Deliverable 4.5
Report on secondary waste management
Date 30.4.2024 version Final

Dissemination level Public

Kateřina Čubová

Czech Technical University in Prague
Brehova 7, 115 19 Prague 1

katerina.cubova@fjfi.cvut.cz
tel.: +420771276701

Project acronym PREDIS	Project title PRE-DISposal management of radioactive waste	Grant agreement No. 945098	
Deliverable No. D4.5	Deliverable title Report on secondary waste management		Version Final
Type Report	Dissemination level Public		Due date M44
Lead beneficiary Czech Technical University in Prague (CTU)			WP No. 4
Main author Kateřina Čubová, CTU	Reviewed by Abdesselam Abdelouas, IMT, WP4 Leader	Accepted by Maria Oksa, VTT, Coordinator	
Contributing author(s) Mathurin Robin, Tomo Suzuki and Abdesselam Abdelouas, IMT Atlantique			Pages 21

Abstract

This Deliverable 4.5 „Report on secondary waste management" summarizes output of the Task 4.3 „Development and optimization of decontamination processes" aiming on treatment of radioactive waste. During the project, two different fields focused on developing and optimising decontamination processes, recycling and secondary waste minimisation were studied.

The first part is dedicated to the development of the process for the decontamination and treatment of radioactive liquid effluents, in particular those generated during the chemical decontamination of metal alloys. The primary goal of this study was to develop and optimise a precipitation protocol that can be adapted to the effluent produced during the COREMIX process. This precipitation protocol should make it possible to reduce the amount of resin needed to decontaminate contaminated wastewater while concentrating the radioactivity into the solid phase, which should reduce disposal costs.

The second section aims at optimization of the process developed for the regeneration and reuse of contaminated effluents with the use of ionic liquids. Due to the enhanced selectivity the use of ILs in liquid-liquid extraction seems to be very promising way for the separation of metals and radionuclides in the solutions resulting from the processes of decontamination and decommissioning or treatment of an industrial waste. Liquid-liquid extraction of the metals and the radionuclides of interest was studied, the screening of the optimum extraction parameters was carried out. The main aim was to find the optimum conditions for the extraction of radionuclides of interest from model decontamination solutions containing organic complexants like oxalic (H_2Ox) and citric (H_3Cit) acids to ionic liquid medium.

Both of these methods seem to be promising in the field of waste treatment and minimization and worth further research, development and potential application. The main results obtained from both fields are described in the report.

Keywords

Secondary waste, waste management, decontamination, recycling, waste minimisation

Notification

Acknowledgement

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1   Introduction

Any decontamination process always generates large volumes of the secondary waste containing the removed contaminants. The main part of this type of waste is usually represented by liquid waste containing low amount of the radioactive substances (usually types of ILW or LLW) but its volume is rather large. Technologies for the treatment of such liquid radioactive wastes are therefore focused on removing radionuclides from the bulk of the liquid and to concentrate the radioactivity into a small volume for subsequent conditioning and disposal. Many various mechanical, chemical or electrochemical methods have been proposed for this purpose. They range from non-aggressive techniques that use only simple tools and water, to very complex and expensive processes which demand complicated devices and/or toxic chemicals, but all of them generate secondary waste containing the removed contaminants. Therefore, strong demand for new technologies enable to remove the radionuclides and recycle the residue is required especially from the industrial fields. Resulting procedure would enable to reduce negative impact on the environment coming from related chemical processes. In addition, needs for money-savings coming from economics have to be considered as well.

Two different approaches to solving this problem are described in the report. First one is based on developing and optimisation of the precipitation protocol that can be adapted to the effluent produced during the COREMIX process. This precipitation protocol should provide a mean of reducing the quantity of resin required to decontaminate contaminated effluent, while concentrating the radioactivity into a solid phase, thereby limiting disposal costs while fulfilling waste acceptance criteria requirements.

Second approach is focused on liquid waste minimization by solvent extraction process enhanced with the use of ionic liquids - compounds that can be widely used in many applications and which properties can be adjusted for the specific usage. In the solvent extraction, ionic liquids can be designed as extractant or can be also used as the alternative to traditional volatile organic solvents. Main emphasis is put on recycling of chemicals and media used and potentially also possible separation and concentration of radionuclides for further use. Two-step separation method consisting of extraction of radionuclides from the decontamination solutions by using the ionic liquids, followed by the separation of radionuclides from ionic liquids by electrodeposition was proposed.

2   Development of a decontamination process for metallic radioactive effluents using precipitation

This section is dedicated to the development of a process for the decontamination and treatment of radioactive liquid effluents, in particular those generated during the chemical decontamination of metal alloys. The main results obtained on different types of samples (synthetic, surrogate and active) and the different optimisations carried out are presented here.

2.1   Context and objectives

During maintenance and dismantling, a significant amount of waste is generated, primarily consisting of metal alloys. Steam generators, in particular, can contain several tonnes of waste, the majority of which is classified as Low-Level Waste (LLW) or Intermediate Level Waste (ILW) due to the deposition and migration of radionuclides from the primary circuit into the metal. Therefore, these metal parts require decontamination prior to packaging and dispose of in accordance with the standards applicable to each type. To meet these challenges, various decontamination methods have been developed and implemented. These include chemical decontamination techniques that dissolve the metal oxide layer on the surface of radioactive materials.

The COREMIX process (Chemical Oxidation Reduction using Nitric Permanganate and Oxalic Acid MIXture), is a sequence of alternating steps designed to achieve this chemical decontamination. It is based on the established CORD process, which has been proven effective in decontaminating radioactive metal surfaces. In this two-step process, the chromium oxide layer is first oxidised by the addition of permanganate ions (MnO_4^-), and then oxalic acid is added to reduce these ions and dissolve the iron and nickel present in significant quantities in the oxide layer [1,2]. Deliverable 4.3 provides details of the COREMIX process and how it differs from the CORD process.

This process produces a significant amount of radioactive effluent that also needs to be decontaminated. To treat this type of effluent, the common approach involves the use of ion exchange resins. However, they can be prohibitively expensive due to their specificity and the complexity of the effluents, which typically contain many metals and radionuclides ([54]Mn; [55]Fe; ^{60}Co; [63]Ni; [65]Zn; [144]Ce and more). One of the ways to reduce the amount of resins, and therefore the cost of treatment, is to pre-treat liquid waste upstream with, for example, a precipitation step. In this reaction, a precipitating agent is added to the effluent solution, resulting in the formation of insoluble metal precipitates. The equation with the example of iron hydroxide precipitation is shown below.

$$Fe^{3+} + 3OH^- \leftrightarrow Fe(OH)_{3(s)}$$
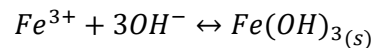
The main objectives of this study are therefore to develop and optimise a precipitation protocol that can be adapted to the effluent produced during the COREMIX process. This precipitation protocol should provide a mean of reducing the quantity of resin required to decontaminate radioactive effluent, while concentrating the radioactivity into a solid phase, thereby limiting disposal costs. The development of this pre-treatment step will be carried out in accordance with current waste acceptance criteria (WAC) and will also be the subject of an environmental cost analysis (LCA) detailed in milestone MS16 of the WP2.

