2. CHEMISTRY OF NUCLEAR FUEL CYCLE, RADIOCHEMICAL PROBLEMS IN NUCLEAR WASTE MANAGEMENT (NFC)

Lectures

NFC.L01 (Id: 92)
KINETICS OF REDUCTION OF HEXAVALENT NEPTUNIUM BY NITROUS ACID IN SOLUTIONS OF NITRIC ACID

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Extraction of hexavalent and tetravalent actinides with tributylphospate (TBP) from their solutions in nitric acid is the most industrially mature process for reprocessing spent nuclear fuel and is the basis for the development of advanced reprocessing schemes like UREX and TRUEX. One of the less resolved issues is the management of neptunium in the extraction system, because of not clearly defined redox speciation. Neptunium is present in both pentavalent and hexavalent oxidation states that differ greatly in their extractability to the organic phase (hexavalent state being very well extracted by TBP, whereas pentavalent neptunium is almost not extracted). As a result, neptunium is distributed in both organic and aqueous streams of the separation process. Apparently, the most important factor determining the redox speciation of neptunium is the presence of nitrous acid that is formed during the dissolution of spent fuel and also by radiolysis. Nitrous acid HNO_2 is relatively well extracted by TBP ($\log D \approx 1$) and is therefore distributed from the source raffinate solution in further stages of the separation system. If present in small quantities, it autocatalyzes the oxidation of Np(V) by nitric acid, whereas large concentration of HNO_2 leads to reduction of Np(VI) back to the pentavalent state - the kinetics of this reaction have been covered in detail by many authors. The kinetics of reduction of Np(VI) by HNO_2 have so far attracted only little interest and are the subject of this study. UV-VIS-NIR absorption spectrophotometry (OceanOpticsTM) in a stirred cuvette was employed in order to study the reaction: $2Np(VI) + HNO_2 + H_2O \leftrightarrow 2Np(V) + NO_3^- + 3H^+$ The reaction progress was recorded by following the absorbance at characteristic peak of Np(V) at 981 nm and simultaneous observation of the broad absorption peak of HNO_2 between 350-400 nm. The reaction orders with respect to concentrations of Np(VI) and HNO_2 were found to be close to one. Increasing the concentration of nitric acid at constant ionic strength (μ = 4M H/$LiNO_3$) had a decreasing effect on the reaction rate with an order of -0.8. The dependence of the rate constant on the ionic strength and temperature will be also reported.

NFC.L02 (Id: 164)
ELECTRO-FLUID ANALYSIS OF A MOLTEN-SALT ELECTROREFINER FOR PYROCHEMICAL NUCLEAR WASTE TREATMENT

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Pyrochemical technologies offer the capability to treat spent nuclear fuels and were acknowledged to meet the proliferation-resistant principles. These processes could play an important role in reducing the long-term hazards of a spent nuclear fuel by separating uranium and transuranic actinides, which in turn may be transmuted in a fast breeder reactor. The most effective way to accelerate the development of these technologies is to formulate physical models of the underlying electrochemical and transport processes. The multi-physics computational models can be essential for design and operational analysis of advanced processors and offer an efficient approach to implementing these processes. In this study, the electrochemical principles and forced convection of molten eutectic (LiCl-KCl) electrolyte in a uranium electrorefining cell are considered to establish an appropriate electro-fluid model within the 3-dimensional framework of a conventional computational fluid dynamic model. Diffusional mass transport as a controlling step is modeled for the surface resistance of charge transfer between the electrode and molten-salt phase in which a constant composition is provided by an intense forced mixing of the bulk solution. The approach in this study is focused on the mass transport and current arising due to the concentration and the surface overpotential based on a cell configuration. This computational platform includes the electrochemical reaction rate of charge transfer kinetics which is described by a Hitler-Volmer equation, while mass transport is considered using an ionic transport equation. The coupling of the local overpotential distribution and uranium concentration gradient makes it possible to predict the local current density distribution at the electrode surfaces.

NFC.L03 (Id: 295)
ELECTROCHEMICAL SEPARATION OF ACTINIDES FROM MOLTEN LiCl-KCl ON SOLID Al CATHODES

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An electrorefining process in molten chloride salts using solid aluminium cathodes is being developed in the Institute for Transuranium Elements to recover all actinides from metallic spent nuclear fuel. In this process, actinides are group-selectively electrodeposited on the cathode in a form of solid actinide-aluminium alloys. Fission products are anodically co-oxidised from the fuel together with actinides to the electrolyte. Without purification of this carrier salt, the process would have to be stopped after concentration of the dissolved fission products would become too high to prevent selective deposition of actinides on the cathode. A multiple-steps procedure is considered for cleaning of the salt and a process refered as 'exhaustive electrolysis' is proposed for the first purification step. Similarly to the electrorefining process, this technique is based on the group-selective electrodeposition of actinides on solid aluminium cathodes forming actinide-aluminium alloys. On the anodic side, chlorine gas is produced by electrochemical decomposition of the carrier salt. The presented work was carried out in order to prove feasibility of the method. Two galvanostatic electrolyses were realised and the potentials of both electrodes were constantly followed. Uranium was successfully recovered from LiCl-KCl melts containing UCl_3 and a mixture of UCl_3-$NdCl_3$ and its concentration decreased from 1.7 to 0.1 wt. % with no co-deposition of neodymium. Although the maximum applicable current densities were relatively low, the results are promising, showing high current efficiency and selectivity of the proposed method. A design and application of a special chlorine gas producing inert anode is also discussed.

NFC.L04 (Id: 279)
ADVANCED ORIENT CYCLE - PROGRESS ON RESEARCH, WITH FOCUSING ON SAFETY AND ENGINEERING

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A multi-functional separation process is proposed on the Advanced-ORIENT Cycle (Advanced Optimization by Recycling Instructive Elements) concept [1]. The tertiary pyridine-type anion-exchange resin embedded in silica beads was proposed for the separation process using spent fuel. In this process, hydrochloric acid (HCl), mixture of nitric acid (HNO_3) and methanol (MeOH) are used as eluents. In order to apply this process to engineering scale, two important subjects should be solved so as to prove the availability. One is the environmental aspect for the use of HCl solution, because of its corrosive property to the material. The other is explication of the reactive safety between IER (ion exchange resin) and solvent (HNO_3 - MeOH). The four candidate metals of Ta, Zr, Nb, Hastelloy-B (28%Mo-Ni) and SUS316L as a reference were tested. The conditions of immersion and acid mist-exposure tests were conducted in 0.5~12 M pure and simulated high level liquid waste (SHLLW) HCl at room temperature for maximum 7200 h and at 90 °C for 72~1440 h. In addition, corrosion potential was evaluated by electrochemistry measurement under the same conditions. From the result of the corrosion experiment, Ta was anti-corrosive in HCl media, and Hastelloy-B seemed to be acceptable at RT, with evidence of low corrosion rate (<0.1 mm/y) and general type corrosion. Thermal analysis by DSC was performed to investigate the thermal stability of TPR itself and the mixtures of TPR/MeOH/HCl or HNO_3. Moreover, the thermal stability of TPR mixtures of TPR and SHLLW-NO_3 was investigated and the stability of presence or absence of coexistent elements was compared. Sudden exothermic heat and release of fumes were observed with a mixture of TPR-NO_3/MeOH/HNO_3 when the temperature of the heater reached 220 °C regardless of the HNO_3 concentration. The temperature increased slowly to 175 °C followed by a sudden increase in temperature. Violent reaction occurred in TPR under high temperature in the HNO_3 system. The reaction occurred regardless of HNO_3 concentration and presence or absence of MeOH. However, it was confirmed that the reaction did not occur when the heating temperature decreased. In this report, outline of current progress of Adv-ORIENT research as well as detailed evaluation results of this safety and engineering study are described.

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NFC.L05 (Id: 191)
COBALT BIS(DICARBOLLIDE) IONS WITH COVALENTLY BONDED TODGA-LIKE SUBSTITUENTS FOR ACTINIDE AND LANTHANIDE EXTRACTIONS

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The partitioning and transmutation of long-lived nuclides such as minor actinides from high level waste (HLW) issued from nuclear fuel reprocessing is a method how to reduce the long-term environmental burder of HLW. In recent years, several HLW partitioning processes using different extractant agents have been developed. Among them, the tridentate ligands like N,N,N´,N´-tetraoctyl diglycolamide (TODGA) are one of the most promising extractants for the recovery of acti-

nides and lanthanides in the nuclear fuel treatment. In this work, the recently developed extractants based on cobalt bis(dicarbollide) ion(1-), [(1,2-$C_2B_9H_{11}$)2-3-Co)]- (COSAN) functionalized with TODGA like substituents were evaluated for extraction of trivalent actinides and lanthanides from acidic waste solutions. The extractants under study differed in substitution of the amide nitrogen (e.g., by butyl-, octyl-, tert-octyl-, dodecyl-, benzyl- groups) and the mode of attachment of two cobalt bis(dicarbollide) anions (with or without spacer) to diglycolyl acid platform by amidic bonds. It was found that the compounds with longer diethyleneglycol connectors between COSAN cage and diglycolamide group extracted trivalent lanthanides and actinides very effectively even from highly acidic nitric acid solutions. Additionally, the extraction efficiency of such derivates was significantly higher than that of comparable organic TODGA molecules without COSANs. The most perspective compound from this series corresponds to the formula X-[(8-CH_2-$CH_2O)_2$-1,2-$C_2B_9H_{10}$)(1',2'-$C_2B_9H_{11}$)-3,3'-Co]$_2$, where central amidic unit X corresponds to [(n-C_8H_{17}-$NCOCH_2)_2O$]. We shall demonstrate that this extractant enables good extraction of trivalent lanthanides and actinides from majority of fission products presented in the simulated PUREX feed. Trivalent radionuclides can be effectively stripped using complexants. This extractant will be further studied for possible technological applications.

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NFC.L06 (Id: 35)
EXTRACTION OF RADIONUCLIDES WITH SOLUTIONS OF COMPLEXING AGENTS IN SUPERCRITICAL FLUIDS AND COMPRESSED GASES

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One of the main advantages of extraction with supercritical fluids (SCF) or liquid gases (LG) is a possibility of the reagent-free regeneration of "solvent", which sharply decreases the secondary waste volume. As a result, in the last 20 years the researchers in many countries focused their attention on the supercritical fluid extraction (SFE) of the trace amounts of radioactive and heavy metals for treatment to remove and decontamination of various solid objects (including soils) and on SFE of actinide macroamounts for reprocessing the spent nuclear fuel of the nuclear power plants (SNF NPP). In this work we analyze the similarities and differences between the liquid-liquid extraction of radionuclides and extraction with SCF and LG and the prospects of extraction using supercritical and liquid gases in radiochemistry. In the last 20 years the data on SFE of a series of metals were published in more than 100 papers. The detailed data was presented on SFE of U, Th, rare-earth elements (REE), Co, Cu, Mn, Pu, Np, and Am. The SFE of U, Th, and REE with tri-n-butyl phosphate (TBP) and its mixture with β diketones were also extensively studied. Rather detailed data were presented on SFE of transuranium elements and fission products using carbon dioxide solutions of TBP, β diketones and their mixtures and even on recovery of these elements from non-irradiated nuclear fuel and from SNF NPP. SFE of Cs and Sr with solutions of organic acids and polyethers was also well studied. The detailed data are published of the extraction of U, REE, Cu, Pb, Zn, Cd, Cr, and As using carbon dioxide solutions of various acids such as di-2-ethylhexyl phosphoric, bis(2,4,4-trimethylphenyl) phosphoric (cyanex 272), bis(2,4,4-trimethylphenyl)monothio phosphoric (cyanex-302), bis(2,4,4-trimethylphenyl)dithio phosphoric (cyanex-301), and di-2-ethylhexylthio phosphoric acids. Our analysis showed only slight differences between the extraction of macro- and microamounts of metal cations with solutions of complexing agents in liquid and supercritical CO_2 and liquid-liquid extraction. At the same time it should be noted that:

- low viscosity and high diffusion rate allows performance of extraction in CO_2 without mixing of the phases;
- CO_2 can affect pH of the liquid phase being in equilibrium with it;
- main difference between the extraction of metal cations with solutions in liquid and supercritical CO_2 and liquid-liquid extraction are observed for microamounts of metals.

Moreover, it should be mentioned that the technologies of SNF reprocessing and procedures of deactivation in supercritical and compressed CO_2 and Freons are most promising for radiochemistry. The advantages of these processes are sharp decrease in the volume of secondary liquid radioactive wastes; absence of organic solvents and toxic compounds, and rather low operation temperature (25-80°C). It should be noted that the use of Freons instead of CO_2 allows to decrease the working pressure to 1- 4 MPa.

NFC.L07 (Id: 81)
REMOVAL OF ANTIMONY-124 FROM PWR COOLANT WATER

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Selective ion media, e.g. inorganic adsorbents and ion exchangers, are increasingly used for the removal of key radionuclides such as ^{60}Co, ^{90}Sr and ^{137}Cs from nuclear waste effluents due to their radiation stability, high processing capacity and high decontamination efficiency. The materials used that are commercially available (e.g. zeolites, titanates, silicotitanates, hexacyanoferrates) are cation exchangers or adsorbents, which can remove efficiently cationic and neutral radioactive species. Inorganic anion exchange materials are quite rare and do not possess high selectivity. Considering radiation doses to personnel and environment, $^{58,60}Co$ and ^{137}Cs are the most critical radionuclides in nuclear power plant (NPP) waste liquids and water streams. Improved processing systems have been able to reduce markedly the discharges of these radio-

nuclides at many utility sites and further efforts have been directed to remove other radionuclides such as ^{51}Cr, ^{110m}Ag and ^{125}Sb that dominate in solution after cesium and cobalt elimination. Much attention has been paid recently to ^{125}Sb. It may exist completely in soluble form in the Floor Drain Waters. In solution, antimony can exist in two oxidation states (+3,+5) and in several hydroxyl species (e.g. $Sb(OH)_6^-$, $Sb(OH)_3$ (aq), $Sb(OH)_4^+$), depending on the pH and redox conditions. This indicates that antimony is difficult to remove from solution. Recent tests showed that standard demineralizer resins and ion selective media are ineffective for the removal of Sb from liquid radwaste. However, some commercially available inorganic cation exchangers, such as CoTreat, can remove cationic species of ^{125}Sb from NPP Floor Drain water with good efficiency in some cases. Chemical additives coupled with ultra filtration have been shown to be effective method for ^{125}Sb removal in a test program conducted at Duke Power Company's Oconee plant. Study of other methods such as electrodeionization and hollow-fibre filtration is underway e.g. in the EPRI Low-Level Waste program. In Loviisa NPP (PWR, Finland) about 50 % of the radiation dose received by personnel during the service shut-down period is caused by ^{124}Sb. Immediately after shut-down, ^{124}Sb is released from fuel into the primary coolant water at levels greater than 100,000 Bq/L ($>3x10^{-3}$ μCi/mL). The mixed-bed organic resin demineralizer system used for activity removal under routine reactor operation is inefficient in removing the released ^{125}Sb. Loviisa NPP has thus established a project to study and assess various ^{124}Sb abatement technologies. As a part of this project, Laboratory of Radiochemistry has just initiated a laboratory study to remove ^{124}Sb from the primary coolant water of Loviisa NPP using novel zirconium oxide (ZrO_2) sorbents. Test samples were obtained from service shut-down of Loviisa Unit 1. Water samples contained 600,000 Bq/L of soluble ^{124}Sb after filtration.

