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DELIVERABLE D4.1

HoT in D&D manuals for practical tasks

Lead Beneficiary: POLIMI

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EXECUTIVE SUMMARY

Within the A-CINCH project, a Hands-on Training course has been proposed within the Decontamination and Decommissioning (D&D) areas, in order to provide a contribution in a topic that is becoming more and more relevant in the nuclear industry, but it is not yet well supported from the educational point of view.

The Hands-on Training (HoT) course will be a modular course where the participants will have the opportunity to cover their needs and to gain practical experience.

The whole course foresees some theoretical parts to be delivered as distance learning materials, that will be made available on the CINCH Moodle platform, and onsite activities organized in practical tasks. In particular, the HoT in D&D foresees the following four practical tasks:

- Decontamination of surfaces and solutions, developed by CTU;
- Determination of Sr-90 for radioactive waste characterization, developed by JSI;
- Decontamination of metallic waste and waste conditioning, developed by POLIMI;
- Application of the CORD process on a metallic sample, developed by IMT..

These tasks should provide students with a basic overview of the chemical procedures used for decontamination of devices, equipment, and materials contaminated with radionuclides. Additionally, parts dealing with separation and determination of significant contaminants are included. The course is compiled as a set of simple and self-standing tasks, each containing one procedure (and its variants), which can be combined into more complex exercise in relation to the chemical properties of the decontaminated material and the monitored radionuclide.

This deliverable contains the HoT in D&D manuals for the abovementioned practical tasks. The manuals provide list of reagents, materials and equipment needed as well as procedures to be followed during the practical sessions of the course.

CONTENT

INTRODUCTION

The Hands-on Training course in Decontamination and Decommissioning offers relevant practical activities organized in different practical tasks.

Each of them aims to let the student acquire the knowledge, competences and skills that are necessary to face the decontamination activities that arise from the decommissioning operations.

Decontamination methods are widely used in the whole industry for decreasing amount of undesired chemical compounds, elements, or radionuclides in the treated volume or surface. Especially in relation to nuclear industry, implementation of the methods, their efficiency, and costs are supposed to be the key parameters together with secondary waste production and related dose received by personnel or population.

Various decontamination methods exist and their particular chemistry is reflecting origin of the contamination, chemistry of contaminants, and operation conditions (chemical and industrial) of the contaminated device, facility. In case of nuclear power plants, distribution and behaviour of radioactive contamination is based on nuclear reactor operation and, substantially, chemical regimes of the primary circuit.

In the deliverable, brief descriptions of each practical task are provided together with the manuals to be followed to carry out the exercises.

TASK 1 - DECONTAMINATION OF SELECTED MATERIALS

This part is dedicated to CTU laboratory exercise aiming at the decontamination of selected materials. It also represents a batch version of the full task dedicated to flow-through arrangement in decontamination loop. This exercise is designed for students with various background in radiochemistry and nuclear engineering and based on their chemical skills, knowledge and experience, it can be adopted to more complex exercise.

1.1 Task description

The decontamination exercise provides students with practical experience in this field. The exercise consists of three parts/tasks that can be performed separately: characterizing of contamination and material, decontaminating material and handling of spent decontamination solution. All three subtasks play key role in decontamination processes and correct evaluation of each part is necessary for appropriate radioactive materials handling and management.

The benefit of this exercise lies in the following, common decontamination procedure. A student gets several pieces of various materials and the first task aims at identification of the contaminated ones. The characterization of material and radionuclide type and activity for estimation of contamination level lead a student to make decision whether decontamination is needed or not.

The decontamination step is designed as leaching in decontamination solution. In the manual, the universal decontamination solution consisting of mineral acid is used. Contaminated material is immersed into the decontamination bath warmed up to 50°C and left there for one hour. Every 5 or 10 minutes an aliquot is taken for measurement and the increasing activity of the solution indicating radionuclide transfer from material into solution can be observed. After one hour, the material is taken out, dried and measured and the evaluation of decontamination efficiency calculated. Several ways of calculation are recommended – measurement using the equipment for surface contamination, measurement of material using HPGe or NaI:Tl detector in appropriate geometry, and the activity of spent decontamination solution can be compared with known activity of solution used for contamination. All results can be compared, and the differences offers space for discussion. The goal of this part Is to show students that measurement of contamination, its accuracy and precision, plays vital role in decision-making processes and it is crucial to keep in mind all the potential errors (for various methods and even without analytical statistical calculations).

The last subtask focuses on possibilities of spent decontamination solution treatment. Resulted solution belongs among low-level radioactive wastes and minimizing the volume is desirable. In this task, the concentration of radionuclide using cation exchanger is used. Spent decontamination solution is poured through the resin, the fractions of eluent are measured and the efficiency of radionuclide capture on resin can be evaluated.

Manual for this exercise is attached in Appendix 1.

1.2 Exercise modifications

The exercise is designed as a simple laboratory task to ensure accessibility for students of various background. However, teacher or even student (according to their skills and experiences) can suggest variant of the task e.g., material to be decontaminated (glass, cloth, PVC, rubber etc.), radionuclide used for contamination (short-lived gamma emitters are preferred: ^{57}Co, ^{59}Fe, ^{85}Sr, ^{90}Y, ^{99}Mo, ^{99m}Tc, ^{134}Cs), chemicals as decontamination agent (complexing agents, universal decontamination detergents), treatment of spent decontamination solution (anion exchanger,

mixed exchangers, extraction, electrodeposition). Moreover, in a group of students, each of them can go through the different variant of the task to compare the results.

1.3 Task´s problematic parts and demands on students

The efficiency of decontamination process is highly dependent on many parameters. The structure and chemical composition of material chosen to be decontaminated as well as the chemical properties of radionuclide and the composition of leaching solution highly influence the efficiency of the cleaning process. All such problematic parts are the possible objects for discussions and suggestion. However, the depth and relevance of such discussions is connected to the students´ knowledge of chemistry.

The measurement of contamination and all samples can be identified as another critical point. Students needs to have at least basic knowledge of principles of ionizing radiation detection to correctly evaluate measured data.

1.4 Task impact

Practical aspects of complex cleaning procedures will provide students experience with ideas behind decontamination processes and performance as well as it will improve their laboratory skills. Each subtask is separately evaluated and provides student with overall impact on decontamination process. Obtained results are fundamental in application of continuous decontamination process.

Greater impact can be expected when modifications of the task are performed. In case of working in groups, sharing results and experiences can lead to the discussions on decontamination methods and parameters that can influence the overall efficiency.

TASK 2 - DETERMINATION OF ^{90}Sr FOR RADIOACTIVE WASTE CHARACTERIZATION

This part is dedicated to JSI laboratory exercise aiming at the determination of ^{90}Sr in different matrices. Indeed, ^{90}Sr is of critical importance in nuclear waste management, environmental monitoring, and radiation protection due to high radiation energy and its similar chemical properties to calcium.

This exercise is designed for students with various background in radiochemistry and nuclear engineering and it can be adapted according to their chemical skills, knowledge and experience.

2.1 Task description

The ^{90}Sr is a beta-emitting radionuclide (maximum decay energy 0.546 MeV) with a half-life of 28.8 years that decays to ^{90}Y (half-life 2.67 days and maximum decay energy of 2.27 MeV) and then on to stable ^{90}Zr. The ^{90}Sr is of critical importance in nuclear waste management, environmental monitoring, and radiation protection. Additionally, ^{90}Sr is a mobile element that can accumulate in soils and plants via precipitation and ion exchange mechanisms, as well as in bones and teeth if inhaled or ingested, because of its similar chemical properties to calcium. This increases the risk of leukaemia and bone cancer.

Radiometric beta-counting techniques, such as liquid scintillation counting or proportional counting, are routinely applied to highly sensitive detection of ^{90}Sr, either through direct measurement of ^{90}Sr, or via ^{90}Y. However, due to the fact that beta spectrum is continuous, radiochemical separation is crucial in accurate determination of ^{90}Sr. The overlapping spectra of these two radionuclides can be resolved by calculating an in-growth of ^{90}Y, or more commonly waiting for 2 weeks for the establishment of secular equilibrium, followed by long count times, depending on the detection limits required.

The major challenge of the radiochemical separation procedure is ^{90}Sr separation from interfering radionuclides and matrix elements, most notable being calcium due to its abundance and similarity to strontium. Detection is most often done by liquid scintillation counting or with a proportional gas flow counter. Most widely used methods used are either method based on selective precipitation or extraction chromatography.

Selective precipitation method is based on precipitation with oxalate and use of fuming nitric acid. Low solubility of strontium nitrate is exploited for separation from calcium, consequently the method is most applicable for samples containing large amounts of calcium (e.g., sediments). Further purification is done by co-precipitation using $Fe(OH)_3$ and $BaCrO_4$. The procedure is robust but time-consuming and requires fuming nitric acid handling.

