, Inc.). This material is comprised of the aliphatic quaternary amine Aliquat 336 impregnated on Amberchrom^{TM} CG-71 as inert polymeric support [1]. Recently, modified poly-acrylonitrile (PAN) was proposed as an inert support for liquid extractants in extraction chromatography [2]. The aim of this work was to study properties of the solid extractants with Aliquat 336 in the matrix of PAN and to compare properties of these new materials with the commercial TEVA resin.

EXPERIMENTAL

Solid extractants (SEX) further referred to as A336-PAN were prepared by direct incorporation of Aliquat® 336 into PAN binding matrix. Two different solvents were used to prepare PAN polymer solution, concentrated nitric acid or dimethylsulfoxide (DMSO). The use of the former solvent yielded solid extractant with better properties, therefore the properties of the material prepared using DMSO are not discussed here. The SEX material further referred to as PAN-A336 was prepared by impregnation of ready-made PAN beads with Aliquat® 336. All materials with PAN matrix were prepared to contain theoretically 40 % (w/w) of the active component. TEVA Resin also contained 40 % (w/w) of Aliquat^{TM} 336. Procedures for determination of weight distribution ratios D_g, extraction isotherms, dynamic extraction capacities and break-through curves are described in detail elsewhere [3]. In these experiments radiotracers ^{186}Re and ^{188}Re were used, which were prepared by rhenium irradiation in VVR-15 nuclear reactor of the Nuclear Research Institute Řež, plc. Activities of these radioisotopes were measured by γ-spectrometry with various HPGe detectors coupled to a Canberra Genie 2000 γ-ray spectrometric system.

RESULTS

Fast kinetics of rhenium uptake for all PAN-based materials and TEVA Resin was found in batch experiments for all the materials studied, the extraction equilibrium being reached within 5-10 min. of contact. Therefore, a contact time of 30 min. was chosen as sufficient for further batch experimrnts. Fig. 1 shows weight distribution ratio D_g as a function of HCl or HNO$_3$ concentration for SEX materials and TEVA resin. The D_g values decrease with the increase of HCl or HNO$_3$ concentration for all the materials studied, the D_g values measured in HNO$_3$ solutions being about two orders of magnitude lower than in HCl solutions.
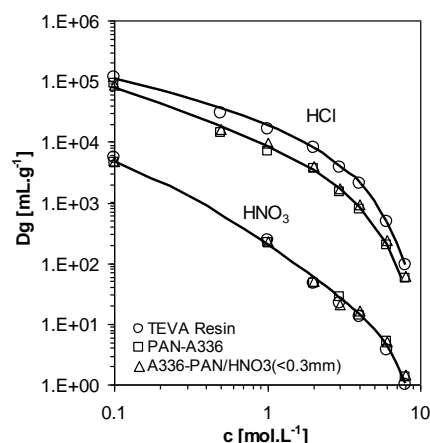

Fig. 1. D_g as a function of HCl or HNO$_3$ concentratrion (10^{-5} M NH$_4$ReO$_4$, V/m=250 mL·g^{-1}, contact time 30 min.)

The D_g values determined in HCl solutions for TEVA Resin were somewhat higher compared with those measu-red for PAN-based materials. However, a comparison of theoretical capacities Q_0, maximum capacities Q_{max} and mass practical capacities Q_m for Re retention, which is given in Tab. 1, shows that the newly prepared SEX materials are fully comparable with the commercially available TEVA Resin.

Tab. 1. Comparison of Q_0, Q_{max} and Q_m capacities[a]

Material	Q_0 (mmol·g^{-1})	Q_{max} (mmol·g^{-1})	Q_m (mmol·g^{-1})
A336-PAN	0.861	0.742	0.593
PAN-A336	0.861	0.742	0.746
TEVA Resin	0.813	0.731	0.596

[a] – for their meaning and determination Cf. [3]

The main advantage of the new PAN-based materials is a low price of the polymer support and the possibility to prepare materials with different grain size for required applications. One type of such SEX material was already successfully used for Re separation and its determination by RNAA [4].

REFERENCES

[1] E. P. Horwitz et al. (1995) Anal. Chim. Acta 310, 63-78.
[2] F. Šebesta, unpublished results
[3] M. Lučaníková et al. J. Radioanal. Nucl. Chem., in press.
[4] M. Lučaníková et al. (2006) J. Radioanal. Nucl. Chem. 269, 463-468.

ELECTROLYTIC SEPARATION OF RADIONUCLIDES FROM CONTAMINATED SOILS

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INTRODUCTION

Contamination of soils or environmental areas by various radionuclides is a matter of concern; it can be caused by various accidents, e.g. during shutdowns of nuclear facilities. For the hot spots decontamination, the electrolytic method for radionuclides separation was developed. In the laboratory scale, parameters and procedure efficiency were tested, and the results were used as a basis for the design and construction of a bench-scale decontamination apparatus.

EXPERIMENTAL

Soil samples from the area of Jaslovské Bohunice A1 nuclear power plant were used for the experiments. About 3 g of clay loam samples were electrolyzed at constant current in several types of electrolytes and at different currents and temperatures. The released ^{137}Cs was continuously removed from the electrolyte by sorption in a column filled with composite ion-exchanger based on nickel ferrocyanide and measured in a NaI(Tl) well detector. The efficiency for some additional radionuclides (^{110m}Ag, ^{203}Hg and ^{60}Co) was also tested. The measured activity, temperature and voltage were logged and stored in a PC. The larger electrolytic device was designed to treat more than 250 g of soil at once.

RESULTS

The main results are described on the Fig.1-2. The decontamination efficiency was 61-78% in the phosphate electrolyte at 1 A current, this level was achieved after 20 – 24 hours of the electrolysis. At the 1.5 A current more than 99 % of radiocesium was released in the same electrolyte after approximately 19 hours. At this current, the operating temperature of the electrolyte was ~ 85-90°C. The efficiency of sulphate and nitrate electrolytes was significantly lower, 50 or 30% of ^{137}Cs was released, respectively, at 1 A (see Fig.1).

In the experiments performed at 1A, the operating temperature was increased by external heating to the values typical for the electrolysis at 1.5 A; this increase was applied after the curves reached their plateaus – after 17 h in sulphate or after 22h in the phosphate electrolytes. Consequently, the efficiency increased to 90% (PO_4^{3-}) and 74% (SO_4^{2-}). In the control leaching experiments, 10% (22°C), 43% (50°C), 66% (75°C), and 85% (90°C) of ^{137}Cs was released after 22 hours. The comparison of these values with those achieved in electrolytic experiments demonstrates the net effect of the electrolysis.

The soil artificially contaminated by other radionuclides was electrolyzed in phosphate solution at the 1 A current. As is clear from the Fig.2, the process efficiency depends on the chemistry of the element. The final decontamination levels achieved are > 99,5 % for ^{60}Co, 71,6 % for ^{110m}Ag, 78,1 % for ^{137}Cs, and 31,4 % for ^{203}Hg.

The parameters tested in the bench-scale electrolytic cell were based on the above results. The power supply was designed to provide 10-100 A at 50-85 V, what is enough to electrolyze soil (250-500 g of the soil. The first inactive tests indicated that conditions for efficient release of cesium can be easily achieved.
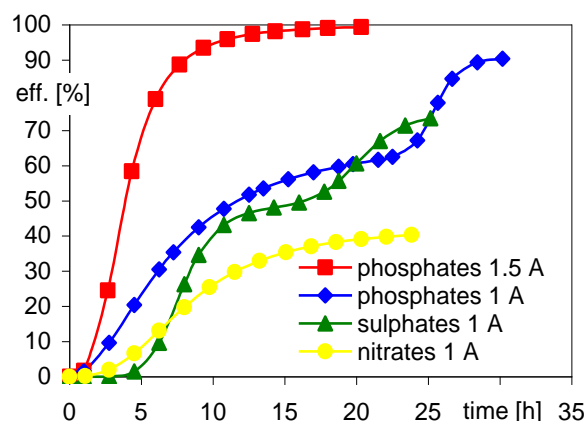

Fig. 1. Soil electrolytic decontamination in different electrolytes (1M H_3PO_4 + 0.1M $NH_4H_2PO_4$, 1M H_2SO_4 + 0.1M $(NH_4)_2SO_4$ and 1M HNO_3 + 0.1M NH_4NO_3), additional heating applied in some cases (see text).
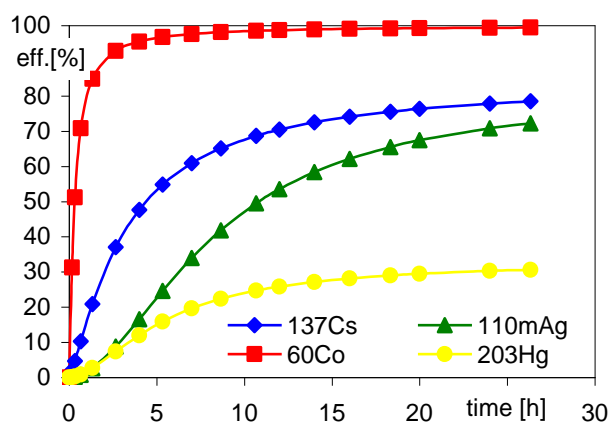

Fig. 2. The efficiency of electrolytic decontamination of the soils contaminated by various radionuclides (phosphate electrolyte, 1A current).