NFC.L08 (Id: 69)
ANALYSIS OF Th, U, Pu, AND Am IN RADIOACTIVE METAL WASTE USING EXTRACTION CHROMATOGRAPHY

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Lots of metal waste the surface of which is contaminated with radionuclides are generated in the decommissioning of nuclear facilities. For the waste management, characterization of radionuclides inventory in the waste is required. In this work, determination method of α nuclides, Th, U, Pu, and Am, contained in the metal waste was developed. Taking into account the half-lives of these α nuclides and their expected concentration in the waste, inductively coupled plasma mass spectroscopy (ICP-MS) and α-ray spectrometry were selected as analytical tools. The determination using these techniques requires that these α nuclides in the metal waste were separated from the large quantities of stable matrix and interfering radionuclides. In our laboratory, we have applied commercially available extraction chromatographic resin to the analysis of α nuclides in a dissolved solution of molten products of low-level radioactive waste; UTEVA resin (for uranium and tetravalent actinide resin) for the analysis of Th and U, and TRU resin (for transuranium resin) for the analysis of Pu and Am. In a similar manner as above, application of these extraction chromatography methods to the metal waste was planned. In the case of the metal waste, we have to take into account the existence of large amounts of Fe, because Fe(III) has significant negative impact on the sorption of trivalent actinides on TRU resin. Hence, the effects of Fe(III) amount and concentration in the sample solution on the uptake of Am, representative of trivalent actinide, on TRU resin were studied in detail with the solution prepared from $Fe(NO_3)_3$. Fortunately, when Fe(III) is reduced to Fe(II) with ascorbic acid, its effect on the sorption of trivalent actinide is practically negligible. The amount of ascorbic acid required to improve the extraction of Am was also studied. Based on this study of the effect of Fe(III) on the extraction of α nuclides on the extraction resin, the schemes to analyze α nuclides in metal waste was optimized. The optimized methods were validated with dissolved solution of stainless steel, SUS304 with added α nuclides. The recoveries of Th and U from dissolved solution of SUS304 were 89±4% and 102±5%, respectively, with optimized scheme using UTEVA resin. The recoveries of Pu and Am were 96±4% and 89±7%, respectively, using TRU resin. Furthermore, Th, U, Pu, and Am in simulated waste prepared by dissolving pipe wastes (the surface ^{60}Co concentration was about 70 kBq) sampled from a coolant system of nuclear reactor and by adding α nuclides were analyzed with the optimized method. The ^{60}Co was sufficiently separated from α nuclides. The recoveries of Th, U, Pu, and Am were 91±3%, 103±4%, 97±4%, and 91±3%, respectively. These recoveries are comparable to that analyzed dissolved solution of SUS304. These results support the usefulness of the optimized schemes.

NFC.L09 (Id: 144)
MICRO-SCALE INVESTIGATIONS OF U(VI) IMMOBILIZATION BY CEMENTITIOUS MATERIALS

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Cement-based materials play an important role in multibarrier concepts developed worldwide for the safe disposal of low- and intermediate-level radioactive waste. Cement is used to condition the waste materials and for the construction of the engineered barrier system (container, backfill and liner materials) in deep geological repositories. The cementitious near field is subject to chemical alteration processes due to the interaction of cement with groundwater infiltrating from the host rock. A molecular-level understanding of the interaction of radionuclides with cement improves long-term predictions of radio-

nuclide retention in cement-based repositories with regards to influences of the heterogeneity of the cement matrix and the chemical evolution of the cementitious near field with time caused by cement degradation. In this study the speciation of U(VI), which is the dominant oxidation state under oxidizing and slightly reducing conditions in cementitious environments, was investigated by a combination of wet chemistry and synchrotron-based (micro-)spectroscopic and micro-diffraction techniques. Wet chemistry experiments were carried out to quantify U(VI) uptake by cement. Sorption isotherm measurements enabled us to distinguish U(VI) retention by sorption from solubility-controlled effects. Complementary to wet chemistry experiments, we carried out synchrotron-based X-ray absorption spectroscopy (XAS) studies on U(VI) doped crushed cementitious materials (bulk-XAS) and micro-X-ray fluorescence (micro-XRF), micro-XAS and micro-diffraction studies (micro-XRD) on U(VI) doped compact hardened cement pastes (HCP) to obtain information on the U(VI) speciation on the molecular level. Micro-scale studies provided structural information on U(VI) binding mechanisms which are essential for the development of thermodynamic models of U(VI) uptake by cementitious materials. To the best of our knowledge, the combined use of bulk-XAS, micro-XAS and micro-XRD techniques for speciation studies on U(VI) doped HCP materials is novel. The synchrotron-based studies showed that in the cement samples with low U(VI) concentration, i.e., in the linear range of U(VI) sorption, U(VI) was predominantly bound onto calcium silicate hydrates (C-S-H). The latter phases are among the most important cement phases governing immobilization processes. The coordination environment of U(VI) was found to resemble that of U(VI) in uranyl silicate minerals under these conditions. At high U(VI) loadings, however, where U(VI) immobilization is controlled by a solubility-limiting process, a second U(VI) species was observed in addition to uranyl-silicate-like U(VI) coordination. The coordination environment of this species was similar to that of U(VI) in Ca-uranate. This study demonstrates that C-S-H are the uptake-controlling phase for U(VI) in HCP. This finding, in combination with the observed long-term existence of C-S-H phases in an evolving cementitious near field, implies that safe disposal of U(VI) in a cement-based repository should be possible over a very long period of time.

NFC.L10 (Id: 80)
NEW f-ELEMENT PHOSPHATES WITH LANGBEINITE-TYPE STRUCTURE

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Crystallochemical principles make possible to create new compounds with expected structure and properties. This approach was used for "constructing" new f-element phosphates with langbeinite-type structure (Lb). Formerly, the same approach was used for the calculation of compositions of tetrahedral-octahedral frameworks for NZP and Lb forms [1], later some new phosphates with Lb structure were prepared [2-4], namely: $K_2RZr(PO_4)_3$, R = Pr-Lu,Y; $K_2R_{3/2}Ta_{1/2}Zr(PO_4)_3$, R = Gd-Yb,Y; $A_2RZr(PO_4)_3$, A = Rb,Cs; R = Pr,Er; $KBaR_2(PO_4)_3$, R = Yb,Er; $CsBaR_2(PO_4)_3$, R = Dy-Yb; $ABaFe_{2-x}Pr_x(PO_4)_3$, A = K,Cs, x = 0.25; 0.5; 0.75. As a development of this research we have calculated the formula phosphate compositions with expected Lb-type structure with tri- and tetra-valent elements in the interframework sites: $[A_{3/2}R_{1/2}]^{3+}$; $[A_{5/3}M_{1/3}]^{3+}$; $[AR]^{4+}$; $[A_{4/3}M_{2/3}]^{4+}$, A,R,M - uni-, tri-, tetra-valent cations, also f-elements. We were going to prepare the phosphates: $A_{3/2}Ln_{1/2}MgZr(PO_4)_3$, $A_{3/2}Ln_{1/2}Fe_2(PO_4)_3$ and ALnMg$_{3/2}$Zr$_{1/2}$(PO$_4$)$_3$, where A = K, Rb, Cs; Ln = Pr, Sm, Yb. Synthesis was carried out by sol-gel technology. The IR, X-Ray and DSC analyses have been used for samples characterization. Optimum conditions were as follows: pH = 7-9; T = 600 and 800°C during 24 h on every stages, quick addition of H_3PO_4 solution; ultrasonic activation was ineffective. The phosphates $A_{3/2}Ln_{1/2}MgZr(PO_4)_3$ and $A_{3/2}Ln_{1/2}Fe_2(PO_4)_3$ higher presented with cubic structure, sp. gr. P213 were formed. An attempts to prepare phosphates with bigger concentration of Ln-cations in the interframework positions such as ALn or $A_{1.2}Ln_{0.8}$ was unsuccessful. The additional X-ray reflections of the monazite type phases presented on XRD patterns. Monazite phase as an admixture was also present in all phosphate samples prepared. The temperature limits of existence of Lb type phases were established: from 750 - 800 up to 900 - 1150 °C. The thermal decomposition products were identified as phosphates with NZP- or monazite-type structures and as phosphate $Cs_7Fe_7(PO_4)_8O_2$ in the case of iron-containing compounds. The lanthanide ions in LnO_n polyhedra in the structure of new phosphates are characterized by ninefold coordination in cavities. In known phosphates with such structure with Ln-cations located in framework sites the coordination is n = 6 [2,3]. Crystal chemical principle allows to predict new phosphate compositions with expected Lb-type structure containing lanthanide cations in sites of both types simultaneously. This may be realized as the subject of future investigations.

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NFC.L11 (Id: 23)
DETERMINATION OF ^{237}Np, ^{93}Zr AND OTHER LONG-LIVED RADIONUCLIDES IN MEDIUM AND LOW-LEVEL RADIOACTIVE WASTE SAMPLES

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The majority of long-lived radionuclides produced in the nuclear fuel cycle can be regarded as "difficult-to-determine nuclides" due to the low activities and/or the absence of γ-radiation of medium or high energies in their decay schemes. Most isotopes of actinoides are α-emitters, ^{90}Sr (fission product) and ^{93}Zr (activation product) emit almost exclusively β-particles, ^{93m}Nb (activation product) decays by isomer transition or electron capture and emits only X-rays, ^{94}Nb (activation product) emits low intensity γ-radiation due to its low activity. Chemical separation is needed before the nuclear measurement of all the isotopes mentioned above. A combined radiochemical separation method had been developed that enables the simultaneous determination of ^{230}Th, ^{232}Th, ^{234}U, ^{235}U, ^{238}U, $^{239-240}$Pu, ^{238}Pu, ^{241}Am, ^{242}Cm, ^{244}Cm, ^{89}Sr, ^{90}Sr, ^{93m}Nb, and ^{94}Nb. Recently, this method has been extended for the determination of ^{237}Np and ^{93}Zr. The main steps of the method are addition of tracers and carriers, sample destruction, co-precipitation on iron(II) hydroxide and calcium oxalate, separation by extraction chromatography using supported dipentyl-pentylphosphonate (UTEVA), supported N,N-octylphenyl-di-i-butylcarbamoylmethyl phosphine oxide (TRU) and supported bis-(t-butylcyclohexano)-crown(18,6)ether (Sr.Resin), separation on anion exchange resin, α- and β-source preparation, α-spectrometry, liquid scintillation counting (LSC), γ-spectrometry, measurement by inductively coupled plasma mass spectrometry (ICP-MS). ^{237}Np and ^{93}Zr-93 are preconcentrated by co-precipitation on iron(II) hydroxide and zirconium oxide, and separated by extraction chromatography using UTEVA. The key parameter of the method is the adjustment of the oxidation state of the actinoides before adding the sample onto the UTEVA column. This can be done using many redox agents (for example potassium bromate, sodium nitrite or ammonium peroxo disulfate). Highest yields were achieved when ammonium peroxo disulfate was used with silver nitrate as catalyst. As even traces of isotopes with mass number near 237 or 93 cause considerable interferences during ICP-MS detection, a purification step by extraction chromatography was inserted. It was determined by model experiments, that even a small amount of fluoride anions inhibits the retention of Zr on UTEVA, but this problem can be eliminated by addition of boric acid. Analyzing real samples (evaporation concentrates of a nuclear power plant) 66-97% and 31-66% chemical yields were achieved for Np and Zr, respectively.

NFC.L12 (Id: 60)
SORPTION OF Ni AND Eu IN A MULTI-ELEMENT SYSTEM

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At present the immobilisation of High Level Waste (HLW) in vitreous matrices followed by their burial in deep geological repository systems, composed of natural and engineered barriers to isolate the long lived radionuclides from the biosphere, is the most preferred procedure. Granitic rock formations are being considered as host rocks for such geological repositories [1]. The study of the sorption of radionuclides onto geological media is, therefore, an important part of the safety assessment of deep geological disposal of radioactive waste. Due to the many combinations of adsorbents, data collection in multicomponent systems (MCS) is complex; therefore mathematical models have been developed to predict multicomponent (MC) sorption based on the adsorption properties of each element [2]. The problem of predicting adsorption based on the information of single component isotherms is still a challenge in adsorption studies. Multi-element sorption systems were examined in the last century, however, none of these studies dealt with competitive adsorption and only a few dealt with the selectivity of the sorption processes [3]. Several isotherm models have been used to model experimental data obtained from mixed radionuclide systems. One of the commonest of these models is shown below.

- $Q_{mix}/Q_0 > 1$, the sorption is promoted by the presence of other metal ions,
- $Q_{mix}/Q_0 = 1$, there appears to be no observable effect and,
- $Q_{mix}/Q_0 < 1$, the sorption is suppressed by the presence of other metal ions in solution.

Static baTch sorption experiments with 0.2 g of granitic rocks and different granitic minerals with 40 cm^3 of non active Eu and Ni solutions have been performed in systems of single and multiple elements. Solutions were doped with ^{63}Ni and ^{152}Eu, acting as analogues for di- and tri-valent elements. Equilibration periods were between 7 and 10 days, after which radiometric methods (Liquid scintillation counting and γ spectroscopy were used to determine the sorption patterns. The results obtained showed that generally Eu sorption to the 6 granitic materials studied is affected by Ni competition, except in the case of Adamellite granite. Ni sorption to granitic materials was not affected only in the presence of Eu in solution in the case of biotite mica.