Radiochemical separation based on extraction chromatography usin Sr-resin (Sr spec. resin, Eichrom® Industries) offers faster separation but it has also some limitations, most notably Sr retention capacity. Sr-90 is separated from acidic medium as strontium nitrate using crown ethers. The procedure involving Sr-resin has better repeatability, is faster and provides higher separation recoveries. In addition to Sr-resin, other producers utilizing different extraction materials, most notable being TK100, DGA and Dowex 1-X8 resin can be used.

In recent years, mass spectrometry methods are being developed where the main challenges are associated with separation of ^{90}Sr from natural ^{90}Zr isobaric interference and peak tailing from the presence of high concentrations of stable ^{88}Sr in many samples.

Here the method for ^{90}Sr separation using Sr-resin prior to liquid scintillation counting is presented. Calcium phosphate precipitation is used to concentrate strontium from water samples. Stable strontium is used to monitor method chemical recovery. This performed in 5 steps, which are water pre-treatment, sample pre-concentration, strontium separation, preparation of calibration sources for LSC calibration and sample measurements.

Detailed description of each step is shown in Appendix 2.

2.2 Task´s problematic parts and demands on students

The radiochemical procedure requires at least a basic knowledge of chemistry and some laboratory skills. Basic knowledge of LSC measurement is required.

2.3 Task impact

Students could enhance their expertise by learning practical aspects of a radiochemical separation procedure and a radiometric measurement by LSC technique.
Furthermore, they can improve their skills by fruitfully participating in discussion with students and teachers.

TASK 3: DECONTAMINATION OF METALLIC WASTE AND WASTE CONDITIONING

This part is dedicated to the POLIMI laboratory exercise aiming at the decontamination of metallic waste and the subsequent waste conditioning within the Hands-on Training in Decontamination & Decommissioning.

This exercise is addressed to students with various background in radiochemistry and nuclear engineering and based on their chemical skills, knowledge and experience can be adapted to more complex exercise.

3.1 Task description

Nuclear Decommissioning activities generate a huge variety and quantity of radioactive metallic waste that has to be properly managed. Most of them are only superficially contaminated. The superficial contamination usually involves a thickness of about tens of μm, and is due to the gathering of radionuclides such as ^{55}Fe, ^{60}Co, ^{90}Sr, ^{63}Ni, ^{59}Ni, and ^{137}Cs, inside the pores as iron's contaminants in the metallic form (Me) or as metal oxide (Me$_2$Ox). Developing decontamination technology for such metallic waste enables to reduce the impact of the decommissioning activities by enabling the reuse of the biggest part of the material in the industry, after a suitable treatment that has to enable the waste volume reduction and to minimize the generation of secondary waste.

Several decontamination and treatment methods, such as mechanical, chemical, electrochemical and hybrid technologies, are being developed to reduce radioactivity of materials that can be either de-categorized or reach clearance levels. In this context, the Phosphoric Acid Decontamination (PHADEC) process is one of the current chemical methods that contribute to manage contaminated metallic materials coming from dismantling activities in nuclear decommissioning. This technology consists in:

i) phosphoric acid dissolution of the superficial contaminated layer of scrap metals;

ii) recycling of phosphoric solution by adding oxalic acid to precipitate iron oxalate;

iii) re-use of the phosphoric solution by evaporation after removing the precipitate;

iv) thermal treatment of the wet iron oxalate;

v) conditioning of the dry iron oxide powder in concrete for final storage.

Although the PHADEC process has been scaled up from lab to pilot plant to be used during decommissioning activities of Italian nuclear power reactors, some weaknesses are still badly affecting the sustainability of the process.

An innovative chemical and electrochemical decontamination process based on the PHADEC technology is being developed, attempting to overcome drawbacks of the standard PHADEC. A simplified scheme of the process with the primary inputs and outputs of each step is shown in Figure 1.
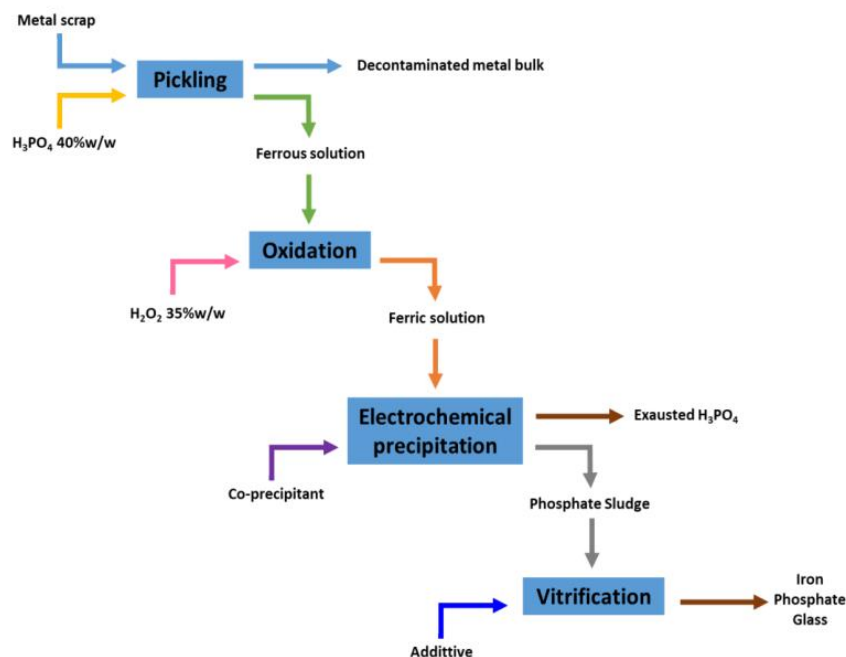
Figure 1 General scheme of the Advanced PHADEC-based process.

The stages involved in this process are:

- **Pickling process**: removal of the superficial contaminated layer by acid attack.

- **Oxidation step**: adjust the iron oxidation state in the solution containing the contamination to the proper value for the following precipitation process.

- **Electrochemical precipitation**: recovering the contaminants present in solution in the form of solid insoluble salts.

- **Vitrification**: conditioning of contamination by direct synthesis of a suitable waste form using the obtained insoluble salts treated at high temperature.

In this new process the phosphoric acid dissolution of the superficial contaminated layer of scrap metals is basically the same as the standard PHADEC one, but the chance to recycle and reuse the phosphoric solution without any evaporation treatment can substantially reduce the energy intensity of the process. The treatment of ferrous solution waste without altering its chemical composition by oxidation of Fe^{2+} to Fe^{3+} to reach the best Fe^{3+}/Fe^{2+} ratio for the following precipitation process is not involved in the standard PHADEC method, where the ferrous solution directly undergoes precipitation process. Furthermore, the chemical decontamination achieved by adding external precipitating agents like oxalic acid in the standard PHADEC process is now overcome by an electrochemical decontamination of the ferric solution, thus improving the precipitation yields, reducing the amount of solid waste, lowering corrosion effects and achieving the best conditions for the final conditioning step. Finally, unlike the standard PHADEC, the advanced process involves a direct conditioning of the solid by-product without any dilution in cement matrices. The final glass waste form obtained at a lower melting temperature than that of borosilicate glass shows higher physical-chemical stability in compliance with the Waste Acceptance Criteria (WAC) of the disposal facility, assuring the isolation of radionuclides from the biosphere.

In this practical course, students can directly experience the procedures that are used for the superficial decontamination of metallic scraps in the advanced PHADEC-based process, leading to

the final release of the metallic materials and the conditioning of the radioactive contamination, minimizing the waste volume and the production of secondary liquid waste. In the course, radioactive contamination is simulated by means of stable isotope of Co, Sr, Cs and Ni.

Detailed description of each step is shown in Appendix 3.

3.2 Exercise modifications

The exercise is organized in 4 steps to ensure the full understanding of the theory behind the experiments for students of various background. However, changes could be done in order to better tailor the course on the students' curricula.

3.3 Task´s problematic parts and demands on students

The efficiency of the decontamination process is highly dependent on many parameters that will be objects of the experimentation and discussion. The activities require at least a basic knowledge of chemistry and some laboratory skills.

3.4 Task impact

Students could enhance their expertise by learning practical aspects of a pickling process and of an electrochemical precipitation. They can gain a better knowledge of the vitrification treatment as conditioning method for nuclear waste. In general, they can improve their skills by fruitfully participating in discussion with students and teachers.

TASK 4: APPLICATION OF THE CORD PROCESS ON A METALLIC SAMPLE

This part is dedicated to the IMT laboratory exercise aiming at the utilization of the CORD process for the treatment of a stainless-steel sample.

This exercise is addressed to students with various background in radiochemistry and nuclear engineering and based on their chemical skills, knowledge and experience can be adapted to more complex exercise.

