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Treatment of spent ion exchange resins: comparison between hydrothermal and acid leaching processes

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Abstract

Ion exchange resins (IERs) are used to treat radioactive liquid effluents from nuclear industry. Today, the management of spent IERs as nuclear waste is an issue. We propose here the use of hydrothermal and leaching treatments to transfer radioactivity from organic solid phase to aqueous phase, in order to connect to existing outlet systems. Co, Cs, Sr and Eu were chosen as α and $\beta\gamma$ radionuclide surrogates. The efficiency of the treatment was assessed in terms of extraction yields and contaminant concentrations in wastewaters. The highest extraction efficiencies of 90–100% were obtained in supercritical water in batch and semi-dynamic mode in the presence of oxidant. In subcritical conditions, yields adequate are lower but suitable with the disposal criteria for the residual solid waste. Complete extraction was also achieved by leaching with ethylenediaminetetraacetic acid solutions. The optimal choice between all these processes is therefore discussed with regards to the requirements of effluent treatment plant including post-treatment steps such as coprecipitation and advanced oxidation.

Keywords: Ion exchange resin, hydrothermal treatment, oxidation, leaching, batch, semi-dynamic

1. Introduction

Water treatment systems in the nuclear industry use ion exchange resins (IERS) to control the chemistry of the effluents, minimize corrosion and remove radioactive contaminants. Spent IERS can be damaged by chemical, mechanical and thermal processes as well as by irradiation [1]. This can destroy the covalent bonds in the resin and lead to swelling. Nuclear power plants typically consume around 5–7 m³ of IERS per reactor per year. The regeneration of spent IERS containing radioactive ions would therefore produce large volumes of liquid waste but this step is so complicated that spent IERS are typically replaced without any reuse. Spent IERS can be immobilized in an inert matrix (cement, bitumen, or polymer) or mineralized to inorganic residues before solidification or disposal. The high flammability and radioactivity of spent IERS mean that recycling is particularly difficult, with no satisfactory treatment currently available, but safe disposal is also problematic for the most radioactive waste, making the treatment of spent IERS a critical issue.

Supercritical water has properties allowing to totally decompose organic polymers such as resins into CO₂ and aqueous phase containing inorganic salts. This allows the total destruction of the IERS and transfer all the contamination from the organic solid to the aqueous effluent that must be compatible with existing outlet system.

Considering safety and cost issues, a fast and easy way to operate alternative to supercritical water treatment consists in reducing pressure and temperature in order to carry out subcritical water extraction under the critical point of water. In these sub-critical conditions, the diffusion rate of water increases because of reduction of its viscosity, surface tension and permittivity. Ionization constant is much higher than in water in ambient temperature. Moreover, the modulation of redox conditions is possible by adding suitable amount of oxidant. Considered resins contain respectively sulphur or nitrogen, which may be converted in situ into H₂SO₄ and HNO₃ during the waste decomposition, avoiding to add other corrosive chemicals. Therefore, released metallic species react with acids formed in situ, so as to get ionic species in aqueous phase. Another way consist of using metal complexing reagents to leaching out radionuclides entrapped in spent IER. In subcritical mode, and

in leaching mode, the spent IERs can be degraded and most of the contamination transferred from the solid phase to the aqueous phase. The objective is to have, as final waste, solids and an aqueous effluent compatible with the outlets.

Gupta et al.'s investigations of acid leaching to treat spent Dowex[®] IERs from the PUREX process suggest that this may be a viable approach for organic radioactive waste [2]. Another possibility to mineralize the organic backbone of IERs and recover radionuclides as secondary waste from liquid effluents is hydrothermal oxidation. Milder hydrothermal treatments can also be used to extract radioactive species from spent IERs so that they can be immobilized in an inert matrix. Sub-critical hydrothermal processes are generally used to reduce the solid content of organic waste for disposal or to remove harmful heavy metals. The feasibility of wet air oxidation for nuclear grade cationic and anionic IERs was demonstrated by Dubois et al. (1996), with carbon degradation yields of up to 96% at 380–435 °C and 220–260 bar, and with residence times of few hours [3]. Koda subsequently investigated the kinetics of the hydrothermal oxidation of cationic IER as a function of temperature (300–450 °C) and oxidant stoichiometry [4]. Advanced oxidation processes, such as Fenton oxidation, have also been investigated for the degradation of cationic resins [5–7]. These processes have been implemented alone [5] or with wet air oxidation for mineralization [6]. Wan & Wang used Fenton oxidation to completely dissolve cationic resins using Fenton oxidation with 95.8% weight reduction [7].

