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Recycling metal waste in nuclear decommissioning by advanced phosphoric acid decontamination process

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Summary. — The heavy burden of nuclear waste is currently the driver for the development of advanced technologies for treatment and conditioning of radioactive materials. Nuclear decommissioning generates a huge quantity of contaminated metal scraps to be managed. An advanced PHADEC-based process is under study to obtain further volume savings of the final waste and recycle metallic materials after treatment. This process consists of phosphoric acid dissolution of the superficial contaminated layer, subsequent oxidation of the pickling solution, electrochemical precipitation and vitrification of the dried iron phosphate precipitate. The research activity aims to optimize the electrochemical precipitation and separation steps to produce a suitable precipitate for the following vitrification unit. Pickling, oxidation and precipitation tests were performed at lab and intermediate scale. Stable Co, Cs, Sr and Ni were chosen as representatives of the radionuclides of the metallic dissolution liquor. To enhance decontamination and recycle the pickling solution in a pilot plant, screening tests were conducted thus exploring the potential role of co-precipitation agents in the electrochemical precipitation step. A promising abatement of contaminants from the phosphoric solution was observed by adding 0.3 M $BaSO_4$ during the electrochemical precipitation. Ongoing activities point to improve the decontamination yields by testing more co-precipitation agents.

1. – Introduction

Nowadays, the heavy burden of nuclear waste management represents the driving force for the development of innovative technologies for treatment and conditioning of radioactive materials. Decommissioning of a nuclear facility generates a large amount of contaminated metallic materials [1]. Most of the metal waste meet clearance levels in terms of radiation exposure to be released from the regulatory control as radiologically unrestricted materials, while the remaining part has different levels of radioactivity and needs to be managed [2,3]. Therefore, recycling and reuse of scrap metals could be

pursued to minimize the environmental footprint of dismantling activities, reduce high costs and save repository capacity [4,5]. The decision-making process on decommissioning and waste management is actually very hard, and a life cycle assessment could be vital for choosing the best strategy to undertake [6]. 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. 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) reuse 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 [7]. 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 in this research project, attempting to overcome drawbacks of the standard PHADEC. The new process depicted in fig. 1 is being carried out by the following steps:

- Phosphoric acid dissolution of the superficial contaminated layer of scrap metals at very low pH. The pickling process 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.

- 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. This step is not involved in the standard PHADEC method, where the ferrous solution directly undergoes precipitation process.

- Electrochemical precipitation of iron and contaminants phosphates. 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
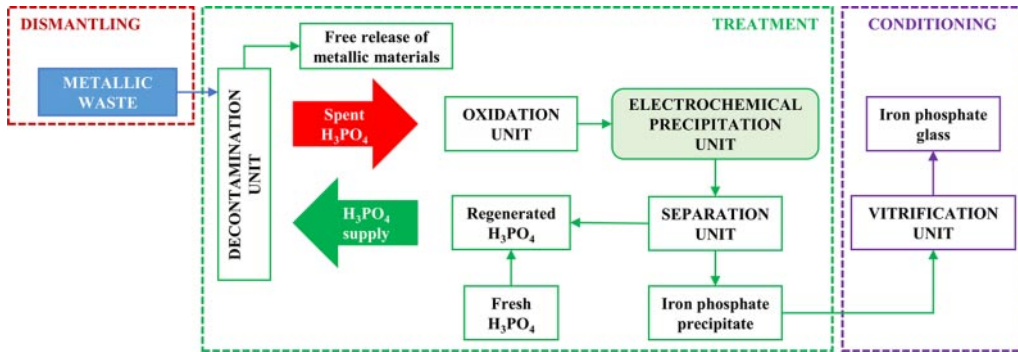

Fig. 1. – Treatment and conditioning steps of the advanced PHADEC-based process.

amount of solid waste, lowering corrosion effects and achieving the best conditions for the final conditioning step [7].

- Conditioning of the dried iron phosphate precipitate by vitrification. 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 shows higher physico-chemical stability in compliance with the Waste Acceptance Criteria (WAC) of the disposal facility [8,9]. The scope is to achieve the fundamental safety target of isolating radionuclides from the biosphere [10].