4.1 Task description

Nuclear power generation is present in many countries worldwide, but more than 60% of the nuclear capacity is over 25 years old. In Europe 90% of all nuclear reactors, need to be shut down by 2030, unless their operation life will be prolonged. The major nuclear decommissioning activity is the application of decontamination technology, which are used to reduce the occupational exposures, to limit the potential releases of radioactive materials and to permit the reuse of components.

The reactor vessel and the piping system of the primary coolant is typically made up of austenitic stainless steel and Ni-alloy. The alloys are subjected to corrosion on the internal side under exposure to the primary circuit water; therefore, on the surface of these a duplex corrosion layer is formed. The upper layer is mainly magnetite, the main part of the corrosion film contains Cr, Ni, and Fe mixed oxides. Generally, the thickness of this corrosion layer is 5-6 µm for stainless steel.

The Chemical Oxidation Reduction Decontamination (CORD) method is a world-wide known 2-steps decontamination process for metallic structure in nuclear power plants. The following photos show the oxidized stainless steel before and after treatment using the CORD method. The examination of the treated confirmed the total dissolution of the oxidized layer, highlighting the efficiency of the CORD method.

Oxidized stainless steel embedded in silicon and showing a black oxidation layer.

Stainless steel embedded in silicon and decontaminated using the CORD method.

In the first step permanganate ion (MnO_4^-) is used to oxidize the chromium oxide-layer and to release chromate ions. Permanganate ions are derived from potassium permanganate, which can be used in nitric acid media, which is known as NP CORD, or in alkaline media (KOH) which is known as AP CORD.

A third type of the CORD process, HP CORD makes use of permanganic acid, which is prepared from $KMnO_4$ using a strong acid cation resin.

The reaction is as follows:

$$Cr_2O_3 + 2MnO_4^- + H_2O \rightarrow 2HCRO_4^- + 2MnO_2$$

In the next step, oxalic acid is added to reduce the permanganate ion to aqueous Mn^{2+} ions and dissolve the MnO_2 formed.

The reaction are as follows:

$$2MnO_4^- + 5H_2C_2O_4 + 6H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

$$MnO_2 + H_2C_2O_4 + 2H^+ \rightarrow Mn^{2+} + 2CO_2 + 2H_2O$$

The oxalic acid dissolves the Fe and Ni enriched oxide layer from the surface of the alloys according to reaction:
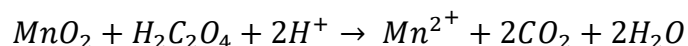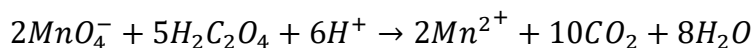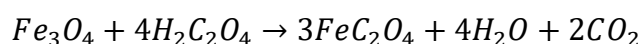
$$Fe_3O_4 + 4H_2C_2O_4 \rightarrow 3FeC_2O_4 + 4H_2O + 2CO_2$$

This constitutes one-step of the process.

The whole process is repeated several times. The solutions are treated with ion exchange resin to extract the dissolved metals; however, this process is only used in the second step, because of the incompatibility of the resins with the MnO_2 precipitate that can be formed in the oxidation stage. In most cases, the remaining oxalic acid is removed from the solutions by addition of H_2O_2 and the presence of a UV-source (CORD UV technology) and/or heating the solution.

For destruction using H_2O_2, the reaction is as follows:

$$H_2O_2 + H_2C_2O_4 \rightarrow 2CO_2 + 2H_2O$$

Detailed description of each step is shown in Appendix 4.

4.2 Task´s problematic parts and demands on students

The efficiency of the process is highly dependent on many parameters that will be objects of the experimentation and discussion. The activities require at least a basic knowledge of chemistry and some laboratory skills.

4.3 Task impact

Students could enhance their expertise by learning practical aspects of the chemical process. In general, they can improve their skills by fruitfully participating in discussion with students and teachers.

GENERAL CONCLUSIONS

The practical tasks provided within the Hands-on Training course on Decontamination and Decommissioning have been designed as well as the specific actions to be developed during the onsite phase of the course. The manuals describing the reagents, materials, equipment and procedures to be used are complete and will be made available on the CINCH Moodle platform.

APPENDIX 1: DECONTAMINATION OF SELECTED MATERIALS

Hands-on Training in Decontamination and Decommissioning

Manual for practical exercise

2022

Version: 1.0

1 Decontamination of selected materials contaminated with radionuclides

Abstract:

Decontamination of surfaces and of various materials is one of basic procedures used in nuclear facilities during and after their operation. Decreasing of activities is required either for radiation protection or for waste management. This decontamination task is focused on quantification of decontamination process, evaluation of efficiency of the process with attention to any common complications, and management of generated wastes.

1.1 Introduction:

Radionuclide contamination can occur during the operation of any nuclear facilities and there is a requirement to decrease them using various decontamination processes. The reasons for decontamination usually range from decreasing of radiation exposure of people, through cleaning of equipment for further usage, to reducing the volume of equipment and materials requiring disposal. Besides removing of radionuclides, the treatment can also result in fixing the unremovable radionuclides inside material to avoid their release into environment during disposal. Decontamination processes are usually part of decommissioning planning.

The contamination can be assessed by the strength of binding between radionuclide and material. When the contaminants can easily be spread from material to another one only by touching, we classify the contamination as *loose* or *free*. This type of contamination can be easily removed from contaminated material using simple decontamination methods for example by washing with water or by smears, because radionuclides are mostly bonded to the surfaces by intermolecular forces. When The interaction between material and radionuclides bonded by chemical adsorption or ion exchange is stronger than bonding by intermolecular forces and penetrating deeper layers can occur. Such f*ixed* contamination usually requires more complex decontamination methods (chemical, electrochemical, mechanical etc.) and radionuclides cannot be easily spread around. The most difficult contamination removal is caused by deep diffusion of radionuclides or activation of material by ionizing radiation, especially by neutrons.

The type of contamination and interaction of contaminant with material play role in deciding whether and how the decontamination will be carried out. Other important parameters in the decision-making process are the economic aspects related to the cost of decontamination but also to the treatment of secondary waste.

Decontamination techniques are based on physical or chemical treatment:

- Mechanical methods use physical forces to remove radioactive contaminants such as scrubbing, brushing or wiping. Novel methods can include treatment with high-pressure (liquid jetting), low or high temperatures (dry ice blasting, laser-based cleaning, plasma treatment) or both (supercritical fluids cleaning).
- Chemical methods are based on chemical reactions (oxidation, reduction, dissolution or complexation) between radionuclide or material and decontaminating agents. The cleaning agents can be used as water solution (washing bath), foams or gels. Besides water the decontamination solution typically contains mineral or organic acids, complexing agents, redox agents or surfactants. Each component plays its own role in decontamination process: redox agents change the oxidation state of surface or radionuclides, acids can dissolve metal oxide layers, chelating agents are usually used for treatment of fixed contaminants where

simple methods are inefficient, surfactant decreases the surface tension and increase contact of liquid with the material. Chemical decontamination can be enhanced with electrochemical processes like electrolysis, electrophoresis, and electroosmosis.

In the decontamination process, a secondary waste of various volumes and types are produced. The activity of secondary waste varies in dependence on decontamination technique. In the case of chemical decontamination, resulting spent decontamination solution usually belongs to low-level radioactive waste. Treatment of such type of waste for disposal is not economically and ecologically advantageous and usually consists of volume reduction by evaporation. Alternative ways such as ion exchange, liquid-liquid extraction, electrodeposition treatment enable re-use of the solution in decontamination process after radionuclide removal.

1.2   List of tasks

This exercise consists of three tasks, which are following real decontamination process modified for laboratory exercise:

1. Characterization of contaminated material
2. Decontamination of material by leaching
3. Treatment of spent decontamination solution

1.3   Task 1: Characterization of contaminated material

One of the first decision making steps how to handle contaminated material is its characterization. There are several important parameters playing main role such as level of radioactivity, type of radionuclides, chemical and physical properties of contaminated material. Activity of the material is also a limiting key parameter dictating weather material can be released into environment or must be treated as radioactive. Radioactive material can be treated for disposal, or decontaminated and reused, or released into environment. Identification of radionuclide and determination level of its activity is the aim of Subtask 1.

Procedure:

1. With surface contamination monitor identify contaminated material: Find clean spot and measure background value. Place one piece from heap of materials at the time on clean spot and measure it with the monitor. Identify contaminated piece and take it for further characterization and treatment.
2. Insert contaminated material in appropriate plastic container or bag and measure gamma spectra in the given geometry using HPGe detector for 300 s. Evaluate the spectra. With built-in library, identify the contaminating radionuclide. Record net areas of selected peaks.
3. Measure standard of identified radionuclide with known activity using HPGe detector for 300 s.
4. Based on identified radionuclide, calibrate monitor of surface contamination if necessary. Measure the activity of contaminated material and background in Bq. Record values. If the calibration is not possible, use only cps values.
5. Determine the weight and estimate the surface of contaminated material. Record values.