REFERENCES

[1] L. B. Prozorov et. al (2000) J. Radioanal. Nucl. Chem. 246(3), 571-574

[2] M. Němec (2008) Thesis, CTU in Prague, p. 98

SEPARATION OF RADIONUCLIDES FROM CONTAMINATED SOILS BY ELECTROMIGRATION

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INTRODUCTION

At larger contaminated sites, soils are often excavated but disposal of these large amounts of soils into nuclear waste repositories is inconvenient from both the economic and spatial points of view. Therefore, various methods for in situ or ex situ remediation were sought and tested. Electrochemical methods are now in focus, because of their high efficiency and ability to concentrate the radionuclides and to drive their flows. In this study, the soils contaminated before 30 years by ^{137}Cs were used as the model material for experiments. The main aim of the laboratory tests is to find conditions or parameters which can provide high efficiency for cesium separation from soils contaminated long time ago and help then to propose, develope and optimize an in situ decontamination method.

EXPERIMENTAL

The experiments were performed in two types of electrophoretic cells with the suspension of soil from the area of Jaslovské Bohunice A1 nuclear power plant in 0.5 M phosphoric acid at the ratio approx. 5:4. In the first cell – horizontally oriented – the soil activity profile along the length of the column was measured during the process. For more precise tests, the second, vertical, cell was made, where the anode was in direct contact with the suspension and the cathodic solution was treated by a separation column filled with cesium-selective composite ion exchanger. In both cases, the electrophoresis ran in the constant current regime, which was more convenient for logging, the maximum electric input was limited to 5 or 3 W respectively.

RESULTS

On the Fig. 1, the scheme of the horizontal cell is shown. The main result of the tests in this cell was the proof that even in the soils contaminated long time ago the cesium ions may be mobilized by electric field and that temperature, higher input and electroosmosis negatively influence the process – they dry the soil and hence increase the system resistance and decrease the ion flow.
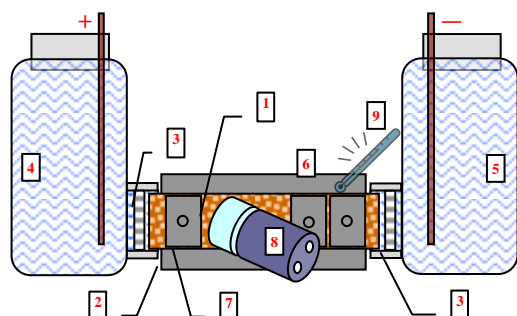

Fig. 1. The horizontal electrophoretic cell.
1-soil suspension, 2-column holders, 3-porous plugs, 4,5-electrode vessels, 6-Pb shielding, 7-Pb cubes, 8-NaI(Tl) detector, 9-thermocouple
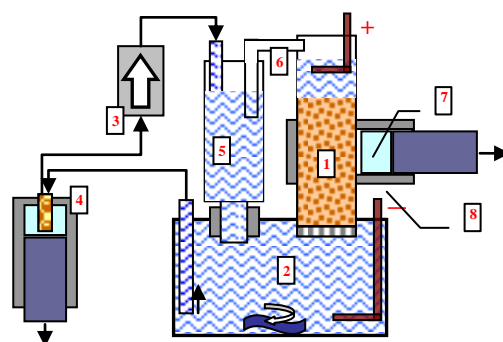

Fig. 2. The vertical electrophoretic cell.
1-soil suspension, 2-cathodic solution, 3-pump, 4-NaI(Tl) with separation column, 5-reservoir, 6-catholyte overflow, 7-NaI(Tl), 8-Pb shielding.
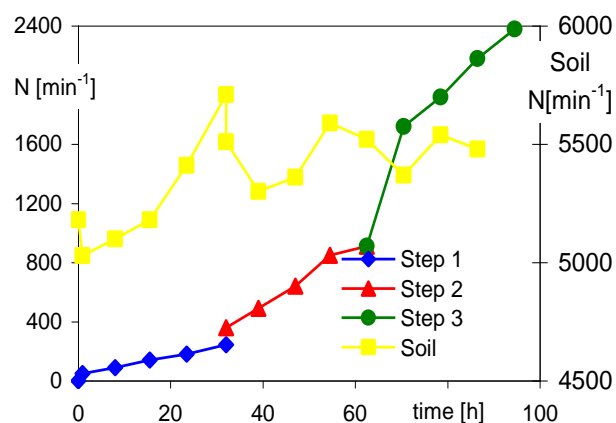

Fig. 2. The record of the soil activity (yellow, right Y) and the increase of activity of released ^{137}Cs on the ion exchanger.

During the tests in the vertical cell, the activity of the soil, the voltage at the constant current and the activity of the separation column were measured. In the Fig. 3, it is shown that, at the parameters 35 mA – 75 V – 3 W (upper limits), cesium is released relatively fast and the process accelerates with time. The measured activity variations in the soil were caused by the geometry changes cased by the electroosmotic flow and soil column contraction.

REFERENCES

[1] L. B. Prozorov et. al (2000) J. Radioanal. Nucl. Chem. 246(3), 571-574

[2] M. Němec (2008) Thesis, CTU in Prague, p. 98

STUDY OF SORPTION PROPERTIES OF NOVEL TODGA–PAN MATERIAL

J. Šuľaková, J. John, F. Šebesta

INTRODUCTION

The majority of the recent hydrochemical partitioning strategies are based on utilization of liquid-liquid extraction technology. Using methods based on extraction chromatography in partitioning of minor actinides (MAn) is rare, however, in some countries this approach is seriously considered as an alternative to liquid-liquid extraction.

The aim of this research was to evaluate sorption properties of the composite material based on one of the extraction agents prospective for co-separation of lanthanides and MAn from high level liquid waste – N,N,N',N'-tetraoctyl-3-oxapentanediamide (TODGA) [1] – incorporated in the support based on polyacrylonitrile (PAN).

EXPERIMENTAL

The solid extractant tested in this work was prepared by a method where the extraction agent is incorporated in PAN as inert support by coagulation of the solution of TODGA in PAN solution in DMSO. The extraction agent used was synthesised and supplied by Katchem, Czech Republic. Its molecular structure is shown in Fig, 1.
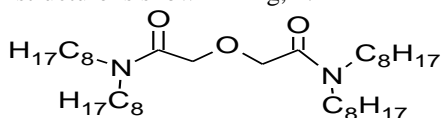
Fig. 1. Molecular structure of TODGA

The characterisation of the extraction properties of the materials studied was carried out through weight distribution ratios determination, kinetics experiments, dynamic extraction capacity determination, and extraction isotherm determination.

RESULTS

The studied materials were characterised by determination of the actual content of the extractant, microphotography, and thermogravimetric analysis (TG, DSC and/or DTA). The microphotography confirmed that the materials are macroporous, thus allowing easy contact of the aqueous phase with the embedded extractant.