Several approaches have been considered in the literature to improve carbon degradation yields and completely mineralize IERs. Worl et al. [8] used pyrolysis to convert solid organic waste mixtures (e.g. solvents, liquid scintillation cocktail, rubber gloves and IERs) into pumpable liquids. Sugiyama et al. [9] investigated supercritical water oxidation with a RuO₂ based catalyst. Akai et al. [10] achieved degradation yields greater than 99% at 400 °C, 300 bar, using stoichiometric excesses of strong oxidant, while in our laboratory, degradation yields of up to 99.9% were obtained for crushed IERs using isopropanol as a co-fuel [11]. Finally, Kim et al. [12] established optimal operating parameters for sub- and supercritical water oxidation of IERs by experimental design using

the chemical oxygen demand, the total nitrogen concentration, and the concentrations of different metals in the effluent to monitor the efficiency of the process. These studies provided the technical background for the development of commercial IER treatment plants in Japan [13] and South Korea [14] with treatment capacities of up to 150 kg/h.

Previous studies have mostly focussed on acidic resins in hydrogen form or basic resins in hydroxyl forms rather than exchanged forms of IERs. However, in cationic resins, the counterion has been shown to have a significant effect on the degradation process, with lower yields obtained with Li⁺-exchanged IERs compared with those exchanged with Na⁺ or K⁺ [11].

The aim of this study was to evaluate hydrothermal processes with and without an oxidant, at sub and supercritical conditions, for the removal of contaminants from spent IERs **and the transfer of radioactivity from organic solid phase to aqueous phase to connect to existing outlet systems.** Experiments were performed on laboratory-contaminated non-radioactive IERs but in view of applications with radiocontaminated, structurally deteriorated IERs, mild hydrothermal conditions were favoured and the samples were not preprocessed. Moreover, to accommodate uncertainties in IER particle sizes and chemical structure, batch and semi-dynamic processes were investigated instead of the continuous stirred reactor process developed previously in our laboratory [15]. Different operating conditions (pressure, temperature and oxidant concentration) were assessed and the hydrothermal processes were compared with acid leaching in terms of extraction yields and effluent compositions.

2. Material and methods

2.1. Reagents

2.1.1. Ion exchange resins

The IERs used in this study (Amberlite[®] IRN77 and IRN78, The Dow Chemical Company) consist of polystyrene backbones reticulated with divinylbenzene and functionalized with either sulfonic groups (in IRN77, a strong cationic resin) or trimethylammonium groups (in IRN78, a strong

anionic resin). The physical and chemical characteristics of the two resins are summarized in Table 1.

Table 1

Properties of the ion exchange resins used in the study

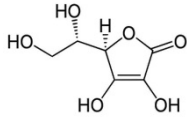
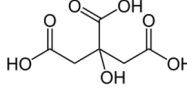
	IRN77	IRN78
Type	cationic	anionic
Functional group	SO ₃ ⁻	NH ₄ ⁺
Crosslinking rate (%)	8	8
Ion exchange capacity		
(eq·L ⁻¹)	1.9	1.2
(meq·g ⁻¹ dry IER)	4.7	3.5
Particle size range (mm)	0.6–0.7	0.58–0.68
Density (g·L ⁻¹)	800	690
Moisture content (%)	49–55	54–60

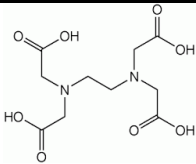
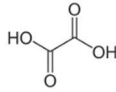
2.1.2. Other chemicals

The metal salts used to contaminate the IERs and the acids used for leaching experiments are listed in Table 2. Hydrogen peroxide was used as an oxidant.

Table 2

Chemical structure and purity of the chemical products used in this study.

<i>Chemical name</i>	<i>CAS N°</i>	<i>Source</i>	<i>Chemical formula/structure</i>	<i>Purity (wt%)</i>
Ascorbic acid	50-81-7	Aldrich		> 99
Citric acid	77-92-9	Aldrich		>99.5

EDTA	60-00-4	Aldrich		>99
Nitric acid	7697-37-2	Aldrich	HNO ₃	70
Oxalic acid	144-62-7	Aldrich		> 99
Sodium carbonate	497-19-8	Aldrich	Na ₂ CO ₃	> 99
Ammonium sulfate	7783-20-2	Aldrich	(NH ₄) ₂ SO ₄	> 99
Sulfuric acid	7664-93-9	Aldrich	H ₂ SO ₄	95-98
Cobalt (II) nitrate hexahydrate	10026-22-9	Aldrich	Co(NO ₃) ₂ ; 6H ₂ O	99.999
Cesium nitrate	7789-18-6	Aldrich	Cs(NO ₃)	99.999
Europium (III) nitrate pentahydrate	63026-01-7	Aldrich	Eu(NO ₃) ₃ ; 5H ₂ O	99.9
Strontium nitrate	10042-76-9	Aldrich	Sr(NO ₃) ₂	99.995
Hydrogen peroxide	7722-84-1	Aldrich	H ₂ O ₂	30