Data evaluation:

- Calculate the measurement efficiency for identified radionuclide.

- Calculate specific activity of material from value measured by monitor of surface contamination in Bq/cm^2 and Bq/g or in cps/cm^2 and cps/g. Calculate specific relative activity of material from value measured by HPGe in cps/cm^2, cps/g.

1.4 Task 2: Decontamination of material by leaching

Wet chemical decontamination consists in affecting chemical properties of radionuclides or matrix material resulting in transfer of radionuclides into the solution. The composition of decontamination solution varies depending on radionuclides and materials. Mineral acids such as nitric or hydrochloric acids or complexing acids (citric, oxalic acid, EDTA) are the most used decontaminating agents. The evaluation of decontamination using nitric acid solution is the aim of Subtask 2.

Procedure:

1. Prepare 250 mL of 0.1M HNO_3 as decontamination solution.
2. Pour the solution into 500mL beaker, insert teflon stirrer and warm it up to 50°C.
3. Take the blank aliquot of 1-2 mL and measure using appropriate detector (NaI:Tl well type for 60 s or HPGe for 300 s).
4. Using nylon thread immerse contaminated material into decontamination solution so that is completely submerged but not lying on the bottom.
5. For 40 minutes, take aliquots of 1-2 mL every 5 minutes. For next 50 minutes take aliquots of 1-2 mL every 10 minutes. Measure all aliquots using appropriate detector (NaI:Tl well type for 60 s or HPGe for 300 s).
6. After 90 minutes of leaching, take decontaminated material out and dry it on air.
7. Using monitor of surface contamination measure activity of dry decontaminated material in Bq or in cps to compare with values from subtask 1.
8. Insert decontaminated material in the same type of plastic container or bag as at the beginning and measure gamma spectra in the same geometry as before for 300 s. Record net areas of desired peaks.

Data evaluation:

- Calculate specific activity of material from value measured by monitor of surface contamination in Bq/cm^2 and Bq/g or in cps/cm^2 and cps/g. Calculate specific relative activity of material from value measured by HPGe in cps/cm^2, cps/g. Compare calculated data with data gained in Subtask 1. Calculate the efficiency of decontamination as the ratio of activity after and before.
- Calculate total activity of the spent decontamination solution in cps and using the efficiency of the measurement calculate the activity in Bq.
- Plot the dependency of net cps/ml of the solution on the time of leaching.

1.5 Task 3: Treatment of spent decontamination solution

Spent decontamination solutions usually belong to the category of low-level radioactive wastes. Separation of radionuclides from such solution reduces total volume of radioactive wastes and offers the possibility of decontamination solution reuse. One of possible processes for radionuclide separation is ion-exchange when radionuclides in cationic form can be concentrated on cation exchanger. The radionuclide separation on cation exchanger from spent decontamination solution is the aim of Subtask 3.

Procedure:

1. Wash swollen strongly acidic cation exchanger in column (BV = 5mL) with 3x BV of 3M HNO_3 (speed given by gravity) to convert exchanger into H^+ form.
2. Wash column with 2x BV of fresh decontamination solution (0.1M HNO_3).
3. Pour the spent decontamination solution through the cation exchanger, take 20mL fractions and measure the fractions or aliquots from fraction using appropriate detector (NaI:Tl well type for 60 s or HPGe for 300 s).

Data evaluation:

Plot the dependency of net cps/ml of the solution on the volume of treated spent decontamination solution. Compare the volume activity of eluate with the initial volume activity of spent decontamination solution.

1.6 Summarising the task:

Discuss the discrepancies in values of decontamination efficiency calculated from measurement by monitor of contamination and from measurement by HPGe or NaI:Tl. Compare the activity of spent decontamination solution with the activity of the material before and after leaching and discus the discrepancies. Compare activities after decontamination with national limits. Discuss possibilities of enhancing the decontamination process.

Notes for teachers - modifications:

Materials for contamination:	
Radionuclides:	cloth, tile, concrete, rubber, PVC, glass, ceramics
	gamma emitters (Co-57,58,60, Fe-59, Mn-54, Zn-65, Tc-99m, Mo-99)
	beta emitters (Y-90)
Detection:	HPGe
	NaI:Tl
	LSC
Decontamination solution:	0.1M HNO_3
	10mM H_2Ox + 5mM H_3Cit
	10mM H_3Cit pH ≈ 8
Exchanger:	strongly acidic catex (radionuclides in cationic forms)
	strongly basic anex (radionuclides in anionic forms)
Arrangement:	Flow-through/loop arrangement possible

APPENDIX 2: MANUAL FOR DETERMINATION OF ^{90}Sr FOR RADIOACTIVE WASTE CHARACTERIZATION

Hands-on Training in Decontamination and Decommissioning

Task 2 – Determination of ^{90}Sr for radioactive waste characterization

Manual for practical exercise

<div align="right">

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Version 1.0

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EXECUTIVE SUMMARY

This document contains manual for practical task Determination of ^{90}Sr for radioactive waste characterization prepared by JSI to be used in HoT Decontamination and decommissioning.

CONTENT

1   INTRODUCTION

The ^{90}Sr is a beta-emitting radionuclide (maximum decay energy 0.546 MeV) with a half-life of 28.8 years that decays to Y-90 (half-life 2.67 days and maximum decay energy of 2.27 MeV) and then on to stable ^{90}Zr. The ^{90}Sr is of critical importance in nuclear waste management, environmental monitoring and radiation protection. Additionally, ^{90}Sr is a mobile element that can accumulate in soils and plants via precipitation and ion exchange mechanisms, as well as in bones and teeth if inhaled or ingested, because of its similar chemical properties to calcium. This increases the risk of leukaemia and bone cancer.

Radiometric beta-counting techniques, such as liquid scintillation counting or proportional counting, are routinely applied to highly sensitive detection of ^{90}Sr, either through direct measurement of Sr-90, or via Y-90. However, due to the fact that beta spectrum is continuous, radiochemical separation is crucial in accurate determination of ^{90}Sr. The overlapping spectra of these two radionuclides can be resolved by calculating an in-growth of ^{90}Y, or more commonly waiting for 2 weeks for the establishment of secular equilibrium, followed by long count times, depending on the detection limits required.

The major challenge of the radiochemical separation procedure is ^{90}Sr separation from interfering radionuclides and matrix elements, most notable being calcium due to its abundance and similarity to strontium. Detection is most often done by liquid scintillation counting or with a proportional gas flow counter. Most widely used methods used are either method based on selective precipitation or extraction chromatography.

Selective precipitation method is based on precipitation with oxalate and use of fuming nitric acid. Low solubility of strontium nitrate is exploited for separation from calcium, consequently the method is most applicable for samples containing large amounts of calcium (e.g. sediments). Further purification is done by co-precipitation using $Fe(OH)_3$ and $BaCrO_4$. The procedure is robust but time-consuming and requires fuming nitric acid handling.

Radiochemical separation based on extraction chromatography usin Sr-resin (Sr spec. resin, Eichrom® Industries) offers faster separation but it has also some limitations, most notably Sr retention capacity. The ^{90}Sr is separated from acidic medium as strontium nitrate using crown ethers. The procedure involving Sr-resin has better repeatability, is faster and provides higher separation recoveries. In addition to Sr-resin, other producers utilizing different extraction materials, most notable being TK100, DGA and Dowex 1-X8 resin can be used.

In recent years, mass spectrometry methods are being developed where the main challenges are associated with separation of ^{90}Sr from natural ^{90}Zr isobaric interference and peak tailing from the presence of high concentrations of stable ^{88}Sr in many samples.

Here the method for ^{90}Sr separation using Sr-resin prior to liquid scintillation counting is presented. Calcium phosphate precipitation is used to concentrate strontium from water samples. Stable strontium is used to monitor method chemical recovery. This performed in 5 steps, which are water pre-treatment, sample preconcentration, strontium separation, preparation of calibration sources for LSC calibration and sample measurements. Detailed description of each step is shown in following chapters.