2.2 Optimisation of the precipitation process

Firstly, there are a large number of possible precipitants for removing metal cations in aqueous solution (hydroxide, sulphide, phosphate, oxalate, fluoride and many others). Secondly, it is necessary to adapt to the main cations present in the solution to be decontaminated in order to obtain optimum precipitation efficiencies. In the case of radioactive effluents from the COREMIX process, the main metals are iron, nickel, manganese and chromium, most of which come from the metal base of the contaminated material. Additionally, specific radionuclides should also be considered, such as ^{60}Co or [144]Ce as they contribute to the contamination of metal components. It's essential to consider the toxicity of the reagents must be considered when selecting the precipitant, as well as waste acceptance criteria and environmental standards.

All these criteria point in the direction of metal hydroxide precipitation. The reagents (NaOH, KOH, etc.) used to produce these precipitates are inexpensive, not very toxic to the environment and their effectiveness has already been proven on several types of solutions and metals [3,4].

2.2.1 pH

One drawback of metal hydroxides is their high dependence on pH. Their solubility varies considerably over narrow pH ranges. This is shown in Figure 1, representing the theoretical solubility values of various metal hydroxides as a function of pH using the geochemical Phreeqc software.
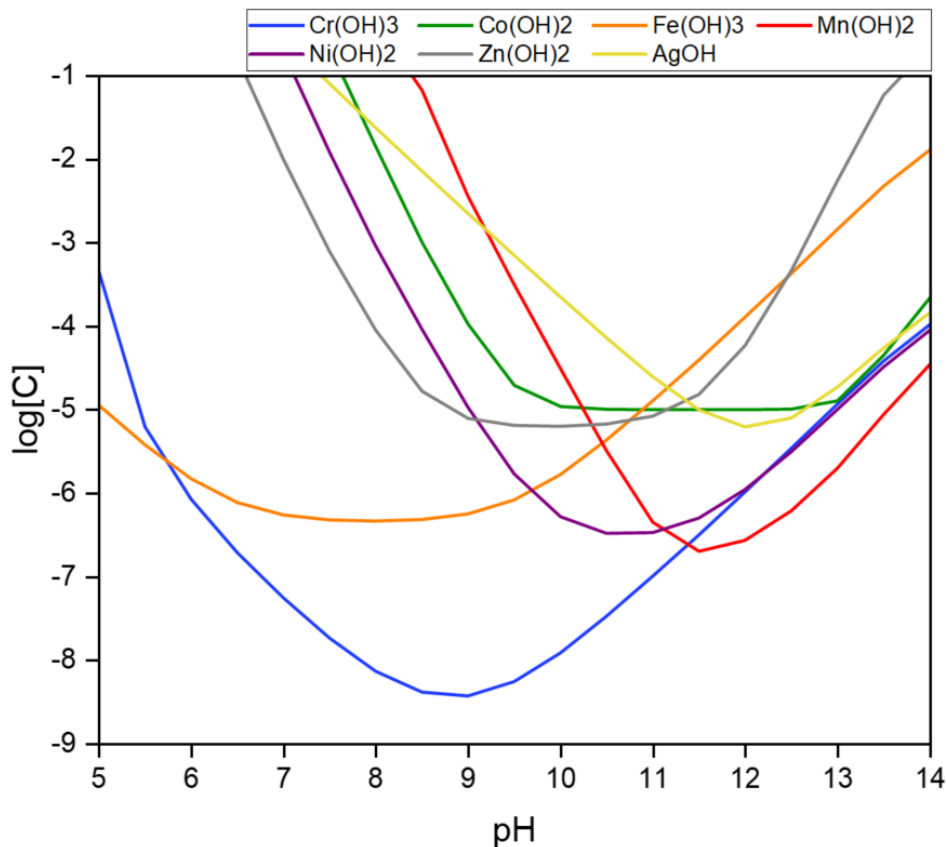
Figure 1: PHREEQC solubility modelling of several metal hydroxides as function of pH

As shown above, the modelled metal hydroxides have solubility minima at different pH values, ranging from pH 7-8 for iron to pH 12 for silver and cobalt. It is therefore not possible to precipitate all metal cations at a single pH. For this reason, pH values of 8.5 and 12 were chosen in order to precipitate all the cations. The first precipitation at pH 8.5 removes iron, chromium and zinc, while the second precipitation at pH 12 removes nickel, manganese, cobalt and silver. The choice of these two pH values also makes it possible to precipitate other metals that may be present in small quantities, such as copper [5], lead [6] or cerium [7].

2.2.2   Solid characterisation

The two precipitates (pH 8.5 and 12) obtained using the developed precipitation protocol were dried and characterised using different analytical methods, with the following results:

1) Fourier-transform infrared spectroscopy (FTIR)
The FTIR spectra of the two precipitates are very similar and show the presence of unbound water molecules and hydrogen bonds between the molecules. In addition, iron-oxygen (Fe-O) bonds were observed in the precipitate obtained at pH 8.5 and manganese-oxygen (Mn-O) bonds in the precipitate obtained at pH 12. These results support the hypothesis that the sludge is a mixture of oxides and hydroxides.

2) Thermogravimetric analysis (TGA)
For further chemical characterization of the sludge, a thermogravimetric analysis was carried out from 20 to 950°C.
For the first precipitate (pH 8.5), a significant mass loss is observed as the temperature rises, corresponding to the loss of water molecules previously observed in the FTIR spectra. A reduction in heat flow around 200°C is also observed, which may be due to crystallisation from a hydroxide to

an oxide form. Finally, a characteristic peak of iron (structural transformation of iron oxide) is observed at 520°C, confirming the predominant presence of iron in the first precipitate.

For the second precipitate (pH 12), water loss is also observed as for the first precipitate. On the other hand, no change in heat flow observed, indicating that no crystallisation takes place during the temperature increase and that iron is not the main component. These observations lead to the hypothesis of a precipitate that can be in the form of oxide at room temperature.

3) X-ray diffraction (XRD)

The X-ray study of the sludge obtained was carried out after drying the sludge at different temperatures in order to observe its influence on the sludge crystallisation, and to confirm the observations made during the thermogravimetric analysis.

The diffraction pattern obtained on the solid at pH 8.5 shows a completely amorphous or nanocrystallised phase up to 200°C. These observations would be consistent with a hydroxide phase. After increasing the temperature to 400°C, characteristic peaks of iron oxide (Fe_2O_3, Fe_3O_4) are visible, confirming that crystallisation took place between 200 and 400°C, as observed in TGA.

For the solid precipitated at pH 12, the diffraction patternobtained are identical between 20 and 600°C. Many characteristic peaks of the manganese oxide Mn_3O_4 (or $MnO.Mn_2O_3$) are observed, as well as some other oxides such as Mn_2O_3 and Fe_3O_4. These results show that manganese is the main element precipitated at this pH and that it forms oxide compounds.

The results obtained using different analytical techniques confirm the hypothesis that the first precipitate obtained at pH 8.5 is mainly composed of iron hydroxide $Fe(OH)_3$ or oxo-hydroxide $FeO(OH)$, while the second precipitate obtained at pH 12 is mainly composed of manganese oxide Mn_3O_4. More details on the characterisation results (XRD, FTIR, TGA) are planned to be published [8].

