

Development of New Processes for the Decommissioning Decontamination and for Treatment and Disposal of the Secondary Low- and Intermediate-Level Radioactive Waste

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As an example of research activities in decontamination for decommissioning, new data are presented on the options for corrosion layer dissolution during the decommissioning decontamination, or persulfate regeneration for decontamination solutions re-use. For the management of spent decontamination solutions, new method based on solvent extraction of radionuclides into ionic liquid followed by electrodeposition of the radionuclides has been developed. Fields of applications of composite inorganic-organic absorbers or solid extractants with polyacrylonitrile (PAN) binding matrix for the treatment of liquid radioactive waste are reviewed; a method for americium separation from the boric acid containing NPP evaporator concentrates based on the TODGA-PAN material is discussed in more detail. Performance of a model of radionuclide transport, developed and implemented within the GoldSim programming environment, for the safety studies of the LLW/ILW repository is demonstrated on the specific case of the Richard repository (Czech Republic). Continuation and even broadening of these activities are expected in connection with the approaching end of the lifespan of the first blocks of the Czech NPPs.

Keywords: Liquid radioactive waste, Decontamination, Ionic liquids, Composite absorbers, Solid extractants, Safety assessment

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1. Introduction

The Czech Republic, as a part of the former Czechoslovakia, is one of the handful of nuclear countries that were able to build, manufacture, launch and operate a complete nuclear power plant (NPP). The A-1 NPP, using a heavy-water moderated, gaseous CO₂-cooled experimental reactor KS-150 with thermal output of 560 MWt designed and produced in Czechoslovakia, and metallic natural (unenriched) uranium fuel was built between 1958 and 1972. During the construction and operation of the A-1 NPP, a significant base of top experts and technicians was created for all nuclear industries, including mining and milling of rich local uranium deposits. Not only their experience and knowledge, but also mastery of the production of materials, components and equipment were used in the construction of the later more advanced VVER reactors in Czechoslovakia. The today's Faculty of Nuclear Sciences and Physical Engineering of the Czech Technical University in Prague (CTU in Prague–FNSPE) became and remains one of the cornerstones of the nuclear fuel cycle and nuclear power related research and education in the Czech Republic.

The aim of this paper is to summarize results of the recent and ongoing research activities in decontamination for decommissioning, treatment, and disposal of low- and intermediate-level radioactive waste carried on at the Department of Nuclear Chemistry of the CTU in Prague–FNSPE. Since most of this research has been integrated into the ongoing joint European efforts, the key European project in this field are briefly introduced below.

2. Joint European efforts in the field of management and disposal of low- and intermediate-level radioactive waste

The research and development in the field of management and disposal of low- and intermediate-level

radioactive waste has been supported within the “nuclear fission and radiation protection” part of the Euratom Programme—a complementary research programme for nuclear research and training under Horizon 2020—the biggest EU Research and Innovation programme ever. Among the on-going Euratom supported projects, broad multi-partner projects such as PREDIS, EURAD, or SHARE, or more specialised projects such as TRANSAT [1] play the key role and are worth of mentioning.

The project “Pre-disposal management of radioactive waste” (PREDIS) aims at developing and increasing the Technological Readiness Level of treatment and conditioning methodologies for wastes for which no adequate or industrially mature solutions are currently available, including metallic materials, liquid organic waste and solid organic waste. PREDIS project also develops innovations in cemented waste handling and pre-disposal storage by testing and evaluating. The project started 1.9.2020 with four years duration. The consortium includes 47 partners from 18 EU Member States (MSs); the overall budget of the project is 23.7 M€. PREDIS high-level objectives are to [2] develop solutions for future treatment and conditioning of waste, for which no industrially mature or inadequate solutions are currently available, and/or improve existing solutions with safer, cheaper or more effective alternative processes.

EURAD—“European Joint Programme on Radioactive Waste Management” is a project that will help MSs obtain the know-how required to implement safe and long-term management of radioactive waste. EURAD will also provide management knowledge to operate disposal facilities, and help transfer that knowledge between countries and organisations [3].

In practice, this will encompass supporting MSs in developing and implementing their national R&D programmes for the safe long-term management of their waste, and/or consolidating existing knowledge for the safe start of operation of the first geological disposal facilities for spent fuel, high-level waste, and other

long-lived radioactive waste.

The project started 1.6.2019 with five years duration. The consortium gathers 51 mandated organisations with 54 linked third parties from 25 countries. The overall budget of the project is 59.9 M€.

The project SHARE–“A roadmap for research in Decommissioning”– aims at increasing coordination between the various stakeholders involved in research activities related to decommissioning and who have an interest in ensuring that decommissioning can be implemented in a safe, effective and sustainable manner [4]. The SHARE consortium will provide an inclusive roadmap for stakeholders in Europe and beyond. The aim of this roadmap will be to jointly improve safety, reduce costs and minimize environmental impact in the decommissioning of nuclear facilities for the next 10 to 15 years.

The project started 1.6.2019 with 29 months duration. The consortium includes 11 partners supported by an expert review panel that includes 16 entities from 11 countries. The overall budget of the project is 1.5 M€.

As stated above, the vast majority of the current research in the field of low- and intermediate-level radioactive waste management and disposal at the Department of Nuclear Chemistry has been amalgamated into these projects or their predecessors.

3. Recent and ongoing studies in the field of management and disposal of low- and intermediate-level radioactive waste at the CTU in Prague

The recent and/or ongoing studies aimed at safer LLW and ILW management and disposal carried on at the CTU in Prague can be classified into three fields: Decontamination for decommissioning, Treatment of liquid radioactive waste, and Safety studies of the near-surface repository of LLW and ILW. This is also how the key results are discussed below.

3.1 Decontamination for decommissioning

Decommissioning is inevitable for each nuclear facility and, lately, it has become one of the most topical issues. Closing the life cycle of nuclear power plant is complicated and long-term operation. Among the “hot” operations after transport of the used nuclear fuel, dismantling and fractionation of the primary circuit play the most significant roles. In order to protect the personnel on place and minimize their dose, the first and crucial step is the activity reduction of all contaminated components.

3.1.1 Process requirements and design

Several decontamination methods have been successfully applied worldwide; however, it was found out that the process of decontamination is influenced not only by the decontamination agent itself and the conditions of its use (e.g. temperature, contact time of the solution) and/or different composition of the construction materials, but also by the properties of the decontaminated surface affected by the chemical and operational history of the surface. This means that even a well-tuned decontamination system developed for a particular type of nuclear facility is not directly and easily applicable for another type of facility. This situation leads us to look closer at the chemistry of the most often used decontamination methods in decommissioning and routine operations and the differences in various types of nuclear facilities.