2 REAGENTS, MATERIALS AND APPARATUS

1. Liquid scintillation counter
2. ICP-MS
3. Filtration unit
4. 0.45 μm polysulfone filter
5. Deionized water
6. Source of vacuum (water pump or vacuum pump)
7. HDPE container
8. Concentrated HNO_3
9. pH indicator paper
10. 500 mL measuring cylinder
11. 1000 mL glass beaker
12. Hot plate
13. Magnetic stirrer
14. 3M HNO_3
15. 3M HNO_3 – 0.05M oxalic acid solution
16. 0.05M HNO_3
17. 8M HNO_3
18. 5 mg/mL Sr carrier solution
19. 1.25M $Ca(NO_3)_2$ solution
20. 3.2M $(NH_4)_2HPO_4$ solution
21. 50mL plastic centrifuge tube
22. 1M $Al(NO_3)_3$
23. 2mL plastic column
24. Column rack
25. 250mL glass beaker
26. Sr-resin
27. Plastic column reservoir
28. Calibrated ^{90}Sr standard solution
29. 20mL scintillation vial
30. UltimaGold LLT scintillation cocktail
31. Ethanol

3   WATER PRE-TREATMENT

First step after sampling is sample filtration. Even if it looks like that our sample is transparent with no suspended solids, often we are surprized on the amount of undissolved solids in it once we filter it. Therefore, filtration step is very important. For some applications, we may not want to filter our sample, for instance if we want to determine dose from drinking water since usually nobody filter drinking water through 0.45 μm pore size filter before drinking it.

But we have to be careful with this because undissolved solids might cause problems during different analysis steps. Sample is filtered following these steps:

1. Connect sample collecting flask with filter support with frit where we will place the filter and filtration funnel, which is attached to the filter support.

2. Place polysulfone filter with 0.45 μm pore size on the filter support.

3. Wet the filter with deionized water and then attach filtration funnel.

4. Connect receiving flask to source of vacuum and apply vacuum to the filtration system.

5. Check for leaks of the filtration system.

6. Pour the sample on the filtration funnel and wait that it is filtered.

7. Repeat step 6 until you fill up the collecting flask with filtered sample.

8. Detach filtering flask from the vacuum line and transfer filtered sample to clean HDPE container.

9. Repeat steps 6.-8. to filter the whole sample.

10. Acidify sample with adding 3 mL of conc. HNO_3 per litre of sample.

11. After acid addition, cap the sample and shake it thoroughly.

12. Check pH of the sample with pH indicator paper.

13. If pH is not 1-2, repeat steps 10-12.

14. Store sample for next steps.

4 SAMPLE PRECONCENTRATION

With pre-concentration we reduce volume of water samples that we can load it on Sr-resin column. Pre-concentration of water samples is needed when expected Sr-90 activity concentration is too low to enable direct separation on Sr-resin extraction chromatographic column. Sample volumes up to approximately 20 mL could be directly loaded on the Sr-resin column, but for larger volumes pre-concentration is preferred option before we load the sample to the column.

The procedure for pre-concentrating water sample using calcium phosphate is as follows:

1. Measure the sample volume of pre-filtered and acidified sample using a standard graduated cylinder and transfer volume to an appropriate size glass beaker. Sample volume depend on the expected ^{90}Sr activity concentration or required detection limit. We will take 500 mL of sample.

2. Place beaker with sample on a hotplate, insert magnetic stirrer and start stirring.

3. Add 1 mL of 5mg/mL of strontium carrier to the sample. Strontium carrier is added to be able to trace radiochemical recovery of the procedure.

4. Add 2 mL of 1.25M $Ca(NO_3)_2$ to sample and heat it to 60-80°C.

5. Add 5 mL of 3.2M $(NH_4)_2HPO_4$ solution per litre of sample and adjust pH to 9-10 with slowly adding 12M NaOH to form a calcium phosphate precipitate. Continue heating and mixing for 15-20 minutes.

6. Cool sample to room temperature. Allow precipitate to settle until solution can be decanted.

7. Decant supernatant and discard to waste. Transfer sample to centrifuge tube and centrifuge it to remove remaining supernatant.

8. Dissolve precipitate in 7 mL of concentrated HNO_3 and 8 mL of 1M $Al(NO_3)_3$.

5 STRONTIUM SEPARATION

Before measurements ^{90}Sr needs to be separated from interfering radionuclides. This can be achieved by using Sr-resin, which is selective for Sr, following this procedure:

1. Place a plastic column in the column rack and place a beaker below the column.

2. Fill the column with Sr-resin previously dispersed in deionized water and wait that water passes through.

3. Attach column reservoirs to each column and add 5 mL of 8M HNO$_3$ into each column reservoir to condition the Sr-resin. Allow solution to drain.

4. Take aliquot for ICP-MS determination of stable Sr and transfer dissolved sample into the appropriate Sr-resin column reservoir. Allow solution to drain.

5. Add 5mL of 8M HNO$_3$ to rinse to each sample beaker or tube. Transfer the rinse solution into the appropriate Sr-resin column reservoir. Allow solution to drain.

6. Rinse each column with 5mL of 3M HNO$_3$ - 0.05M oxalic acid. Allow solution to drain.

Note: The 3M HNO$_3$ - 0.05M oxalic acid removes Pu(IV), Np(IV), Zr(IV), or Ce(IV), which are retained by Sr-resin. If these interference's are known to be absent, this step may be skipped.

7. Add 5 mL of 8M HNO$_3$ to each column reservoir. Allow the rinse solution to drain through each column.

Note: This additional 8M HNO$_3$ rinse removes any residual oxalic acid and ensures full removal of K$^+$ and Ba^{2+} that may be present.

8. Record the time when the last rinse completely drains through each column as the start of yttrium ingrowth.

9. Place clean, labelled vial below column.

10. Add 10 mL of 0.05M HNO$_3$ to each column reservoir to elute Sr. Allow solution to drain.

11. Take aliquot for ICP-MS determination of stable Sr for chemical recovery determination.

6 PREPARATION OF CALIBRATION SOURCES FOR LSC CALIBRATION

For the calibration of liquid scintillation counter, we need to prepare ^{90}Sr standard solution separated from ^{90}Y and count it in different time intervals after separation to evaluate response of the counter with respect to ^{90}Y ingrowth. Therefore, first we have to perform ^{90}Sr separation using these steps:

1. Add an appropriate volume of calibrated ^{90}Sr standard solution to a beaker, add 1 mL of 5mg/mL solution of Sr carrier and evaporate the solution to dryness.

2. Re-dissolve the residue in 5 mL of 8M HNO_3.

3. Place a plastic column into column rack and place waste vial below each column.

4. Fill column with Sr-resin dispersed in deionized water and add 5 mL of 8M HNO_3 to column to condition resin and allow to drain.

5. Take aliquot from the re-dissolved residue with ^{90}Sr standard for ICP-MS measurements and transfer remaining solution into the appropriate Sr-resin column. Allow solution to drain.

6. Add 5 mL of 8M HNO_3 to rinse the beaker. Transfer the beaker rinse into the appropriate Sr-resin column. Allow solution to drain.

7. Repeat step 6.

8. Add 5 mL of 8M HNO_3 to the Sr-resin column. Allow solution to drain.

9. Place a clean, labelled centrifuge tube below each column for ^{90}Sr elution.

10. Add 10 mL of 0.05M HNO_3 to the column to strip the ^{90}Sr. Allow solution to drain.

11. Take aliquot for ICP-MS determination of Sr and chemical recovery.

7 SAMPLE MEASUREMENTS

Sample solutions after separation of ^{90}Sr are measured using liquid scintillation counter according to the following steps:

1. Take 5 mL of separated solution and transfer it to plastic liquid scintillation vial.

2. Add 17 mL of UltimaGold LLT scintillation cocktail, close the vial tightly, and mix it thoroughly. Sample should be completely mixed with the cocktail.

3. Wipe counting vial on the outer surface with ethanol to remove any contamination.

4. Place vials with samples in the liquid scintillation counter and initiate counting protocol. Procedure for setting up counting protocols differ depending on the LSC instrument used.

5. After end of counting print out counting reports with results of the measurements.

APPENDIX 3: DECONTAMINATION OF METALLIC WASTE AND WASTE CONDITIONING

Hands-on Training in Decontamination and Decommissioning

Task 3 – Decontamination of metallic waste and waste conditioning

Manual for practical exercise

Author: Elena Macerata, Mario Mariani, Francesco Galluccio, Marco Giola, Gabriele Magugliani, Eros Mossini, Maddalena Negrin, Andrea Santi
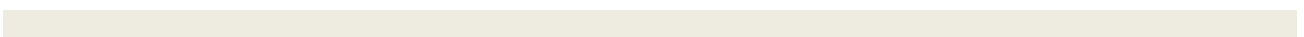
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EXECUTIVE SUMMARY

This manual contains a detailed description of the reagents, procedures and analytical techniques to be used in the practical task devoted to the decontamination of metallic waste and the subsequent conditioning of the recovered contamination within the Hands-on Training in Decontamination and Decommissioning.

CONTENT

1 INTRODUCTION

Nuclear Decommissioning activities generate a huge variety and quantity of radioactive metallic waste that has to be properly managed. Most of them are only superficially contaminated. The superficial contamination usually involves a thickness of about tens of μm, and is due to the gathering of radionuclides such as ^{55}Fe, ^{60}Co, ^{90}Sr, ^{63}Ni, ^{59}Ni, and ^{137}Cs, inside the pores as iron's contaminants in the metallic form (Me) or as metal oxide (Me$_2$Ox). Developing decontamination technology for such metallic waste enables to reduce the impact of the decommissioning activities by enabling the reuse of the biggest part of the material in the industry, after a suitable treatment that has to enable the waste volume reduction and to minimize the generation of secondary waste.