The kinetics of Eu uptake by the TODGA–PAN solid extractant was found to be relatively fast; the equilibrium has been reached approximately in 1 hour. An example of the dependencies of weight distribution ratios D_g on nitric acid concentration is shown in Fig. 1. The shape of the dependences and the order of actinides extraction obtained for the new material are in agreement with the behaviour of TODGA in liquid-liquid extraction. The behaviour of the TODGA–PAN material towards americium and curium is practically the same, while the D_gs measured for californium are significantly higher. An unexpected finding was the almost two orders of magnitude difference of the D_g values of thorium and plutonium as tetravalent ions.
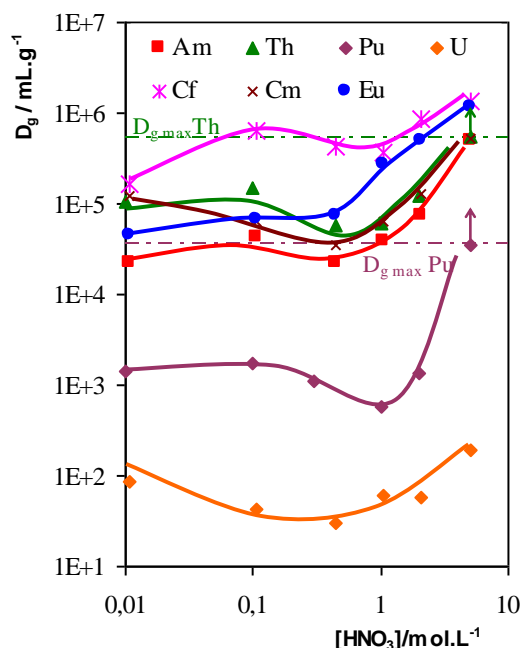

Fig. 1. Dependence of weight distribution ratios D_g of Eu, Th, U, Pu, Am, Cm and Cf on TODGA–PAN solid extractant on nitric acid concentration. (0.1M NaNO$_3$ + HNO$_3$ [+ 10^{-5}M Eu in experiments with Eu and Am], V/m = 250 mL.g^{-1}, 20 hrs contact time)

A mechanistic study was performed to determine the stoichiometry of the extracted complexes for Eu and Th as the representatives of trivalent Ln and An, or tetravalent An ions, respectively. Mass practical capacities Q(m), determined in the dynamic experiments, together with the maximum loadings Q$_{max}$, determined from the measured extraction isotherms, were used to elucidate the Eu : TODGA and Th : TODGA ratios in the complexes. The stoichiometry calculated fom Eu is Eu(TODGA)$_4$, which is identical with the published composition of complexes extracted in liquid-liquid extraction. However, the stoichiometry calculated for Th is Th(TODGA)$_2$ which shows that the mechanism of thorium extraction with pure TODGA incorporated without any solvent into the PAN based binding matrix differs from its mechanism in liquid liquid extraction with TODGA dissolved in solvents where formation of 1 : 3 (Th : TODGA) complexes was reported.

REFERENCES

[1] Y. Sasaki et al. (2002) Solv. Extr. Ion Exch. 20(1), 21-34

DEVELOPMENT AND OPTIMISATION OF NOVEL C5BTBP–PAN MATERIAL

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INTRODUCTION

Achieving effective separation of minor actinides (MAn) from high active waste issuing the reprocessing of spent nuclear fuel is one of the conditions of launching the Partitionin and Transmuatation technology. This is difficult namely due to the chemical similarity of MAn(III) and Ln(III) which results in co-extraction of the lanthanides with An(III) by most of the extractants.

As a new family of extractants prospective for achieving this goal, the so-called bi-pyridines have been recently identified [1]. The aim of this research was to develop a solid extractant incorporating this prospective extraction agent in the support based on polyacrylonitrile (PAN).

EXPERIMENTAL

Two methods of preparation of the composite material studied were used: coagulation of the suspension of the extractant in the solution of PAN, or impregnation of ready-made PAN beads by the solution of the extractant in a suitable diluent. The extractant studied was the 6,6'-Bis-5,6-dipentyl-[1,2,4]triazin-3-yl[2,2']bi-pyridine (C_5-BTBP), it was synthesised at the University of Reading, UK. Its molecular structure is shown in Fig. 1.
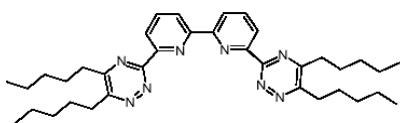

Fig. 1. Molecular structure of C_5-BTBP

The characterisation of the extraction properties of the materials studied was carried out through weight distribution ratios determination and kinetics experiments.

RESULTS

The preliminary scouting experiments revealed that the material prepared by direct granulation of the extractant, that contained the extractant in solid state, is not effective. The first successful results, where mutual separation of Am from Eu was reached, were obtained after wetting the original material with appropriate diluent (Fig. 2). A significant problem with this material was the very slow kinetics of Am uptake observed.

In order to find a system with advanced extraction properties and faster kinetics of Am uptake, influence of different diluents was investigated. The Am/Eu separation factors (SF) observed for these systems at 3M HNO_3 are compared in Fig. 3.

The most prospective systems were found to be the materials prepared by impregnation of PAN with solutions of C_5-BTBP dissolved in tetrachloroethane, nitrobenzene, or cyclohexanone. With these materials, high separation factors SF >94, 103, or >65, respectively, were achieved as well as a reasonable kinetics – in 3 hours ~ 80 % of the Am equilibrium uptake was achieved.
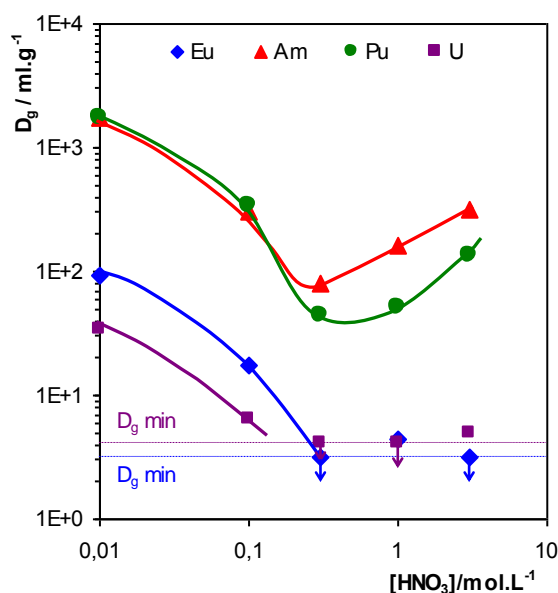

Fig. 2. Dependence of weight distribution ratios D_g of Eu, Am, Pu, and U on C5BTBP–PAN solid extractant modified by wetting with octanol on nitric acid concentration. (0.1M $NaNO_3$ + HNO_3 [+ 10^{-5}M Eu in experiments with Eu and Am], V/m = 250 mL.g^{-1}, 20 hrs contact time)
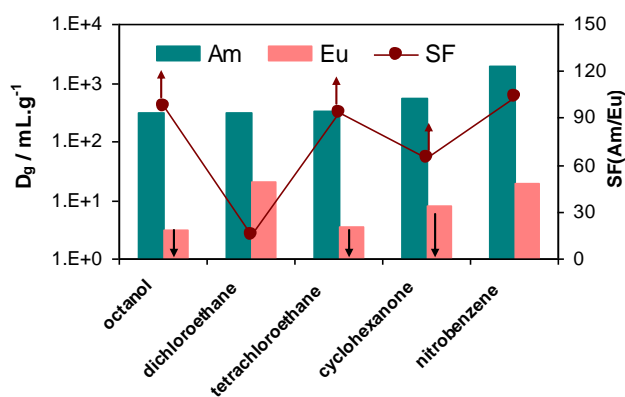

Fig. 3. Dependence of weight distribution ratios D_g for Am and Eu, and Am/Eu separation factors SF(Am/Eu) on diluents used in PAN–C5BTBP[diluent] solid extractant. (3M HNO_3, 10^{-5}M Eu carrier for Am + Eu, V/m = 250 mL.g^{-1}, 20 hrs contact time)

REFERENCES

[1] M. Nilsson et al. (2005) Solv. Extr. Ion Exch. 24(3), 299-318

RADIATION REMOVAL OF IONIC FORMS OF LEAD AND CADMIUM FROM AQUEOUS SOLUTIONS

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INTRODUCTION

Due to extensive contamination of the environment with heavy toxic metals, more efficient and economically more convenient methods of their removal from wastewater and groundwater are pursued. The utilization of ionizing radiation for radiation removal of heavy metals from aqueous solutions could be a possibility in this case. This application could be ecological, less time-consuming, and requires a rather low number of partial operations, if compared with conventional chemical methods of heavy metal removal [1,2]. The aim of this work is to investigate whether and under what conditions picked heavy metals can be removed from aqueous solutions under irradiation.