2.2.3 Efficiency on synthetic sample

In addition to the aforementioned investigation, various parameters were studied, including the stirring time, the influence of the metal concentration or the choice of reagent used. The various tests carried out made it possible to establish a robust and operational protocol, applied on a synthetic sample representing the equivalent of one gram of nickel alloy dissolved by the COREMIX process. The sample was obtained by dissolving metal chlorides and nitrates in an acidic aqueous solution. In the first step of the protocol, potassium hydroxide (KOH) is added to the effluent until a pH of 8.5 is reached, allowing the precipitation of Fe, Cr and Zn. Stirring is maintained for at least 1 hour. Filtration or centrifugation (depending on the amount of sludge) is then required to separate the solid phase from the aqueous phase. Once the sludge has been removed from the solution, the pH is adjusted a second time by adding KOH until a pH of 12 is obtained to remove Mn, Ni and Co. A second filtration (or centrifugation) is then carried out to obtain the second precipitate on one side and an almost metal-free solution on the other [1]. The solution treated by the precipitation protocol is then analysed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) to determine the concentration of metal cations at each stage of the protocol (initial, pH 8.5 and pH 12). These results can be seen in Figure 2.
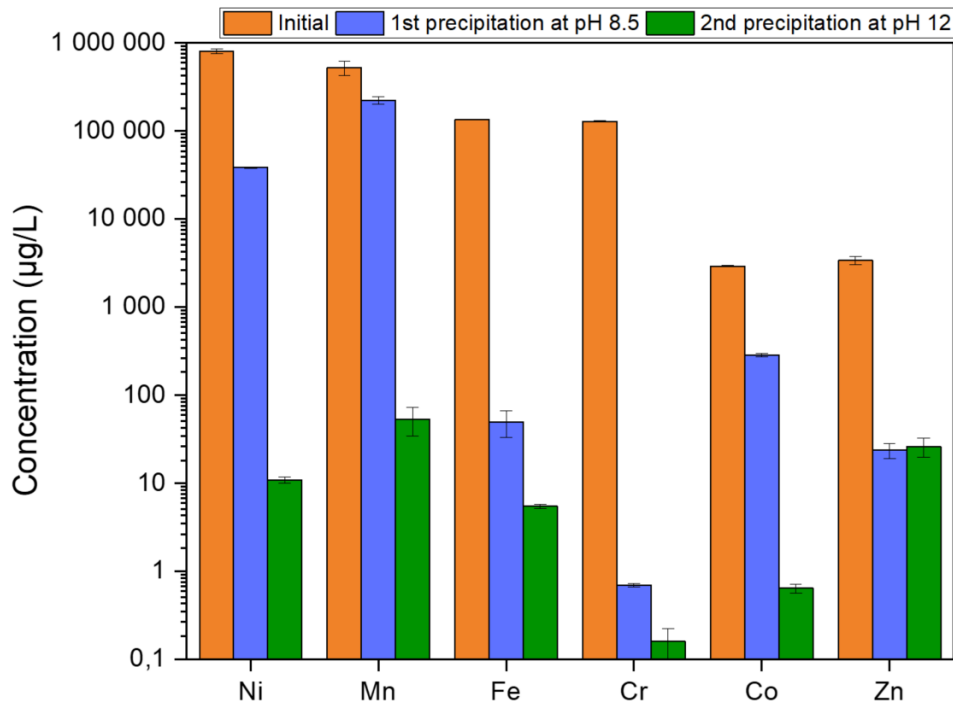
Figure 2: Metal concentrations after each stage of the precipitation protocol on a synthetic sample

Tests carried out on a synthetic sample show that two precipitations are required to remove all the metals in solution. Figure 2 shows a significant decrease in the concentration of Fe, Cr and Zn after the first precipitation at pH 8.5, while the other metals appear to be removed only during the second precipitation at pH 12, with a decrease in the concentration of Ni, Mn and Co. The protocol applied to this synthetic sample removed approximately 100% of the metals in solution, with an 84% reduction after the first precipitation at pH 8.5. Final concentrations ranged from 0.4 to 23 µg/L from initial concentrations of 2.3 to 840 mg/L. These results are in agreement with the data obtained when modelling the metal hydroxides shown in Figure 1.

2.3 Application to surrogate and complex samples

2.3.1 Efficiency on surrogate sample

After carrying out tests on a synthetic sample, the precipitation protocol was tested on an oxidized surrogate stainless steel sample treated by 3 cycles of the COREMIX process ($KMnO_4$ + $H_2C_2O_4$). The effluents generated during the cycles were pooled and treated according to the precipitation protocol presented above. The results of this test on a surrogate sample were compared with those obtained on a synthetic sample to observe any change in performance. Only the concentrations of Fe, Mn, Ni and Cr were compared as the other metals (Zn and Co) were not present in the original stainless steel sample. Table 1 compares the percentage of metals precipitated at the end of these two experiments and the overall efficiency of the precipitation.

*Table 1: Comparison of hydroxide precipitation efficiency (%) for two different samples*

	Ni	Mn	Fe	Cr	**Total**
Synthetic sample	100	100	100	100	**100**
Surrogate sample	100	100	100	49	**99**

The precipitation efficiencies for iron, nickel and manganese were identical, reaching 100% for both samples analysed. On the other hand, half of the chromium seems to remain in solution in the surrogate sample, since only 49% of it is found in the solid phase. However, the overall precipitation efficiency remains very high (> 99%) because the chromium concentration is much lower than iron and manganese concentration. Its effect on the overall efficiency is therefore very small.

The drop in the precipitation efficiency of Cr can be explained by the formation of highly soluble Cr-oxalate salts such as $Cr_2(C_2O_4)_3$ [8]. Indeed, the oxalic acid used in the reduction stage of the COREMIX process acts as a reductant for Cr(VI), converting it to Cr(III) in solution [9].

2.3.2 Oxalic acid destruction

To ensure a proper precipitation of chromium in solution, a preliminary oxalic acid destruction step has been developed prior to the precipitation protocol. To prevent the introduction of additional contaminants into the effluent, and in compliance with waste acceptance criteria, only hydrogen peroxide is required for the oxalic acid destruction stage. Several tests have been carried out to ensure and verify the complete destruction of oxalic acid. This stage requires the effluent to be heated at 80°C. Once this temperature reached, H_2O_2 is added and the solution is stirred for 48 hours while maintaining a temperature of 80°C. Hydrogen peroxide reacts with oxalic acid to form water and carbon dioxide according to the following equation:

$$H_2O_2 + H_2C_2O_4 \rightarrow 2CO_2 + 2H_2O$$
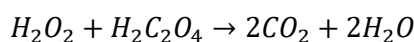
In addition, the presence of metals in solution, particularly Mn^{2+}, promotes the reaction by catalysis, as does Fe^{3+}, which acts as a reagent in the Fenton mechanism [10,11]. These two cations present in the effluent therefore allow oxalic acid to be rapidly destroyed without using UV light [12].

In order to demonstrate the influence of oxalic acid on chromium precipitation, the amount of chromium precipitated in the solid phase was measured according to different percentages of oxalic acid destruction and the results are shown in Table 2.

Table 2: Effect of oxalic acid destruction on chromium precipitation in solution

Oxalic acid destroyed (%)	Precipitated chromium (%)
0	49
90	84
100	100

According to the results obtained, the precipitation yield of chromium seems to be related to the amount of oxalic acid destroyed. Indeed, only 49% of chromium is precipitated when the oxalic acid is not destroyed, compared to 100% when it is completely destroyed by the addition of H_2O_2 at 80°C for 48 hours. An intermediate value of 84% precipitated chromium for 90% destroyed oxalic acid also confirms this hypothesis.