Based on the information obtained, the research has been focused on the development of a specific system for decontamination of the primary circuit before its dismantling based on a general scheme (Fig. 1). The system was designed with respect to materials used and operating and chemical history typical for VVER-type NPPs. From this study, several main requirements towards searched decontamination system followed:

- Simple, fast and aggressive
 - At low concentrations of chemicals
 - At low temperature/pressure

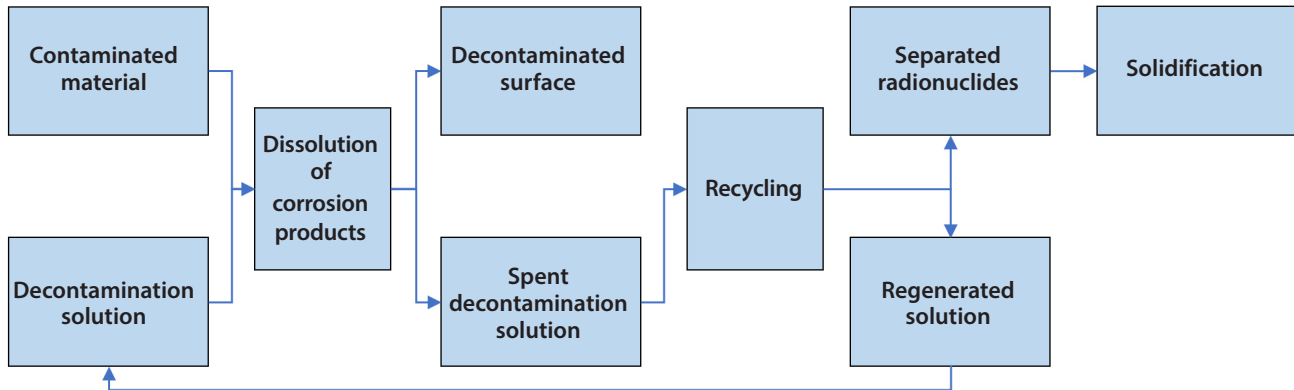


Fig. 1. Simplified block diagram of the decontamination system.

- Capable of oxidizing and dissolving chromium(III) oxides/spinel-based corrosion layers
- Comparable efficiency to other systems (e.g. systems based on HBF_4)
- Suitable for circulation through primary circuit pipelines of VVER-type NPPs
- Suitable for regeneration/recycling
- Separation of radionuclides in minimum steps
- Separation and regeneration possible without ion exchangers
- Resulting waste suitable for cementation or bituminization.

The decontamination of primary circuits focuses mainly on the removal of inner corrosion layers of steel components which contain activated corrosion products adsorbed and/or incorporated during the NPP operation, and very often also immobilized fission products coming from microcracks in fuel cladding.

In such cases, the key process in steel decontamination, is to dissolve surface corrosion layer and thus remove radionuclides. Main goal of the research was inspired by decontamination processes originally based on the fluoroboric acid and taking into account the conditions and the specific corrosion layers typical for the material of primary circuit of the VVER nuclear power plants [5-7]. From the corrosion studies on the surface

of stainless steel under primary circuit conditions of pressurized water reactors, it can be concluded, that the dissolution of the corrosion layer is associated with the oxidation of insoluble built-in Cr^{3+} to soluble Cr^{6+} and similarly Fe^{2+} to Fe^{3+} . Because of this fact, the experiments of dissolving corrosion layers started with dissolution of chromium(III) oxide in the solutions usable and suitable for treatment during decommissioning.

3.1.2 Experimental results and conclusions

The studies performed were focused at dissolving the most resistant chemical present in the corrosion layers, chromium(III) oxide, using redox chemistry and further testing of the selected redox systems on stainless steels and corrosion compounds of the primary circuits of the Czech and Slovak VVER NPPs. The oxidation and dissolution of common corrosion layer compounds was investigated in acidic environment of HBF_4 and H_2SO_4 at various concentrations and temperatures. Addition of potassium persulfate $\text{K}_2\text{S}_2\text{O}_8$ as oxidizing agent and various charge transferring ions as catalysts at different concentrations were tested. As simulants of the corrosion layer compounds, chromium(III) oxide, magnetite and several spinel minerals synthesized to mimic spinels created in the primary circuit of nuclear power plant during its operation were used.

From the results obtained several main conclusions

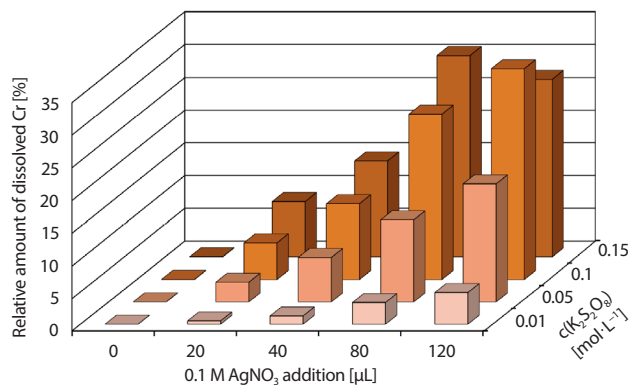


Fig. 2. Dissolution of Cr₂O₃ in 5% H₂SO₄ at various concentrations of K₂S₂O₈ and/or AgNO₃, t = 5 hrs, T = 50°C.

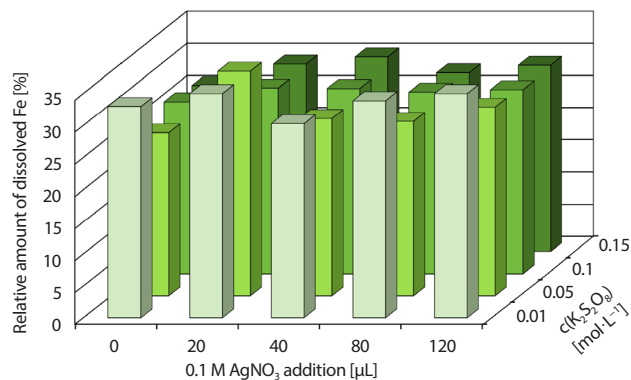


Fig. 3. Dissolution of Fe₃O₄ in 5% H₂SO₄ at various concentrations of K₂S₂O₈ and/or AgNO₃, t = 5 hrs, T = 50°C.

could be drawn [8]:

- Decontamination medium based on persulfates with Ag ions in acidic media at T = 50°C was proposed. The medium was successfully tested for dissolution of chromium(III) oxide, magnetite and several spinel minerals.
- The dissolution of chromium(III) oxides, that are present in corrosion layers of the stainless steel of NPP primary circuits, is a key step in decontamination methods.
- The results show that it is possible to corrupt and dissolve highly stable corrosion layer compounds.
- The solubility of chromium oxide increases with increasing concentration of persulfate and silver ions. Its solubility depends on the presence of both components (Fig. 2).
- The amount of dissolved iron is significantly less dependent on the concentration of persulfate and silver nitrate—the solubility of iron in magnetite is around 30% over the whole range of concentrations of persulfate and silver nitrate (Fig. 3).
- The kinetics of the dissolution of Cr₂O₃ and Fe₃O₄ are different, the more resistant Cr₂O₃ dissolves more slowly. In the case of Cr₂O₃, almost 30% of the chromium was transferred to the solution in 42.5 hours, while more than 97% of iron was dissolved in the

same time.