The optimization of the electrochemical precipitation step conducted in this research project is needed. The small concentration of contaminants could hinder their precipitation; therefore, the potential role of a co-precipitation agent is being investigated. This advancement will allow the PHADEC process to completely decontaminate the phosphoric acid solution and recycle it for a new pickling process, without generating very large amounts of secondary liquid waste [7,11].

2. – Materials and methods

2.1. *Chemicals*. – Metal scraps used in the dissolution experiments were commercial steel, named Fe-52/Fe 510/S 355, containing $< 1.5\%$ Mn, 0.55% Si, 0.22% C and 0.045% P and S. Phosphoric acid (H_3PO_4, 40% w/w) and hydrogen peroxide (H_2O_2, 35% w/w), purchased from Chimitex Italy, were of technical grade. 1 M phosphoric acid solution was prepared by dilution of the concentrated acid.

Cobalt (Co, 99%), nickel (Ni, 99%), strontium (Sr, 99.5%) and caesium (Cs, >99%) nitrates, purchased from Carlo Erba and Fluka, were used to prepare the metal stock solution in H_3PO_4 (40% w/w).

$Pb(CrO_4)$, $Ca(NO_3)_2$, CaF_2, $CaHPO_4$, $Al_2(SO4)_3$, $BaSO_4$ were purchased from Sigma-Aldrich (Reagent Grade). All chemicals were used as received.

Ultrapure nitric acid (purchased from Santis Analytical Italia) and ultrapure water (Millipore, Billerica, USA; $18.2\,M\Omega \cdot cm$) were used to properly dilute samples for mass spectrometry analysis.

2.2. *Procedures*. –

2.2.1. Pickling. Metal scraps were dissolved in H_3PO_4 (40% w/w) into a three-neck round-bottom flask for 72 hours at controlled temperature lower than $55\,°C$ and vigorous mixing. The resulting ferrous solution was filtered to remove insoluble fine powder, and properly characterized as described in sect. **2**.3 (fig. 2). The pickling step was performed at both lab (1 L) and intermediate (25 L) scale.

2.2.2. Oxidation. The ferrous solution was 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 complete in 60–80 minutes (fig. 3). The ferric solution was properly characterized (see sect. **2**.3) and used within two days since the preparation. The oxidation step was performed at both lab (1 L) and intermediate (25 L) scale.
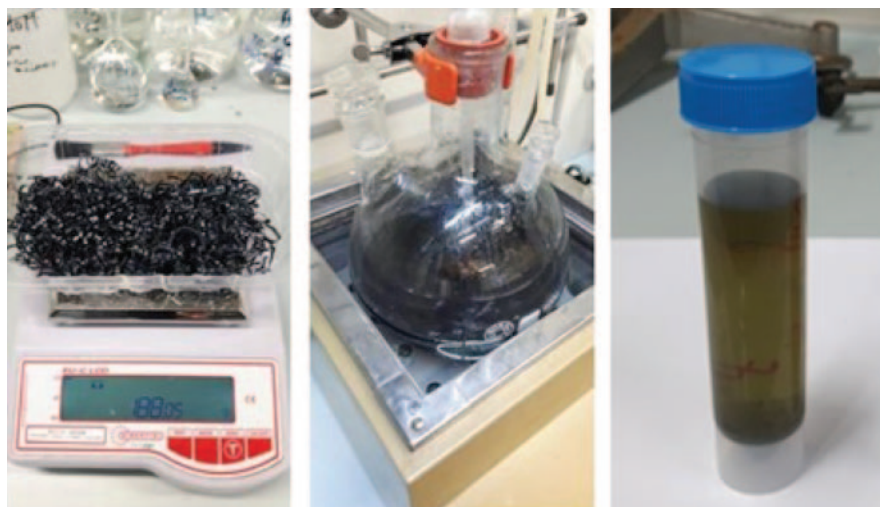
Fig. 2. – Dissolution process of scrap metals at lab scale (1 L) and ferrous solution after filtration.