EDTA; Ethylenediaminetetraacetic acid

2.2. Protocol for the preparation of contaminated IER

Samples of IRN77 were contaminated as described by Lafond et al. [16]. Acidic IERs exchange reversibly with metal cation solutions. The target concentration was 10 mg/g, chosen as a compromise between realistic contamination levels and analytical detection limits. A set of samples with 20 mg/g metal contaminations was also prepared for the batch experiments on 50:50 wt% mixtures of IRN77 and (uncontaminated) IRN78 to keep the overall metal concentration approximately constant between experiments. Typically, 10 g of IER beads in H⁺ form was added to a vessel containing 500 mL of the Cs, Co, Eu and Sr nitrate solution at the desired concentration and stirred continuously for 4 h. The evolution of the ion-exchange reaction was monitored using pH measurements and inductively coupled plasma atomic emission spectroscopy (ICP-AES) and atomic absorption spectroscopy (AAS). The solutions were analysed before and after contacting with the IER to determine the concentration of each element in the IER samples before leaching or hydrothermal treatment. The initial metal contents of the samples for the batch (B1–B10), dynamic

(D1,D2) and leaching experiments (L1–L10) ranged from 9.4 to 10.6 mg/g for Cs, 9.5 to 10.4 mg/g for Co, 8.9 to 9.8 mg/g for Eu, and 9.3 to 10.4 mg/g for Sr.

2.3 *Hydrothermal treatment experiments*

2.3.1. *Batch experiments*

The apparatus used for the hydrolysis/oxidation experiments under subcritical and supercritical hydrothermal conditions has been described in detail elsewhere [17]. It consists of an Inconel 625 autoclave with a flexible internal titanium vessel, which confines the aggressive chemical species (e.g. H₂SO₄) and protects the reactor walls from corrosion. The flexibility of this vessel makes it possible to compensate for pressure differences between the internal and the external contents. The device is designed for operating pressures and temperatures up to 300 bar and 600 °C. Temperature and pressure were measured in the reactor and in the vessel using K-type thermocouples (uncertainty $\pm 0.4\%$) and Keller PA-23 SY pressure sensors (uncertainty $\pm 0.25\%$).

The titanium vessel was filled with a mixture of the IER sample and demineralized water or a water/H₂O₂ mixture, in which case the H₂O₂/IER stoichiometric ratio was set to 1.3 based on the average composition of the IER stated by the manufacturer. To minimize pressure differences and avoid damaging the titanium vessel, the filling factors of the reactor and the titanium container were equalized by adding water to the reactor. The filling factor was adjusted to reach the target pressure at each operating temperature as calculated using the Peng-Robinson equation of state. The mass of water in the reactor was set to 71 g and the corresponding water/H₂O₂ masses in the titanium container are listed in Table 3. After filling the autoclave and the container, the temperature was increased to the desired value and the pressure increased autogenously. Each experiment was run for 2 h after the target temperature had been reached.

Table 3.

Solution compositions and operating conditions used for the batch hydrothermal extraction experiments.

Experiment	T (°C)	P (bar)	IER	m_{IER} (g)	m_{H_2O} (g)	$m_{H_2O_2}$ (g)
B1	300	69	IRN77	1.2	18	0
B2	300	67	IRN77	1.2	18	0
B3	450	263	IRN77	1.3	18	0
B4	250	58	IRN77	1.2	2	16.7
B5	300	63	IRN77	1.2	2	16.3
B6	450	289	IRN77	1.2	1.2	16.5
B7	300	74	IRN77/IRN78	0.6/0.6	18	0
B8	450	281	IRN77/IRN78	0.6/0.6	18	0
B9	300	77	IRN77/IRN78	0.6/0.6	1.2	16.5
B10	450	284	IRN77/IRN78	0.6/0.6	1.2	16.5

IER, ion exchange resin

2.3.2. Semi-dynamic experiments

The device designed for batch operation was adapted to perform semi-dynamic experiments in which the pressure and temperature were adapted and the hydrothermal stream was renewed (Fig. 1). In this setup, the treatment capacity was 50 g of IER per experiment. The internal basket containing the IER(s) (IRN77 by itself in experiment D1, or mixed with IRN78 in experiment D2) was equipped with a 90 μm mesh to avoid mechanical entrainment and plugging. The reactor was heated to operating temperatures of up to 200°C using heating shells. A 70/30 wt% water/H₂O₂ mixture was injected at a constant flow rate of 5 mL·min⁻¹ and a pressure of 50 bar using a high-pressure pump (PU-4180, Jasco). The exchanged (contaminated) IERs were loaded into the basket before being placed in the reactor and contacted with the water stream, which was fed from the bottom of the basket. Each experiment lasted about 4 h. The metal contaminants were recovered in the aqueous

phase. The flow (water + mineral species + IER degradation products) was collected downstream after cooling and depressurization using a back pressure regulator. The effluents were sampled every 10 min, weighed, filtered with a 45 μm syringe filter and analysed by ICP-AES to determine the Cs, Co, Eu and Sr concentrations.