- Based on the known composition of the chemical system for decontamination, the possibility of separation of radionuclides from spent decontamination solution and regeneration of persulfate was successfully achieved.

3.2 Treatment of liquid radioactive waste

3.2.1 Application of ionic liquids in liquid LLW and ILW treatment

Ionic liquids (ILs) are low-melting salts (melting point below 100°C) usually composed of large asymmetric organic cation (based on e.g. imidazolium, pyridinium, or many others) and organic or inorganic anion [9]. Among their main advantages belong relatively high thermal and radiation stability, possibility of designing for enhanced selectivity, low vapour pressure compared with the volatile organic compounds used in common processes, and possible application as solvent for agents providing high separation factors [10-12]. Compared to traditional solvent extraction, the metal-ion partitioning in ionic liquid-based extraction systems exhibits high complexities and the designability of ionic liquids could offer a suitable tool for the separation of radionuclides from decontamination solutions [12, 13].

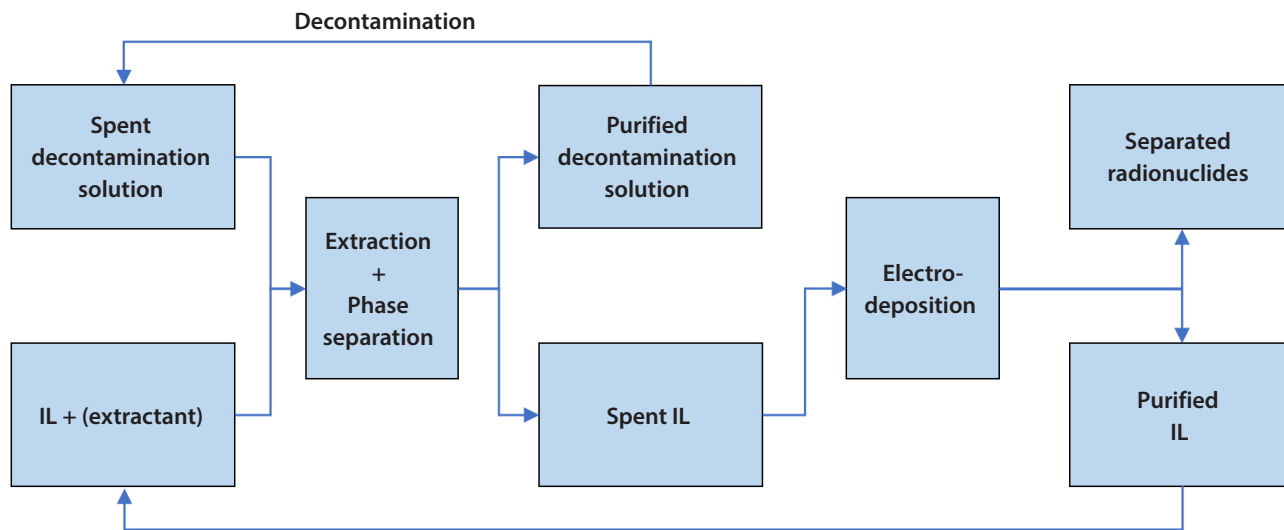


Fig. 4. Principle scheme of the developed method for secondary waste treatment based on the application of ionic liquids.

3.2.1.1 New separation method for secondary waste treatment

The main goal of our research in this field was to propose and test new separation method for treatment of the secondary waste (usually types of ILW or LLW) coming from the decontamination procedures. The two-step method proposed (see Fig. 4) is based on solvent extraction of radionuclides into selected ionic liquid, potentially containing additional extractant, followed by electrodeposition of the radionuclides directly from the ionic liquid phase. Parameters strongly influencing each step of this process as ionic liquid type, pH of aqueous phase, concentration of extractant and presence of organic complexing agents were studied as well as the parameters of electrodeposition. The developed procedure was focused on treatment of spent decontamination solution and was tested on a model solution of the selected corrosion products—iron and cobalt—with complexing agents [14]. This model solution consisted of nitric acid at various concentrations, or oxalic or citric acid solutions or their mixture. The organic phase consisted of one of the selected ionic liquids from imidazolium or ammonium family: 1-alkyl-3-methylimidazolium bis(trifluoromethanesulfonyl) imide ionic liquids, tributyl-

methylammonium bis(trifluoromethanesulfonyl)imide, and methyltrioctylammonium bis(trifluoromethanesulfonyl) imide (all supplied by IoLitec). As the extractant, 8-hydroxyquinoline in various concentrations was used. Electrochemical behaviour of metals in the ionic liquid phase was tested using cyclic voltammetry.

3.2.1.2 Results and conclusions

The procedure developed was successfully tested for the extraction of cobalt (^{60}Co) from solution containing citric and oxalic acid. Cobalt was almost fully extracted into 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl) ionic liquid with 8-hydroxyquinoline at $\text{pH} > 2.5$ and more than 99.8% of the extracted cobalt could be deposited on the working electrode in the subsequent step. The method described was patented [15] and detailed results were published [14]. In summary, it was found out that the solvent extraction with ionic liquids followed by direct electrodeposition from organic phase could be effectively used for the removal of metals and radionuclides from the aqueous solutions containing organic complexing agents like oxalic or citric acid.

This procedure represents very promising system for

Table 1. PAN-based composite absorbers

Code	Active Component	Code	Active Component
AMP-PAN	Ammonium molybdophosphate	TiO-PAN	Titanium oxide
NiFC-PAN	Nickel ferrocyanide	ZrO-PAN	Zirconium oxide
KNiFC-PAN	Potassium-nickel ferrocyanide	MgO-PAN	Magnesium oxide
CoFC-PAN	Cobalt ferrocyanide	G-PAN	Goethite (α -FeOOH)
KCoFC-PAN	Potassium-cobalt ferrocyanide	MAG-PAN	Magnetite (Fe_3O_4)
CuFC-PAN	Copper ferrocyanide	NM-PAN	Manganese dioxide and Nickel ferrocyanide
KCuFC-PAN	Potassium-copper ferrocyanide	C-PAN	Activated carbon
ZnFC-PAN	Zinc ferrocyanide	NiFCC-PAN	Nickel ferrocyanide and activated carbon
NiFIC-PAN	Nickel ferricyanide	MAG/F	Magnetite and nickel ferrocyanide
CoFIC-PAN	Cobalt ferricyanide	ZrOP-PAN	Zirconium oxide and zirconium phosphate
CuFIC-PAN	Copper ferricyanide	NaTiO-PAN	Sodium titanate
ZnFIC-PAN	Zinc ferricyanide	CSbA-PAN	Crystalline antimonite acid
ZrP-PAN	Zirconium phosphate	SnSbA-PAN	Tin(IV) antimonate
MnO-PAN	Manganese dioxide	Ba(Ca)SO ₄ -PAN	Barium sulfate activated by calcium
NiS-PAN	Nickel sulphide	BS-PAN	Biomass
CuS-PAN	Copper sulphide	M315-PAN	Synthetic mordenite M315
FeS-PAN	Ferrous sulphide	CLIN-PAN	Natural clinoptilolite
ZnS-PAN	Zinc sulphide	HPM-PAN	Sr- and Ra- selective ternary ion-exchanger
Na-Y-PAN	Synthetic zeolite Na-Y		

potential recycling of decontamination solutions and thereby volume reduction of the final waste. The ionic liquids could be a future alternative to present-day solvents used in separation of metals and radionuclides from solutions containing organic complexing agents, especially in the processes of decontamination and decommissioning or treatment of an industrial waste.