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NFC.L13 (Id: 63)
SORPTION OF Tc(IV) TO GEOLOGIC MATERIALS ASSOCIATED WITH A GEOLOGICAL DISPOSAL FACILITY

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Technetium-99 is one of the most important isotopes likely to be disposed of in the proposed UK geological disposal facility (GDF) for higher-activity radioactive wastes. This is due to its long half life (2.13×10^5 y), fission yield (6%), and its ability to migrate through soils and other environmental components when in its oxidised, pertechnetate, TcO_4^- form. However, much of the technetium in the GDF is likely to be in the lower oxidation state of Tc(IV) as TcO_2(am) or $TcO(OH)_2$(aq). Therefore, an important aspect of the behaviour of technetium in the near- and far-fields of a GDF is its sorption to geologic and cementitious materials in its reduced (Tc(IV)) oxidation state. BaTch sorption experiments on technetium in both oxidised and reduced forms have been conducted in the presence of various materials which are associated with a deep geological disposal facility. These solids can be placed in the following categories: Single minerals; Sedimentary rocks; Crystalline rocks; Carbonates; Clays and clay minerals; Concretes and cements. Tc(IV) was produced by electrochemically reducing a solution of ^{95m}Tc, ($t_{1/2} = 60$ days) pertechnetate which was used as a spike added to a carrier solution of reduced ^{99}Tc pertechnetate solution. Tc(IV) solutions were used at concentrations from 10^{-9} to 10^{-11} mol dm^{-3}. The results for these studies show R_d values ranging from 0 - 39 000 mL g^{-1} depending on pH and solid material. The results for both oxidised and reduced technetium in the presence of solids associated with a geological disposal facility are presented here. It is noticeable that the R_d is very dependent on the pH. For example, for a 10^{-9} mol.dm^{-3} technetium solution in contact with bentonite at pH 7, $R_d = 21$ mL.g^{-1}, however, at pH 10 for the same concentration of technetium $R_d = 2974$ mL g^{-1}. Surface complexation modelling of the data generated has been performed, as well as characterisation of the solids. In general using bidentate constants give best agreement between model and data, e.g. for bentonite: Bent-OH + H^+ ↔ Bent-OH_2^+ (Log K = 4.5 [1]) Bent-OH ↔ Bent-O^- + H^+ (Log K = -7.9 [1]) Bent-OH + Na^+ ↔ Bent-ONa + H^+ (Log K = -0.1) Bent-OH + TcO_2^+ + H_2O ↔ (Bent-$O)_2TcO(OH)^-$ + $3H^+$ (Log K = -0.75)

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NFC.L14 (Id: 71)
EFFECT OF Ca^{2+} ON THE SORPTION OF URANIUM(VI) AND HUMIC ACID ON NATURAL CLAY

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Actinide migration in clay formations has been studied by sorption experiments. Also the influence of humic acid (HA) was investigated as it is ubiquitously found in natural environments and can interact with actinides of the nuclear waste. Natural clay contains HA and fulvic acid like organic matter, which can be released from the clay [1]. HA also forms stable colloids. Due to this behavior HA can influence the mobility of actinides, e.g. U(VI), in a nuclear waste repository. Opalinus clay (OPA) from Mont Terri, Switzerland, was studied. BaTch sorption experiments were performed to determine the sorption ability of U(VI) ([U] = 1×10^{-6} M) onto OPA in the absence and presence of HA ([HA] = 10 mg/L, 50 mg/L) and of HA in the absence and presence of U(VI) using synthetic OPA pore water (OPAWA, [2], pH 7.6, I = 0.39 M) and $NaClO_4$ (pH 3-10, I = 0.1 M) as background electrolyte. During these studies a large influence of calcite on the sorption behavior of U(VI) and HA was found. Calcite represents only a fraction of 13% in OPA and its ions occur also in the OPAWA ([Ca^{2+}] = 0.03 M, [CO_3^{2-}] = 5×10^{-4} M). In OPAWA, U(VI) forms with the ions in solution the neutral aquatic complex $Ca_2UO_2(CO_3)_3$ [3]. This complex dominates the speciation with a fraction of 99%. It was shown that this complex adsorbs weakly onto OPA. Normalized to the specific surface area of OPA (BET = 41.6 m^2/g) the U(VI) sorption was determined to be 0.05 ± 0.002 µg U/m^2 clay. It was also shown that HA has no influence on the U(VI) sorption onto OPA. This was proved by speciation calculations, which showed that also in the presence of HA the $Ca_2UO_2(CO_3)_3$(aq) complex is the dominating species in solution. In order to interpret the sorption data onto OPA, additional ζ potential measurements were performed, where between pH 0 and 7.5 a negative ζ potential for OPA was determined. The HA sorption onto OPA in OPAWA was determined to be 3.57±0.01 µg HA/m^2 (10 mg/L) and 17.28±0.15 µg HA/m^2 (50 mg/L). In the presence of U(VI), a slight increase of HA sorption (D = 0.3 µg HA/m^2) was observed for [HA] = 50 mg/L. Species calculations showed that Ca^{2+} ions affect also the HA speciation, because Ca^{2+} is complexed by HA. Ca^{2+} is present in such a high concentration that it saturates the binding sites of HA. Thus, only few binding sites, about 0.1% according to speciation calculations, are available for the complexation of U(VI). Consequently, U(VI) and HA have no effect on each other during the sorption studies. These experiments show the large effect of the calcite fraction of the OPA and thus the resulting composition of the OPAWA on the U(VI) and HA sorption. Thus, calcite should be taken into account for the safety case analysis of a nuclear waste repository.

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NFC.L15 (Id: 103)
SORPTION OF Pd, ONE LONG LIVED FISSION PRODUCT, ONTO SYNTHETIC HYDROXYAPATITE

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The chemistry of several B-metals in the +II oxidation state is of concern for nuclear waste management. Isotopes of ruthenium (Ru), rhodium (Rh) and palladium (Pd) fission products formed in nuclear spent fuels can have an important contribution to the long-term radiotoxicity of high level wastes. The sorption of one long lived fission product, Pd on hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) has been studied at 25 °C as a function of pH, from 0.025 M $Ca(ClO_4)_2$ and 0.025 M NaH_2PO_4 aqueous background electrolytes, trying to minimize some types of reactions, such as dissolution of solid and precipitation of metal. The radiotracer palladium, ^{109}Pd, obtained by the neutron irradiation of $Pd(NO_3)_2$ salt in Triga Mark III research reactor of the ININ (Mexico), has been used to measure their partition coefficients between aqueous phase and hydroxyapatite. In the interpretation of the sorption measurement, we take into account the existence of active sites at the hydroxyapatite surface and the aqueous solution chemistry of palladium as well as the effect of phosphate anions from solid dissolution. The results can be interpreted as evidence of sorption of the species $PdOH^+$, and of a mixed hydroxo complex of Pd^{2+} fixed onto Ca-OH surface sites of the hydroxyapatite.

NFC.L16 (Id: 100)
THE ADSORPTIVE BEHAVIOUR OF CADMIUM ON CLAYS

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Heavy metals present in the environment such as cadmium are considered harmful due to their toxicity. Adsorption-desorption reactions of metals from aqueous solutions to the soil play an important role in influencing the accumulation and transport of metal contaminants. These are affected by the surface and chemical properties of the soil components. Sorption and desorption of Cd^{2+} has been examined on a series of clays bentonite, illite, illite-smectite, kaolin and montmorillonite through γ-spectroscopy as a function of pH and ionic strength. Experimental data acquired for the systems studied have been used to determine the isotherms. The order of increasing cadmium adsorption onto the clays in the absence of organic matter has been found to be:

illite<≈ kaolin<montmorillonite<illite-smectite< bentonite

Further, to gain mechanistic insights to the sorption and desorption processes NMR and XRD have been used to probe these systems.

NFC.L17 (Id: 221)
SPECIATION AND SURFACE COMPLEXATION MODELLING OF Np(V) SORPTION ON MONTMORILLONITE

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The sorption of Np(V) on Na-montmorillonite (STx-1) has been studied by baTch experiments, spectroscopic measurements, and surface complexation modelling with the aim to contribute toward a better understanding of the sorption of ^{237}Np ($t_{1/2} = 2.1 \times 10^6$ a) in the near field (bentonite backfill material) and far field (argillaceous rocks) of high-level nuclear waste repositories. BaTch experiments were performed in the absence of inorganic carbon and under air-equilibrated conditions with 0.1 and 0.01 M $NaClO_4$ as background electrolyte, 8×10^{-12} and 9×10^{-6} M Np(V), and $3 \leq pH \leq 10$. At pH > 8 the presence of inorganic carbon has a strong influence on the sorption behavior of Np(V) due to the formation of aqueous Np(V) complexes with carbonate. Neptunium LIII-edge extended X-ray absorption fine structure (EXAFS) measurements on Np(V)/montmorillonite samples with Np(V) loadings in the range of 0.3-3.5 µmol/g have been performed to determine the speciation of Np at the solid-liquid interface. The EXAFS spectra of samples prepared under ambient air conditions (pCO_2 = 10-3.5 atm) revealed the formation of Np(V)-carbonate complexes at the montmorillonite surface. The results of the baTch experiments obtained under CO_2-free conditions could be modeled using the two site protolysis non-electrostatic surface complexation and cation exchange (2SPNE SC/CE) model described in [1]. For modeling the sorption behavior of Np(V) on montmorillonite in the air-equilibrated system, the aqueous complexation of Np(V) with carbonate [2] was included and the following additional surface complexation reaction was required: $\equiv SOH + NpO_2^+ + CO_3^{2-} \leftrightarrow \equiv SONpO_2CO_3^{2-} + H^+$.

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NFC.L18 (Id: 41)
AN APPROACH FOR ACQUIRING DATA FOR DESCRIPTION OF DIFFUSION IN PERFORMANCE ASSESSMENT OF RADIOACTIVE WASTE REPOSITORIES

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Repositories for radioactive wastes are sited in the environment with very low permeability. One of the most important processes leading to the release of radionuclides to the environment is diffusion and therefore data for its evaluation are very important for the results of performance assessment of these repositories. These data are obtained usually from the evaluation of laboratory through-, in- or out-diffusion experiments, which are evaluated by various mathematical methods that have to take into account also deficiencies of real experimental equipments. E.g., a very long experimental time is needed for sorbing radionuclides to achieve stationary conditions under which the standard evaluation of the through-diffusion experiment is applicable. In such cases only values of apparent diffusion coefficients are usually obtainable from evaluation of in or out-diffusion experiments. A robust performance assessment codes, however, require knowledge of effective diffusion coefficients and equilibrium sorption coefficients, which cannot be easily obtained by the evaluation of in- and/or out-diffusion experiments. This fact can lead to the propagation of uncertainties in performance assessment of radioactive waste repositories. In this paper a new approach is proposed for the evaluation of diffusion data for performance assessment. This approach consist in the following steps: i) experimental measurements of material diffusion parameters (tortuosity, transport porosity) under various conditions (e.g. different density, different ionic strength of water) using non-sorbing radionuclides such as tritium and chlorine for which it is easy to reach conditions under which mathematical solution of diffusion equation is applicable, ii) to measure sorption isotherms for sorbing radionuclides by baTch methodology, iii) to calculate diffusion coefficients for sorbing radionuclides from well-defined diffusion coefficients in free water and determined tortuosity, transport porosity and sorption coefficients, iv) to carry out the relatively short in-diffusion experiments with sorbing radionuclides and v) to compare experimental results with simulated curves using the performance assessment computer code. We see the advantage of this approach in the use of the same computer code both for verification of the laboratory diffusion results and for the performance assessment. The diffusion description uncertainty in performance assessment is therefore decreased. The relationships between measured data and parameters used in performance assessment are discussed on the basis of baTch sorption and diffusion experiments performed for HTO, ^{36}Cl and ^{137}Cs with different types of bentonite.

NFC.L19 (Id: 54)
THE COMPLEXATION OF Tc(IV) WITH ORGANIC LIGANDS IN RADIOACTIVE WASTE

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The preferred option in the UK for the management of higher-activity radioactive wastes is to store it in a deep Geological Disposal Facility (GDF). This may then be backfilled with a cementitious material. Once closed, the GDF will become saturated with groundwater and highly alkaline porewater will develop with an initial pH of ca. 13.4. This will decrease to 12.5 as groundwater flow removes the NaOH and KOH present. Mineral phases in the cement will then act as a buffer and maintain the pH at 12.5 for ca. 105 years. Corrosion of waste-containing steel canisters will lead to the gradual formation of reducing conditions. Thus, the behaviour of radionuclides in the waste must be understood in the context of this chemistry. Organic complexing agents will be present as inherent components of the waste, especially isosaccharinic acid (ISA) and other polyhydroxylated carboxylic acids which will be formed by the degradation of cellulose. These are highly complexing and can cause significant increases in radionuclide solubility at high pH. The GDF will not be homogenous, there are likely to be areas of reducing and oxidising potential. This heterogeneity could mean that both Tc(VII) and Tc(IV) are present within the GDF. If TcO_4^- migrates into an area in which reducing conditions exist, the organics may complex with technetium during reduction to form water-soluble complexes. Also of relevance is the possibility of increased solubility when organics are in contact with reduced technetium (TcO_2(am)). In other words, do organics affect the reduction of Tc(VII) to Tc(IV)? Therefore, studies have been undertaken in which TcO_4^- was reduced electrochemically, and by Sn(II) and Fe(II), in the presence and absence of ISA, gluconic acid, EDTA, NTA and picolinic acid, to determine whether they caused an increase in Tc solubility when TcO_2(am) was contacted with them. In the presence of ISA and gluconic acid a lowering of [Tc(aq)] took place on reduction, showing such ligands did not prevent some reduction occurring. If this reduction was to Tc(IV), then the final aqueous concentration should be the same as that produced by the addition of the same ligands to Tc(IV) solution at steady state, i.e. the Tc(IV) complexes would again be formed, but by 2 different routes. However, the final [Tc](aq) in the system where reduction took place in the presence of ISA and gluconate was higher than when starting from TcO_2(am). This indicates that Tc(VII) may not have been reduced to Tc(IV) but an intermediate oxidation state complex such as Tc(V) may have formed. This concept is well known in ^{99m}Tc radiopharmaceuticals, where polyhydric complexes of Tc(V) can be formed by the reduction of pertechnetate in aqueous solution of excess O-donor ligand, although in pharmaceuticals this is not carried out at high pH.

NFC.L20 (Id: 95)
CHARACTERIZATION OF PORTUGUESE GEOMATERIALS, THE CLAY COMPONENT OF RAÑAS, AS POTENTIAL LINERS FOR LOW AND INTERMEDIATE RADIOACTIVE DISPOSAL SITES

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Safety assessment of low and intermediate level waste repositories requires the understanding of radionuclides sorption-desorption mechanisms, mainly the degree of interaction between radionuclides and mineral surfaces with the aim to analyse processes that can affect the safety of the repository at both near- and far-field zones. Among the different radionuclides that are part of the radwastes' inventory produced by industrial, medical, teaching and research activities carried out in Portugal, ^{137}Cs is one of the most important nuclides from the radiological point of view due to its half-live (30 years) and high radiotoxicity. The clay component of natural geomaterials named rañas, originated from an area located in the NE Mainland of Portugal, were studied for their potential as effective barriers to avoid or reduce the impact of radionuclides migration. Characterization of these geomaterials is the first step towards identification of the adsorption/desorption mechanisms involved. Cationic exchange capacity (CEC), specific adsorption capacity on frayed edge sites (FES), and radiocesium interception potential (RIP) for potassium ion, using γ spectrometry were determined for three selected grains-size fractions (<63 μm, <36 μm and <20 μm). Organic content and pH were also determined. The selected fractions were mineralogically analysed by X-ray diffraction and by Instrumental Neutron Activation Analysis for chemical elemental composition. Smectite, illite and chlorite-smectite mixed-layers were identified in the clay fractions analysed. The overall values obtained for CEC ranged from 184.9 ± 11.7 to 349.5 ± 22.1 mmol kg^{-1}, while FES values were scattered between 0.55 ± 0.06 and 1.55 ± 0.16 mmol kg^{-1}. The RIP values, defined by a clear plateau at higher potassium concentrations, varied from 1.77 ± 0.05 mmol kg^{-1} to 2.90 ± 0.11 mmol kg^{-1}. However, these values are clearly overestimated since they are 3 to 8 times higher than the correspondent exchangeable RIP values. A possible explanation for this deviation could be the fixation of cesium in non-specific sites during the procedure. The ionic capacity of FES is related to the sample granulometry. The values obtained for the FES were shown to decrease for higher grain-size fractions. Also, the presence or absence of an expanded mixed-layer (hydrous) phyllosilicates (i.e., one-or two-layers smectite) in the fractions analysed was found to increase or decrease the radiocesium adsorption. Preliminary results concerning the characterization of these specific geomaterials with regard to the behaviour of radiocesium are very promising in terms of a possible application as lining materials in a hypothetic LILW repository. Further studies involving the sorption, fixation and selective coefficients onto clay minerals related to rãna deposits, are currently under progress.