2'2.3. *Precipitation.* The ferric solution was used as it is or after adding a known amount of the contaminants stock solutions. The electrochemical precipitation was performed by loading a weighed amount of the ferric solution in the cathodic half-cell and a weighed amount of 1 M phosphoric acid solution in the anodic half-cell. Two electrochemical cells of different sizes (lab and intermediate scale half-cell volume of about

Fig. 3. – Oxidation process at lab scale (1 L); comparison between ferrous and ferric solutions.

TABLE I. – *Features of electrochemical cells used at lab and intermediate scale in this research project.*

Cell A		
Volume half-cell	0.5 L	
Electrode materials	niobium	platinum titanium
Electrode size	2.5×2.5 cm^2, micro-mesh	4×4 cm^2, large mesh
Electrode surface	6.25 cm^2	16 cm^2
Separator dimensions	8×11 cm^2	
Cell B		
Volume half-cell	25 L	
Electrode materials	platinum titanium	
Electrode size	15×20 cm^2, large mesh	
Electrode surface	300 cm^2	
Separator dimensions	30×25 cm^2	

0.5 L and 25 L, respectively) equipped with an anion-exchange membrane (Fumasep$^®$ FAD-PET-75, purchased from FUMATECH BWT GmbH) separating the two half-cells were used. Table I reports some details about the cells and the electrodes [11].

Optimization experiments were performed by using different configurations (half-cell geometry) and process conditions (voltage values and duration). Current and voltage profiles during the electrochemical process were recorded.

Cell A with contaminants. The lab scale precipitation test was carried out by using electrochemical cell A (0.5 L) according to the procedure developed by ECIR S.R.L., with electrodes distance of 8.5 cm and applied voltage of about 10 V [11]. Stable Co, Sr, Ni and Cs were added to 557 g of a catholyte solution to have about 50 ppm each. The electrochemical process lasted about 18 hours.

Cell B with contaminants. The electrochemical precipitation was also performed at intermediate scale by cell B (25 L) with electrodes at a certain distance and applied voltage. The stable contaminants were added to 31691 g of catholyte at a concentration of about 50 ppm each. The test was conducted for 29 hours.

2˙2.4. *Separation.* At the end of the process, the catholyte was quantitatively recovered and centrifuged under previously optimized conditions (relative centrifugal force equivalent to 3000 g, for 15 minutes). A wet sludge was obtained by decanting the supernatant. Both the fractions were weighed for evaluating the precipitation yield, that is defined as the ratio between the mass of the obtained wet sludge and the mass of the initial catholyte solution. Supernatant and anolyte were properly characterized (sect. **2**˙3).

2˙2.5. *Co-precipitation.* The choice of the co-precipitant was driven by the general physico-chemical principles of the co-precipitation procedure. It was chosen on the basis of its solubility product constant with respect to the insoluble phosphates of the present contaminants [12]. The aim is to optimize the final concentration of the best co-precipitation agents to improve the decontamination yields, without compromising

the following vitrification step [11]. The first series of screening experiments were conducted by adding a weighed amount of the co-precipitation agent as powder to small volumes (10 mL) of i) the supernatant coming from the precipitation tests and of ii) the ferric solutions before electrochemical precipitation. The solutions were first visually observed and then analysed by ICP-MS before and after the addition of the co-precipitation agent. The scope was to select an effective co-precipitation agent able to promote further formation of precipitate from the solutions under investigation. The effect of the most promising co-precipitation agent among those tested has been further checked during an electrochemical process at lab scale (120 mL) in a simple electrochemical cell configuration (no anion exchange membrane, electrode section 4×4 cm^2 and distance 2.5 cm, applied voltage 8 V, process time 4 h 30′). After centrifugation, an aliquot of the supernatant was taken for ICP-MS analysis.

2˙3. *Characterization*. – Density and pH were measured for the ferrous and ferric solutions. The Fe^{2+} concentration in the ferrous solution was determined by spectrophotometric measurements (Lambda 650, Perkin Elmer, USA). Inductively Coupled Plasma-Mass Spectrometry (ICP-MS, NexION 2000, Perkin Elmer, USA) was used to characterize the adopted commercial steel after dissolution by acid attack in a microwave oven, and to measure Fe, P, Co, Ni, Sr and Cs concentrations in the liquid solutions.