3.2.2 Composite inorganic-organic absorbers for liquid waste management

For liquid waste management, synthetic or natural inorganic ion exchangers are frequently used. Their main advantages are high selectivity for sorption of some radionuclides and good radiation, temperature and chemical stability; their main disadvantage being their fine to powdery nature. Technological application of such fine materials is

often limited by the need of their separation from the aqueous waste streams treated. In practise there exist number of technological possibilities how to use or pre-treat such materials [16, 17]. One of the frequently used options is to convert the powdered or microcrystalline ion exchangers into granular “engineered” beads suitable for application in column beds.

3.2.2.1 Composite absorbers with polyacrylonitrile (PAN) binding matrix

At DNC, a universal procedure for the production of such beads was proposed and developed. In this procedure, modified polyacrylonitrile (PAN) as a universal binding polymer for inorganic ion exchangers (active components) and production of the so called “composite sorbents” was used [17, 18]. The list of such composite materials

produced in our laboratory is shown in Table 1.

In the early phase of the studies, main attention was paid to the study and evaluation of the properties of these materials [18]. It was confirmed that neither the kinetics of ion exchange nor the capacity of the ion exchangers is influenced by the presence of the binding polymer. The content of the active component can be varied in the broad range of 5–90% of the active component in the final material. Properties of such composite absorbers can be “tailored” to the specific application by mixing suitable active components to the particular waste stream. The possibilities of regeneration of composite absorbers are determined solely by the nature of the active component. Positive effect of the binder was found in the case of (non-regenerable) insoluble ferrocyanides. The binder allows their regeneration by oxidation of the active component to ferricyanides and back-reduction to ferrocyanides [19]. Chemical and radiation stability of the binder (B-PAN beads) and/or some composite sorbents in acidic or alkaline simulant solution was studied under technical and financial support of U.S. DOE [20, 21]. The binder itself is stable in aqueous solutions of all common electrolytes, except for concentrated solutions of acids and alkalis or some concentrated salts [20, 21]. The beads of composite sorbent AMP-PAN and B-PAN beads demonstrated excellent stability in 1 M HNO₃ + 1 M NaNO₃ solution during 1 month. In alkaline solution, 1 M NaOH + 1 M NaNO₃, and also in dependence on temperature, the stability of B-PAN beads was sufficient for time period up to 7–10 days which is sufficient for most applications expected.

Radiation stability of B-PAN and AMP-PAN or TiO-PAN absorber in distilled water was studied in a radiation dose range 10³–10⁶ Gy. No influence of radiation on the stability of B PAN beads was observed. Cross-linking of PAN polymer during irradiation was detected, which can positively influence PAN chemical stability in alkaline solutions [21]. In the frame of general studies, treatment of PAN-based composite absorbers for solidification for the final disposal was also studied [23, 24]. Immobilization of

the spent sorbents in cement matrices was studied at first, as it is the primary process considered for their final disposal. Here, their main advantage is that the binding polymer does not swell (contrary to organic ion exchangers) and the radionuclides are bound to the inorganic active component which is more stable against radiation and chemical damage. Up to 5–9 % of the dry composite absorber KNiFC-PAN was possible to be loaded into the cement grout. The final products are comparable with the solidified “pure” inorganic ion exchangers and were stable after several freeze/thaw and soak/dry cycles. Leachability of ¹³⁷Cs from the cemented samples in dynamic tests and after their irradiation was tested, too [24, 25]. Spent absorbers can be frequently classified as intermediate or even high level waste and immobilisation of such material in cement may not be acceptable or safe enough. Therefore, in trial experiments vitrification of KNiFC-PAN absorber was also tested [23]. Hydrolytic resistance of the product, measured as electrical conductivity of the leachate, was 20 μS·cm⁻¹ and lower and vitrification was evaluated as prospective for long term storage of such high-level radioactive waste.

3.2.2.2 Selected applications of composite absorbers

Application of composite absorbers was tested for different aqueous streams ranging from model simulant solutions, underground or surface water to real samples of radioactive wastes. Many possible applications of these materials were performed and reported earlier, together with full-scale applications [18, 21, 22].

Significant effort was targeted on the waste at NPP A-1 (Slovak Republic), produced during its decommissioning after an accident. For the treatment of 350 m³ of biological shield water before discharge into the environment, technology using 35 L of NiFC-PAN (separation ¹³⁷Cs) and 10–15 litres of NaTiO-PAN absorber (separation ⁶⁰Co and ⁹⁰Sr) was developed.

Extensive research activities have been carried out [26] for decreasing the long/term fuel storage pond water

activity (approx. 200 GBq $^{137}\text{Cs}\cdot\text{m}^{-3}$ and volume approx. 550 m^3) before the planned removal of damaged fuel cassettes in cans from the pond water. In a bench scale experiment with fluidised NiFC-PAN composite absorber, flow rate of 500 $\text{BV}\cdot\text{hr}^{-1}$ (BV = bed volume) was used and the water was returned to the pond. A mathematic model of circulation of pond water predicted that 8.6 times total volume of the pond water has to be treated to decrease the ^{137}Cs activity by three order of magnitude, using fluidized bed with volume of 3 L. For the final treatment, AEA Technology (U.K.) was responsible [27]. 200 L of NiFC-PAN composite absorber were produced at DNC. Two columns in series were used and in total three columns were needed for the treatment of 550 m^3 of pond water and the ^{137}Cs activity was decreased by two orders of magnitude. The spent columns were hot air dried, filled with inert gas and sealed into shielded steel containers. These columns are stored as high level radioactive waste in a temporary repository.

Cooperation under technical and financial support of U.S. DOE was also directed on solution of practical problems with real waste. A hot-cell demonstration experiment at Idaho National Engineering Laboratory (INEEL) was performed with the with WM-183 tank real “Sodium Bearing Waste”-SBW [28]. Cumulative breakthrough of caesium was as low as 0.013% even after treatment of 1,000 BV (max. permissible volume of treated waste) using AMP-PAN/SF01 optimized absorber. The same type of absorber was tested during the study of caesium sorption from INEEL concentrated acidic tank wastes [29]. Evaluation of the results revealed that this absorber represents a more effective option for the removal of caesium in comparison with other sorbents. More than 20 PAN based composite absorbers prepared at the DNC were also tested at Los Alamos National Laboratory during screening study of many absorbers potentially prospective for treating the Hanford HLW tanks [16, 30-33].