NFC.L21 (Id: 114)
LONG TERM DIFFUSION EXPERIMENT (LTD) IN GRIMSEL URL: COMPARISON OF MODELING AND IN-SITU RESULTS

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Phase 1 (2005 - 2008) of the long term diffusion experiment (LTD) project has taken place in the Grimsel underground research laboratory (GTS, Switzerland) in a joint effort between NAGRA (Switzerland), University of Bern (Switzerland), NRI Řež (Czech Republic), HYRL (Finland), JAEA (Japan) and AIST (Japan). The project aim was to study matrix diffusion of radionuclides relevant to performance assessments of deep geological repositories (DGR) of nuclear waste, and confirm the role of matrix diffusion for radionuclide retardation within the repository. Work Package 1 of Phase 1 focused on the study of radionuclide diffusion from a single borehole into the undisturbed rock matrix. Within this framework a radionuclide cocktail was injected into a defined borehole interval sealed by packers (8 m depth from Grimsel URL tunnel) in June 2007. The cocktail consisted of a conservative tracer (^{3}H), a weakly sorbing cation (^{22}Na), a non-sorbing anion (^{131}I), and a strongly sorbing cation (^{134}Cs). The injection was preceded by series of preliminary modeling studies. The predictive studies were performed using different codes, namely; a FORTRAN based code, created in NRI, a code based on SW GoldSim with radionuclide migration module integrated (NRI, JAEA), CrunchFlow (UniBern), Nflow (CSCI, Spain). Compiled results predicted ^{3}H migration up to 30 cm depth from the borehole wall, ^{22}Na and ^{131}I migration up to several cms and ^{134}Cs sorption within the first centimeter of the rock. A significant decrease of radionuclide activity level in the circulation water was predicted only for ^{134}Cs. In reality, the radionuclide cocktail was left in contact with the undisturbed rock matrix under real crystalline rock conditions in GTS for 26 months (June 2007 to August 2009). The radionuclide activity level in the circulation water was checked by regular sampling of small aliquots of contact solution and by activity measurements at PSI. As expected, significant activity decrease in in-situ circulation water was determined only for ^{134}Cs. The activity decreased rapidly within 100 days down to the 35% of original level, which was far faster than predicted. Meanwhile short lived ^{131}I ($T_{1/2}$ 8 days) decayed during the first few weeks, ^{3}H and ^{22}Na activity levels decreased down to 80% and 85%, respectively, of the original activity over the 2 year period. Only the results of in-situ reservoir sampling can be compared and re-evaluated with the simulated results. The real extent of radionuclide migration into the rock matrix will be detected after borehole overcoring, followed by core sampling and activity measurements by the

end of October 2009. The NRI FORTRAN based code, developed specially for LTD, was used for re-evaluation calculations. This is a 1-D model with cylindric coordinates, that is solved with a finite difference method. Translator G77/GFORTRAN was used for calculations, implementing the results of laboratory and analytical results.

NFC.L22 (Id: 124)
THE EFFECT OF COMPETITION FROM OTHER METALS ON NICKEL COMPLEXATION BY A-ISOSACCHARINIC, GLUCONIC AND PICOLINIC ACIDS

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The UK has an underground repository concept with a combination of engineered and natural barriers. Cementitious materials will produce high pH conditions for at least 1 Ma and surfaces for sorption which will greatly reduce the solubility of many radionuclides. Likely to be in the repository are many organic ligands, as inherent components of wastes or due to the degradation of organics, e.g. cellulose. It has been shown that cellulose degradation products, e.g. α-isosaccharinic acid (ISA), can substantially increase the solubility of radionuclides. Picolinates are in some waste-streams due to the use of picolinic acid in decontamination. Gluconic acid is structurally similar to ISA, a strong ligand useful for comparison purposes and may occur in a repository as a cement additive. From pH 11.5 to 13.5, Ni is fairly insoluble. The 3 ligands increase its solubility by forming aqueous complexes - a process that is fairly well understood. The purpose was to investigate the effects on Ni complexation, of competition from other metals. A repository will also contain Fe metal so experiments were performed in its presence and absence. Predictions of Ni solubility were made for each system to aid the interpretation of competitive effects. Measured [Ni] in the absence of other metals showed good correlation with calculated values. There was evidence for slight sorption of Ni to Th and Eu phases formed. There was no significant effect due to other metals and/or solid phases being present. In general, the calculated [Ni] trend was followed with picolinate. Th and Hf had little effect on Ni solubility in the presence of picolinate, Co reduced [Ni], which might be expected as it complexes in a similar fashion, above pH 13 all metals caused a significant reduction in [Ni]. This may have been due to sorption to solid phases, or coprecipitation, with Ni being scavenged out as the lowest inventory metal. All the Ni was complexed by gluconate. Eu had no significant effect at the highest Ni concentration. Hf, Co and Th reduced [Ni] across the pH range, probably due to complexation with gluconate. Eu had a marginally greater effect at a [Ni] = 10^{-3} M, suggesting a very slight amount of complexation. Hf again had little effect. The Th results were the most difficult to explain. At [Ni] = 0.01 and 0.0001 M, Th affected [Ni] as though forming strong gluconate complexes, but not at 0.001 M. At the lowest [Ni], all competing metals significantly reduced [Ni]. Th had complexed strongly with gluconate, causing Ni to precipitate. Hf had a similar effect to. Co significantly reduced [Ni] in line with its predicted effect. Eu had a significant effect on [Ni] reducing it from the predicted 10^{-4} M to ca. 2 x 10^{-6} M. Fe was predicted to have no effect on [Ni] by complexation with ISA. The measured [Ni] was lower than the calculated in virtually all cases, including those with no competing metal. This may have been caused by sorption to Fe(s). No significant competition effects from other metals were observed.

NFC.L23 (Id: 249)
MIGRATION CHARACTERISTICS OF ROCK SAMPLES STUDIED BY ELECTROMIGRATION METHOD: METHODOLOGY: PROCEDURE MODIFICATION

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In several concepts of deep geological repository (DGR) development granites are considered as potential host rocks (Sweden, Finland, Czech Republic). Safety calculations, evaluating safety functions of DGR barriers, require information about radionuclide migration within fractured rock formations, where advection and matrix diffusion are considered as the most important processes for activity decrease. Radionuclide diffusion into rock matrix can be studied both in laboratory and in-situ (e.g., Long term diffusion project, Grimsel URL, Switzerland). However, due to diffusion speed the lab experiments usually take longer time than, e.g., baTch experiments, even in year perspective. Moreover, some parameters, e.g., formation factor F_f, are difficult to determine using conventional methods. Hereby, the through electromigration methods (TEM; [1]) can be used for diffusion parameter studies, especially due to speeding up the experimental work in comparison with standard through-diffusion methods. The TEM experiments gain both formation factor (F_f) and effective diffusion coefficient (D_e) values. In NRI the experimental cells for TEM method, based on the work of Löfgren [1], were assembled, modified in order to increase its function and tested. Iodide anion as a tracer in sodium chloride background electrolyte of different concentration was used. Blank experiments with Plexiglas piece, substituting rock sample, were performed for in order to test the experimental apparatus for leakage failures, sample sealing and non-conductive cell materials. Subsequently, TEM experiments with rock samples were accomplished, including samples of crystalline rocks (granite, granodiorite) from the Czech Republic, Sweden and Switzerland. The results (F_f and D_e) obtained were compared and evaluated, taking into account rock sample properties. The research on samples from Sweden (Forsmark and Laksemark) was funded by SKB Sweden that also provided the rock material.

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NFC.L24 (Id: 61)
JOINT DETERMINATION OF ^{99}Tc AND ^{108m}Ag IN L/ILW LIQUID WASTES

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The low- and intermediate-level liquid wastes produced by the Paks Nuclear Power Plant (NPP) contain routinely measureable γ-emitting nuclides (e.g. ^{54}Mn, ^{60}Co, ^{110m}Ag, and ^{137}Cs) as well as many so-called "difficult-to-measure" isotopes. Despite of their low specific activity compared to the total, the reliable determination of these isotopes is an important issue of nuclear waste management. The increasing amount of waste samples to be qualified yearly by our laboratory put a pressure on revising the existing procedure of ^{99}Tc separation applied. We have managed to halve the initial amount of the sample required to achieve the same level of MDA of technetium. Furthermore, one of the new purifying steps introduced have proved to be able to separate more than 99% of ^{108m}Ag (and ^{110m}Ag) keeping the ^{99}Tc content of the product almost intact. As intended, this new procedure has a major impact on the chemical reagent as well as the electricity requirement of the separation making it more cost-effective.

NFC.L25 (Id: 113)
TRITIUM (HTO) AS A CONSERVATIVE TRACER USED FOR CHARACTERIZATION OF CONTAMINANT MIGRATION IN POROUS ROCK ENVIRONMENT

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Chemical leaching of uranium in Northern Bohemia (Stráž pod Ralskem) took place in between 1972 to 1996. Acid technology solutions, mainly consisting of sulphure acid (more than 4 mil tons), nitric acid, ammonia and fluoric acid, were pumped into uranium bearing layers and caused contamination of Cenomanian and Turonian water reservoirs. Cenomanian aquifer containing U was contaminated by more than 5 mil tons of dissolved species, including mainly H_2SO_4, sulfates, Fe, Al, NH_4. However, trace metals are also presented in a broad range of mobile species - e.g., Th, As, V, Mn, Tl, and be both released and migrate within contaminated aquifer and neighbouring layers. Contaminant migration within different layers must be considered during evaluation of measures and methodologies to be used during remediation process. Target rock layers include both porous „friable" sandstones with permeability coefficient up to 10^{-5} m/s (majority of contamination) and upper „fucoid" sandstones, containing more impermeable clay and organic fraction with permeability coefficient from 10^{-8} to 10^{-7} m/s. Diffusion transport of potential contaminants is expected to dominate mainly within fucoid sandstone layers. In the presented study ^{3}H (HTO) was used as a conservative tracer in order to study diffusion of non-sorbing, i.e. the most mobile contaminants, within porous environment saturated with groundwater. The through-diffusion technique was used for different samples, including both friable and fucoid sandstones. Breakthrough curves were evaluated using GOLDSIM diffusion module (NRI Řež/CTU), enabling to take into account the unsteady boundary condition in the inlet reservoir. Although the determined values of effective diffusion coefficient D_e fell into relatively narrow interval of ($2.0x10^{-10}$ - $6.34x10^{-10}$) $m^2.s^{-1}$, the dependence of tracer diffusion through sandstone sample on rock properties could be distinguished. It was found that ^{3}H diffusion rate was dependent on pore size distribution, even though the total porosity of different samples did not differ significantly (22-27 % range), and furthermore on mineral content. Kaolinite was finally identified as the main influencing factor for species diffusion rate within sandstone as its content in pores results in different pore size distribution. In samples with higher content of kaolinite (max. 16 %) mainly pores with small size were observed in which tracer diffusion movement was slowed down, and vice versa. Moreover, this phenomenon influences also out-diffusion process of species/contaminants, retained in sandstone samples: faster out-leaching was observed for samples with lower kaolinite content and larger pores.

NFC.L26 (Id: 234)
EXTRACTION OF THORIUM FROM THE FEN DEPOSIT IN NORWAY

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After the renaissance of nuclear power and thorium breeding in particular, the interest for the Norwegian thorium deposits has revived. However, the economic potential for exploitation is depending on several parameters, i.e. heterogeneity of ore, content of carbonaceous minerals, other valuable elements present, eTc. Fen is the site where the largest Norwegian thorium deposits are found. The thorium minerals at Fen are reported to be oxide and silicate, but experience obtained indicates that some thorium must also be present in carbonate rock. Based on experience from extraction of rare earth elements from red rock ("rødberg") at Fen the possibilities for thorium extraction are assessed. The Fen complex in Telemark, Norway is a geological region noted for an unusual suite of igneous rocks. Several varieties of carbonatite are present in the area as well as highly alkaline rocks. The Fen complex is a roughly circular area about three kilometers in diameter. It is located just west of the Oslo graben, on the south side of Lake Norsjø, from Ulefoss in NW some three km eastbound. The area covers some 6 km^2 and has been known for its complex mineralogical composition for almost a century. Rødberg rock in the local area called GruveÅsen is covered with soil and vegetation.

GruveÅsen has the highest concentration of thorium in the area. The thorium concentration in GruveÅsen is reported to reach 0.4%, but ordinarily it is 0.1 - 0.2%. Only in GruveÅsen the amount of Th is expected to be of the order of 5 000 tonnes. The whole Fen area is populated and used as residential and recreational areas. Not only is the heterogeneity large, the mineral grains are small, less than 0.1 mm. The content of carbonaceous rock requires a high consumption of acid to leach it. In a pilot plant operation to extract rare earth elements (REE) HCl was chosen as the dissolving species. 700 kg HCl per tonne rødberg was consumed to leach a yield of 100% Ca and Mg and 80% of REE. Thorium was also leached indicating that Th is not solely present as silicate or oxide. However, small amounts of silicic acid were also present in the leachate causing severe problems. To extract thorium also other valuable elements must be cost carriers and the rare earths are an obvious choice. Another possible element present is niobium, but it is not present in the same minerals as REE. Thorium from Fen will hardly ever be recovered as the main element, but may be a valuable by-product. However, the main obstacle in developing an economic feasible process is the carbonaceous rocks consuming too much acid or energy.

NFC.L27 (Id: 262)
TECHNETIUM CHEMISTRY AT THE UNIVERSITY OF NEVADA LAS VEGAS

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The chemistry of technetium is being explored at the University of Nevada Las Vegas. Our goal is to investigate both the applied and fundamental aspects of technetium chemistry, with a special emphasis on synthesis, separations, and materials science. The synthetic chemistry focuses on metal-metal bonding and binary halides. Recently, two new multiply metal-metal bonded dimers and technetium tribromide and tetrabromide were prepared and characterized. These compounds were used as precursor for synthesis of low valent technetium complexes. The structure of $(n\text{-}Bu_4N)_2Tc_2Br_8$ was solved by single crystal XRD and its electronic structure analyzed by first principles calculations. Separation and materials chemistry is related to the nuclear industry. The separation of uranium/technetium from acidic solution, and synthesis of Tc containing waste forms have been investigated. The facilities at UNLV include modern radiochemistry laboratories where investigators can work with multi-milligram quantities of ^{99}Tc, and analytical instrumentation dedicated for radioelement characterization and analysis.

NFC.L28 (Id: 299)
RECENT DEVELOPMENTS OF NUCLEAR FORENSIC SIGNATURES OF YELLOW CAKES

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Natural uranium is the starting material for the production of nuclear fuels. Uranium of natural isotopic composition is mined from uranium containing ores in different geological formations. The uranium is extracted, chemically purified and pre-concentrated. As an industrial scale material, uranium ore concentrates will carry signatures that provide information on the history and on the origin of the uranium. These signatures may be source material inherited or process inherited. In the present work we investigated the significance and potential application of parameters such as the rare earth elemental patterns or strontium and lead stable isotope ratios. The methodology developed and its application to uranium ore concentrates from different mines around the world will be presented.