Several decontamination and treatment methods, such as mechanical, chemical, electrochemical and hybrid technologies, are being developed to reduce radioactivity of materials that can be either de-categorized or reach clearance levels. In this context, the Phosphoric Acid Decontamination (PHADEC) process is one of the current chemical methods that contribute to manage contaminated metallic materials coming from dismantling activities in nuclear decommissioning. This technology consists in:

    i)   phosphoric acid dissolution of the superficial contaminated layer of scrap metals;

    ii)   recycling of phosphoric solution by adding oxalic acid to precipitate iron oxalate;

    iii)   re-use of the phosphoric solution by evaporation after removing the precipitate;

    iv)   thermal treatment of the wet iron oxalate;

    v)   conditioning of the dry iron oxide powder in concrete for final storage.

Although the PHADEC process has been scaled up from lab to pilot plant to be used during decommissioning activities of Italian nuclear power reactors, some weaknesses are still badly affecting the sustainability of the process.

An innovative chemical and electrochemical decontamination process based on the PHADEC technology is being developed, attempting to overcome drawbacks of the standard PHADEC. A simplified scheme of the process with the primary inputs and outputs of each step is shown in Figure 1.
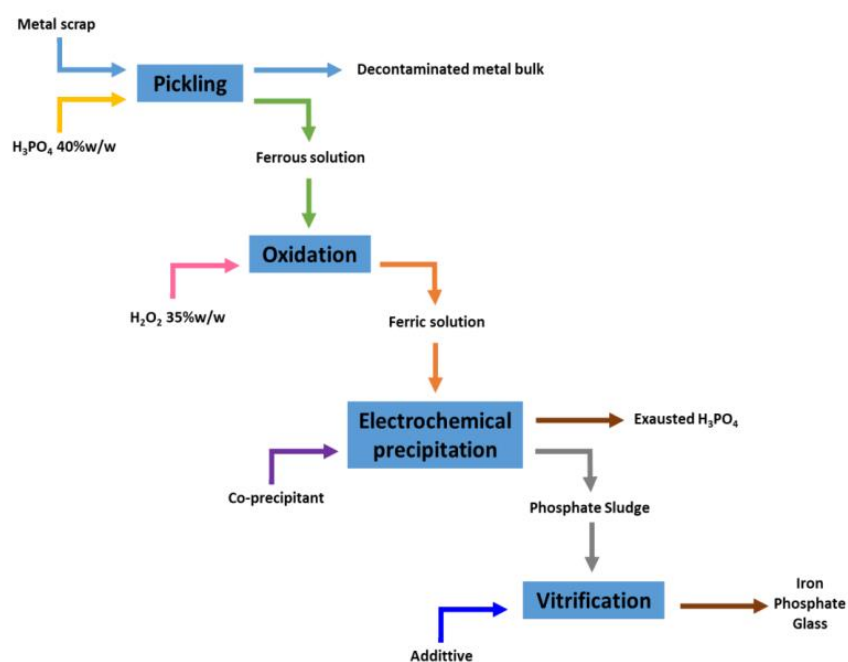

Figure 2 General scheme of the Advanced PHADEC-based process.

The stages involved in this process are:

- **Pickling process**: removal of the superficial contaminated layer by acid attack.

- **Oxidation step**: adjust the iron oxidation state in the solution containing the contamination to the proper value for the following precipitation process.

- **Electrochemical precipitation**: recovering the contaminants present in solution in the form of solid insoluble salts.

- **Vitrification**: conditioning of contamination by direct synthesis of a suitable waste form using the obtained insoluble salts treated at high temperature.

In this new process the phosphoric acid dissolution of the superficial contaminated layer of scrap metals is basically the same as the standard PHADEC one, but the chance to recycle and reuse the phosphoric solution without any evaporation treatment can substantially reduce the energy intensity of the process. The treatment of ferrous solution waste without altering its chemical composition by oxidation of Fe^{2+} to Fe^{3+} to reach the best Fe^{3+}/Fe^{2+} ratio for the following precipitation process is not involved in the standard PHADEC method, where the ferrous solution directly undergoes precipitation process. Furthermore, the chemical decontamination achieved by adding external precipitating agents like oxalic acid in the standard PHADEC process is now overcome by an electrochemical decontamination of the ferric solution, thus improving the precipitation yields, reducing the amount of solid waste, lowering corrosion effects and achieving the best conditions for the final conditioning step. Finally, unlike the standard PHADEC, the advanced process involves a direct conditioning of the solid by-product without any dilution in cement matrices. The final glass waste form obtained at a lower melting temperature than that of borosilicate glass shows higher physical-chemical stability in compliance with the Waste Acceptance Criteria (WAC) of the disposal facility, assuring the isolation of radionuclides from the biosphere.

In this practical course, you can directly experience the procedures that are used for the superficial decontamination of metallic scraps in the advanced PHADEC-based process, leading to the final release of the metallic materials and the conditioning of the radioactive contamination, minimizing the waste volume and the production of secondary liquid waste. In the course, radioactive contamination is simulated by means of stable isotope of Co, Sr, Cs, and Ni.

2 SURFACE DECONTAMINATION OF METALLIC SCRAPS: PICKLING PROCESS

2.1 Reagents, materials and apparatus

1. Metallic slab made of commercial steel
2. H_3PO_4 40%wt
3. Deionized water
4. Ultrapure water
5. Solution of 1% ultrapure nitric acid in ultrapure water
6. 50mM H_2SO_4
7. 0.3% Phenanthroline solution in water
8. 0.5mM $(NH_4)_2Fe(SO_4)_2$ solution in 50mM H_2SO_4

9. Pipettes
10. Thermostatic bath
11. Glassware (beaker, cylinder, funnel)
12. Plastic containers of different volumes
13. Plastic cuvette

14. pH-meter
15. Laboratory balance
16. Inductively coupled plasma mass spectrometry - ICP-MS
17. UV-vis spectrophotometer

2.2 Procedure

This step aims to dissolve the contaminated superficial layer on the metallic waste by a suitable acid attack, thus decontaminating the metal without any deterioration, making it possible for further reuse/recycling in the industry.

The pickling is performed by using concentrated orthophosphoric acid (H_3PO_4 40% w/w) by heating the solution to favour the reaction from a kinetic and thermodynamic point of view for several hours according to the desired final Fe concentration. The so-obtained solution is referred to as ferrous solution, which shows a bright green colour and a total Fe content of about 8.57% w/w, thus a saturated solution. In the perspective of the process economy, it is more convenient to produce a saturated Fe solution, even if, because of the several species present in the solution and the complex equilibria that are involved, the solution could exhibit some chemical instability, that could be observed as the presence of black solid particles in the solution.

The pickling process is performed following these steps:

1. Weigh the metal slab on a weighing boat

2. Put it in a plastic 500 mL container

3. Weigh the necessary amount of phosphoric acid at 40%w/w in a cylinder

4. Put the plastic container in the thermostatic bath, set the temperature and take note of the date and time

5. Stop the heating and remove the plastic container from the thermostatic bath

6. Remove the steel slab from the container, dry it and weigh it

7. Recover the solution, weigh it and filter it on filter paper

8. Measure density and pH of the green ferrous solution

9. Dilute an aliquot of the green ferrous solution by the proper dilution factor with ultrapure water and nitric acid for ICP-MS analysis to determine the concentration of Fe, P and other elements from steel

10. Dilute an aliquot of the green ferrous solution by a factor 4000 with 50mM H_2SO_4 for the UV-vis spectrophotometric analysis to determine the concentration of Fe(II): for the measurement prepare 5 samples of 10 mL each, containing 1 mL of diluted ferrous solution, 0.8 mL of 0.3% phenanthroline solution, a variable amount of $(NH_4)_2Fe(SO_4)_2$ solution (0, 0.1, 0.2, 0.3 and 0.4 mL) and sulfuric acid (8.2, 8.1, 8, 7.9 and 7.8 mL). Add 4 mL of each solution in a plastic cuvette for the spectrophotometric measurements.