2.3.3 Test on complex sample

The tests were conclusive after the addition of an oxalic acid destruction stage prior to the precipitation stages, and a study was carried out on more complex samples containing more than twenty five different metals. To achieve this, the National Nuclear Laboratory (NNL) developed a

controlled boiling acid technique to produce SS-304 oxidised samples, replicating the conditions at the Sellafield reprocessing plant. Details of the process and the different metals used are given in Deliverable D4.4. These stainless steel samples were then treated by the COREMIX process through three cycles, and the resulting effluents were collected and combined to enable a full test of the complete precipitation protocol, including the destruction of oxalic acid, over a wide range of metal. The results obtained in Figure 3 show the measured concentrations of metals in solution in the original sample, after the first precipitation at pH 8.5 and after the second precipitation at pH 12. The measurements were performed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS).
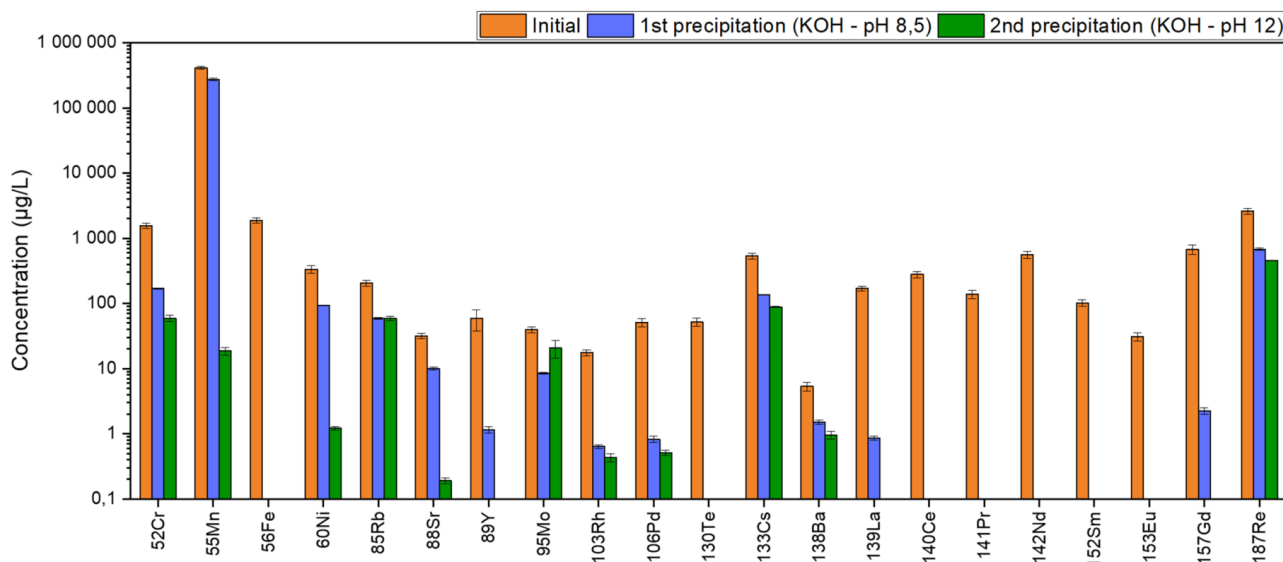

Figure 3: Liquid characterisation of the complex sample after each step of the precipitation protocol

Out of the 28 different elements initially present in the original stainless steel sample, only 21 could be analysed in the effluents generated. Some non-metallic elements (P, N, Na and K) require other analytical methods and their precipitation are not investigated here, while some metals (Al, Zr) require complex analytical matrices. Also for V, it was not detected in the effluents produced by the COREMIX process. The ICP-MS results show that certain transition metals (Cr, Fe, Y, Rh and Pd) precipitate preferentially at pH 8.5, as do most of the lanthanides (La, Ce, Pr, Nd, Sm, Eu and Gd). Tellurium is also one of the metals removed from solution at pH 8.5. The second precipitation stage, at pH 12, precipitates Mn, Ni and Sr. Fewer different metals are removed from the solution at this pH, but this stage remains important because of the high concentration of Mn that must be removed before conditioning. With the exception of strontium, the elements belonging to the alkali and alkaline earth families (Rb, Cs and Ba) were not removed from the effluent, or only to a very limited extent. This is also the case for Mo and Re. The remaining traces of metal cations in the effluent can be then removed by a purification step using ion exchange resins for example.

2.4   Discussions and perspectives

A hydroxide-based precipitation protocol has been developed and partially optimised in order to reduce the volume of effluent generated during the decontamination of metallic materials using the COREMIX process. The manipulations carried out on synthetic and surrogate samples allowed the establishment of a functional protocol for a large number of metals and radionuclides. The characterisation of the precipitates produced during the process shows that the sludge obtained at pH 8.5 differs from that obtained at pH 12. Indeed, the former contains a large amount of iron hydroxide $Fe(OH)_3$ or oxo-hydroxide $FeO(OH)$, whereas the latter mainly contains manganese oxide Mn_3O_4. This information will enable us to better adapt the future conditioning and storage stages for

these sludges. Approximately 100% of the metals in solution were removed from the treated effluent using this process, including metals present in large quantities such as iron, nickel and manganese. This significant reduction in metal concentration will allow the volume of ion exchange resin to be reduced by more than 99% for the metals mentioned [1].

Combined with the oxidation-reduction decontamination process, the oxalic acid destruction stage and the precipitation stage form a complete metal alloy decontamination process called COREMIX-HP (Chemical Oxidation REduction using nitric permanganate and oxalic acid MIXture with Hydrogen peroxide treatment and Precipitation). This complete process was also tested on a nickel alloy contaminated with ^{60}Co. The details of this experiment and the associated results will be the subject of a future publication [14].
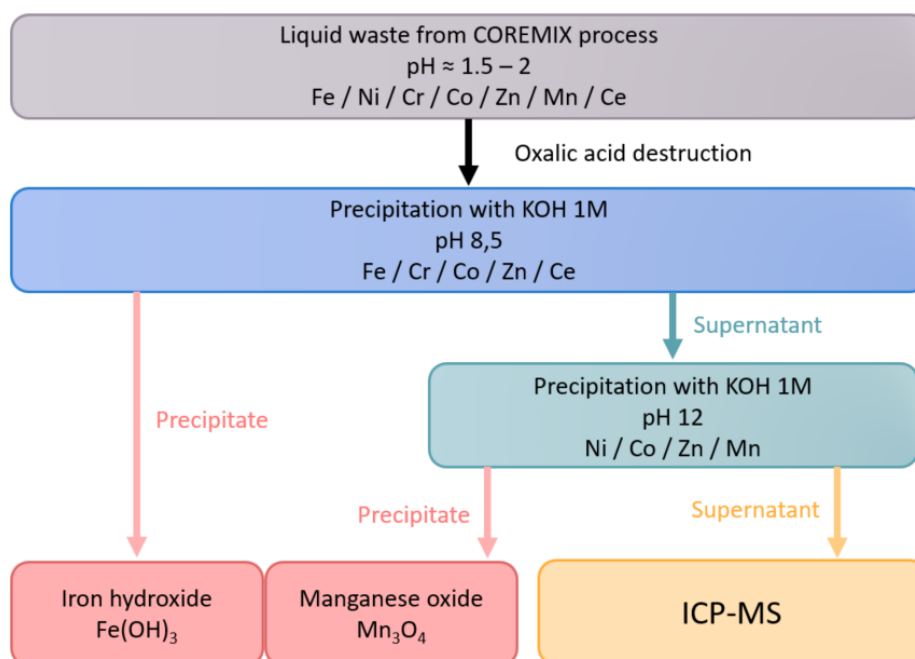

Figure 4: Optimised hydroxide precipitation protocol

The hydroxide precipitation process illustrated in Figure 4 offers several advantages when used to treat the liquid effluents produced by the COREMIX process. Firstly, it provides a cost-effective technique of removing radioactive metals from industrial effluents. In addition, the technique exhibits remarkable selectivity, allowing the precise extraction of specific metal ions while reducing the impact of other non-radioactive contaminants.