Posters

NFC.P01 (Id: 22)
EVALUATION OF DIHEXYLOCTANAMIDE AS EXTRACTANT UNDER PLUTONIUM RICH FEED CONDITIONS

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Tributyl phosphate (TBP) has been the work horse of Nuclear Fuel Reprocessing Technologists for more than five decades. However, based on five decades of experience on spent fuel reprocessing, certain problems have also been identified with the use of TBP as extractant. Prominent amongst them are: (a) high aqueous solubility, (b) poor radiation stability and interference of degradation products during stripping of Pu/U, (c) poor decontamination factor (DF) values of Pu/U with respect to fission products, (d) low limiting organic concentration (LOC) of Pu(IV), and (e) a large volume of secondary (phosphate) waste. In addition, as a consequence of the radiolytic degradation of TBP, the extraction and stripping behavior of U/Pu, and hydrodynamic properties such as viscosity, density, and phase disengagement time, are adversely affected. These problems are of particular concern to the separation scientists and technologists during the reprocessing of short-cooled thermal reactor fuels as well as of fast reactor fuels. In this context, completely incinerable N,N-dialkyl amides have been evaluated extensively as alternative extractants to TBP. Studies carried out at Radiochemistry Division, BARC, India, on the development of new extractants for the reprocessing of spent fuel suggested that a straight chain N,N-dihexyloctanamide (DHOA) was promising alternative to TBP for the reprocessing of irradiated uranium based fuels. This paper deals with the evaluation of DHOA vis a vis TBP as an extractant for plutonium rich feed solutions encountered in fast reactor spent fuel reprocessing. Solvent extraction studies were carried out to evaluate the two extractants DHOA and TBP using pure 20 g/L Pu as well as simulated Pu rich feed solution containing 20 g/L Pu, 7 g/L U, fission products (FPs) and structural materials (SMs) at 4 M HNO_3. D_{Pu} values were higher for 1.1 M DHOA (26.4±1.2) for pure Pu as well as for simulated feed solution as compared to those for 1.1 M TBP (16.6±2.2) under identical conditions. Under simulated feed conditions, two successive stages were sufficient for quantitative extraction (>99.9 %) of Pu(IV) employing 1.1 M DHOA as extractant and maintaining organic-to-aqueous phase ratio (O/A) as 1. On the other hand, three stages were required in the case of 1.1 M TBP as extractant. Plutonium stripping experiments using 0.5 M HNO_3 as strippant (without any reductant) showed that only six stripping stages were sufficient for quantitative stripping of Pu from loaded DHOA phase. On the other hand, >10 stages were required for Pu stripping from loaded TBP phase and it became further difficult with the aging of the organic phase. By contrast, no problem related to Pu retention was observed for aged DHOA solution. These studies also suggested that DHOA is a promising extractant for coprocessing of U/Pu from spent fuels. In addition, DHOA was found distinctly better than TBP with respect to FPs and SMs decontamination.

NFC.P02 (Id: 283)
COMPREHENSIVE INVESTIGATION OF THE CORROSION STATE AND SURFACE PROPERTIES OF THE STAINLESS STEEL TUBES OF STEAM GENERATORS

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Evaluating the water chemistry in the primary circuit and the effect of chemical decontamination of the heat exchanger tubes performed by the AP-CITROX (AP: alkaline permanganate; CITROX: citric and oxalic acid) procedure at Paks NPP (Hungary), a project dealing with the comprehensive investigation of the general corrosion state of the steam generators (SGs) has been initiated. Owing to the fact that there is no investigation method available for the in-situ monitoring of the inner surfaces of heat exchanger tubes, a research program based on sampling as well as on ex-situ electrochemical (voltammetric) and surface analytical measurements (SEM-EDX, CEMS, XRD, XPS) was developed and elaborated. In the time period of 2000-2008 - within the frame of the above project - 45 stainless steel specimens, cut out from various locations of the steam generators of the Paks NPP were investigated. Based on the measured corrosion characteristics (corrosion rate, thickness and chemical composition of the protective oxide-layer) it was found that these parameters are strongly dependent on the decontamination history of steam generators. The present work gives a brief overview on the general corrosion state of the heat exchanger tubes of SGs, concerning the long-term effects of the AP-CITROX procedure on the chemical composition and structure of the protective oxide-layer.

NFC.P03 (Id: 142)
PYROCHEMICAL AND ELECTROCHEMICAL SEPARATIONS STUDIES ON PLUTONIUM (PART 2)

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Pyrochemical separations, involving molten salt and metal media, by liquid/liquid extraction or electrorefining are studied with nuclear defense and civil applications. The electrochemical properties of plutonium have been studied in molten salt - ternary eutectic mixture NaCl-KCl-$BaCl_2$, equimolar mixture NaCl-KCl and pure $CaCl_2$, and in liquid gallium at 1073 K. These processes concern actinide separations. However, lanthanides, such as cerium, are often used as surrogates. The first steps of a pyrochemical process development consist in the solvent media. Activity coefficients of the solutes in the two phases, that describe the solvent-solute interaction, are important thermochemical parameters to predict separations efficiency and to assess the solvents influence. As nuclear defense scientist, I discuss the advanced developments to separate plutonium by electrochemical method that has been supporting the developments of pyrochemical processes involving plutonium as main goal and actinides separations.

NFC.P04 (Id: 145)
EXTRACTION OF Ln/An FROM HIGHLY ACIDIC SOLUTIONS USING COBALT BIS(DICARBOLLIDE) FUNCTIONALIZED WITH COMPLEXING CMPO GROUP.

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Nuclear fuel reprocessing issues an important problem with respect to the family of actinides representing the main source of radiotoxity during long-term storage. The separation of long-lived radionuclides from liquid radioactive waste enables these hazardous elements to be either conditioned more safely in specific matrices or destroyed by transmutation. Thus, elimination of minor actinides would lead to significant reduction of volume and radiotoxicity of the waste for the final storage and should consequently minimize the possible risks to biosphere. Several extraction concepts were proposed for separation of Ln and An from fission product mixture during the last ten years. In this paper, extraction of trivalent lanthanides and actinides using a compound based on covalent combination of cobalt bis(dicarbollide) (1-) anion (COSAN) and CMPO (N,N- dialkyl carbamoyl methyl diphenyl phosphine oxide) complexing group of the formula [8-$Ph_2P(O)$-$CH_2C(O)N$-t-C_8H_{17}-$(CH_2CH_2O)_2$-1',2'-$C_2B_9H_{11}$)-3,3'-Co]- will be presented. This compound was selected for detailed tests from a broad panel of other derivatives differing in the substitution at the CMPO function and its bonding to the COSAN cluster [1,2] due to very effective extraction of Ln(III) and An(III) from highly acidic solutions (3M HNO_3), good solubility characteristics and an easy synthetic accessibility in a large scale. Extraction efficiency under different conditions (acidity, reagent concentration, macro amounts of metals, eTc.), solubility in different solvents and chemical stability were tested to evaluate a possible technological use. The composition of extracted complex was studied. Extraction from fission product mixture revealed very effective separation from the majority of fission products with separation factor exceeding 1000. For some fission products, the presence of complexing agents was necessary.

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NFC.P05 (Id: 167)
STUDY OF PROPERTIES OF EXTRACTION-CHROMATOGRAPHIC MATERIAL TBP-PAN

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This project is focused on studying properties of extraction-chromathographic material prepared by embedding tributylphosphate (TBP) into the matrix of polyakrylonitrile (PAN). After elementary characterization of the prepared materials, the kinetics of uranium extraction from 3 mol L^{-1} HNO_3 was examined. The influence of nitrates and nitric acid concentration on the values of weight distribution coeficient D_g as well as "extraction isoterm" was specified. For determination of ^{233}U in aqueous solution, liquid scintillation spectrometry was used. After evaluation of all experiments it can be concluded that TBP-PAN material behaves like TBP in liquid-liquid extraction.

NFC.P06 (Id: 222)
ELECTROCHEMICAL BEHAVIOUR OF SELECTED ACTINIDES AND LANTHANIDES IN MOLTEN FLUORIDE SALTS FLINAK AND FLIBE

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The presented work is focused on research of basic electrochemical properties of several actinides and lanthanides representing the fissile material and fission products in suitable molten fluoride melt. The general framework of this work is to study the electrochemical behaviour of systems relevant for possible future use in the Generation IV reactor concepts. Results of cyclic voltammetry, chronopotentiometric and electrolytic experiments with uranium and several lanthanides in the LiF-NaF-KF (acronym FLINAK) are presented. Mechanisms of electrochemical reduction were investigated. Recorded reduction steps were investigated and described in terms of reversibility, number of exchanged electrons, diffusion coefficients eTc. For the lanthanides, it seems impossible to reach solid deposit of studied lanthanide on the electrode. For uranium, deposition depending on electrode material and shape was studied with special attention given to its deposition on reactive (Ni) working electrode. Beryllium based molten salts 7LiF-BeF_2-ZrF_4 and 7LiF-BeF_2 were used as a carrier melts during Molten Salt Reactor Experiment and Molten Salt Breeder Reactor projects [1] and are considered as key systems also for the future use. In the LiF-BeF_2 melt (acronym FLIBE), the work was focused on research of uranium behaviour in the melt and the influence of its composition between two eutectic points of FLIBE (eutectic compositions of FLIBE melt are defined by molar ratio of BeF_2 x = 0.328 and x = 0.531). Also the general consequences of the obtained data for the development of separation process are concluded.

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NFC.P07 (Id: 291)
EPR MEASUREMENTS ON N-BEARING LIGANDS USED IN SPENT NUCLEAR FUEL REPROCESSING FOR An(III)/Ln(III) PARTITIONING

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A future goal for the reprocessing of spent nuclear fuel is the transmutation of long-lived minor actinides, such as americium and curium, into short-lived isotopes by means of neutron irradiation. In order to develop an effective transmutation process, it is necessary to separate the trivalent minor actinides, An(III), from the trivalent lanthanides, Ln(III), by means of two subsequent solvent extraction processes: i) DIAMEX to extract both Ln(III) and An(III) from PUREX raffinate and ii) SANEX to obtain the selective extraction of An(III) from the output of DIAMEX process. The present work concerns the degradation due to ionizing radiation released by radionuclides to the selected solvent system involved in the SANEX process. The high-energy radiations are able to modify the ligands molecules structures changing their extractant capabilities. In particular, several aspects must be considered when selecting a molecule to be used in the mentioned process: chemical stability; solubility in organic diluents; extraction capability of metal ions with appropriate distribution ratios; and resistance towards irradiation. Some aza-heterocyclic extractant molecules C2-BT (5,6 diethyl (1,2,4 bis-triazine), C2-BTP (2,6-diethyl(1,2,4-triazine-3-yl)pyridine), C5-BTBP (6,6'-bis-(5,6-dipentyl-[1,2,4]triazine-3-yl[2,2']bipyridinyl) and CyMe4BTBP (2,6-bis-(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo[1,2,4]triazin-3-yl)-[2,2']bipyridinyl), constituted by pyridine and triazine aromatic rings with chelating nitrogen donor atoms, have been studied during the European Research Project EUROPART. Furthermore, the mentioned molecules present aliphatic side groups as n-carbon alkyl substituents (methyl, ethyl or penthyl chains) or cyclohexyl moieties to ensure their lipophilic behavior after coordination of trivalent metal ions during liquid-liquid extraction processes. To carry out studies concerning radical mechanisms, the abovementioned molecules were irradiated in a ^{60}Co γ irradiation facility (up to 113 kGy with a dose rate of 0.5 kGy/h), at 77 K to reduce radicals reactivity before investigations by EPR spectrometry. A preliminary EPR screening on the four ligand molecules shows the presence of radiation-induced radicals on both the aromatic and aliphatic sides of the ligands. In particular, irradiation of C2-BTP in alcoholic solutions highlighted the formation of azacyclohexadienyl radical as intermediated species. The azacyclohexadienyl radical has been recognized by simulated spectra using appropriate hyperfine constants, and similar signals have been collected also for irradiated solution of C5-BTBP. The EPR spectra collected on samples of C5-BTBP powder, irradiated in air, disclosed the formation of peroxide radical species $ROO^{\bullet}$. Further simulations on the EPR spectrum collected at 208 K revealed definitively the presence of peroxide species on C5-BTBP. In conclusion, taking into account the peroxide radical formation proven on C5-BTBP powder, it was possible to propose several radical mechanisms able to modified the extractant capabilities of the investigated molecules.

NFC.P08 (Id: 342)
REMOVAL OF Cs, Sr, Pu AND Am FROM CONTAMINATED SOLUTIONS BY INORGANIC SORBENTS

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Recently growing concern about contamination of the environment with radioactive and non-radioactive pollutants resulted in intensive studies related to the development of new technologies for separation of radionuclides from liquid waste. These new technologies should be based on highly selective materials (e.g., crystalline titanium silicates) which are hard to decompose over a wide range of pH, which remain stable at high temperatures, which are resistant to ionizing radiation and which are able to operate in the presence of a great excess of competitive ions, organic solvents and oxidants. However, complicated technologies, high capital and regeneration costs stimulated studies to develop low-cost and efficient technologies based on naturally occurring minerals such as zeolites and clay minerals. Another option could be an application of amorphous porous mixed oxides - a rapidly developing class of materials prepared by sol-gel procedures, the main benefit of which are very simple procedures conducted under mild reaction conditions in the ambient atmosphere. Ferrites and a variety of iron-containing minerals such as akaganeite, feroxyhyte, ferrihydrite, goethite, hematite, lepidocrocite, maghemite and magnetite are also a promising class for the treatment of liquid wastes containing radioactive and hazardous metals. The aim of this study was to prepare amorphous TiSi by sol-gel procedures, to synthesize various iron oxides, to characterize them using IR, XRD, Mössbauer spectroscopy and to carry out a comparative assessment of possible application of these low-cost synthetic inorganic sorbents with conventional and natural sorptive materials in liquid waste treatment technologies to remove long-lived radionuclides such as Cs, Sr, Pu and Am. Results obtained using a bath method, ICP-MS, γ, α spectrometry and β counting revealed that titanium silicates, synthesized using $TiOSO_4$ without reference to the chosen method - a precipitation or sol-gel, showed the highest sorption ability towards studied radionuclides. Magnetite and clay minerals showed better sorption ability towards americium. The highest Pu K_d values and better Pu sorption kinetics were found for synthetic iron oxides. An increase in the Pu K_d value by a factor of 6.8 found for magnetite/hematite composite in comparison with the pure magnetite suggests that this sorbent is efficient for plutonium removal and it is promising for its separation from contaminated solutions. TiSi tested in this study showed close sorption ability towards studied radionuclides in comparison with crystalline TiSi, whereas they were synthesized under mild conditions using cheaper materials. In addition, TiSi prepared by the sol-gel method has certain advantages in comparison with the fine powder TiSi because of a huge potential for tailoring of chemical composition, porosity and surface properties, as well as for the production in the granular form, which is especially important for practical purposes.

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NFC.P09 (Id: 34)
IMPROVEMENT OF RADIONUCLIDE FIXATION IN CEMENT MATRIXES DURING IMMOBILIZATION OF LIQUID RADIOACTIVE WASTE

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Cementation provided by mixing of concentrated radioactive waste (RAW) and cement is the most common procedure for immobilization of medium- and low-level radioactive salt-containing waste of radiochemical industry. However, low degree of inclusion of solidified waste in concrete (especially from concentrated salt-containing solutions owing to deterioration of the concrete properties) and noticeable leaching of some fission elements require development of additional barriers at storage of such RAW. Therefore, addition of RAW into the concrete not in the form of solutions but in the form of sorbents saturated with radionuclides can decrease leaching and, in turn, can improve degree of cesium inclusion without decrease in the strength and some other properties of the concrete monolith. Our studies were aimed at treatment of the solutions with complex chemical composition from the units of RAW concentration and fractionation and of the spent decontamination solutions. To include radionuclides containing in liquid RAW in the concrete the possibility of using of superstoichiometric sorption was studied. This method allows a saturation increase with respect to many radionuclides by a factor of 5-20. Chemical treatment of the sorbent preliminarily saturated with cesium provides stronger fixation of given radionuclide in the solid matrix. Inclusion of sorbents saturated with radionuclides in the concrete increases ^{137}Cs content in the solidified matrix by one-two orders of magnitude without any changes in the strength properties of the resulting composites. At the same time, the leaching rate of ^{137}Cs decreases by a factor of 4-5. Surface treatment of the resulting composites liquid and supercritical CO_2 (so-called carbonization procedure) was also studied to improve fixation of radionuclides in the concrete blocks. Combination of above procedures allows reducing cesium leaching from the concrete blocks by more than two orders of magnitude.