3   PREPARATORY STEP FOR AN OPTIMAL PRECIPITATION: OXIDATION OF THE FERROUS SOLUTION

3.1 Reagents, materials and apparatus

1. Ferrous solution
2. H_2O_2 35%wt
3. Solution of 1% ultrapure nitric acid in ultrapure water
4. 50 mM sulfuric acid
5. 0.3% phenanthroline solution in water
6. 0.5mM $(NH_4)_2Fe(SO_4)_2$ solution in 50 mM sulfuric acid

7. Pipettes
8. thermostatic bath
9. stirring rod
10. glassware (beaker, cylinder, dropping funnel, multi-neck round bottom flask)
11. plastic containers of different volumes
12. plastic cuvette

13. pHmeter
14. Laboratory balance
15. Inductively coupled plasma mass spectrometry - ICP-MS
16. UV-vis spectrophotometer

3.2 Procedure

The oxidation process is necessary to enable the subsequent decontamination of the solution by electrochemical precipitation. Indeed, it is possible to exploit the precipitation of the most abundant cation Fe(II) as iron phosphate to co-precipitate insoluble phosphate salts of the other cations, present in solution at lower concentrations. However, having a look at the solubility and solubility products of such compounds, the compound that could be easily precipitated is ferric phosphate, where iron is in the oxidation state III. Therefore, it is necessary to oxidize Fe^{2+} to Fe^{3+} using a suitable oxidizing agent to precipitate in the subsequent stage efficiently. The ferrous solution is oxidized by dropwise addition of hydrogen peroxide (35% w/w) at controlled temperature (below 5 ◦C) under vigorous agitation. The stoichiometric amount of H_2O_2 was calculated on the basis of the Fe(II) concentration previously determined in the ferrous solution by a spectrophotometric measurement.

The oxidation process is performed following these steps:

1. Weigh the ferrous solution in a multi-neck round bottom flask
2. Put it in a thermostatic bath set at 5°C

3. Add a thermometer for temperature check to the flask

4. Add the stirring rod to the flask

5. Weigh the necessary amount of hydrogen peroxide 35%w/w in a cylinder

6. Put hydrogen peroxide in a dropping funnel and add it to the flask

7. When the solution is at 5°C, start to add dropwise hydrogen peroxide by the dropping funnel and turn on stirring

8. Check the temperature of the solution and adjust the bath temperature to keep the solution temperature in the range 5-7°C

9. Keep stirring for some minutes once the addition is concluded

10. Turn off the thermostatic bath and remove the flask

11. Weigh the ferric solution

12. Measure density and pH of the reddish-brown ferric solution

13. Dilute an aliquot of the reddish-brown ferric solution as done previously for the UV-vis spectrophotometric analysis to determine the residual concentration of Fe(II)

14. Dilute an aliquot of the reddish-brown ferric solution by the proper dilution factor with ultrapure water and nitric acid for ICP-MS analysis to determine the concentration of Fe, P and other elements from steel

4 RECOVERY OF THE CONTAMINATION IN A SOLID FORM: ELECTROCHEMICAL PRECIPITATION OF THE FERRIC SOLUTION

4.1 Reagents, materials and apparatus

1. Ferric solution
2. 100g/L $Sr(NO_3)_2$ solution in H_3PO_4 40%
3. 100g/L $CsNO_3$ solution in H_3PO_4 40%
4. 100g/L $Co(NO_3)_2$ solution in H_3PO_4 40%
5. 100g/L $Ni(NO_3)_2$ solution in H_3PO_4 40%
6. Co-precipitation agent
7. Solution of 1% ultrapure nitric acid in ultrapure water
8. Concentrated hydrochloric acid (37%)

9. Pipettes
10. Electrodes
11. Power supply
12. Glassware (glass rod, beaker, cylinder)
13. Plastic containers of different volumes

14. Centrifuge
15. pH-meter
16. Laboratory balance
17. Inductively coupled plasma mass spectrometry - ICP-MS
18. UV-vis spectrophotometer

4.2 Procedure

Radioactive contamination removed from the metallic scraps has still to be recovered in a form suitable for the subsequent conditioning, that is, in this case, the vitrification as iron phosphate glass. Furthermore, it is necessary to minimize the generation of secondary liquid waste. The electrochemical precipitation step aims to reach these two objectives.

The radioactive contaminations is simulated by adding known amounts of stable Cs, Co, Ni, and Sr to the ferric solution before the precipitation. The electrochemical precipitation is performed by immersing the electrodes in the ferric solution and applying a voltage by a suitable power supply and setting a limit to the current. As the current flows, there is gas release at the electrodes and the formation of sludge in the proximity of the cathode. At the end of the electrochemical precipitation process, a white pinkish sludge is formed in the cell and the liquid still present is called supernatant: they are separated by centrifugation. The so-obtained sludge is made of iron phosphates and mixed iron-contaminants phosphate: it contains most of the contamination removed from the metallic

pipes and is further treated in the next conditioning step. The supernatant could contain some remaining contamination: it is characterized in order to evaluate its recycling.

The electrochemical precipitation of ferric solution is performed following these steps:

1. Weigh the ferric solution in a plastic cell
2. Put the plastic cell in a water bath
3. Add a known amount of each contaminant from the stock solutions to the ferric solution.
4. Mix the solution and set aside an aliquot for the ICP-MS analysis
5. If required, add a weighed amount of the selected co-precipitation agent
6. Immerse the electrodes in the solution and connect them to the power supply
7. Set the current and voltage values and start the electrochemical precipitation
8. Once no more variation in the voltage are observed, turn off the power supply
9. Weigh the plastic cell with the electrodes
10. Remove the electrodes and weigh them
11. Remove the mixture from the plastic cell into centrifuge tubes and centrifuge them
12. Separate the supernatant, put it in a clean bottle and weigh it
13. Separate the wet sludge, put it in a clean bottle and weigh it
14. Calculate the precipitation yield, R, defined as the ratio between the weight of the wet sludge after centrifugation and the initial amount of ferric solution.
15. Measure density and pH of the supernatant
16. Dilute an aliquot of the supernatant as done previously for the UV-vis spectrophotometric analysis to determine the residual concentration of Fe(II)
17. Dilute an aliquot of the supernatant by the proper dilution factor with ultrapure water and nitric acid for ICP-MS analysis to determine the concentration of Fe, P and other elements from steel
18. Calculate the decontamination yields for Co, Sr, Ni, and Cs
19. Dissolve the wet sludge in concentrated hydrochloric acid in the ratio 1:12 w/w
20. Dilute an aliquot of the sludge solution by the proper dilution factor with ultrapure water and nitric acid for ICP-MS analysis to determine the concentration of Fe, P and other elements from steel

5 CONDITIONING OF THE CONTAMINATION BY VITRIFICATION OF THE IRON PHOSPHATE SLUDGE IN IRON PHOSPHATE GLASS

5.1 Reagents, materials and apparatus

1. Iron phosphate sludge
2. Sodium tri-polyphosphate

3. Plastic spoon
4. Ceramic crucibles
5. Single use aluminium containers
6. Gloves for high temperature
7. Tweezers
8. mortar

9. Balance
10. Oven
11. Furnace
12. X-ray fluorescence spectroscopy - XRF

5.2 Procedure

The simulated contaminants recovered from the ferric solution are now concentrated in the iron phosphate sludge, mainly in the form of phosphates. The sludge composition is suitable to directly obtain an iron phosphate glass by means of a proper thermal treatment at high temperature. Iron phosphate glasses are considered the better waste form for low activity waste due to their chemical stability and high fluidity, which helps quickly melt at lower temperatures than borosilicate glasses.

The vitrification of the sludge is performed by adding to the sludge a flux, having the role of lowering the melting temperature of the mixture under vitrification, thus reducing the energy consumption for the thermal treatment. The sludge is treated at 1025°C following an optimized thermal cycle.

The vitrification of the sludge is performed following these steps:

1. Weigh the sludge in plastic container
2. Add a weighed amount of flux and mix
3. Put the sludge added by the flux in the crucible and weigh it
4. Put the crucible in the furnace and follow the thermal cycle
5. At the end of the thermal cycle, turn off the furnace and recover the sample
6. Grind the glass obtained to fine powder and prepare the sample suitable for XRF analysis to determine the Fe, P and contaminants percentage in the glass.
7. Evaluate weight and volume reduction in the vitrification step

6 STRUCTURE OF THE HANDS-ON TRAINING COURSE

The Hands-on training course is organized in five days mainly devoted to practical sessions accompanied by theoretical lessons in person as recap or data analysis. Distance learning via CINCH Moodle will take place before the practical course. At the beginning of the course a training by means of a VR exercise will be proposed to the students.

APPENDIX 4: APPLICATION OF THE CORD PROCESS ON A METALLIC SAMPLE

Hands-on Training in Decontamination and Decommissioning

Task 4 – Application of the CORD process on a metallic sample

Manual for practical exercise

Author: Abdesselam ABDELOUAS, Aditya RIVONKAR

Version 1.0

IMT Atlantique
Bretagne-Pays de la Loire
École Mines-Télécom

EXECUTIVE SUMMARY

This document contains manual for practical task for the utilization of the CORD process for the treatment of a stainless steel sample. The CORD decontamination chemical process is a known method for decontamination of metallic structure in nuclear power plants. The following photos show the oxidized stainless steel before and after treatment using the CORD method. The examination of the treated confirmed the total dissolution of the oxidized layer, highlighting the efficiency of the CORD method.