Other precipitation protocols are being developed to suit all types of effluent. Phosphates and sulphides can be used as alternatives to hydroxides for the treatment of more complex liquid wastes. In order to reduce the environmental impact of the COREMIX-HP process, a Life Cycle Assessment (LCA) study has been carried out and optimisations are currently being made to the oxalic acid destruction stage and the precipitation stages. In this way, the concentration of hydrogen peroxide (H_2O_2) tends to be reduced, as well as the heating time during the destruction of oxalic acid.

In addition, the precipitation of hydroxides by electrocoagulation is also being studied in order to limit the use of chemical reagents and salts (Na^+ or K^+), thus reducing the financial and environmental costs of the process. Finally, the COREMIX-HP process has been developed and implemented at laboratory scale. Scale-up tests are required to assess the feasibility of this process on an industrial scale.

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3   Optimization of treatment of secondary waste streams – Liquid waste minimization process based on application of Ionic Liquids

This section is dedicated to the optimization of a process for the decontamination and treatment of secondary radioactive liquid waste such as that generated during the chemical decontamination of metal alloys. The main results obtained with different radionuclides out are presented here.

3.1   Context and objectives

Chemical decontamination of nuclear facilities generates large volumes of low-level radioactive waste. Following worldwide efforts to reduce spent chemical reagents and radioactive waste volumes, new methods of regeneration and reuse of spent decontamination solutions are studied. The replacement of traditional volatile organic solvent by ionic liquids seems to be promising way for enhancing the extraction with the potential for their recycling and reuse and liquid-liquid extraction is one of possible ways for processing of low-level radioactive waste originating for example from decontamination processes.
Ionic liquids as compounds that can be widely used in many applications, are the object of many studies. Their properties can be adjusted for the specific usage. Many of them seems to be promising in the field of separation processes including solvent extraction. Ionic liquids can be designed as extractant or can be also used as the alternative to traditional volatile organic solvents [1-4].
Research was focused on liquid waste minimization by ionic-liquids-based processes. Main emphasis was put on recycling of chemicals and media used and potentially also possible returning of radionuclides for other use. Two-step separation method consisting of extraction of radionuclides from the decontamination solutions by using the ionic liquids, followed by the separation of radionuclides from ionic liquids by electrodeposition was proposed and tested [5,6].

The effect of solvent (chloroform, imidazolium or ammonium based ionic liquid) on radionuclide extraction was studied in wide range of pH values. Besides extraction into pure solvent, different extractants were used. Extraction efficiency varies depending on extracted radionuclide and its chemical properties. Representatives of activation products (Co, Fe) and fission products (Sr, Mo, Tc) were tested in this work.
For the first set of experiments ^{60}Co, ^{99m}Tc and ^{99}Mo were selected as the part of group of problematic radionuclides from NPP and institutional waste. Tc is also a representative of highly mobile anionic contaminants. ^{99m}Tc and ^{99}Mo can be taken as the analogues of problematic DTM nuclides ^{93}Mo and ^{99}Tc. As the simulants for decontamination solutions in the experiments oxalic (H_2Ox) and citric (H_3Cit) acids were used.

Suggested procedure:
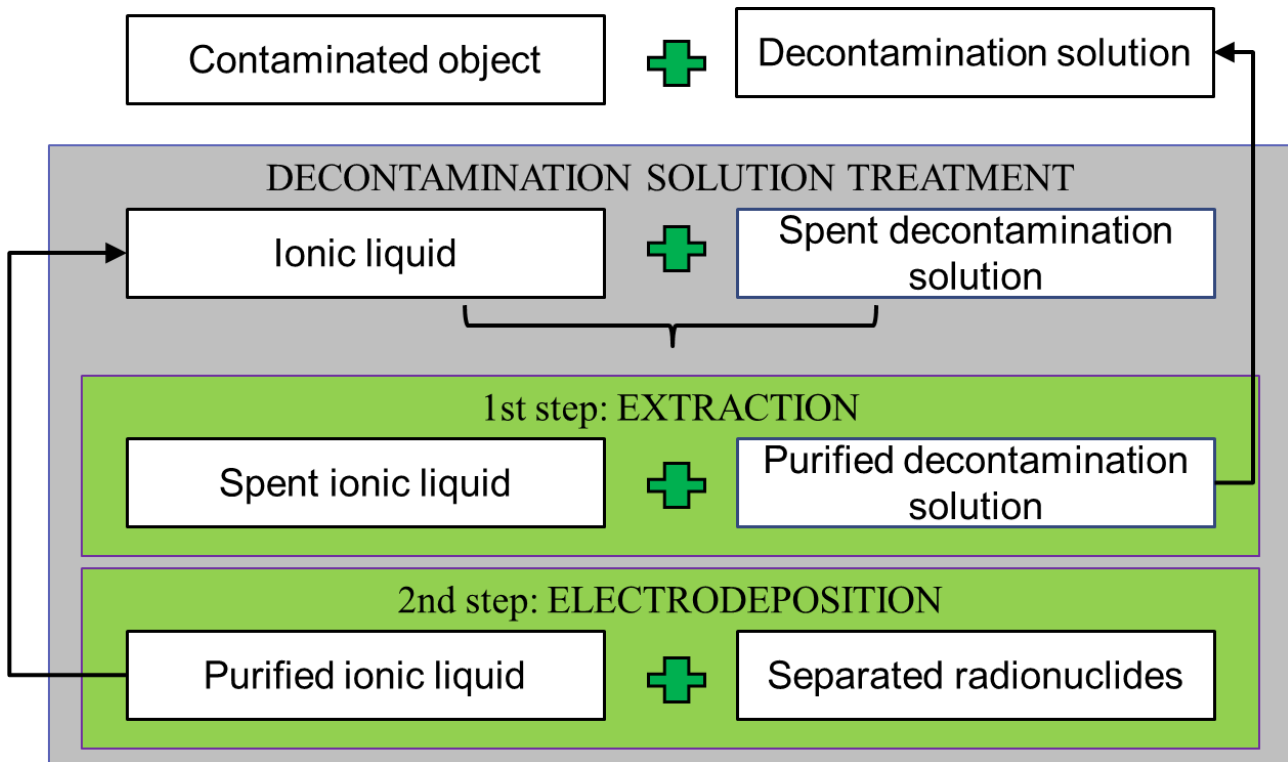
3.2 Extraction of cobalt

The ^{60}Co was chosen for the experiments as the representative of activation products. These experiments followed and complemented previous research on possibility of extraction metals into ionic liquids [5,6]. Five extraction reagents acetylacetone (AcAc), Di(2-ethylhexyl)phosphoric acid (DEHPA), Tributylphosphate (TBP), Aliquat 336 (A336), 2-theonyltrifluoroacetone (TTA), N-nitroso-N-fenylhydroxylamin) were selected to evaluate their suitability for extraction. These reagents were tested for miscibility / solubility in $[C_2mim]$ $[NTf_2]$. Based on the results, acetylacetone, TTA and N-nitroso-N-fenylhydroxylamin were selected for extraction experiments.