NFC.P10 (Id: 85)
THE SOLUBILITY OF Ni(II) AND Eu(III) IN THE PRESENCE OF CEMENT SUPERPLASTICISERS

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One of the illustrative disposal concepts considered by the NDA-RWMD (Nuclear Decommissioning Authority - Radioactive Waste Management Directorate) for the disposal of intermediate-level wastes and some low-level wastes is that of grouted waste packages surrounded by a cementitious backfill. The potential use of superplasticisers to improve flow properties of waste encapsulation grouts offers benefits in some applications, e.g. for infilling or self-levelling. However, their impact on the post closure performance assessment of a geological disposal facility (GDF) needs to be considered. First generation superplasticisers such as naphthalene formaldehyde and sodium lignosulphonate showed the ability to increase the aqueous concentrations of radionuclides. The observed effects were not consistent and the use of such additives was, in general, discouraged, however, the composition of modern superplasticisers ('comb' polymers) is better controlled than the composition of compounds used in the past. This suggests that their effects may be better understood and they may behave in a more predictable manner. To determine whether the presence of comb superplasticisers will have an effect of the solubility of radionuclides within the near field of a radioactive waste repository, a study of the solubility of Ni(II) and Eu(III) in high pH (12-13.5) aqueous solutions of the superplasticiser ADVA Cast 551 was conducted. The solubility experiments were approached from oversaturation and were conducted in the following aqueous solutions: 95% saturated $Ca(OH)_2$, 0.1 mol dm^{-3} NaOH and cement equilibrated solutions containing Ordinary Portland Cement (OPC), Pulverised Fly Ash (PFA) or Blast Furnace Slag (BFS). ADVA Cast 551 was present at between 0 and 10% (w/v). Samples were taken at regular intervals over the period of 1 month and measured by Liquid Scintillation Counting or Gamma Spectrometry for Ni and Eu quantification respectively. Results for Ni(II) have shown that the concentration of Ni(II) measured in solution increases with the presence of the cement superplasticisers. The increase observed was greatest in the 95% saturated $Ca(OH)_2$ solution. Results observed in the cement equilibrated solutions were less significant with the solubility increase being within an order of magnitude even in the presence of 10% ADVA Cast 551. Results for Eu(III) will also be presented.

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NFC.P11 (Id: 134)
IMMOBILISATION OF CESIUM AND DIVALENT METALS INTO SINGLE-PHASE STUFFED TRIDYMITE-BASED CERAMICS

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The mixed phosphates with high cesium concentration of the compositions $CsMePO_4$ (Me - divalent metal with a tetrahedral coordination) adopting a stuffed β-SiO_2 tridymite structure are studied as perspective materials for ^{137}Cs γ-radiation sources to be used in medical applications. For the purpose of ^{137}Cs source production from commercial wastes (nitrate cesium solutions containing Me impurities) it is necessary to know the possibilities of single-phase composition formation in the systems $CsMe'_{1-x}Me_xPO_4$ with different Me cations. Phase formation regularities and thermal behavior of mixed complex phosphates $CsMg_{1-x}Me_xPO_4$ (Me = Mn, Co, Ni, Zn, Cu) have been studied. The samples were synthesized by precipitation method. The aqueous solution of phosphoric acid taken in accordance with the stoichiometry sample was added to stoichiometric mixture of cesium and metal (Me) nitrate or chloride solutions. The reaction mixture was dried at 353 K and thermally treated at 873 and 973 K. All the thermal treatment stages were alternated with careful grinding. Crystalline powders were obtained. X-ray powder diffraction measurements indicated that continuous (Me = Mn, Co, Ni, Zn; $0 \le x \le 1.0$) or limited (Me = Cu; $0 \le x \le 0.4$) solid solutions of the tridymite type were obtained. The samples homogeneity and conformity of their compositions to the theoretical values was monitored by scanning electron microscopy and electron microprobe analysis. The phase formation regularities and the dependences of the unit cell parameters of $CsMg_{1-x}Me_xPO_4$ solid solutions on their compositions x were studied. Three polymorphic forms are possible: monoclinic (sp. gr. P21/a) and two orthorhombic (sp. gr. Pn21a and Pnma). For many phosphates phase transitions P21/a → Pn21a → Pnma are observed with temperature increase. Due to the differential scanning calorimetry results, the phosphates $CsMePO_4$ with Me = Co and Zn had two polymorphic transitions in the temperature interval from 423 to 583 K. The phosphate $CsMgPO_4$ underwent phase transition at 236 K. The second harmonic generation results showed phosphate crystallization in centrosymmetric (P21/a or Pnma) or non-centrosymmetric (Pn21a) space groups. The transition from Pnma to Pn21a space group was accompanied by absorption band disappearance of valency symmetric vibrations in IR-spectra of phosphates. A leaching rate of approximately 10^{-5} $g.cm^{-2}.d^{-1}$ for Cs was determined from Soxhlet leaching of $CsMgPO_4$. Thus, the possibility of simultaneous incorporation of cesium and different metals with oxidation degree +2 (present in commercial radiocesium wastes) is shown in the tridymite structure with formation of wide or continuous solid solutions. Such tridymite-like phosphates

may be a perspective candidate both for radiocesium immobilisation and cesium isotopic source production instead of soluble CsCl used nowadays.

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NFC.P12 (Id: 138)
PRODUCTION OF ARTIFICIAL METAL RUTHENIUM FROM IRRADIATED TECHNETIUM

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Long-lived nuclide ^{99}Tc is accumulated as a fission product in 1-3 kg/t quantities in fuel of nuclear power plants. Transmutation of technetium by the action of neutrons is the most cardinal method for its neutralization and disposal; this leads to the production of artificial stable ^{100}Ru, ^{101}Ru. Several technetium targets have been irradiated at SSC RIAR. Metal technetium in the form of disks was irradiated in the neutron trap of the SM reactor. Specimens resulting from the irradiation were found to represent Tc-Ru alloys. Prior to our work no description of the production of artificial metal ruthenium from irradiated technetium was available elsewhere. This paper presents two different procedures for the production of artificial metal ruthenium from irradiated technetium targets. In one of these procedures the targets were dissolved in KOH solutions at the presence of KIO_4 followed by precipitation of Ru(IV) hydroxide with ethanol. To purify the produced ruthenium from technetium traces, it was distilled as RuO_4 into the ethanol aqueous solution where it was reduced and precipitated as Ru(IV) hydroxide. To produce metal ruthenium, Ru(IV) hydroxide precipitate was calcinated up to RuO_2 and then reduced to metal in hydrogen flow. According to the other procedure for separation of stable ruthenium from the irradiated technetium target use was made of a catalytic oxidation with ozone. Firstly, a Tc-Ru alloy specimen was placed into HNO_3 or $HClO_4$ solution containing Ag(I) (or Co(II)) ions. Then the ozone-oxygen mixture was bubbled through the solution. Formed by action of ozone Ag(I) (or Co(II)) ions oxidized the alloy (Tc and Ru) components transferring them to the solution. Then RuO_4 and some part of $HTcO_4$ were distilled to NaOH solution where RuO_4 was reduced to sodium ruthenate. At the next process stage the Ru(IV) hydroxide was precipitated from the solution by the action of ethanol acting as a selective reducer of Ru(IV). The precipitate was placed into water and the ozone-oxygen mixture was bubbled through the hydroxide suspension formed in water. The Ru(IV) hydroxide was reduced to RuO_4 with ozone, which was distilled to ethanol aqueous solution by the bubbled gas flow. The produced Ru(IV) hydroxide was transformed to RuO_2, which was reduced to metal in the helium-oxygen mixture.

NFC.P13 (Id: 185)
STUDY OF NEW FILTER PROPERTIES ^{137}Cs VAPOUR CAPTURE AT HIGH TEMPERATURE

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Vitrification of radioactive wastes and high-temperature synthesis of glass and ceramics for ionizing radiation sources, containing ^{137}Cs, is accompanied by discharge of its vapours. The off-gas contaminated by ^{137}Cs must be cleaned up using different trapping systems. In general two methods of ^{137}Cs vapour caTching are possible, differing both in process character (nature) and realization place in technological scheme:

- "wet" method - "low-temperature" ^{137}Cs vapour condensation in system of gas cleaning (condensers, scrubbers, HEPA-filters). This method leads to contamination of communications and to formation secondary liquid RAW, which require additional repossessing.
- "dry" method - "high-temperature" ^{137}Cs vapour chemisorptions. This method allows fixing ^{137}Cs in stable crystalline and amorphous phases. Earlier it was shown that porous inorganic materials with high content of silica- alumina amorphous phase could be used for effective capturing of ^{137}Cs vapours. Effectiveness of filter depends on the total porosity, porous structure and aerodynamic resistance to off-gas flow. To study these parameters a laboratory scale test facility was built at the KRI.

The following three methods are used to evaluate dust and aerosol capture efficiency at room temperature:

- weighing method: sampling of the dust using special certificated analytical filters followed by weighing of the absorbed precipitate. The filters are sealed in the filter holders;
- radiometric method: if an isotope spike is used, the dust is sampled using the analytical filters as described above followed by measurements of absorbed activity using conventional methods;
- aerosol particle concentration measurements: using laser counters for aerosol particle concentrations. This method determines fraction decontamination factors for the particle sizes ranging from 0.2 to 5 μm.

Report will summarize the obtained analytical data and describe the dependence of filter effectiveness at different rates off-gas flow.

NFC.P14 (Id: 230)
RADIOACTIVE WASTE DESTRUCTION USING MOLTEN SALT OXIDATION

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A molten salt oxidation (MSO) process is being studied for the safe and effective destruction of organic components of radioactive waste. The work involves a laboratory-scale molten salt oxidation system where solid or liquid waste is injected into a bed of molten carbonate salt in the presence of an oxidizing gas. The relatively simple MSO process completely destroys organic compounds, and the carbonate salt neutralizes any generated acid gases and retains the radioactivity. In the past, high melting point salts have been used with air oxidation. In these studies, the use of low melting point salts and stronger oxidizing agents are being investigated for the destruction of radioactive waste oil and ion exchange resins. Work on the recovery of uranium from lignites will also be presented.

NFC.P15 (Id: 255)
FUNCTIONALIZED LATEX PARTICLES FOR PREPARATION OF COLLOID-STABLE NANOSIZED SELECTIVE SORBENTS AND COMPOSITE MATERIALS FOR DECONTAMINATION OF RADIOACTIVE WASTES

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Preparation of a new type of colloid-stable nanosized sorbents based on functionalized latex particles is discussed, which can be directly applied for decontamination of liquid and solid radioactive wastes or used for construction of fibrous or mesoporous composite sorption materials. Carboxylic latex (siloxane-acrylate and polystyrene-acrylate) functionalization is performed via immobilization of nanocrystals of sorbents selective to radionuclides (ferrocyanides of transition metals and sulfates of calcium/barium) into the polymer matrix. The presence of anionic centers on the latex particle surfaces stipulates for the possibility of binding to them ions of divalent metal-precursors of selective sorbents. With the added metal concentration increase one can observe the decrease of electrokinetic potential (by module) at the constant particle size. The residual negative charge on the surface provides the system with high colloid stability. To form stable nanoparticles of a selective sorbent it is crucial to limit the amount of introduced divalent metal ions by the beginning of the plateau on the dependence of electrokinetic potential on the metal concentration in solution. AFM imaging of the functionalized latex particles shows that, as a result of introducing cobalt ferrocyanide nanoparticles, the initially spherical polystyrene-acrylate (PA) particles transform into a cubic shape, which is characteristic for ferrocyanide macrocrystals. Due to immobilization into stable polymer colloids, the selective sorbents nanoparticles preserve high stability at filtration in porous media. After 50 filtration cycles of emulsion of the siloxane-acrylate (SA) latex with immobilized nanoparticles of cobalt ferrocyanide through a layer of natural zeolite, the cobalt content in the emulsion remained nearly constant. When such colloid-stable sorbents are directly applied for decontamination, after radionuclides sorption the stability of such systems can be controllably reduced by addition of cationic flocculants, thus providing high efficiency of radionuclide removal from solution. The combination of high selectivity of nanosized sorbents immobilized into latex particles with ease of their removal from solution by flocculation/coagulation process enables us to recommend the developed schemes for different materials decontamination, first of all, for solid bulky wastes - soils, grounds, metal constructions. To extend suggested approach to the production of different types of sorption materials pre-formed colloidal-stable selective sorbents were deposited on carbon fibers by electrochemical method or used as a template during formation of mesoporous SiO_2, ZrO_2 and TiO_2 sorbents. The selective sorption materials obtained showed good kinetics of radionuclides sorption and distribution coefficients for cesium up to $1x10^7$.

NFC.P16 (Id: 284)
COMPARATIVE STUDY OF THE CORROSION AND SURFACE ANALYTICAL EFFECTS OF THE DECONTAMINATION TECHNOLOGIES

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Decontamination technologies are generally developed to reduce the collective dose of the maintenance and operation personnel at NPPs. The highest efficiency (i.e., the highest DF values) available without detrimental modification of the treated surface of structural material is the most important goal in the course of the application of a decontamination technology. The AP-CITROX procedure has mainly been used for the decontamination of the primary coolant circuit's components (e.g. main circulating pump (MCP) and steam generators (SGs)) at the Paks NPP. While decontamination of the dismountable devices (e.g. main circulating pump) has been carried out in big tanks with heating potential, separable equipments (e.g. heat exchangers) have been treated with special decontamination facilities. The AP-CITROX procedure was used 24 times for the SGs decontamination at units 1-3 of the

Paks NPP during the period of 1993-2001. Our previous studies have revealed that a "hybrid" structure of the amorphous and crystalline phases is formed in the outermost surface region of the austenitic stainless steel tubes of SGs as an undesired consequence of the industrial application of the AP-CITROX decontamination technology. In this presentation, we report some comparative findings on the corrosion and surface analytical effects of the AP-CITROX procedure and the decontamination technology elaborated at our institution. After optimizing its operational parameters the latter technology is suitable for the decontamination of both dismountable (e.g. MCP swivel) and separable (e.g. heat exchanger) equipments. In this semi-plant scale experiments, the passivity, morphology and chemical compositions of the treated surfaces of tube specimens were investigated by voltammetry, and SEM-EDX methods. The newly developed decontamination technology can be effectively applied for the decontamination of the austenitic stainless steel samples; the total oxide-layer can be removed by this technique. The SEM-EDX results revealed that the oxide removal is surprisingly uniform even after 2 or 3 consecutive cycles. The electrochemical studies provided evidences that no unfavorable tendencies in the general corrosion state of the tube samples can be detected in the course of the chemical treatments.