Oxidized stainless steel embedded in silicon and showing a black oxidation layer.

Stainless steel embedded in silicon and decontaminated using the CORD method.
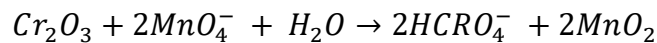
CONTENT

1 INTRODUCTION

Nuclear power generation is present in many countries worldwide, but more than 60% of the nuclear capacity is over 25 years old. In Europe 90% of all nuclear reactors, need to be shut down by 2030, unless their operation life will be prolonged. The major nuclear decommissioning activity is the application of decontamination technology, which are used to reduce the occupational exposures, to limit the potential releases of radioactive materials and to permit the reuse of components.

The reactor vessel and the piping system of the primary coolant is typically made up of austenitic stainless steel and Ni-alloy. The alloys are subjected to corrosion on the internal side under exposure to the primary circuit water; therefore, on the surface of these a duplex corrosion layer is formed. The upper layer is mainly magnetite, the main part of the corrosion film contains Cr, Ni, and Fe mixed oxides. Generally, the thickness of this corrosion layer is 5-6 μm for stainless steel.

The Chemical Oxidation Reduction Decontamination (CORD) method is a world-wide known 2-steps decontamination process. In the first step permanganate ion (MnO_4^-) is used to oxidize the chromium oxide-layer and to release chromate ions. Permanganate ions are derived from potassium permanganate, which can be used in nitric acid media, which is known as NP CORD, or in alkaline media (KOH) which is known as AP CORD.
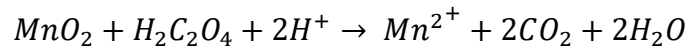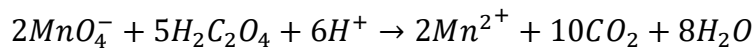
A third type of the CORD process, HP CORD makes use of permanganic acid, which is prepared from $KMnO_4$ using a strong acid cation resin.
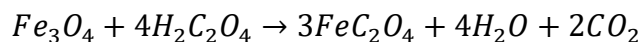
The reaction is as follows:

$$Cr_2O_3 + 2MnO_4^- + H_2O \rightarrow 2HCRO_4^- + 2MnO_2$$

In the next step, oxalic acid is added to reduce the permanganate ion to aqueous Mn^{2+} ions and dissolve the MnO_2 formed.
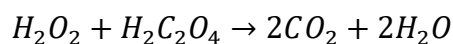
The reaction are as follows:

$$2MnO_4^- + 5H_2C_2O_4 + 6H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

$$MnO_2 + H_2C_2O_4 + 2H^+ \rightarrow Mn^{2+} + 2CO_2 + 2H_2O$$

The oxalic acid dissolves the Fe and Ni enriched oxide layer from the surface of the alloys according to reaction:

$$Fe_3O_4 + 4H_2C_2O_4 \rightarrow 3FeC_2O_4 + 4H_2O + 2CO_2$$

This constitutes one-step of the process.

The whole process is repeated several times. The solutions are treated with ion exchange resin to extract the dissolved metals; however, this process is only used in the second step, because of the incompatibility of the resins with the MnO_2 precipitate that can be formed in the oxidation stage. In most cases, the remaining oxalic acid is removed from the solutions by addition of H_2O_2 and the presence of a UV-source (CORD UV technology) and/or heating the solution.

For destruction using H_2O_2, the reaction is as follows:

$$H_2O_2 + H_2C_2O_4 \rightarrow 2CO_2 + 2H_2O$$

2 REAGENTS, MATERIALS AND APPARATUS

1. ICP-MS
2. Filtration unit
3. 0.45 μm filters
4. 5ml syringes
5. Deionized water
6. 1M HCl solution for cleaning
7. HDPE container
8. pH indicator paper
9. Hot plate
10. Small magnetic stirrers
11. 4M HNO_3
12. 50mM $KMnO_4$ Solution
13. 0.5M Oxalic acid solution
14. 5mL plastic bottle
15. 250mL glass beaker
16. 50mL measuring flask
17. SS sample to be treated (1cm*1cm*4mm)
18. Parafilm
19. Ethanol
20. Hydrogen peroxide (30%)
21. Paper filter

3 SAMPLE PREPARATION AND TEST

Before using the CORD process, the required solutions are needed to be prepared. This involves dilution of the $KMnO_4$ and oxalic acid solution until the required concentrations, in this case 6mM $KMnO_4$ in 3mM HNO_3 and a total of 21mM oxalic acid. For both solutions, 50 ml are prepared.

Dilution calculation:

$$C_1V_1 = C_2V_2$$

Where C_1= Concentration of stock solution

V_1= Required volume of stock solution

C_2= Desired concentration of final solution

V_2= Desired volume of final solution.

Using the equation, for 6mM $KMnO_4$ at 50 ml using 50 mmol·l^{-1} stock solution, we need a 6 mL of solution. Similarly, for HNO_3, a volume of 37.5 µl is needed. In addition, 4 mL of oxalic acid are required.

The procedure for application of the CORD process therefore is as follows:

1. It is very important to have all glassware chemically clean before beginning the experiment. To do this, rinse the 50 mL measuring flask and the 250 mL glass beaker using deionized water. Repeat at least 3 times. Then rinse using the 1M HCl solution for at least 3 times. Finally rinse using deionized water 5 times.

2. In the 50 mL measuring flask, add 20 mL of deionized water followed by 6 mL of 50mM $KMnO_4$ solution and 37.5 µl of 4M HNO_3 using a micro-pipette. Add water and adjust to 50mL.

3. Pour the solution in the 250mL glass beaker.

4. Add the sample and the magnet into the beaker and close the beaker using the parafilm.

5. Put the beaker on the hot plate and heat to 80℃ and turn on the magnetic stirrer.

6. Let the solution heat and stir for 4 hours.

7. Rinse the 50mL measuring flask once again using the same protocol as step 1.

8. In the meantime, the oxalic acid solution can be prepared. In the cleaned 50mL measuring flask, add 10 mL deionized water. Then add 4 mL of oxalic acid and finally adjust to 50 mL using deionized water. Set aside.

9. After 4 hours, remove the beaker and let it cool for 30 minutes before opening, as it can be **HOT**.

10. Using a 5 mL syringe, take out 5 mL from the solution. Pass the solution through the 0.45µm filter and store in the 5mL bottle. Label the bottle. This is the end of the step one of the solution.

11. To the glass beaker, add the 50 mL oxalic acid solution prepared in step 8.

12. Cover with parafilm once again and keep the solution on the hot plate and heat to 80℃.

13. Let the solution heat and stir for 4 hours once again and repeat steps 9, 10 and 11.

14. Using forceps remove the stainless steel sample from the solution, rinse it with ethanol, and let air dry.

15. The remaining solution can then be stored in the HDPE container and disposed of as liquid waste or can be used for oxalic acid destruction experiments.

This process completes one cycle of the process and it can be repeated as desired.

4   SAMPLE MEASUREMENTS

For the sample measurements, the ICP-MS is utilized for detection of Fe, Ni, and Cr dissolved in solution. To be within the detection limits of the device, the solution needs to be diluted using 2% HNO_3. Let us consider a dilution of 100 times and a volume of 10 mL per sample.

$$Volume\ required = \frac{Final\ volume}{Dilution\ factor} = \frac{10}{100} = 0.1\ ml$$

1. Take 0.1 mL of solution from the 5mL bottle in a tube.

2. Add 9.9 ml of 2% HNO_3.

3. Mix well and repeat for the second sample.

4. Pass through the ICP-MS as per protocol.

5. If the metals are not within detection limits of the device, adjust the dilution factors as required and prepare fresh dilutions accordingly.

6. After completion of the measurement, treat the data accounting for the calibration curve and the dilution factors utilized.

5 TREATMENT OF WASTES

After completing the treatment of the metal samples, the liquid waste is rich in oxalic acid and it needs to be treated before disposal. This can be done using hydrogen peroxide (H_2O_2) which is added to the oxalic acid solution (approximately 100 mL/cycle).

Calculating the H_2O_2 needed for preparing 100 mL of $1 mol·l^{-1}$ solution, we need 11.3 ml of 30% H_2O_2.

1. Transfer the remaining oxalic acid solution into a glass beaker. Each cycle should have approximately 100 mL of solution, if multiple cycles are used, the solutions can be mixed together.

2. Heat the solution up to 80℃ while stirring using the magnetic stirrer.

3. Carefully add 11.3 mL of 30% H_2O_2 solution. Adjust the volume if volume is greater than 100 mL.

4. Cover with parafilm and let react for 48 hours while stirring continuously.

5. After 48 hours, take off from heating and let cool completely.

6. If there is a precipitate, filter the solution using filter paper.

7. The solution and filter can then be disposed as per protocol.