3. – Results and discussion

3˙1. *Pickling and oxidation*. – The pickling process carried out at lab and intermediate scale resulted into an olive-green solution, mainly composed of Fe^{2+} (8.06–8.61% w/w). It has a density of 1.42–1.45 g/mL and pH between 1–1.2. A total Fe/P ratio of about 0.746–0.781 was measured, suitable for the subsequent vitrification step [11].

The brick-red solution obtained from the oxidation process at lab and intermediate scale is completely Fe^{3+} and it is herein also called ferric solution. It has a density of around 1.40–1.42 g/mL and a pH value in the range 0.8–1.

3˙2. *Precipitation*. – The electrochemical precipitation ended with the formation of a substantial milky sludge into the cathodic half-cell of both configurations as depicted in fig. 4. The process carried out in the electrochemical cell A showed a volume reduction of the catholyte ($\sim$15%) and the anolyte ($\sim$19%). Variations of pH were observed for the catholyte and in particular for the anolyte (from 0.9 to 0.5).

At the end of the process carried out with the electrochemical cell B, a smaller volume
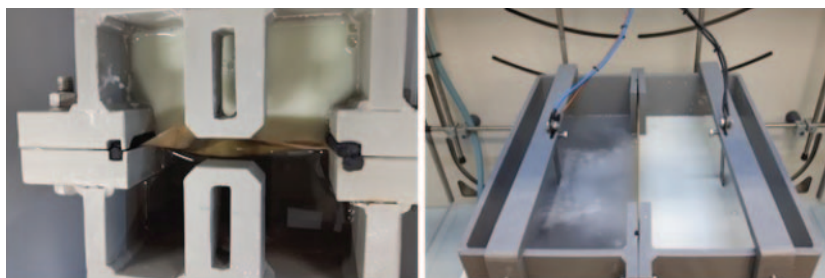

Fig. 4. – Final stage of the electrochemical precipitation process conducted at lab (left) and intermediate (right) scale. The cathodic solution turned into a huge quantity of milky precipitate.

reduction was observed for both the catholyte ($\sim$5%) and the anolyte (7%). Similarly, small variations of pH were observed.

$3`3$. *Separation*. – The process carried out with the electrochemical cell A resulted in 240.7 g of supernatant and 234.8 g of wet sludge thereby obtaining a precipitation yield of about 0.42. The fraction of Co, Ni, Sr and Cs in the supernatant was 56%, 62%, 63% and 7%, respectively. Remarkably, the anolyte also contained 1%, 0.2%, 1.7% and 0.9% of initial Co, Ni, Sr and Cs content, respectively. By the electrochemical cell B, 17697 g of supernatant and 13570 g of wet sludge were obtained. This resulted into a precipitation yield of about 0.41. The supernatant contained about 69% each of initial Co, Sr, Ni and 3% of Cs after the separation, while the percentages in the anolyte were much lower than before ($\leq$0.1%).

$3`4$. *Co-precipitation*. – The first screening experiments conducted with the supernatant solutions resulted in a conspicuous amount of precipitate for CaF_2 and $BaSO_4$, while small precipitate for $CaHPO_4$ and poor chemical stability over time for $Pb(CrO_4)$ and $Ca(NO_3)_2$ were observed (fig. 5). Despite the small quantity of precipitate obtained by $Al_2(SO_4)_3$, the ICP-MS analysis carried out on the supernatant after centrifugation showed a promising abatement of Co and Sr. The second series of screening tests were run with CaF_2, $CaHPO_4$ and $BaSO_4$ on small volumes of the ferric solution before the electrochemical precipitation. They resulted in a greater amount of precipitate, but ICP-MS analysis did not lead to notable abatement of contaminants.