Several PAN based composite absorbers were tested for potential application during radionuclide separation from boric acid containing liquid waste produced during

operation of Nuclear Power Plants [34] or as possible accidental nuclear waste [35]. NiFC-PAN, NaTiO-PAN, MnO-PAN, M315-PAN and Na-Y-PAN absorbers were tested for the separation of $^{137+134}\text{Cs}$, $^{60+58}\text{Co}$ or ^{54}Mn . Combination of two columns in series was used for radionuclide separation from Waste Condensate Tank, Boron Recycle Hold-up Tank and Waste Hold-up Tank solutions from NPP Krško, Slovenia. The best results for radiocaesium separation were achieved for the NiFC-PAN absorber while MnO-PAN absorber showed to be most effective for radiocobalt separation. Separation of cobalt was complicated by its speciation in the solutions. NM-PAN, TiO-PAN and CSbA-PAN absorbers were tested for the Pu and Am separation from simulated accident solution containing 5 g or 20 $\text{g}\cdot\text{L}^{-1}$ of boric acid at pH approx. 5.8 and/or 7.3. The batch and column experiments performed revealed that Pu sorption is low and is affected by plutonium hydrolysis. The most effective Am absorbers were NM-PAN or TiO-PAN. With NM-PAN absorber as column bed, Am could be removed from the solution (5 $\text{g}\cdot\text{L}^{-1}$ boric acid at pH = 5.8 and volume of 3,500 BV) with decontamination factor $D_f = 10^5$.

As presented above, different applications of composite ion exchangers (absorbers) for the concentration and separation of radionuclides were demonstrated to be useful and many additional applications were presented elsewhere [17, 18, 22]. The universal procedure for their production enables preparation of absorbers “tailored” for practically any aqueous waste stream contaminated with radionuclides or other toxic contaminants; the materials are prospective also for different radioanalytical purposes. Also, preparation of solid extractants containing extraction agents (with or without a diluent) impregnated onto the B-PAN beads of neat polyacrylonitrile has been demonstrated.

3.2.3 Minor actinides separation from ILW

Elevated activities of minor actinides, among them ^{241}Am , can be expected in boric acid containing light water reactor (LWR) based NPP evaporator concentrates in case of emergency, such as e.g. fuel cladding damage. The presence

Table 2. Chemical composition of the used boric acid containing evaporator concentrate

Component	Concentration
H ₃ BO ₃	74.2 g·L ⁻¹
Cl ⁻	2 g·L ⁻¹
(CO ₃) ²⁻	10.8 g·L ⁻¹
NH ₃	21.6 mg·L ⁻¹
Mn	130 mg·L ⁻¹
CHOC-Cr	2.8 g O ₂ ·L ⁻¹
(NO ₃) ⁻	52.8 g·L ⁻¹
(SO ₄) ²⁻	3.5 g·L ⁻¹
(NO ₂) ⁻	3.2 g·L ⁻¹
Oxalates	1.5 g·L ⁻¹
Citrates	1.2 g·L ⁻¹
Na ⁺	46.8 g·L ⁻¹
K ⁺	5.6 g·L ⁻¹

of alpha-emitting radionuclides then disqualifies the waste for disposal in near-surface repositories. Therefore, reliable and effective method for ²⁴¹Am separation from boric acid containing medium was developed. The targeted emergency evaporator concentrates contain not only the primary circuit cooling solution, but also decontamination solutions, laundry waste-waters, laboratory waste-waters and so on. Moreover, their high pH (ca 11) and salinity also complicates the separation process.

3.2.3.1 Process requirements and design

In addition to the studies involving composite inorganic-organic absorbers mentioned above [35], extraction chromatography was the method of choice for a more detailed study as several resins were reported prospective for americium separation [36-38]. Among those, DGA Resin (TrisKem International), containing the N,N,N',N'-tetraoctyldiglycolamide (TODGA) extractant on an inert support, showed good separation properties for americium at wide pH range including the possibility of elution [39]. This is

why DGA Resin and DGA Resin-like materials were used in this study. Specifically, TODGA-PAN extraction-chromatographic resin comprising TODGA-impregnated PAN beads (developed and prepared at the DNC [40]) was utilized. Real boric acid containing evaporator concentrate from the Dukovany NPP (Czech Republic) with pH 11.3 was used throughout the study (Table 2).

Introductory experiments performed revealed that pH and salinity of the concentrate has to be adjusted to achieve efficient uptake of americium by TODGA-PAN. As optimal parameters, pH 2.1–2.3 and 40% dilution of concentrate were determined. Such dilution enabled to increase 12-times the volume of the solution processed by the same amount of the solid extractant [41]. For the experiments, the solution was spiked with ²⁴¹Am.

3.2.3.2 Experimental results and conclusions

The kinetics of ²⁴¹Am uptake by the solid extractant was studied in batch experiments performed at volume-to-mass ratio (V·m⁻¹) equal to 250 mL·g⁻¹. Filtration by a glass microfiber filter Whatman GF/A was used to separate the filtrate from the solid extractant.

The kinetic experiments revealed that not only kinetics of the process is very fast, but also TODGA-PAN is even faster than the commercial DGA Resin. About 97% of americium uptake has been reached after half an hour of phase contact with TODGA-PAN, while DGA Resin needed three times higher time to reach the same result.

For the determination of the TODGA-PAN practical sorption capacity, breakthrough curves were measured in column experiments. Small columns filled with 0.24 mL of TODGA-PAN were used; the flow rate was maintained at 2 BV per hour. For the elution experiments, the loaded column was washed with boric acid solution acidified with nitric acid to pH 2.1–2.3. Then, the bound americium was stripped with 0.25 M oxalic acid solution; the reverse direction of flow, that rated also 2 BV per hour, was used. In all column experiments, alpha-spectrometry was used in parallel to the LSC counting. Sources for alpha-spectrometry

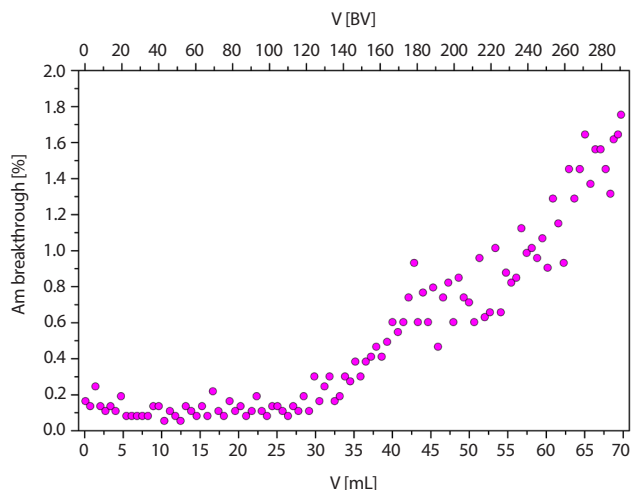


Fig. 5. Breakthrough (a_{out}/a_{in}) of americium through a column of TODGA-PAN solid extractant (grain size 0.3–0.8 mm) as a function of the volume of the treated 40%-diluted real evaporator concentrate (a_{out} , a_{in} — ^{241}Am activities at the column outlet and the inlet, respectively; pH = 2.2; BV = 0.24 mL; flow rate 2 BV·hr⁻¹).