NFC.P17 (Id: 285)
OBSERVATION OF EFFICIENCY OF THE DECONTAMINATION TECHNOLOGIES IN NUCLEAR POWER PLANTS

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The version of the AP-CITROX technology (pre-oxidation: alkaline potassium permanganate, oxide-solution: blend of oxalic and citric acid) applied in the steam generators of the Paks NPP (Nuclear Power Plant) was not adequately developed considering its chemical, analytic and corrosion aspects. To replace the AP-CITROX procedure, a new, efficient „soft" chemical decontamination technology has been developed at the Institute of Radiochemistry and Radioecology at University of Pannonia. In the course of the comprehensive characterization of the efficiency of the novel base-technology the chemical composition and morphology of the oxide layer formed on the inner side of the austenitic stainless steel heat exchanger tube specimens before and after the full decontamination process were studied by scanning electron microscopy (SEM), equipped with an energy dispersive X-ray microanalyzer (EDX). The complete decontamination cycle has been performed under laboratory conditions in a pilot plant circulation system elaborated earlier. In different steps of the chemical procedure the concentration of the main alloying components (Fe, Cr, Ni) dissolved from the surface oxide layer into the decontamination solutions was determined by ICP optical emission spectrometric (ICP-OES) method. Based upon the ICP-OES results the average thickness of the oxide layer removed from the surface into the solutions was calculated. When measuring the activity of the removed radionuclides (^{60}Co, ^{58}Co, ^{110}Ag, ^{54}Mn) in the decontamination solutions we drew conclusions concerning the efficiency of certain steps of the technology and depth distribution of the radionuclides on the treated steel surfaces.

NFC.P18 (Id: 49)
STUDY OF CRYSTALLINE CERAMICS FOR IMMOBILIZATION OF ^{99}Tc

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Technetium-99 is β-active long-lived artificial radionuclide (half-life more than 200,000 years). Because of its long-life, high content in spent nuclear fuel, high ability to oxidize under aerobic conditions as TCO_4^- Tc is one of the most dangerous radionuclides. Development of chemically durable host-phase for Tc disposal is important goal of research. There are no natural minerals of Tc, which might be considered as analogues of stable Tc host-phases. Some chemical elements such as manganese, titanium, rhenium can be used as Tc-simulants. They do not reflect however chemical behavior of Tc in detail. It was suggested to consider development of Tc host-phases with structures of spinel; pyrochlore; fluorite; garnet in three oxide systems: Fe-(Mn,Tc)-O, Zr-(Mn,Tc)-O, and (Sn,Tc)-O using different procedures of precursor preparation and ceramic synthesis conditions. Most samples were synthesized at 1150 °C in inert atmosphere from precursors doped with 5 - 12 wt. % Tc. Some samples were obtained in air. All the samples obtained were studied using optical and scanning electron microscopy (SEM); powder X-ray diffraction (XRD); microprobe analysis (EMPA) and static leach test in distilled water at 90 °C for 28 days. Content of Tc varied from 0.5 - 0.8 to 3 - 6 wt.% in oxide host phases and from 54 to 93 wt.% in metallic inclusions. Leach rates were less than $10 - 3$ g/m^2. Development of optimal methods of precursor preparation and synthesis conditions of Tc-doped ceramic are discussed.

NFC.P19 (Id: 6)
THE SORPTION OF CESIUM ON BEISHAN SOIL UNDER DIFFERENT PHYSICOCHEMICAL CONDITIONS STUDIED BY BATCH AND EDS TECHNIQUES

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Adsorption of Cs^+ to Beishan soil (BS) as function of pH, foreign ions, temperatures, contact time and humic substances was studied in detail under ambient conditions using baTch techniques. The results suggested that the adsorption of Cs^+ was strongly dependent on ionic strength, whereas nearly independent of pH values, and the values of K_d were 1388.78 mL/g in 0.01 mol/L $NaClO_4$ and 740.14 mL/g in 0.1 mol/L $NaClO_4$ solution, respectively. The foreign ions competed with Cs^+ in the sequence: $K^+ > Na^+ > Li^+$ and $Mg^{2+} > Ca^{2+} \cdot Na^+$; however, the influence of anions was not obvious which might be attributed to the very low complexing ability with anions (i.e., Cl^-, ClO_4^- and NO_3^-). The adsorption reaction of Cs^+ to BS was very fast; the values of E_a were 8.944 kJ/mol. The positive ΔH_0 and negative ΔG_0 meant that the holistic process of Cs^+ adsorption to BS was an endothermic and spontaneous process. The adsorption isotherms of Cs^+ were well simulated by the Langmuir model at higher concentration of $NaClO_4$, whereas Freundlich model was better than Langmuir model at low ion strengths (i.e., 0.001 mol/L $NaClO_4$); and the values of q_{max} obtained from the Langmuir model ranged from $\sim 3.33 \times 10^{-7}$ to $\sim 5.00 \times 10^{-7}$ mol/g. Humic substances (FA and HA) enhanced significantly the adsorption of Cs^+ to BS.The EDS analysis indicated that the adsorbed Cs^+ were mainly distributed to the fray edges of BS, the locations of these adsorbed Cs^+ coincided with the sodium depletion area, implying the replacement of Na^+ by Cs^+ adsorption.

NFC.P20 (Id: 52)
SELENIUM(IV) RETENTION ONTO ILLITE

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In the context of nuclear waste management, long-term safety assessments have shown that selenium-79, released from the solid waste matrix, could be one of the major isotopes contributing to the global radioactivity potentially reaching the biosphere. Selenium has a quite complex speciation, with four main oxidation states, depending on both the pH and the redox potential of the surrounding environment. Sorption onto minerals can strongly affect the availability and the mobility of selenium. It is thus of great importance to be able to characterize at both macroscopic and microscopic levels the different processes (retention, reduction, surface precipitation, …) that can potentially take place. Regarding the multi-barrier concept considered for deep underground storage of high level and long-lived radionuclides, clays are candidates as host rock as well as backfill materials. Clays like illite, kaolinite, montmorillonite and bentonite constitute the main phases of clay rocks, together with other compounds like iron oxides, titanium oxide, pyrite, calcite and organic matter. We decided to focus our work on illite since it is an abundant and well crystallized clay mineral in soils. Thus, retention properties of illite towards selenium(IV) have been investigated in this study, using a combination of both macroscopic and microscopic measurements. Illite du Puy (France) has been used as the sorbing phase. It has been purified in order to remove auxiliary and minor phases to get a homo-ionic "Na-illite" clay. Then, baTch experiments aiming at studying the sorption behaviour of selenium(IV) onto illite have been performed in $NaClO_4$. The influence of the suspension pH, as well as the ionic strength effect has been investigated. All the experiments have been performed under anoxic conditions in a glove box under N_2 atmosphere ($O_2 < 1$ ppm). Selenium speciation in solution has been checked using Hydride Generation-Atomic Absorption Spectroscopy measurements. The oxidation state of the selenium species once sorbed onto the illite surface has been evidenced using X-Ray Photoelectron Spectroscopy. Electrophoresis measurements have also been performed during this work. Comparison between the ζ potential of the illite surfaces before and after selenium(IV) sorption has been done, to check whether the sorption takes place by chemical bonding formation or rather by electrostatic attraction. Finally, ATR-FTIR measurements have been performed using an ATR ZnSe crystal. By comparison with former IR measurements concerning selenito-ligands containing complexes as well as phases with sorbed selenium species, the fashion binding of selenium(IV) onto illite has been evidenced.

NFC.P21 (Id: 76)
SORPTION OF RADIONUCLIDES TO THE CEMENTITIOUS MATERIAL NRVB UNDER NEAR-FIELD CONDITIONS

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The current concept for the disposal of intermediate- and low-level waste in the United Kingdom involves the emplacement of the grouted waste confined in stainless steel canisters in a cementitious repository deep underground [1]. The NRVB (Nirex reference vault backfill) is a cementitious material specially formulated for this purpose, composed by a mixture of ordinary Portland cement (OPC), hydrate lime ($Ca(OH)_2$) and limestone flour [2]. The movement of the radionuclides away from the repository is expected to be retarded by their limited solubility under the chemical conditions present in the repository (high pH, due to the cement, and low Eh, due to corrosion of the waste canisters) as well as, by sorption processes. In the present work, the sorption of a series of radionuclides (I^-, Cs^+, Ni^{2+}, Eu^{3+}, Th^{4+} and U^{6+}) to NRVB was assessed under near-field conditions (highly-alkaline pH and anoxic conditions).

The experiments were carried using NRVB-equilibrated water (pH ~ 12.6) in NaCl 0.1 mol dm^{-3} as liquid phase, under a N_2 atmosphere (O_2 and CO_2 free), according to the procedure proposed by Sutton et al. [3]. Linear, Langmuir and Freundlich isotherms were studied for all the radionuclides, and in all cases, the sorption of radionuclides fitted well with the linear model. The R_d (C_{solid}/C_{liquid}) observed experimentally varied in a wide interval that ranged from the low values of 0.012 and 0.033 $dm^3\ g^{-1}$ for Ni^{2+} and I^-, respectively, to values as high as 2870 $dm^3\ g^{-1}$, obtained for Cs^+. Results of the effect of cellulose degradation product on sorption to NRVB will also be presented. When the R_d (C_{solid}/C_{liquid}) values of the radionuclides of interest for NRVB, were compared with the experimental R_d values for the individual components of NRVB, i.e. OPC, hydrated lime and limestone, it was observed that in the case of nickel and in absence of the organic ligands, R_d(NRVB) · R_d(OPC) + R_d($Ca(OH)_2$) + R_d(limestone), confirming the validity of the additive model for this material. Acknowledgements Authors express their thanks to the Radioactive Waste Management Directorate of the Nuclear Decommissioning Authority for sponsoring this project

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NFC.P22 (Id: 111)
SORPTION PROPERTIES AND BEHAVIOUR OF ^{137}Cs AND ^{90}Sr ON BENTONITE CLAYS AND MAGNOX SLUDGES

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Within the nuclear industry, waste management and disposal issues, both within the plants themselves and in the surrounding areas, are complex and problematic. This is partially a result of many decades of discharges within the storage site. A major problem is in determining the nature and distribution of contamination within the environment, be this on site in surrounding host rock, or determining whether migration has occurred to such an extent that contamination has breached the boundaries of the site and reached the public domain, or whether contamination has been released to atmosphere, for example. It has been suggested that there may be significant quantities of contaminated land arising from breaches in radionuclide storage. Therefore, an understanding of the transportation of radionuclide waste in the environment around storage ponds and silos on waste sites, as well as an understanding of the behaviour within the ponds, is essential in future waste remediation strategies. One area of significant interest is the migration of ^{137}Cs and ^{90}Sr radionuclides in contaminated clay soils, as migration has been shown to be significantly faster than expected in some areas. Although exact figures are not known, information provided by a UK operator suggests that ^{137}Cs and ^{90}Sr are progressing through the surrounding area quicker than the expected annual rate of 6 cm/year, for this type of material. Sorption studies carried out using ^{137}Cs and ^{85}Sr have returned promising results. ^{85}Sr was used in place of ^{90}Sr as it is easier to work with, yet still exhibits the same behaviour in terms of sorption. Although some previous studies have looked at the sorption properties of these two radionuclides within the two environments studied most have focussed on only one or two variables. In these studies conducted at Loughborough University, numerous variables including pH, ionic strength and the effect of competing ions being present in the system have been investigated, while all the time keeping the remaining contributing variables (all of those not being specifically investigated, plus contact time, solid-to-liquid ratio, eTc) constant. This has provided data which will be extremely valuable as any changes in behaviour can be directly associated with the altered variable and results can be directly compared with those previously obtained. The rheology of clays and clay minerals plays an important role in the transport of these key radionuclides. A key area of the repository LTP (Life Time Plan), for research and development is to be able to link the transport in the materials studied to rheology and organic content. Specific clays of interest are bentonite and montmorillonite, as well as the mineral brucite. A final goal of being able to inhibit transport, either by chemical speciation or barrier systems is an aim of this project.

NFC.P23 (Id: 121)
STUDY OF CESIUM AND STRONTIUM SORPTION ON ROKLE BENTONITE IN DIFFERENT ELECTROLYTES

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In most of deep geological repository (DGR) concepts sorption of radionuclides on bentonite represents an important process of retarding radionuclide migration into geosphere. In the Czech Republic, DGR concept takes local bentonite into account as material for both buffer and backfill. The candidate bentonite comes from the Rokle deposit (NW Bohemia) and represents complex mixture of (Ca,Mg)-Fe-rich montmorillonite, micas, kaolinite and other mineral admixtures (mainly Ca, Mg, Fe carbonates, feldspars and iron oxides). This bentonite differs in composition and properties from worldwide studied Na-bentonite (e.g. MX-80, Volclay) or Na-Ca bentonite (e.g. Febex). This fact leads to the need of investigation of Rokle bentonite in greater detail to verify its suitability as a buffer and backfill in DGR. Despite a number of studies concerning cesium sorption on bentonites, there are still some issues requiring clarification, especially the effect of cesium-selective minerals (micas and mica-type clay minerals). Their amount in bentonite and their effect on cesium sorption at different conditions re-

presents great uncertainty in cesium sorption evaluation. In this study, the general trends of cesium and strontium sorption on Rokle bentonite (different samples) were compared with sorption on the well-defined reference material (Ca-montmorillonite SAz-1). Then, the effect of changing solution ionic composition on both Cs and Sr sorption was investigated in detail for average sample of Rokle bentonite and associated uncertainties in distribution coefficient (K_d) determination were evaluated. The comparison with reference sample demonstrates that cesium-selective minerals are very important for cesium sorption even at its trace concentrations. For strontium there are no selective minerals to sorb it and the sorption is influenced mainly by the cation exchange capacity (CEC) of the bentonite. Comparing different electrolytes for cesium, the potassium has the highest competitive effect (competition on selective sites), in contrast to sodium and calcium. For strontium, calcium has the highest competitive effect (competition on regular ion exchange sites), potassium has a lower one and sodium the least one. No significant differences were found for three selected samples of Rokle bentonite in sorption behavior for cesium and strontium, except the effect of total CEC of bentonite. The main uncertainty sources for cesium arise from the presence of cesium-selective minerals in Rokle bentonite samples in varying amounts. For strontium, the amount of smectite (which has the highest CEC in natural bentonite) represents the main source of uncertainties. It also follows from the performed experiments that the cesium sorption on studied bentonite cannot be described using simple K_d value.

NFC.P24 (Id: 224)
SORPTION BEHAVIOUR AND SPECIATION OF NEPTUNIUM(V) ON OPALINUS CLAY

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The sorption of Np on clay such as Opalinus clay (OPA) is one of many important processes that affect the migration and retardation of Np in the geosphere. Clay formations are under consideration in several European countries as a potential host rock for high-level radioactive waste repositories [1]. We studied the sorption of Np(V) onto OPA (from Mont Terri, Switzerland) both by baTch experiments and X-ray Absorption Spectroscopy (XAS). The aim of this study was to obtain a mechanistic understanding of the interaction of Np(V) with the OPA surface. The obtained information is necessary for the safety assessment and detailed planning of nuclear repositories. The baTch experiments were done under aerobic and anaerobic conditions. The sorption of Np(V) on OPA was studied as a function of many chemical parameters such as pH (6-10), background electrolyte (synth. OPA pore water, saturated calcite solution, and 0.1 M $NaClO_4$), partial pressure of CO_2, and presence/absence of humic acid (HA). The sorption curves for $8x10^{-6}$ mol/L Np(V) in saturated calcite solution obtained under aerobic and anaerobic conditions, respectively, show that the adsorption edge occurs between pH 7-8. Maximum sorption was observed at pH 8.5 with 65% sorption under aerobic conditions and 80% under anaerobic conditions, respectively. Under anaerobic conditions the reduction of Np(V) to Np(IV) by Fe(II) minerals of OPA causes a stronger sorption. At pH > 9 Np sorption decreased due to the complexation of Np with carbonate in aqueous solution [2]. Molecular-level information was obtained by X-ray Absorption Fine Structure (EXAFS). EXAFS spectra were measured in fluorescence mode at the Rossendorf Beamline ROBL at ESRF. Several samples at pH 7.6 and 8.5 with a total Np(V) concentration of ~ $8x10^{-6}$ mol/L were prepared under aerobic and anaerobic conditions. The amount of Np sorbed in the EXAFS samples was in the range of 50-121 ppm. Np L3-edge X-ray Absorption Near-Edge Spectra (XANES) showed that in all aerobic samples the pentavalent oxidation state of Np was the dominating one. The Np L3-edge EXAFS spectra of the anaerobic samples prepared in different background electrolytes showed the same EXAFS pattern, indicating that Np(V)-carbonato complexes are formed at OPA surface. More details as well as additional results will be presented and discussed. The authors acknowledge the ESRF for provision of synchrotron beam time and thank the ROBL team for assistance during EXAFS measurements.