EXPERIMENTAL

The radiation removal of lead (100 mg/L) and cadmium (100 or 27 mg/L) from aqueous solutions in presence of different scavengers has been investigated.

RESULTS

The free, non-complexed lead (100 mg/L) can be completely removed from aqueous solutions (pH ~ 5 – 6) containing OH radical scavengers (1×10^{-2} mol/L of potassium formate HCOOK) already at the dose of 2.5 kGy. The radiation removal of lead is slightly influenced by the presence of some solid modifiers (zeolite, Cu_2O) and enhanced by bubbling with N_2O.

The cadmium requires dose of 15 kGy to be removed from the system containing 1×10^{-2} mol/L of HCOOK.

The experiments show that in acidic solutions, the EDTA (6×10^{-4} mol/L) complexed lead may be reduced at a dose of 30 kGy up to 92 % without the addition of typical OH radical scavengers such as HCOOK. The addition of OH radical scavengers as 1×10^{-3} mol/L HCOOK, 2×10^{-3} mol/L carbonate or 2×10^{-3} mol/L bicarbonate results in no further improvement but the efficiency is the same in such wide range of pH (3.2 – 9.5). The addition of 1×10^{-2} mol/L HCOOK causes strong negative effect. The bubbling of the solution with nitrogen or oxygen also exhibits no positive effect. On the contrary, saturation with nitrous oxide in the presence of scavengers has a modest positive influence, whereas in the system which is scavenger-free, high negative effect (30 %) was observed [fig. 1]. The presence of nitrate (e^-_{aq} scavenger) appears to be important for an effective removal of complexed lead. The behavior of the system with citric acid complexed lead was very similar to the system with $Pb(EDTA)^{2-}$ complex.

The efficient removal of cadmium complexed with EDTA proceeds up to 90 % at dose of 45 kGy with an addition of 5×10^{-3} mol/L of carbonate as the OH radical scavenger and simultaneously pH buffer (pH 10). After irradiation, the cadmium is present in the final form of $CdCO_3$.
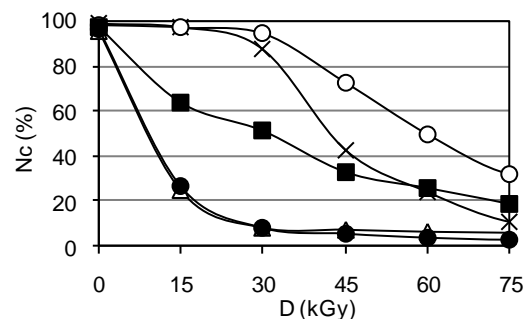
Fig. 1. Dependence of normalized concentration NC of Pb ionic forms on the dose of irradiation D for the sample containing EDTA complexed lead without the addition of a scavenger (Δ), for the sample without the addition of a scavenger bubbled with nitrous oxide (■), for the sample with an addition of 10^{-2} mol/L HCOOK (○),for the sample with the addition of 10^{-2} mol/L HCOOK bubbled with nitrous oxide (x), and for the sample with the addition of 2×10^{-3} mol/L CO_3^{2-} (●).

REFERENCES

[1]   N. Getoff (2001) Res. Chem. Intermed., 343–358
[2]   T. J. Weber (1997) Metal Finishing: Guidebook and Directory issue, 751-770

RADIATION AND CHEMICAL STABILITY OF CALIX[4]ARENE DERIVATIVES AS PROSPECTIVE LIQUID-LIQUID EXTRACTANTS

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INTRODUCTION

Carbamoylmethylphosphine oxides ("CMPOs") are suitable ligands for actinides and lanthanides [1]. The special example (**1**) is used in the so-called TRUEX process. Extraction studies suggest that the extracted Am(III) cation is coordinated by three CMPO molecules and three nitrate anions in an overall neutral complex and more than one CMPO molecule will be also involved in the complexes of other cations. Therefore, improved extractants should be available, by the attachment of several CMPO-functions to a basic skeleton in a mutual orientation, which allows their cooperative action.

In fact we could show, that calix[4]arenes bearing four CMPO-functions on the wide rim (**2**) or on the narrow rim (**3**) show a drastically increased extraction efficiency.

To use a chemical compound as extractant, it must be sufficiently stable under the radiolytic and hydrolytic conditions of the extraction process. This stability can be characterized by measuring the extraction efficiency as a function of the time. However, for potential improvements it is also necessary to characterize the products formed during a potential degradation process. To do this, we included in these stability studies also the compounds (**4**) and (**5**) as models for the calixarene derivatives (**2**) and (**3**).
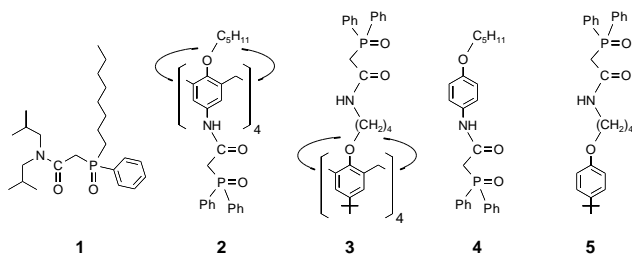

Fig. 1. Chemical formulae of studied compounds

EXPERIMENTAL

For the radiation and chemical stability studies, two diluents were used, 1-octanol and chloroform, since most of the radiation-induced damage to the extractant is expected to originate from the radicals produced in the interaction of ionizing radiation with the diluent, as was shown in previous works [2]. Both the diluents used were of analytical grade. 10^{-3} mol·l^{-1} solutions of the studied calix[4]arene derivatives and their respective model compounds were prepared for the irradiation; For the studies of the kinetics of radiation degradation, the samples were sealed in thin-glass ampoules of 10 ml volume. 250 ml of the solution intended for analysis of the degradation products was irradiated in PET bottle. Besides, the compound (**2**) was irradiated in solid state; the layer of the irradiated material was 1mm thick and it was covered in a plastic envelope. The irradiation was performed using high frequency linear accelerator LINAC 4-1200, with energy of accelerated electrons 4,0 MeV. The doses applied ranged from 0 to 200 kGy. In chemical stability study, samples were contacted with aqueous phase of various acidity for certain amount of time.

RESULTS

Studies on the radiation and hydrolytic stabilities yielded the following results:

1) Radiolysis of the CMPO-functionalised calix[4]arenes is strongly dependant on the diluent used. This is fully in accordance with the assumption that indirect effects of ionizing radiation predominate. Further evidence has been provided by irradiation of one of the compounds in solid phase.

2) The values of radiation chemical yield indicate that radiation degradation does not proceed by chain mechanism.

3) The significant decrease of original compound concentration does not necessarily mean that the extraction properties will be affected to the same degree. The proposed mechanism of gradual stripping of CMPO moieties indicates that significant proportion of the extraction ability may be retained even at relatively high doses of radiation.

4) A complex simulation of actual technological conditions requires irradiation during contact of the organic and aqueous phases. Preliminary experiments showed that intermediates of water radiolysis may significantly accelerate the degradation of calix[4]arene derivatives.

5) When contacted with aqueous phases containing varying concentrations of HNO_3, all the studied compounds demonstrated sufficient chemical stability in both their 1-octanol and chloroform solutions.

REFERENCES

[1] K. A. Martin et al. (1986) *Diluent Extr. Ion Exch. 4*, 1149-1169.
[2] Y. Sugo et al. (2006). Radiat. Phys. Chem. 76 (5), 794-800.

RADIATION CORROSION OF CARBON STEEL UNDER ANOXIC CONDITIONS

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INTRODUCTION

Primary motivation of this work was to investigate corrosive processes occurring in the field of ionizing radiation in deep repository after possible groundwater leakage and also to contribute to general knowledge of kinetics of radiation corrosion of water-steel system. Ionizing radiation can significantly change physical properties of system and chemical properties of its compounds. These changes may lead to different rate of corrosion when compared with non-irradiated system. Mechanism of radiation corrosion is still ill defined and requires further detailed study.