The cobalt extraction was performed from 0.001 M HNO_3 at pH 3 which approximately corresponds to the pH value of the oxalic H_2Ox and citric H_3Cit acids mixture that is commonly used in the decontamination solutions. For the selected reagent with the highest value of the distribution coefficient, the dependences of D on equilibrium pH of the aqueous phase and the concentration of the reagent were performed. The best extraction efficiency from 0.001M HNO_3 was achieved by the mixture $[C_4mim][NTf_2]$ with N-nitroso-N-fenylhydroxylamin, when the maximum determinable value of the distribution coefficient, D_{max}, was exceeded and thus it was selected for further measurement as the most suitable extraction reagent. Unfortunately, in further experiments, the solution of N-nitroso-N-fenylhydroxylamin in ionic liquid was shown to be unstable and therefore TTA in concentration of 0.10 mol/L was selected for the following experiments. The dependences on equilibrium pH of the aqueous phase and the concentration of the extractant were studied. From the results can be seen that from $pH_{eq} \approx 4$, more than 99% of cobalt is quantitatively extracted from the aqueous phase into the organic phase (Figure 5).
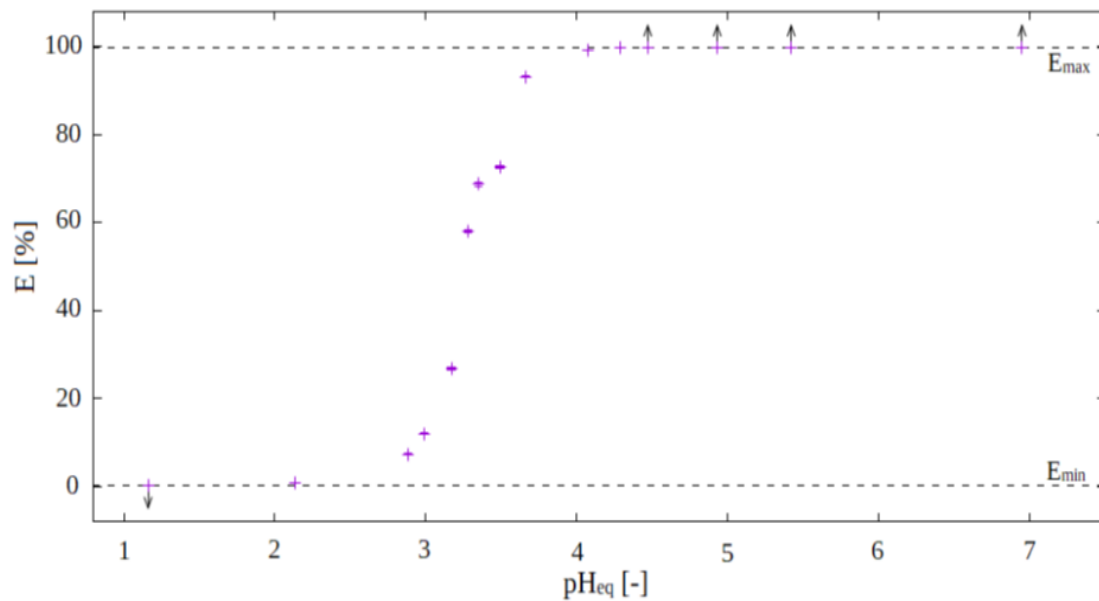
Figure 5: Dependency of the percentage of cobalt extraction on the equilibrium pH of the aqueous phase in the extraction of cobalt up to 0.10 M a solution of TTA in [C₄mim] [NTf₂]

3.3   Extraction of molybdenum

Screening experiments were performed also for ^{99}Mo, and as the extractant 8-hydroxyquinoline (8-HQ) was used. $[C_4mim][NTf_2]$ and 0.1M 8-HQ in $[C_4mim][NTf_2]$ were used as the organic phase, as the aqueous phase, various concentration of HNO_3 and phosphoric buffers were used. In the case of using pure $[C_4mim][NTf_2]$, the Mo extraction was negligible, when 8-HQ was used as an extractant, the trend of the distribution ratio dependence on pH value in $[C_4mim][NTf_2]$ was similar to $CHCl_3$ and at pH 3-8 the positive effect of the ionic liquid was observed and 100% extraction was achieved in the range of pH values 1-6 (Figure 6).
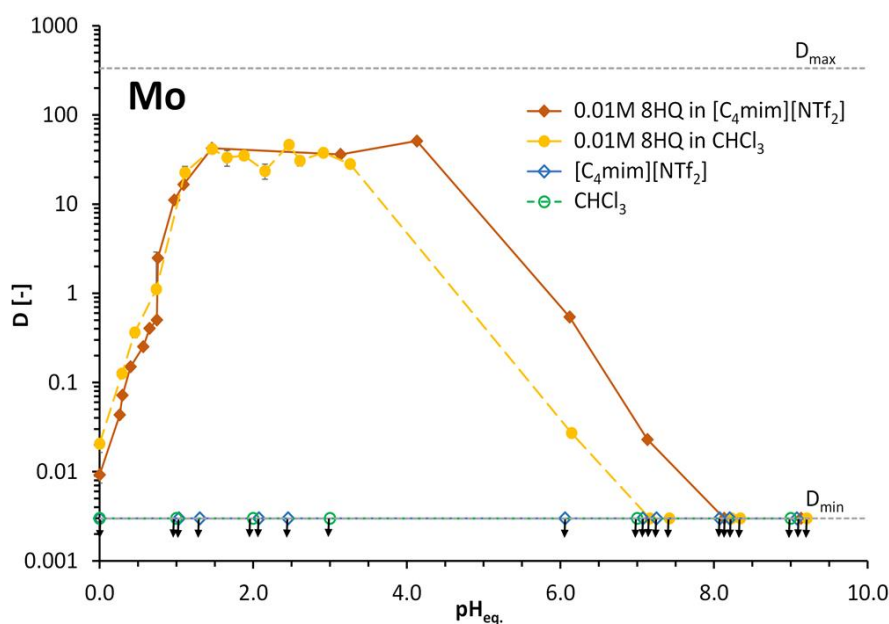

Figure 6: Dependence of molybdenum distribution ratio D on equilibrium pH value in extraction with and without 8-HQ and comparing [C₄mim][NTf₂] and CHCl₃ solvents. Details in text.

3.4 Extraction of technetium

Liquid-liquid extraction experiments were performed with ^{99m}Tc which was obtained from the Mo-Tc generator by elution with 0.9% solution of sodium chloride. Two ionic liquids ([C$_4$mim][NTf$_2$] and [N$_{1888}$][NTf$_2$] and 8-HQ extractant were used as the organic phase. As the aqueous phase, various concentration of HNO$_3$; phosphoric buffers, and complexing agents H$_2$Ox and/or H$_3$Cit were used. The dependence of extraction on equilibrium pH of aqueous phase was studied.