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NFC.P25 (Id: 301)
SORPTION AND DIFFUSION CHANGES OF ^{134}Cs, ^{99}Tc AND ^{129}I RADIONUCLIDES ON BENTONITES AT VARIOUS CONDITIONS

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Radionuclides of ^{99}Tc and ^{129}I belong among the fission products in spent nuclear fuel and make the largest contributions to long-term nuclear waste. The high proportion of risk from these radionuclides is due to their large inventories in many types of waste, long half-lives, and the perception that they are highly mobile in the environment and therefore play potentially large role in long-term dose assessment. Computer-modeling methods were used to calculate equilibrium thermodynamic principles, the distributions of predominant aqueous species, and potential solubility controls for the environmentally important oxidation states of each of the contaminants of

concern. The Eh-pH diagrams of individual chemical species of the tested radionuclides were calculated by the geochemical software tool Geochemist's Workbench. The data obtained from the model calculations corresponded with experimental results. The chemical stability of bentonite was studied on a series of long-term pressure and temperature loaded bentonite samples that were selected with the aim of constructing a behavior profile of the bentonite buffer material in the experimental container. The chemical stability of the loaded bentonite samples was evaluated on the basis of their ion exchange capacity, the migration behavior of selected radionuclides and determination of the leachable components of bentonite into redistilled water. The results obtained in this study were compared with the values for the unloaded bentonite material. It was found that long-term pressure and temperature gradients do not have a significant influence on the changes of the ion exchange capacity of bentonite material. These results make a major contribution towards determining the migration of radionuclides on bentonite, especially cationic forms of radionuclides. Electromigration methods and thin layer chromatography with radiometric detection were used for the identification of technetium and iodine chemical forms in the studied solid-liquid systems. Migration studies of the radionuclides ^{134}Cs in the form of the Cs^+ cation and ^{99}Tc in the form of the pertechnetate anion were described on the basis of two dominant processes that both include sorption and diffusion. The dominant chemical form of technetium under these redox conditions is the insoluble $TcO_2.nH_2O$, which is formed by the reduction of pertechnetate anion to the oxidation state Tc(IV). The determined values of distribution and diffusion coefficients of the loaded bentonite samples corresponded with the values of the unloaded bentonite material. Ion exchange at the surface sites of bentonite corresponded with the control mechanism of Cs^+ cation sorption on bentonite in that both were simultaneously influenced by competitive cations present in the aqueous phase(Na^+, K^+, Ca^{2+}, Mg^{2+}). To retard the migration of selected radionuclides ($^{99}TcO_4^-$, $^{125}I^-$) released from spent nuclear fuel after the failure of a container, the reducing effects on the concentration of these radionuclides by container corrosion products and of some additives on the bases of Fe compounds in various oxidation states were examined in aqueous media in contact with bentonite.

NFC.P26 (Id: 33)
EVOLUTION OF THE REDOX POTENTIAL IN THE CORROSION SYSTEM

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The knowledge of chemical conditions, especially of redox potential, inside waste packages with radioactive wastes is important for the determination of radionuclides speciation and their leaching rate after failure of waste packages. Conditions inside waste packages will be determined primarily by the reactions of thermodynamically unstable iron with groundwater penetrating into waste packages and by the nature of the iron corrosion products formed. The main corrosion products of iron corrosion are Fe(II) ions, hydrogen and products of reactions of these species with species present in water flowing into waste packages. The composition of water will correspond to the composition of ground water affected by other engineered barriers. The rate of the corrosion reaction, the rate of oxidation and hydrolysis of Fe^{2+} and the rate of the formation of precipitation products will govern the development of Eh inside waste packages. One possibility of estimating chemical conditions in such complex systems is to use advanced geochemical models. A great disadvantage of these models is that a lot of important input data must be estimated. This can lead to great uncertainty about the real conditions inside waste packages. The main aim of this work was therefore to measure redox potential (Eh) in simplified systems simulating the conditions inside waste packages and the effect of iron corrosion on Eh development inside waste packages after ingressions of groundwater. The results can then be used to validate geochemical models. The corrosion systems consisted of the carbon steel plates and the synthetic bentonite porewater. The apparatus was put into anaerobic box ($O_2 < 0.1$ ppm), where redox potential was measured by platinum and gold electrodes. The corrosion rate of carbon steel was determined during experiment by measuring hydrogen evolution and then from weight loss of samples. The results show that the values of the redox potential during the experiments firstly sharply decreases and then slowly increases. Opposite behaviour was observed at measuring pH, where values of pH first slightly increased and then slowly decreased. The concentration of Fe^{3+} ions after the experiments was negligible in comparison with Fe^{2+} concentration. The corrosion rate at 50 °C was almost constant during corrosion experiment, while the corrosion rate at 60 and 70 °C was very fast at the beginning of corrosion but then significantly slowed down. It seems that the effect of temperature on corrosion rate is affected by the nature of corrosion products formed on the surface of metal. The experiments provide useful information about evolution of the redox potential and other parameters which can be expected inside waste packages with radioactive wastes, but time of the experiments carried out so far was relatively short (30 days). In the future, long-term experiments must be performed under various conditions to verify the results obtained.

NFC.P27 (Id: 40)
STUDY OF GAS GENERATION IN REAL L/ILW CONTAINERS

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To obtain reliable estimates of the quantities and rates of the gas production in L/ILW a series of measurements was carried in the last seven years in Hungary. Drums filled with

selected original L/ILW coming form the light water PWR type Paks Nuclear Power Plant (Hungary) were placed into special hermetic containers and the gas generation in them was measured carefully. Headspace gas analysis of real radioactive waste vaults closed between 1979 and 1995 in a near surface L/ILW disposal facility of Hungary was also carried out. It was clearly indicated that the gas generation rate is relatively high in the L/ILW drums independently of the chemical type of the main components of the stored waste. Our results showed that the main generated gases in L/ILW are carbon dioxide, methane and hydrogen. The typical rates were 0.05-0.2 STP litre gas/day for CO_2 and CH_4 generation, and less than 0.02 STP litre gas/day for H_2. No explosive gas mixture was indicated in the L/ILW drums during the investigated storage period. Compositions of headspace gases in closed L/ILW vaults were in good agreement with gas generation processes observed in L/ILW drums. The stable carbon isotope measurements show that the main source of the CO_2 gas is the degradation of organic matter in the waste. The low ^{13}C content indicates microbial degradation processes as the main sources of CH_4 in the headspace gas. Typical tritium activity concentrations were between 0.1 and 10 Bq/liter gas in the drums and between 10 and 1000 Bq/liter gas in the vaults. Typical ^{14}C activity values of the headspace gases were between 0.1 and 2.0 Bq/liter gas in the drums and 10 and 1000 Bq/liter gas in the studied vaults.

NFC.P28 (Id: 86)
QUALIFICATION OF LOW AND INTERMEDIATE LEVEL RADIOACTIVE WASTES (L/ILW) WITHIN THE FRAMEWORK OF THE "DEMO" PROJECT BY A TRIATHLER TYPE PORTABLE LIQUID SCINTILLATION SPECTROMETER IN PÜSPÖKSZILÁGY, HUNGARY

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In the Püspökszilágy Radioactive Waste Treatment and Disposal Facility, Hungary, (in operation since 1976) many works started to solve the storage of the non-power-plant radioactive waste of Hungary to fulfil the increasing safety demands. Within the framework of this procedure the exhumation of 66 reinforced concrete near-surface vaults with the size of 70-140 m^3 each (called vault "A") started together with further renewal works. The exhumation of the A11, A12, A13 and A14 vaults was included in the "Demo" project, in the course of which the aim was to find the proper measurement and waste-backfilling technique to adapt them as further vaults. To identify the ^3H, ^{14}C and ^{90}Sr isotopes a Triathler type portable liquid scintillation spectrometer was used together with a rapid and well-reproducible swipe sampling method. The expected total activity value was obtained by evaluating 4000 samples. Certain waste packages were removed to gain space allowing the disposal facility to accept further waste in the future. The measurement technique is therefore well-applicable in the case of the "A type" vaults.

NFC.P29 (Id: 87)
„DEMO" PROGRAM IN PÜSPÖKSZILÁGY, HUNGARY: QUALIFICATION OF LOW AND INTERMEDIATE LEVEL RADIOACTIVE WASTES BY A FIELD γ SPECTROSCOPY SYSTEM

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The Radioactive Waste Treatment and Disposal Facility, Püspökszilágy, Hungary, is in operation since 1976. Low and intermediate level radioactive wastes originating from different industrial, medical, educational and scientific activities are disposed of here. At the beginning of its operation the facility had to fulfil only safety requirements but not regulations pertaining to the form and the quality of the wastes. The recent safety analyses aim to improve these temporary solutions to ensure the further safe and proper operation of the facility. A „Demo" project was launched to remove the wastes containing long-lived and highly active isotopes and to gain excess capacity with more organised backfilling, within the framework of which the exhumation of 4 near-surface reinforced concrete vaults (called „A type") was fulfilled. In the vaults the wastes were in plastic packages. Most of them were undamaged during hoisting, thus the identification of the various isotopes was possible with the help of a field γ spectrometry system. A Genie 2000 Gamma Analysis Software was used together with a Big Mac type CANBERRA γ spectrometry system with a high-purity germanium detector. On the basis of the original records most of the wastes containing different isotopes were identified and the results of the measurements were similar to the ones estimated from the records. After the backfilling it can be seen that the purposes regarding the excess capacity of the vaults can also be achieved. It can be stated that the measurement technique for the further similar vault exhumation procedures is proper and applicable.

NFC.P30 (Id: 294)
IMPACT OF HYDROGEN GENERATED BY IRON CORROSION ON COMPACTED BENTONITE IN DEEP GEOLOGICAL REPOSITORY

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A large number of processes will influence the performance of deep geological repository of radioactive wastes until the activity of radionuclides decay to a negligible level. One of the very important processes is generation of gases, and particularly of hydrogen, which will be formed primarily by anaerobic corrosion of metals and by radiolysis of water. High pressure formed in the vicinity of waste packages due to accumulation of hydrogen can cause failure of sealing materials and contribute to fast release of radionuclides to the geosphere after waste package failure. This contribution presents the results of laboratory experiments, which simulated the phase of repository evolution after ingression of water in failed canister with spent fuel assemblies, which is connected with significant generation and accumulation of hydrogen in free voids of waste packages and at interfaces of waste packages and compacted bentonite used as a sealing material. Corrosion of carbon steel canisters inside walls is simulated by corrosion of iron powder with high surface. It was found that after an increase of pressure of hydrogen to the values exceeding some threshold values, which depends on density bentonite, hydrogen is released to geosphere in pulses due to formation of preferential paths. This is connected with a significant increase of permeability of bentonite from values of approximately 10^{-24} m^2 to 10^{-18} m^2 within the breakthrough time. The pressure needed to reach breakthrough is decreased with the number of breakthrough pulses. Data obtained in experiments enable us to understand more closely the processes occurring in a repository and to avoid conditions that could lead to the failure of sealing materials and fast release of radionuclides to the geosphere and the environment.

NFC.P31 (Id: 39)
DISSOLVED GAS MEASUREMENTS OF THE COOLING PONDS OF PAKS NUCLEAR POWER PLANT, HUNGARY

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The aim of this work was the investigation of the effect of nuclear fuel rods on the composition of the dissolved gas in the cooling water of the cooling ponds of Paks Nuclear Power Plant (Paks NPP). In normal cases after three-year usage in the reactor the spent fuel elements are stored in cooling ponds for years before delivering out from the reactor area. In April 2003 due to the failure of the cleaning procedure of fuel rods from reactor No. 2 some elements remained in service pool No. 1. For better handling of this situation and planning the repairing procedure several parameters must be considered. The gases dissolved in the coolant, especially those produced by fission or decay, are good indicators of the variation in state parameters of the system in this situation as well as in the case of working reactors. Parallel with the measurements of dissolved gases in the coolant for surveying the kilter of the nuclear fuel remained in service pool No.1 we also measured these parameters in the cooling ponds as a reference. The reason was the similar technological situation because in both cases the coolant contains out-of-work fuel elements and the headspace gas above is air with atmospheric pressure. In this work we investigated the effect of the nuclear fuel rods on the composition of the dissolved gas in the coolant of the cooling ponds and the service pool No.1 of the reactor No. 2 of Paks NPP. We measured the quality and the quantity of the dissolved gases and the isotope compositions of the noble gases produced in fission or decay. For these aims sampling and measuring methods were developed. Our results help to ascertain the possible ways and rates of gas generation processes caused by the presence of nuclear fuel rods in the cooling water.

NFC.P32 (Id: 74)
USING NATURAL ORGANIC MATTER AS A REMEDIATION MATERIAL IN ENVIRONMENTAL APPLICATIONS

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Natural organic matter (NOM) is being characterised and investigated for use as a remediation material in various applications. Two readily available environmental materials are being tested: Material A: 68% by weight of the material is organic including 19% humic acid, 28% fulvic acid and 21% humin. 32% of the material is inorganic, containing 23% iron. Material B: 57% by weight of the material is inorganic, 3% is humic acid, 27% is fulvic acid and 13% is humin. The humin fraction of these two materials may contain humic acid that has been immobilised by clays or other minerals. The materials have been tested in three applications; i) As a permeable reactive barrier A permeable reactive barrier is a passive, in situ method that is used to remediate contaminated groundwater. As groundwater flows through it, the barrier extracts contaminants, significantly reducing their concentration. Both materials are capable of extracting metals and organic pollutants from groundwater ii) Extraction of iodine from urine ^{131}I may be given to patients with thyroid problems for diagnosis or treatment. About 30% of the activity (2-3 GBq) is excreted in urine during the first day after administration. In some parts of Europe, the radioactive urine is collected in tanks at the hospital. The objective of this investigation is to determi-

ne whether the radioiodine can be extracted from urine and concentrated in a smaller volume of solid. iii) Extraction of iron and other contaminants from industrial effluents During the production of kaolinite or China Clay, brown discoloration caused by Fe^{3+}-containing impurities is removed by the addition of acid and a reducing agent, forming soluble Fe^{2+}. The latter is then removed from the effluent by precipitation with NaOH and flocculants. This study investigates the use of solid NOM to bind iron and co-contaminants directly, avoiding the need for alkali addition and precipitation of large quantities of slurry.

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