EXPERIMENTAL

All works were performed in glove box under overpressure of inert atmosphere. Plates of carbon steel with dimensions 1x4x1 cm were used as corroding material. Surface of steel plates was treated in 1% solution of HCl for 1 hour for clearing from adsorbed impurities. Distilled or synthetic granitic water were saturated by inert gas (nitrogen or helium). Residual concentration of oxygen in water was continually measured. Following saturation, glass corrosion cells were submerged under water level, completely filled with deoxygenated water and closed by pressure seal to minimize oxygen contamination and possible subsequent re-introduction of air into corrosion system. For study of electrochemical potential, corrosion cells of volume 1L were used. The cells consisted of glass vessel and pressure seal with three slots for electrodes. Three-electrode set-up included argent chloride electrode, platinum electrode and electrode from steel wire (from the same material as steel plates). Cells were treated under the same conditions as their smaller counterparts. Electrochemical potential was measured online during irradiation.
^{60}Co radionuclide gamma source was used for radiation corrosion experiments. For study of corrosion at higher temperatures, samples were inserted in thermostatic cell during irradiation. Dose rate was 0.2 kGy/h. Doses were determined using alanine and Fricke dosimeters.
Corrosive products were analysed using UV/Vis spectrophotometry, their characterization was performed via RTG structural analysis.

RESULTS

Change of temperature of corrosive system influences rate of corrosion both directly via change of corrosion reactions rate and indirectly by change of gases solubility in water (thus affecting equilibrium states of soluble compounds; change of properties of protective layers occurs). With increasing temperature rate of corrosion increases up to maximum at 65-70°C. Rate of corrosion decreases again at higher temperatures due to decreasing solubility of oxygen in water. With increasing temperature, corrosion is less dependent on pH (at 60°C or higher, dependence on pH is non-existent).
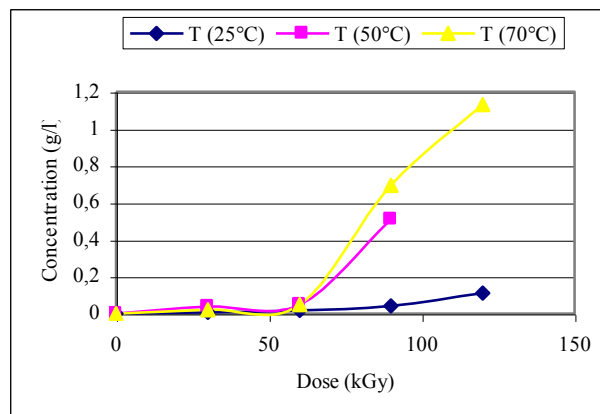

Fig. 1. Dependence of Fe^{2+} concentration on the dose at three different temperatures

REFERENCES

[1] S. M. Sharland et al. (1989) Mat. Res. Soc. Symp. Proc. Vol. 127, Scientific Basis for nuclear waste management XII, Berlin
[2] G. V. Buxton et al. (1988) J. Phys. Chem. Reference Data 17, 513 – 886

MODIFICATION OF REACTIVITY AND CATALYTIC PROPERTIES OF NiO-WO₃ MIXED OXIDES BY IONIZING RADIATION AND ION IMPLANTATION

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INTRODUCTION

Heterogenous catalytic reactions in which various catalysts (precious metals, oxides and sulfides of transition metals, silica, zeolites, atc.) are used, are widely utilized in industry. Properties of catalysts determine efficiency and the economic convenience of the whole process. Therefore, it is necessary to study methods of optimizations of the catalyst properties. Among others, the irradiation and/or reduction of the catalysts based on mixed oxides with the hydrogen are such methods. The catalytic activity was studied with the original, with irradiated and with the hydrogen reduced NiO-WO₃ mixed oxides.

EXPERIMENTAL AND RESULTS

The series of 15 samples of NiO₃ mixed catalysts with various composition in the range 0-100 wt.% of both components was prepared. One of the precursors, nickel hydroxide, was prepared from aqueous solution of nickel nitrate by precipitation with potassium hydroxide. The carefully washed and dried precipitated nickel hydroxide was mixed with aqueous suspension of H_2WO_4 in given ratios. The mixed solids were washed, dried and carefully homogenized by grinding in agate mortar. The optimum temperature for full decomposition of precursors to the final oxide was determined by means of thermogravimetric analysis. Calcination was performed at 450°C in air for 5h. The catalytic activity of all samples was measured by the catalytic decomposition of the aqueous solution of hyrogen peroxide (1.2 mol/l) at different temperatures from 25 to 40°C.

The content of both metals in the mixed oxides was determined chelatometrically. The microstructure of the samples was investigated by X-ray diffraction. The chemical and structure analysis revealed that the samples consist of the cubic nickel oxide, tetragonal tungsten oxide, orthogonal oxide and, in the middle region of composition, nickelous tungstate were found.

Specific surface area of samples was measured by low temperature selective adsorption of nitrogen from N_2/H_2 mixture. The dependence of the specific surface areas on composition has non-monotonous character. The significant maximum in the area of equal amount of both components correlates with presumption that maximum interaction of both components occurs in this area. The content of chemisorbed oxygen (its ionogenic forms expressed as the surface concentration of O^{2-} ions) was determined by iodometric titration.

The content of surface oxygen monotously decreases with decreasing content of nickel oxide with minimum in the middle region of composition and increases in the region with predominant content of tungsten oxide. It can be deduced, that the dissociative chemisorption of molecular oxygen takes place predominantly on the Ni^{2+}-Ni^{3+} centres or on the centres with higher valency of tungsten.

Catalytic activity was also tested on samples pre-irradiated with gama-rays of ^{60}Co and accelerated electrons. Doses of 1 MGy were applied. The catalytic activity of the all samples monotously decreases with decreasing content of nickel oxide, moreover, the samples containing maximum of tungsten oxide were not measurable. The character of dependence of the specific catalytic activity on the composition of the catalysts was not changed by irradiation. Both types of radiation lead only to small change in surface oxidative properties.

One of the objectives of this study was to investigate the influence of implantation of nitrogen ions into the surface of nickel oxide on its catalytic activity. The implanted sample was introduced into the stainless steel cage with the mesh size of 0.1 mm. The whole cage was incorporated into the chamber of implantation equipment. The N^{2+} and N^+ ions (in the ratio 3:1, the energy of 90 keV and the whole ion current of 1.5 mA) were implanted into nickel oxide under vacuum of $3x10^{-3}$ Pa during a rotation of the cage for the time period of 2 h. The both non-treated and implanted samples were tested, of course, under same conditions. No changes were observed in the surface area values. Considerable changes of catalytic activity of pure NiO were caused by implantation of nitrogen ions into the surface of NiO, probably due to farmation of new catalytic sites. The study of hydrogen reduction kinetics was performed using isothermal thermogravimetry in the range 410 to 470°C. Kinetic studies revealed that maximum rate of reduction occurs with samples containing excess of nickel oxide and low amount (about 10 wt. %) of admixture of tungsten oxide. Obtained data were tested in four independent models of reaction mechanism to evaluate which one is best suited for studied system.

REFERENCES

[1] V. Múčka (1986) Pokroky chemie, Academia
[2] M. Pospíšil et al. (1974) Collect. Czech. Chem. Commun., p. 3056
[3] M. Pospíšil et al. (2004) J. Therm. Anal. Cal., 35-50
[4] M. Pospíšil et al. (2001) J. Therm. Anal. Cal., p. 449

RADIATION DECHLORINATION OF ALIPHATIC CHLORINATED HYDROCARBONS IN THE PRESENCE OF SOLID MODIFIERS

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

INTRODUCTION

Chlorinated aliphatic hydrocarbons have been used in a number of industrial processes for many years. There are many methods of their removal from environment. Radiation degradation of molecules of chlorinated hydrocarbons present in water is one of the most effective methods of their removal. The aim of this work is to minimize doses needed for remediation of polluted water. Properties of irradiated system significantly affect efficiency of dechlorination by low doses of radiation. These properties can be further modified by addition of solid modifiers to the irradiated system.