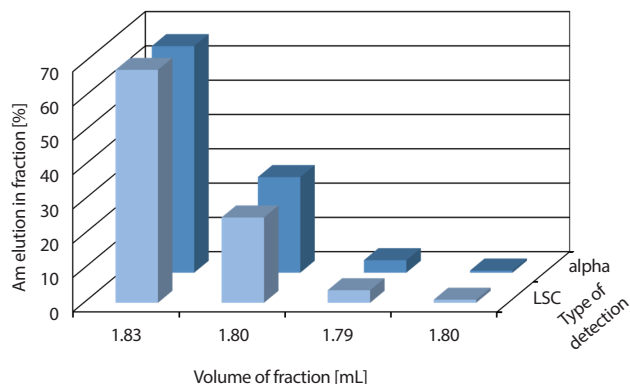


Fig. 6. Elution profile of americium from a column of TODGA-PAN solid extractant (grain size 0.3–0.8 mm) by 0.25 M oxalic acid solution as a function of the volume of the eluant (BV = 0.24 mL; reverse flow rate 2 BV·hr⁻¹).

were prepared by electrodeposition using sulfate-oxalate electrolyte according to Lee et al. [42].

The breakthrough curves measured revealed that more than 200 BV of the feed solution can be treated until the breakthrough of americium exceeds 1% (Fig. 5). The elution profiles measured (Fig. 6) demonstrated a very fast and efficient americium elution from the loaded TODGA-PAN

Table 3. Repeatability of americium elution (E) from a column of TODGA-PAN solid extractant (grain size 0.3–0.8 mm) by 0.25M oxalic acid solution (BV = 0.24 mL; reverse flow rate 2 BV·hr⁻¹)

# of experiment	E [%]
1	98.3 ± 0.3
2	101.3 ± 1.4
3	99.5 ± 1.3
Total	99.7 ± 2.2

column—almost 93% of ^{241}Am could be eluted in the first 3.6 BV of the eluant and the overall elution efficiency reached 99.7 ± 2.2% (Table 3) by as little as 7 BV of 0.25 M oxalic acid solution. Given the results, a very good repeatability of the method can be proclaimed.

Overall, the results achieved allowed to conclude that an efficient, robust and repeatable method for americium separation from boric-acid containing LWR-based NPP evaporator concentrate has been developed.

3.3 Safety studies of the near-surface repository of LLW and ILW

This section describes the mathematical model of radionuclide transport dedicated to safety studies of the near-surface repository of LLW and ILW. Modelling radionuclide transport from nuclear waste repository to the biosphere is not a new problem, it has been solved since the 1970s (e.g. [43-45]). The presented model is in accordance with previous models, adopted for implementation in GoldSim and the specific conditions of the Richard repository managed by the Czech Radioactive Waste Repository Authority (SÚRAO).

A radioactive waste repository is a multibarrier system which shall prevent migration of radionuclides from the disposal chamber to the biosphere. The multibarrier system consists of engineered barriers, such as: waste form or matrix, canister, backfill, and natural geological barriers provided by the host rock. The migration of radionuclides in this environment involves complex transport processes

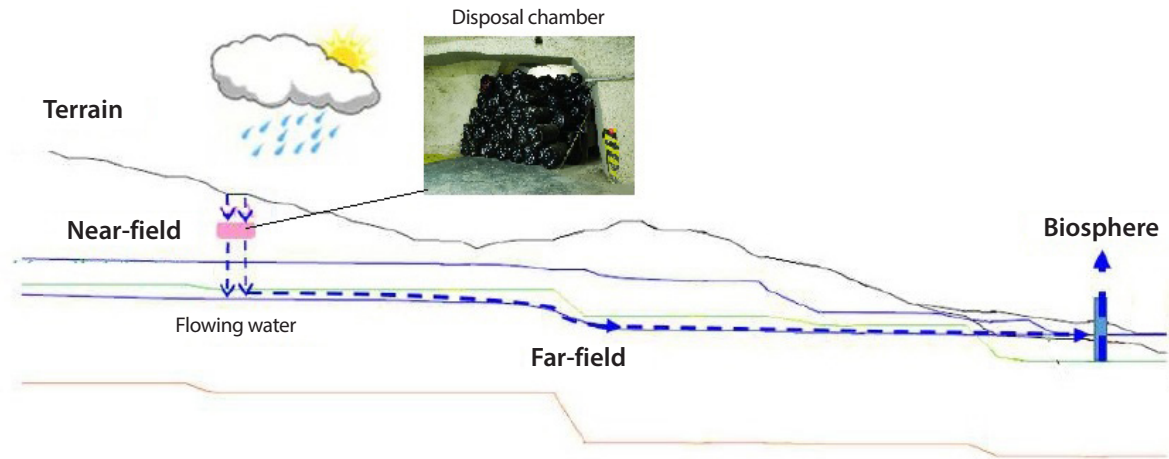


Fig. 7. Scheme of repository conceptual model (adopted from [46]).

which take place in the heterogeneous environment. Considering all these complexities, computationally feasible mathematical models cannot cover all these details, the simplifications are needed. The conceptual model will be described following a top-down modelling methodology. Then, the description will follow with the implementation of the conceptual model within the GoldSim programming environment. The uncertainty in the determination of model parameter values shall be propagated through the model to evaluate the uncertainty in the monitored model outputs. To this end, the methods of uncertainty and sensitivity analysis are also briefly introduced. The model performance is demonstrated on the normal scenario of Richard repository development.

3.3.1 Conceptual model

The repository can be divided into three main parts (Fig. 7): the near-field, the far-field and the biosphere. The near-field is the part of repository that consists of the waste form, engineered barriers and the surrounding host rock that is affected by repository construction and waste emplacement. The far-field is formed by the rock massif between the near-field and the biosphere which can be identified with the area in the landscape that could be contaminated by radionuclide-containing groundwater or surface water

originating from the repository.

The radioactive waste is put into barrel and solidified by concrete [46]. The barrels are placed in a disposal chamber with stabilized walls, the empty space between barrels is filled with concrete of higher strength class than used for barrels and walls. The barrel itself is not considered as an engineered barrier because its lifetime is estimated at only fifty years. From the geometrical point of view, the near field is modelled as a three-layer axially symmetric body with the axis horizontally oriented in a rock environment. The inner layer is considered as a homogeneous mixture of radioactive waste and concrete, the middle layer is made of concrete of a higher strength class, and the outer layer represents stabilizing concrete with a thickness of 0.1 m and of the same properties as in the inner layer. It is assumed that the repository is located above the groundwater level. After repository closure, the presence of water will be possible only from free infiltration of rainwater through the overlying layers of the geological environment. It is conservatively assumed that fractures will occur in concrete layers from the beginning during the setting of the concrete mixture. Later, other fractures can also be caused by seismic events or accidents, but mainly by gradual degradation of concrete due to carbonization.