According to the results obtained in the screening experiments, $Al_2(SO_4)_3$ and $BaSO_4$ were added to the ferric solution at the beginning of electrochemical precipitation. ICP-MS analysis of the supernatant coming from the $Al_2(SO_4)_3$ test showed no remarkable effect on the solution decontamination. Conversely, the use of $BaSO_4$ as co-precipitant during the electrochemical precipitation resulted in a better decontamination of the su-
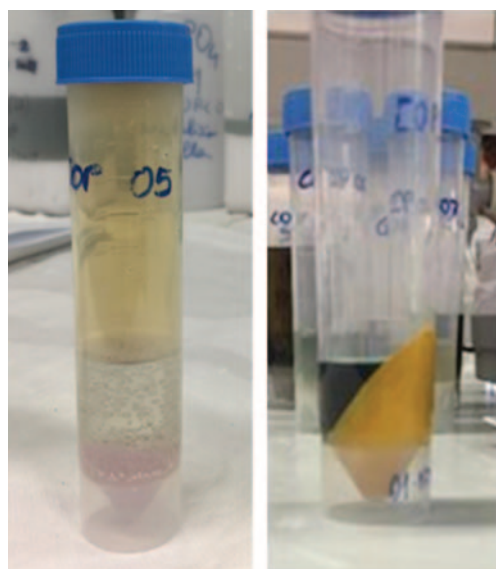

Fig. 5. – Evidence of poor chemical stability over time for $Ca(NO_3)_2$ (left) and $Pb(CrO_4)$ (right).

TABLE II. – *Contaminants in supernatant [%].*

Co-precipitant	Co	Ni	Cs	Sr
Blank (no co-precipitant)	64 ± 1.2	57 ± 1.1	5 ± 0.1	71 ± 1.9
0.3 M BaSO$_4$	40 ± 5.1	40 ± 4.9	4 ± 0.1	47 ± 1.8

pernatant solution, as shown in table II. If compared with the results of the blank (*i.e.*, no co-precipitant), the concentration of Co, Ni and Sr contaminants in the supernatant is reduced by about 20% if BaSO$_4$ co-precipitant is used at 0.3 M. This encouraging result suggests a positive effect of BaSO$_4$ in the abatement of contaminants into the iron phosphate precipitate.

4. – Conclusions

An advanced PHADEC-based process is developed to recycle and reuse metallic materials from dismantling activities in nuclear decommissioning. The process is proposed as a valuable alternative to the standard PHADEC, thereby contributing to minimize the environmental footprint of nuclear decommissioning activities. The possibility to recycle and reuse the phosphoric solution without any evaporation treatment can lead to a lower energy-intensive process, generating low amount of secondary liquid waste. The electro-chemical precipitation performed without adding oxalic acid improves the precipitation yields, reduces the amount of solid waste and limits corrosion effects thus achieving the best conditions for the final conditioning step. The dried iron phosphate precipitate is directly conditioned by vitrification. The final glass wasteform is obtained at lower melting temperature than the borosilicate one, and it shows higher physico-chemical stability.

Pickling, oxidation, and electrochemical precipitation tests were conducted at lab and intermediate scale. The outcomes of the intermediate tests are promising and consistent with those obtained at lab scale. Notably, a total Fe/P ratio between 0.746–0.781 was measured, within the optimal range required by the vitrification process to obtain a very stable wasteform. The electrochemical precipitation tests showed a precipitation yield of about 0.40 and a good abatement of Co, Cs, Sr and Ni from the iron-phosphate solution.

Nevertheless, optimization of the electrochemical precipitation step is needed, and it relies on the effect of potential co-precipitation agents. Promising screening tests were carried out by adding some solid compounds to small volumes of supernatant and to ferric solution before the electrochemical precipitation. The effect of BaSO$_4$ was also checked during the electrochemical process at lab scale in a simple cell configuration. A promising abatement of contaminants ($\sim$55% for Co, Ni, Sr and $\sim$95% for Cs with respect to 30–40% for Co, Ni, Sr and 95% for Cs obtained in the blank test) from the phosphoric solution was observed by adding 0.3 M BaSO$_4$. Ongoing investigations are devoted to corroborating the achieved results, optimizing the precipitation process based on BaSO$_4$ and exploring the efficacy of more potential co-precipitation agents.

These optimization studies will be crucial for the development of this advanced PHADEC-based process since they will allow to completely decontaminate the phosphoric acid solution and recycle it for a new pickling process in a pilot plant.

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