EXPERIMENTAL

Based on previous work of various authors [1-3], the following modifiers were selected for study: cuprous oxide, cupric oxide, titanium dioxide, nickel oxide, active carbon, and bentonite. Aqueous solutions of hydrocarbons or suspensions containing the modifiers were irradiated using linear accelerator LINAC 4-1200, emitting electrons accelerated to the energy of 4.5 MeV (Fig. 1). The absorbed doses ranged from 0 to 5 kGy. Degradation of aqueous solution of two different chlorinated hydrocarbons was studied: tetrachloroethylene (PCE) and trichloroethylene (TCE) with initial concentrations from 1.08×10^{-4} and 0.06×10^{-3} to 9.08×10^{-4} and 4.5×10^{-3} mol dm^{-3}, respectively. After irradiation, analysis of the samples was performed. The concentration of remaining hydrocarbon was measured by gas chromatography. The concentration of produced chlorine anions was determined using ion-selective electrode. Reaction degree, radiation chemical yield and degree of dechlorination were calculated from the acquired results.

RESULTS

The obtained results show that both radiation chemical yields G(-PCE) and G(-TCE) increase with increasing initial concentrations of hydrocarbons. Both these quantities decrease with increasing absorbed doses of irradiation. Cuprous oxide, cupric oxide and nickel oxide negatively affect radiation dechlorination of PCE. Moreover, it was found that presence of CuO- and Cu$_2$O significantly decreases both degree of dechlorination α(Cl$^-$) and radiation chemical yield G(Cl$^-$). This effect does not seem to depend on the amount of the modifier. No effect was observed in the presence of bentonite and titanium dioxide. Finally, in the presence of active carbon the decrease of the concentration of chlorinated hydrocarbon in the solution occurs, due to adsorption properties of the modifier. The irradiation of the system with active carbon leads to degradation of hydrocarbons in solution, succeeded by desorption of adsorbed chlorinated hydrocarbon.

REFERENCES

[1] V. Múčka et al. (2000) Radiat. Phys. Chem. 59, 399-404

[2] J. C. Gonzales - Chuarez et al. (2006) Radiat. Phys. Chem. 75, 768- 772

[3] V. Múčka et al. (2004) Applied Catalysis A: General 271, 195- 201.

Fig. 1. Electron beam output from the linear accelerator

RADIOLYSIS OF OXALIC AND CITRIC ACIDS USING GAMMA RAYS AND ACCELERATED ELECTRONS

M. Semelová, V. Čuba, J. John, V. Múčka

INTRODUCTION

Due to their ability to bind metal ions, complexing agents such as EDTA, NTA, citric acid or oxalic acid are frequently used as the components of decontamination solutions. Specifically, citric and oxalic acids form a part of the majority of decontamination solutions used at nuclear power plants. However, solutions containing impurities, especially radionuclides, bound by complexing agents are generally difficult to treat [1]. Decomposition of complexing agents followed by selective separation of metal ions has been proposed as one of the possible methods of treatment of these complex solutions. Metal ions are released from the complex compound after the degradation of the organic ligand(s) and their effective separation can follow. Various methods to decompose organic compounds were studied, e.g. thermal decomposition, photocatalytic and biological degradation [1]. Radiation degradation of complexing agents is another promising method to achieve aforementioned goal [2]. The aim of this work is detailed study of kinetics of radiolysis of citric and oxalic acids and especially their mixture under various conditions for deeper understanding and for possible optimization of the process of the treatment of spent decontamination solutions or NPP evaporator concentrates.

EXPERIMENTAL

Studied solutions were prepared with regards to composition of real decontamination solutions. Solutions of 0.005 mol/dm^3 citric acid, 0.01 mol/dm^3 oxalic acid, and mixture of 0.005 mol/dm^3 citric and 0.01 mol/dm^3 oxalic acid for irradiation experiments were prepared by dissolution of crystalline compounds in distilled water.

Furthermore, solutions contained sodium nitrate or trihydrogenboric acid as additional compounds. The pH values were adjusted using sodium hydroxide or hydrochloric acid. For evaluating the effect of oxygen and for influencing of the radiation process, several sets of prepared solutions were bubbled at room temperature for 30 min with high purity N_2 or N_2O gases, or with a mixture of air with ozone (20%), prior irradiation. Irradiation was performed using ^{60}Co gamma source and linear electron accelerator.

RESULTS

Both gamma and accelerated electrons irradiation yield comparable results of citric and oxalic acid radiolysis. Both acids degrade faster when alone in solution. Mixing both acids has negative impact on radiolysis. The conversion degree of both acids depends on pH of the solutions; radiolysis proceeds more efficiently at lower pH. (-1) forms of both acids are the most vulnerable to radiolysis. The positive effect of small amount of nitric ions on degradation was observed. However, high amount of inorganic salts (nitric and/or boric ions) decreases the radiolytic effect. Bubbling with various gases has little or no impact on

radiolysis. Obtained results indicate oxidation mechanism of radiation degradation.

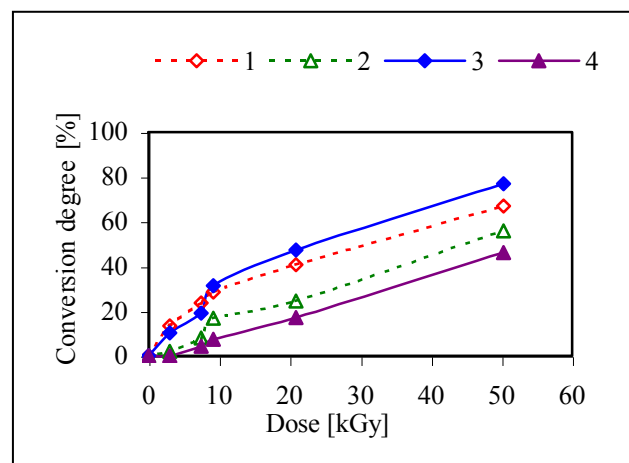Reaction orders were uniformly determined as 2.5.

Fig. 1. Dependence of conversion degree of citric acid on absorbed dose. Solutions: 0.005 mol/dm^3 citric acid and 0.005 mol/dm^3 citric acid + 0.01 mol/dm^3 oxalic acid. 1.3 – citric acid irradiated by gamma rays and accelerated electrons, respectively; 2.4 – citric acid in the mixture with oxalic acid irradiated by gamma rays and accelerated electrons, respectively.