The basic transport mechanisms in the near field are

advection and diffusion, the main retardation processes are solubility and sorption. Transport of radionuclides is considered only in the liquid state, transport of radionuclides in solid and gaseous states is not expected, although the formation of gases cannot be ruled out. Transport in the gaseous state is not considered due to the large thickness of the rock mass above the disposal chamber. Continuous fractures passing through the entire disposal chamber form pathway for advective flow, intact parts of concrete and unconnected fractures allow only the diffusion of radionuclides.

The following hydraulic processes are assumed for the far-field model: infiltration of rainwater from the repository area to the saturated zone of hydraulic collector, and transport of radionuclides by flowing groundwater to the surface, where the contaminated groundwater is taken to the biosphere. The basic transport mechanisms in the far-field are advection and dispersion, the transport is modelled only in a liquid state. The main retardation processes are diffusion into and sorption on a rock matrix.

In the biosphere model, a simple food chain is assumed, in which inhabitants consume local agricultural crops irrigated by ground water pumped from contaminated well, and livestock feed by contaminated water. The same extent of land use by inhabitants is assumed as today. A direct intake of water from contaminated well by inhabitants is conservatively assumed; a standard daily water intake for an adult resp. A child is considered. The use of contaminated water for industrial purposes is not considered.

3.3.2 Mathematical model

The mathematical model of radionuclide transport was implemented within a GoldSim programming environment. The near-field is modelled using a finite volume approach, the body of near field model is divided into 500 cell pathways (CP), which are one of pathway elements provided by GoldSim [47]. The network of CPs is shown on Fig. 8. The red arrows indicate the direction of diffuse transport to flowing water in fractures and into the surrounding

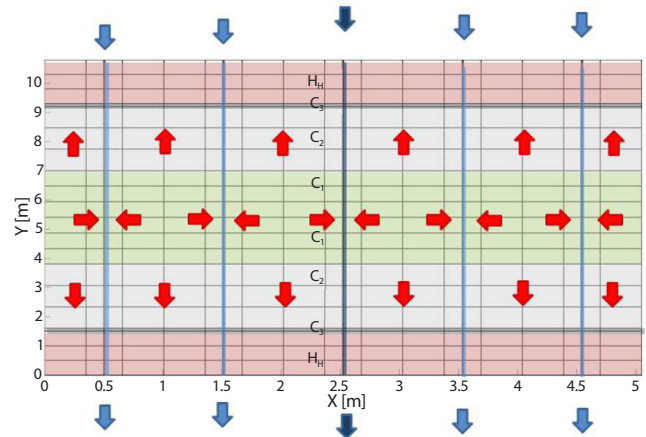


Fig. 8. Network of Cell Pathways used in the near-filed model. C₁ (green-gray) represents a mixture of radioactive waste and concrete; C₂ (light gray) indicates a middle layer filled with concrete of a higher strength class, C₃ is outer layer made of concrete; and H_H (orange) represents rock, (blue) fractures with flowing water (adopted from [46]).

environment, dark blue arrows indicate flow of water in fractures, which are present from the beginning of the simulation, and light blue arrows the flow that occurs during the simulation. The increasing number of fractures is modelled by gradually increasing diffusion areas between the boundary CP layers C₁, C₂, C₃, H_H and CP representing fractures. CP behaves as a mixing cell, in which the mass of each radionuclide is instantaneously and completely mixed and equilibrated among all CP's media [47]. The mass balance equation for CP includes among others a radioactive decay, and advective and diffusive mass transfers. The monitored output from the near field is the total outflow of activity, which is calculated in the model as the sum of the activity outflows from all five fractures.

Transport in the far field was modelled using a chain of three pipe pathways (PP), which is illustrated on Fig. 9. PP is another type of pathway element available within GoldSim that is intended to represent a fluid conduit [47]. The concentration in the mobile zone of PP is governed by the partial differential equation which accounts for radioactive decay, advection and dispersion in the direction of flow, and diffusion and sorption into the rock matrix, in the direction perpendicular to the flow. The solution algorithm for PP

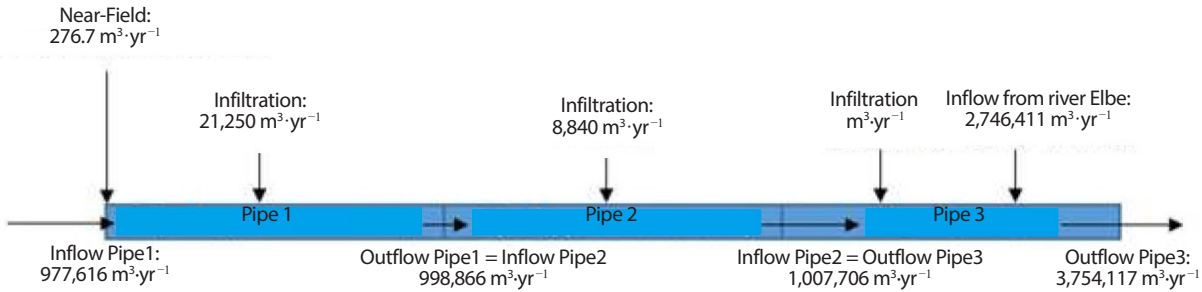


Fig. 9. Scheme of the far-field model showing inflows and outflows from different sources (adopted from [46]).

differential equation is based on the Laplace transform. As a consequence, unlike CP, the solubility constraint cannot be imposed in PP as it represents a linear system. Parameters of each PP were adopted to mimic the results of detailed hydrogeological model. The monitored output of far field model was the volumetric activity at the end of Pipe3.

The biosphere model calculates the dose rates to a representative person ($\text{Sv}\cdot\text{yr}^{-1}$). The model sums doses from three contamination pathways: inhalation, irradiation, and ingestion. The model assumes that main source of those pathways is a soil which is irrigated by contaminated water of the Pipe3 volumetric activity, and that the activity accumulates in soil. Radionuclide activities per soil mass are calculated using a first order differential equation, the rate of change of activities is determined by difference between irrigation intake and effective decay of radionuclides.

The probability analysis provides a quantitative estimation about spread of monitored outputs due to uncertainties in input parameters. The sensitivity analysis aims at identifying those input parameters that are main sources of monitored output variability [48]. Both analyses were performed within a single set of simulations, in which uncertain input parameters were firstly sampled, then monitored outputs for several combinations of input parameters were calculated, and finally, the model outputs were sorted and analysed. In parallel, two methods for probability and sensitivity analysis were used, one based on interval analysis, the other based on decomposition of variance [49].