The difference between technetium extraction with and without extracting agent is small. These results are in agreement with presumption that anionic form of technetium is not extracted with chelating extracting agents such as 8HQ (see Figure 7).
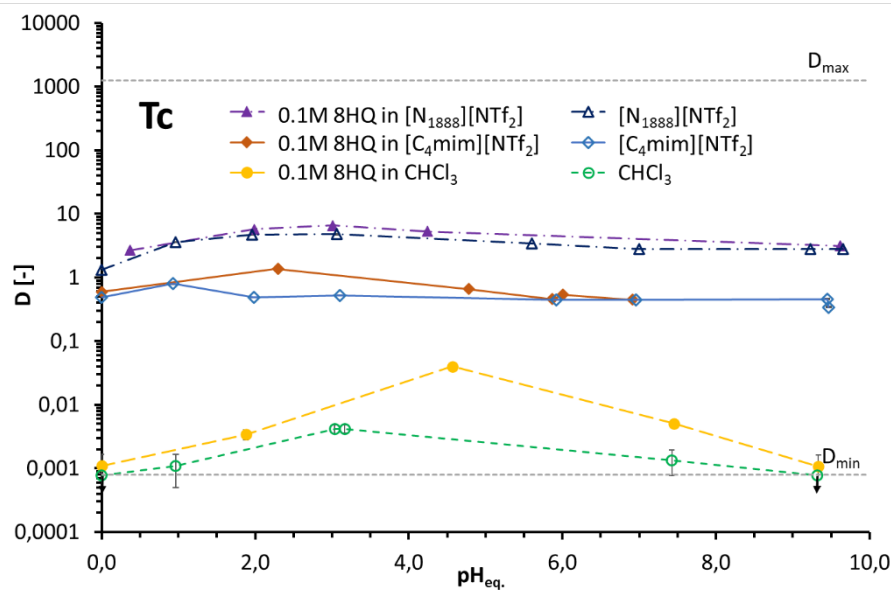

Figure 7: The dependence of distribution ratio D of technetium extraction on equilibrium pH value in extraction with and without 8-HQ and comparing [C$_4$mim][NTf$_2$], [N$_{1888}$][NTf$_2$] and CHCl$_3$ solvents. Details in text.

Nevertheless, comparison of CHCl$_3$ with [C$_4$mim][NTf$_2$] and [N$_{1888}$][NTf$_2$] as a solvent shows that the ionic liquid can increase the technetium extraction.

For the application of the method for decontamination solutions treatment, oxalic (H$_2$Ox) and citric (H$_3$Cit) acids and their mixture in concentration of 0.01M H$_2$Ox or 0.005M H$_3$Cit respectively were used as the aqueous phase. Three different organic phases were tested for this purpose: 0.1M 8-HQ in [C$_4$mim][NTf$_2$], [N$_{1888}$][NTf$_2$], and 0.1M HQ in [N$_{1888}$][NTf$_2$]. The results showed that while [C$_4$mim][NTf$_2$] does not achieve significant extraction, for [N$_{1888}$][NTf$_2$] and 0.1M 8-HQ in [N$_{1888}$][NTf$_2$], the extraction of Tc reached up 70-80% (Figure 8).
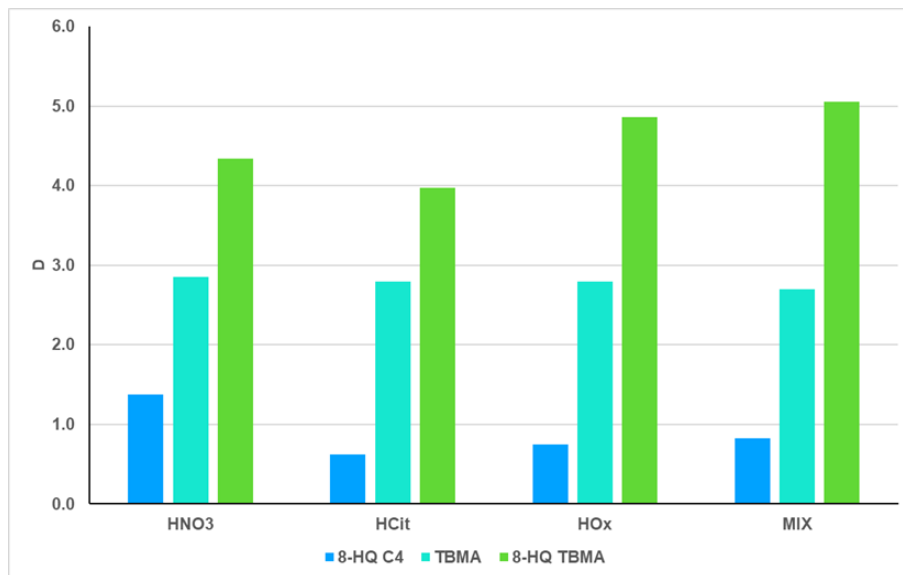
Figure 8: Changes of technetium distribution coefficients in various aqueous and organic phase compositions, details in text.

3.5 Extraction of iron

Similar set of experiments was done for iron as another representative of activation products. Experiments followed and complemented previous research on possibility of extraction metals into ionic liquids [7]. Without extracting agent, ferric cation is extracted only into ionic liquid at pH > 6. For 8-HQ as extractant, the trends of distribution ratio dependence on pH value using ILs are corresponding to results achieved for $CHCl_3$ as solvent. However, the differences between solvents at pH values 3-8 are more noticeable comparing to cobalt extraction results. The positive effect of $[C_4mim][NTf_2]$ as a solvent on iron extraction is the most significant (Figure 9). When H_2Ox and H_3Cit are present, for 0.5 M 8-HQ extraction of Fe > 99% was achieved (Figure 10).
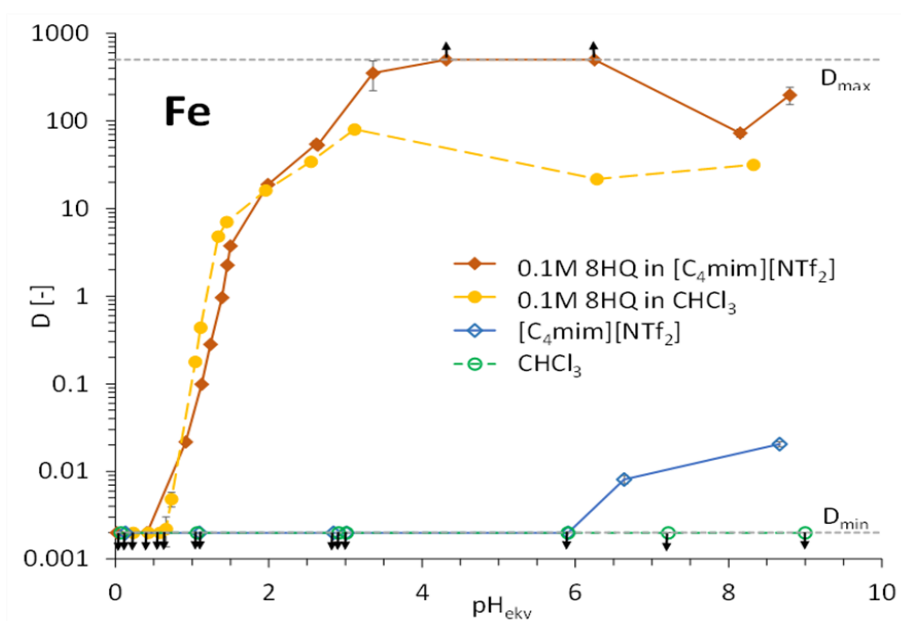