REFERENCES

[1] International Atomic Energy Agency (1994) Technical Report Series No. 370, p. 103
[2] A. P. Toste et al. (1994) Waste Management 14(1), 27-34.
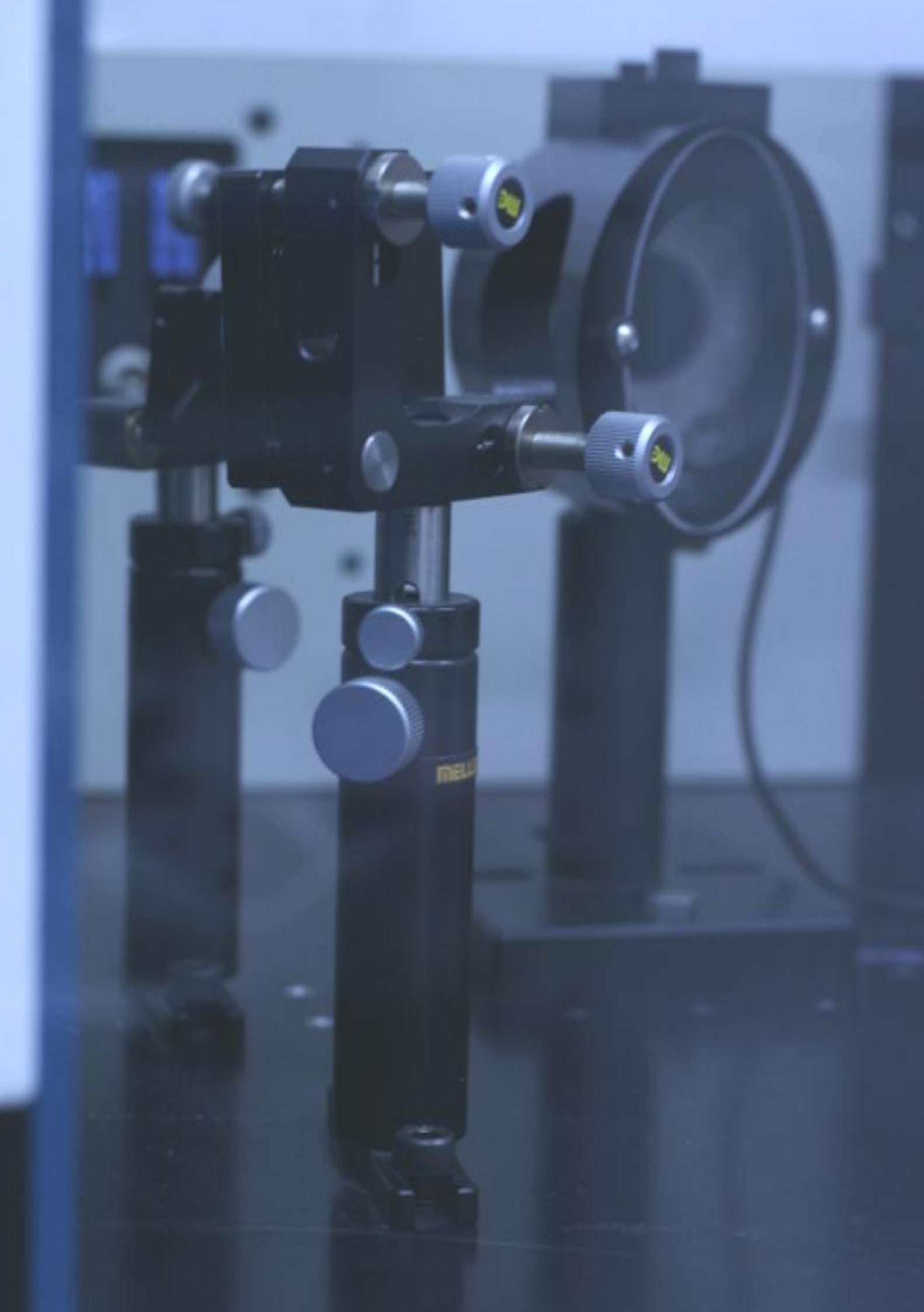
PUBLICATIONS

IAEA TECHNICAL DOCUMENTS

Avramenko, V. - Braet, J. - Bruggeman, A. - Davydov, D. - Davydov, Y. - Dobrzhansky, V.- Drace, Z. - Efremenkov, V. - Forsström, H. - Gan, X. - Halder, S. - Harjula, R. - Igleasias, A.M. - John, J. - Karlin, Y. - Kim, J.H. - Marinin, D. - Manorik, P. - Meyer, A. - Navratil, J. - Parsons, G. - Shin, S.W. - Tusa, E. - Verma, B.B. - Won, J.S. - Yang, H.Y. - Zheleznov, V. **New Developments and Improvements in Processing of 'Problematic' Radioactive Waste.** 1. ed. Vienna: International Atomic Energy Agency, 2007. 320 pp. ISBN 978-92-0-110707-7.

John, J. - Šebesta, F. - Semelova, M. - Čuba, V. - Steinerova, J. - Pavlik, A. – Motl, A. **Separation of Radionuclides from Complex Waste Matrices.** In: New Developments and Improvements in Processing of 'Problematic' Radioactive Waste. IAEA Vienna 2007, p. 134-167. ISBN 978-92-0-110707-7.

PUBLICATIONS / PROCEEDINGS

Čuba, V. - Múčka, V. - Pospíšil, M. - Silber, R.: **Radiation Removal of Contaminants from Groundwater.** In Inovativní in-situ sanační technologie (chemické a biologické metody). Vodní zdroje, Ekomonitor - Chrudim, 2007, p. 24-29. ISBN 978-80-86832-28-9. (in Czech).

Homzová, E. - Mizera, J. - Vetešník, A. - Semelová, M. - Beneš, P. - et al.: **Speciation Study of U(VI) using TRLFS Method.** Chemické zvesti, 2007, No. 1, p. 129. ISSN 1336-7242. (in Czech).

Homzová, E. - Mizera, J. - Vetešník, A. - Semelová, M. - Beneš, P. - et al.: **Speciation Study of U(VI) using TRLFS Method.** In 13. Spektrometrická konference. Spektroskopická společnost Jana Marka Marci - Prague, 2007, p. 96. ISBN 80-903732-2-4. (in Czech).

Klika, Z. - Kraus, L. - Vopálka, D.: **Cesium Uptake from Aqueous Solution by Bentonite: Multicomponent Sorption with Ion-Exchange Models.** Langmuir, 2007, vol. 23, p. 1227-1233. ISSN 0743-7463.

Kobliha, D. - Pospíšil, M. - Čuba, V. - Múčka, V. - Silber, R.: **Influencing of Properties of Mixed Oxides Catalysts using Electromagnetic and Corpuscular Radiation.** Chemické zvesti, 2007, No. 1, p. 162. ISSN 1336-7242. (in Czech).

Kovařík, P. - Pospíšil, M. - Čuba, V. - Drtinová, B.: **Radiation Removal of Co(II) and Ni(II) from Aqueous Solutions.** Chemické zvesti, 2007, No. 1, p. 263. ISSN 1336-7242. (in Czech).

Němec, M. - Zapletal, P. - Dostál, J. - John, J.: **Electrochemical Soil Decontamination – [137]Cs Separation.** In Inovativní in-situ sanační technologie (chemické a biologické metody). Vodní zdroje, Ekomonitor - Chrudim, 2007, p. 82-87. ISBN 978-80-86832-28-9. (in Czech).

Silber, R. - Velický, M. - Vokál, A.: **Dissolution of UO_2 Fuel in Repository Modelling Slightly Alkaline Solution - Electrochemical Approach.** In Proceedings of Workshop 2007. CTU Prague, 2007, vol. B, p. 466-467. ISBN 978-80-01-03667-9.

Silber, R. - Vokál, A. - Dobrev, D.: **Electrochemical Noise Analysis of Carbon Steel Behavior.** In Proceedings of Workshop 2007. CTU Prague, 2007, vol. B, p. 468-469. ISBN 978-80-01-03667-9.

Vetešník, A. - Semelová, M. - Štamberg, K. - Homzová, E. - John, J. - et al.: **The study of Uranium (VI) Speciation in the Sulphate Media by TRLS Method.** Chemické zvesti, 2007, No. 1, p. 167. ISSN 1336-7242. (in Czech).

Vokál, A. - Vopálka, D. - Vejsada, J. - Lukin, D. - Drtinová, B.: **An Approach to Radionuclide Diffusion Modelling in Performance Assessment.** In 11th International Conference on the Chemistry and Migration Behaviour of Actinides and Fission Products in the Geosphere. Forschungscentrum Karlsruhe, 2007, p. 119.

Vopálka, D. - Klika, Z. - Kraus, L. - Vejsada, J.: **Cesium Uptake by Ca/Mg Bentonite: Evaluation by a Multicomponent Two-site Ion-Exchange Model.** In 11th International Conference on the Chemistry and Migration Behaviour of Actinides and Fission Products in the Geosphere. Forschungscentrum Karlsruhe, 2007, p. 75-76.

Vopálka, D. - Laciok, A. - Brennerová, M. - Drtinová, B. - Franta, P. - et al.: **Study of Behaviour of Contaminants in the Fucoid Sandstone on the Stráž pod Ralskem Site.** In Proceedings of Workshop 2007. CTU Prague, 2007, vol. B, p. 462-463. ISBN 978-80-01-03667-9.

REPORTS

Čuba, V. - Vopálka, D. - Neufuss, S. - Múčka, V. - Drtinová, B. - et al.: **Study of Near Field Interactions in Deep Repository. Influence of Radiation on Corrosion Rate of Carbon Steel, Diffusion of Selected Radionuclides in Bentonite (Experiments and Simulation).** CRRC - CTU Prague, 2007, 70 pp. (in Czech).