3.3.3 Results, discussion and conclusions

The implemented model is flexible, an inventory and most of model parameters are entered via an external Microsoft Excel sheet which can be modified by the user. GoldSim has been optimised for probabilistic simulations which require low cost-consuming computational algorithms to allow for many model runs. The model run on a common PC (2.4 GHz CPU) requires in maximum tens of minutes.

The normal scenario of repository development supposes that the representative person from the group of adults and children drinks water from contaminated wells and consumes plant and animal food from the local agricultural production using water from the same contaminated wells to irrigate crops and feed animals.

The total activity outflow from the near field is depicted in Fig. 10(a), the inventory used in the simulation corresponds to the normal scenario considered in [46]. The maximum activity comes from tritium which belongs to non-sorbing radionuclides. The maximum of outflow is reached almost instantaneously. Because of relatively short tritium half-time its dominance disappears after one hundred years. The volumetric activity at the end of Pipe3 is shown in Fig. 10(b). The maximum of tritium activity is delayed by about 80 years, the delay of strongly sorbing radionuclides is larger than hundreds of thousands of years due to sorption to the rock matrix. The total dose is on Fig. 10(c). The main contributor to it is ^{36}Cl and ^{129}I .

To summarize, it can be concluded that a mathemati-

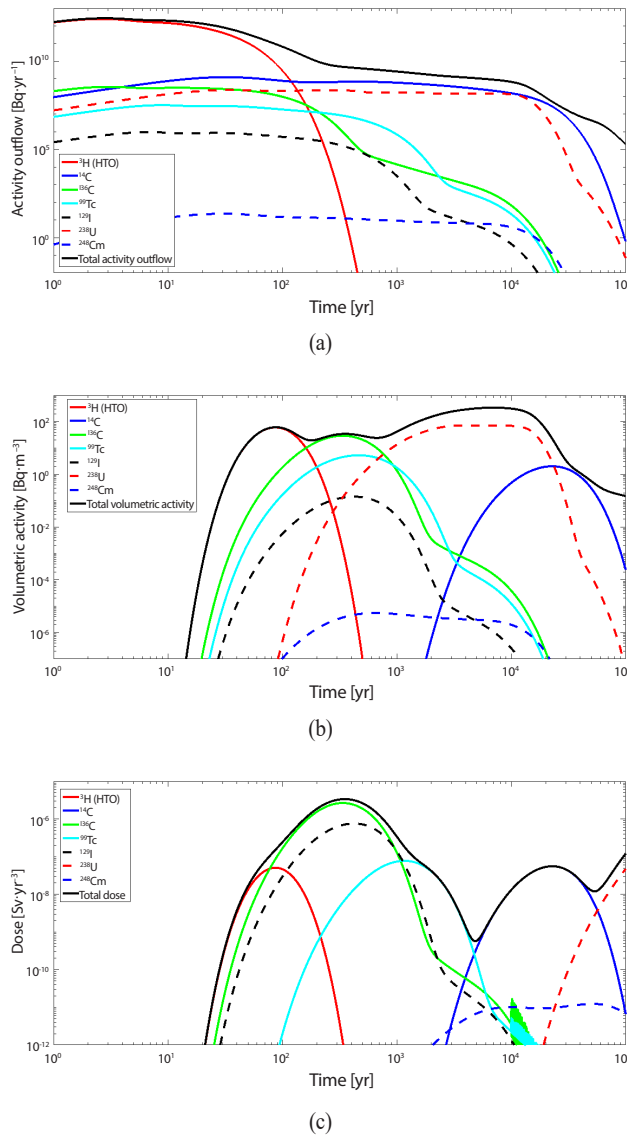


Fig. 10. Results of numerical simulation for the normal scenario of repository development at three model monitoring locations.

cal model of radionuclide transport was developed to evaluate the safety of the near-surface repository of LLW and ILW. It has been shown that developed model is an adequate numerical tool to estimate total dose rates to the representative person under various scenarios [46], even though many simplifying assumptions were used in creating the model. The model developed provides results comparable to the previous study [50]. Our approach to

model radionuclide transport using GoldSim environment has been validated by comparing the simulation results of benchmark tests with other modelling groups [51, 52] and by modelling experimental data of in situ experiments [52]. This gives us confidence in the calculated data. The innovations of developed model lie in a more detailed representation of the near field and model complexity as it includes in one model all three parts of radionuclide transport: near field, far field and biosphere. Therefore, it can be concluded that the GoldSim programming environment provides suitable framework for modelling of advanced transport phenomena. Further development of the model is foreseen.

4. Summary and concluding remarks

Within this paper, recent and on-going research activities in decontamination for decommissioning, treatment, and disposal of low- and intermediate-level radioactive waste at the Department of Nuclear Chemistry of the Faculty of Nuclear Sciences and Physical Engineering at the Czech Technical University in Prague are presented. The scene is set by the presentation of joint European efforts carried on and supported within the “nuclear fission and radiation protection” part of the Euratom Programme—a complementary research programme for nuclear research and training under Horizon 2020. Broad multi-partner projects PREDIS, EURAD, and SHARE are briefly introduced.

The research in the field of novel principles and processes for the decommissioning decontamination of metallic waste such as NPP primary circuit components yielded new data on the options for corrosion layer components, such as spinels, dissolution. The possibility of separation of radionuclides from spent decontamination solution and regeneration of the persulfate for re-use was successfully demonstrated.

Very broad activities are described for the pre-disposal management of liquid radioactive waste. New method for treatment of the secondary waste from the decontamination

procedures has been demonstrated. This two-step method is based on solvent extraction of radionuclides into ionic liquid followed by electrodeposition of the radionuclides directly from the ionic liquid phase that can be then re-used. The properties of composite inorganic-organic absorbers with polyacrylonitrile (PAN) binding matrix that render the powdered or microcrystalline inorganic absorber applicable in packed-bed columns are briefly reviewed. Several recent pilot- to full-scale applications of these materials are described. Next, a method developed for ^{241}Am separation from the boric acid containing light water reactor (LWR) based NPP evaporator concentrates in case of emergency, such as e.g. fuel cladding damage, is described. Using the TODGA-PAN solid extractant, more than 99% of americium could be separated from more than 200 bed volumes (BV) of adjusted real concentrate. Quantitative elution of americium from the loaded solid exchanger is possible by as little as 7 BV of the 0.25 M oxalic acid eluant.

As a part of the safety studies of the near-surface LLW/ILW repository a mathematical model of radionuclide transport was developed and implemented within the GoldSim programming environment. On a specific case of Richard repository (Czech Republic), it has been demonstrated to be an adequate numerical tool [50-52] not only to model the transport but even to estimate total dose rates to the representative person under various scenarios [46].

The studies in all the fields mentioned above are and are expected to be going on even in the foreseeable future since the Czech Republic, as a nuclear country producing currently 35% of electricity in its two nuclear power plants, must be responsible for safe and economic pre-disposal management and disposal of its radioactive waste. A vast majority of the recent and ongoing studies has been carried on within the broad multi-partner joint European projects.

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