Figure 9: Dependence of Fe distribution ratio D on equilibrium pH value for systems with different solvents ($[C_4mim][NTf_2]$ and $CHCl_3$*) and with and without 8-HQ*
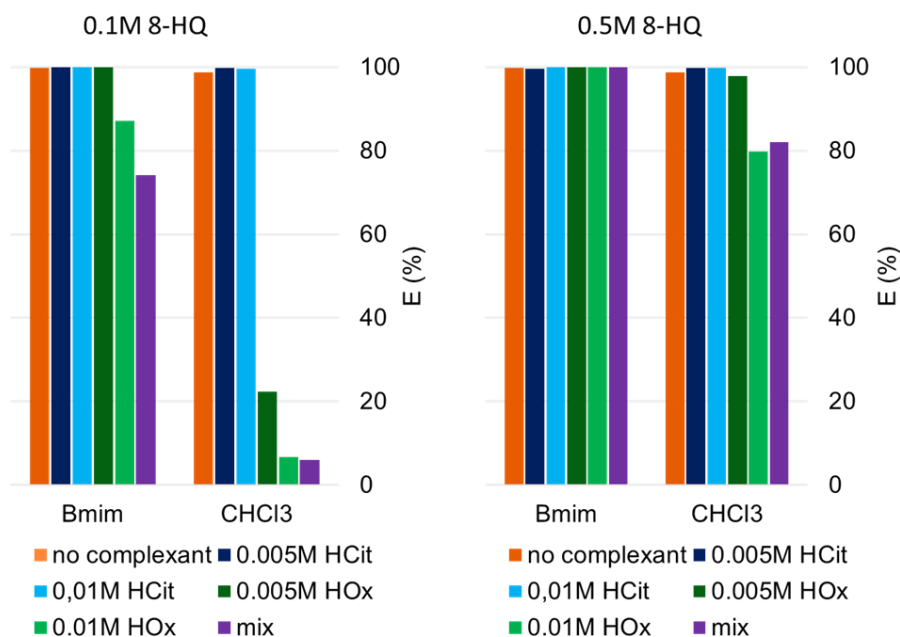
Figure 10: Dependence of distribution coefficients of iron on various aqueous (H_2Ox, H_3Cit and mixture) and organic phase (0.1M, 0.5M 8HQ in ([C_4mim][NTf_2] and $CHCl_3$) composition

3.6 Extraction of strontium

[90]Sr is one of the most monitored fission products. With its half-life, high fission yield and high-energy β^- particles emitted by its decay product, ^{90}Y, it is one of the most hazardous radionuclides in the radioactive waste management process. Experiments in the ionic liquids field were aimed at studying the conditions of separation of strontium as one of the significant fission products. [85]Sr and ^{89}Sr were used as radioactive tracers and the extraction efficiency was evaluated by distribution ratio calculated from count rates of the respective phases. Extractions from HNO_3 solutions into [C_4mim][NTf_2] using various extraction agents were performed. The best results were achieved with dicyclohexano-18-crown-6 (DCH18C6), which has then been used as an extractant in the detailed study of strontium extraction into ILs [8,9]. Extraction efficiency of strontium is highly dependent on the hydrophobicity of the ionic liquid used, with higher distribution ratios obtainable for more hydrophobic ionic liquids. At lower acidities, however, even for the most hydrophilic ionic liquids used in this study, the distribution ratios obtained were much higher than those for commonly used organic solvents ($CHCl_3$ and benzene). Apart from acidity, the extraction of strontium is also affected by other parameters of the aqueous feed solution, such as the presence of interfering cations. At lower acidities, the addition of alkali metal cations (Na+, K+) lowers the distribution ratios of strontium greatly significantly but the effect diminishes with increasing acid concentration (Figure 11). The overall results of this study are consistent with the presumed possible extraction mechanisms [8, 9].
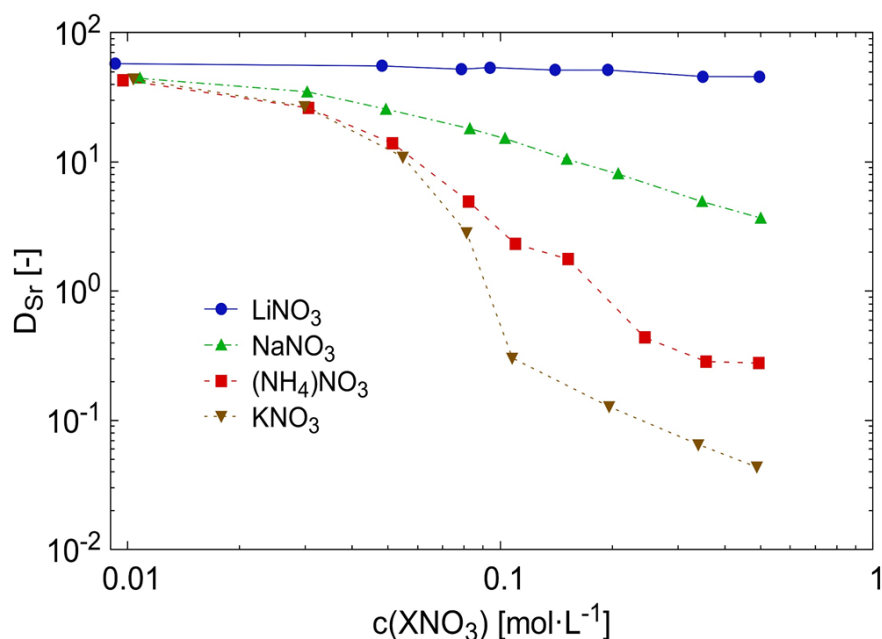
Figure 11: Dependance of strontium extraction on the aqueous concentration of interfering cations, extraction from XNO_3 (X = Li, Na, K or NH_4) solutions in 0.1M HNO_3 into 0.1M solution of DCH18C6 in [C_4mim][NTf_2]

Experiments carried out from solutions containing complexing agents indicate that DCH18C6 could be used to effectively extract radiostrontium from these solutions. Distribution ratios higher than 960 were achieved in the extraction from H_2Ox and H_3Cit solutions (Table 2).

Table 2: Distribution ratios of strontium for extraction from oxalic acid (H_2Ox) and citric acid (H_3Cit) solutions into 0.1M solution of DCH18C6 in [C_4mim][NTf_2]

	H_2Ox	H_3Cit	H_2Ox+H_3Cit
D [-]	> 965	> 965	> 965
E [%]	> 99.8	> 99.8	> 99.8
pH [-]	3.1	3.2	3.1

3.7 Discussion and perspectives

- [C_4mim][NTf_2] as ionic liquid with acceptable properties, can be used as solvent for metal extraction
- Extraction of Co, Fe, Mo, Sr and Tc can be significantly enhanced by using ionic liquids as a solvent, where maximum distribution ratios were achieved
- Extraction with 8-HQ or DCH18C6 in IL is suitable also at H_3Cit + H_2Ox concentrations present in common decontamination solutions.
- Ionic liquids can be regenerated electrochemically [5,6]
- As whole procedure, extraction of radionuclides from model decontamination solution shows possibility to regenerate solution while concentrating them for the next step of electrochemical treatment [5,6]
- Further planned research will aimed at two fields:
    - ✓ group separation of radionuclides of interest
    - ✓ the electrochemical regeneration and closing of the whole cycle

3.8 References

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