Franta, P. - Havlová, V. - Marhol, M. - Polívka, P. - Cvopálka, D. - Kraus, L. - Štamberg, K. - Drtinová, B. - et al.: **Utilisation of Innovative Remediation Technologies and Processes in the Removing of Uranium Chemical Mining Effects.** ÚJV - Řež u Prahy, 2007, 178 pp. (in Czech).

John, J. - Šebesta, F. - Kameník, J. - Šuľaková, J.: **A Proposal of a Chromatographic Process for the Separation of Minor Actinides from Solutions Issuing Reprocessing of Spent Nuclear Fuel.** CTU Prague - CRRC, 2007, 21 pp.

John, J. - Šebesta, F. - Kameník, J. - Šuľaková, J. - Fišera, O.: **European Research Program for the Partitioning of Minor Actinides from High Active Wastes Issuing the Reprocessing of Spent Nuclear Fuels (EUROPART).** CTU Prague - CRRC, 2007, 20 pp.

John, J. - Šebesta, F. - Šuľaková, J. - Kameník, J. - Fišera, O.: **A Proposal of a Chromatographic Process for the Separation of Minor Actinides from Solutions Issuing Reprocessing of Spent Nuclear Fuel.** CTU Prague - CRRC, 2007, 32 pp.

Němec, M. - Zapletal, P. - Dostál, J. - John, J.: **Decontamination of Soils Contaminated by Heavy Metals or Radionuclides.:** ALLDECO CZ a.s. - Hodonín, 2007, 91 pp. (in Czech).

Štamberg, K. - Beneš, P. - Vopálka, D. - Múčková, O.: **The Study of Uranium Sorption Capacity of Ion Exchangers as a Function of pH of Mining Water Taken from Uranium Mine No 19.** Faculty of Nuclear Sciences and Physical Engineering - CTU Prague, 2007, 20 pp. (in Czech).

Štamberg, K. - Beneš, P. - Vopálka, D. - Múčková, O.: **The Study of Equilibrium and Kinetic Dependences of Sorption and Elution of Uranium under the Conditions of Decontamination of Mining Water Taken from Uranium Mine No 19.** Faculty of Nuclear Sciences and Physical Engineering - CTU Prague, 2007, 20 pp. (in Czech).

Vokál, A. - Brůha, P. - Čuba, V. - Dobrev, D. - Hokr, M. - et al.: **Research of Processes of the Near-field Region of the Final Disposal of Spent Nuclear Fuel and High Active Waste - Report No. 3.** Z 1937 CH, ÚJV - Řež u Prahy, 2007, 102 pp. (in Czech).

Vokál, A. - Brůha, P. - Vopálka, D. - Hercík, M. - Landa, J. - et al.: **Annual Report of the Project POKROK 1H-PK/25 - 2007.** ÚJV - Řež u Prahy, 2007, 33 pp. (in Czech).

Vopálka, D. - Beneš, P. - Homzová, E. - Mizera, J. - Semelová, M. - et al.: **Development of Advanced Methods of Speciation- and Sorption Study of Actinides. Part 1.** Faculty of Nuclear Sciences and Physical Engineering - CTU Prague, 2007, 55 pp. (in Czech).

Vopálka, D. - Vokál, A. - Lukin, D. - Vetešník, A. - Sobek, L. - et al.: **Research of Processes of the Near-field Region of the Final Disposal of Spent Nuclear Fuel and High Active Waste. Modelling of the Source Term.** ÚJV - Řež u Prahy, 2007, 34 pp. (in Czech).

THESES

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Promoters in Radiation Processes

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F. Klímek

Pyrochemical Separation Technologies for Fuel Cycles of Generation IV Nuclear Reactors

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M. Žáková

Uranium Speciation Methods in the Environment

D. Vopálka

MASTER / DIPLOMA

P. Kovařík

Study of Radiation Separation of Nickel and Cobalt from Aqueous Solutions

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J. Mihalík

Kinetics of Photopolymeral Reaction in the Holographic Recording Material

P. Fiala (Department of Physical Electronics, CTU in Prague)

M. Přeček

The Fuel Cycle of the Molten-salt Transmutation Reactor

J. Uhlíř (Nuclear Research Institute, Řež)

B. Andris

Determination of ^{99}Tc in Radioactive Wastes

F. Šebesta

M. Buňata

Radiation Dechlorination of Some Chlorinated Aliphatic Hydrocarbons

V. Múčka

D. Dobrev

Kinetics of Carbon Steel Corrosion under Conditions of Nuclear Waste Repository

R. Silber

H. Chaloupková

Labeling of Biomolecules and their Subsequent Quality Control

M. Fišer (Nuclear Physics Institute of the AS CR, Řež)

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Kinetics of Dissolution of Uranium Dioxide under Waste Disposal Conditions

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Radiation Removal of Ionic Forms of Lead and Cadmium from Aqueous Solutions

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H. Švecová

Proposal of Quality Control Methods for Antibodies and their Fragments Labelled by Radioactivity

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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

European Research Program for the Partitioning of Minor Actinides from High Active Wastes Issuing the Reprocessing of Spent Nuclear Fuels (EUROPART), FI6W-CT-2003-508 854, EU FP6; J. John and F. Šebesta

FUNMIG: Fundamental Processes of Radionuclide Migration, associated group, EU FP6; P. Beneš and D. Vopálka

Network for Actinide Science (ACTINET-6), FI6W-CT-2004-508 836, EU FP6; P. Beneš

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

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

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

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

Collaboration with the Federation of European Chemical Societies (FECS), 1P05LA263, Ministry of Education, Youth and Sports, Czech Republic; J. John

Modification of Reactivity and Catalytic Propeties of NiO-WO$_3$ Mixed Oxides by Ionizining Radiation and Ion Implantation, CTU0708314, Czech Technical University in Prague; D. Kobliha and M. Pospíšil

Advancement of Nuclear Education at the Universities in the Czech Republic (CENEN), Development project CTU 174, Ministry of Education, Youth and Sports, Czech Republic; V. Múčka and J. John

Harmonisation of the Infrastructure of CTU with the Valid Legislature: Extension of the Dosimetric Instrumentation at CTU Controlled Zones, Development project CTU 31, Ministry of Education, Youth and Sports, Czech Republic; J. John and M. Němec

Innovation of Instrumentation for Education in Nuclear Chemistry, Development project CTU 16, Ministry of Education, Youth and Sports, Czech Republic; V. Múčka and V. Čuba

Study of Near-field Processes of the Final Disposal of Spent Nuclear Fuel and High-Level Nuclear Waste, FJFI 40-05038, Nuclear Research Institute Řež plc; D. Vopálka

Determination of the Dependence of Ionex Capacity for Uranium on the Mine water pH, FJFI 40-07003, DIAMO Příbram; K. Štamberg

Determination of Equilibrium and Kinetic Dependencies of Uranium Sorption for Two Anion Exchangers, FJFI 40-07022, DIAMO Příbram; K. Štamberg

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

Proposal of a Chromatographic Process for the Separation of Minor Actinides from the Solutions Issuing the Reprocessing of Spent Nuclear Fuels, CRRC/práv/07/01; RAWRA Czech Republic, J. John and F. Šebesta

RESEARCH FELLOWSHIPS / VISITING SCIENTISTS

OUTGOING:

B. Drtinová

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

Oregon State University, Radiation Center, Corvallis, USA, July - October 2007

J. John, J. Kučera, M. Němec

Atomic Mass Spectrometry (AMS) Laboratory and Development of Analytical Method Based on this Technique

Paul Scherrer Institute, Villigen, and ETH Zürich, Switzerland, August 2007

INCOMING:

V. Böhmer

Optimisation of Radiation Stability of Functionalised Calix[4]arenes

DAAD Project 350506, Johannes Gutenberg Universität, Mainz, Germany, February 2007

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Experimental Study and Modelling of Radionuclide Sorption on Clays, Suspended Solids and Bottom Sediments from Natural Waters

Institute of Physics, Savanorių ave 231, Vilnius, LT-02300, Lithuania

EXPERT MISSION

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Evaluate of Categorization and Processing of Liquid RW Containing Transuranic Elements and Organic Material

IAEA Project C3-UKR/3/002-11-01, Chernobyl, Ukraine, August 2007

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