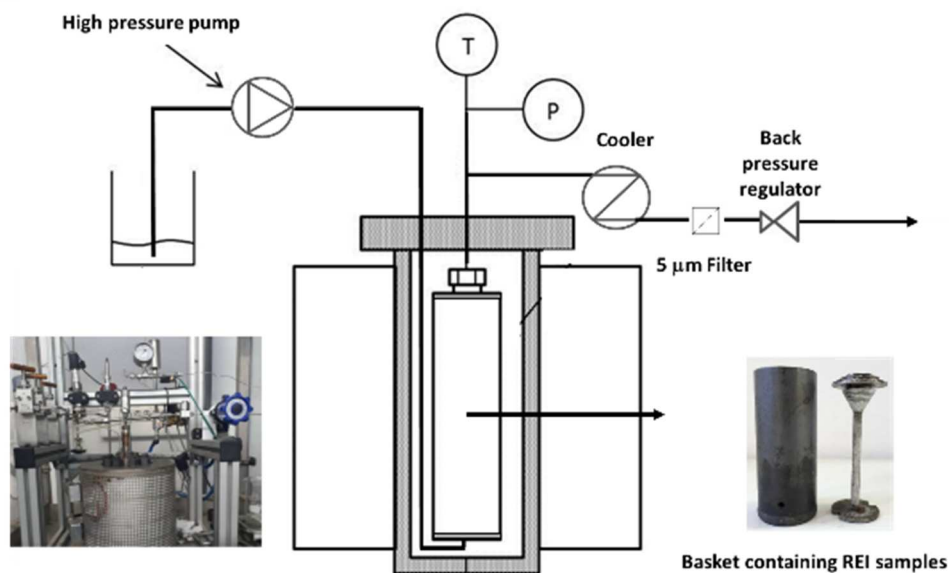


Fig. 1. Schematic diagram of the setup used for the semi-dynamic hydrothermal treatments of ion exchange resins.

2.4. Leaching experiments

Leaching experiments were performed at ambient temperature using 100 mL of 10 different acid solutions (Table 4). In each case, 10 g of contaminated IRN77 was leached for 3 h. The leaching solutions were then weighed, filtered with a 45 μm syringe filter and analysed by ICP-AES to determine the Co, Eu and Sr concentrations.

Table 4

Composition of the acid solutions used for the leaching experiments

Experiment	Leaching solution
------------	-------------------

L1	HNO ₃ (0.1 mol·L ⁻¹)
L2	HNO ₃ (1 mol·L ⁻¹)
L3	C ₆ H ₈ O ₇ (1 mol·L ⁻¹) – (NH ₄) ₂ SO ₄ (0.01 mol·L ⁻¹)
L4	C ₆ H ₈ O ₇ (0.3 mol·L ⁻¹) – (NH ₄) ₂ SO ₄ (0.005 mol·L ⁻¹)
L5	EDTA (1 mol·L ⁻¹)
L6	EDTA (0.1 mol·L ⁻¹) - Na ₂ CO ₃ (0.01 mol·L ⁻¹)
L7	EDTA (0.05 mol·L ⁻¹) - Na ₂ CO ₃ (0.3 mol·L ⁻¹)
L8	C ₂ H ₂ O ₄ (0.1 mol·L ⁻¹)
L9	C ₆ H ₈ O ₆ (0.1 mol·L ⁻¹)
L10	H ₂ SO ₄ (2 mol·L ⁻¹)

2.5. Analysis

The IER and liquid effluent samples from each hydrothermal treatment and leaching experiment were analysed by ICP-AES and AAS to determine the concentration of the metal contaminants (Cs, Co, Sr and Eu); the total organic carbon (TOC) content of the samples was also measured.

The extraction yields for Cs, Co, Sr and Eu was calculated using Eq. (1):

$$R_X = \frac{m_{X_{sol}}}{m_{X_{IER}}} \times 100 \quad (1)$$

where $m_{X_{sol}}$ and $m_{X_{IER}}$ are respectively the final mass of metal X in the aqueous phase after hydrothermal treatment and the initial mass of metal X in the IER. The uncertainties on these extraction yields was less than 10%.

The degradation yield for carbon was calculated using Eq. (2):

$$R_C = \left(1 - \frac{m_{C_{sol}}}{m_{C_{IER}}}\right) \times 100 \quad (2)$$

where $m_{C_{sol}}$ and $m_{C_{IER}}$ are defined as above for the metals. The uncertainties on these measurements was less than 2%.

3. Results and discussion

3.1. Batch hydrothermal treatments

The results obtained for the batch hydrothermal treatments using sub- or supercritical water are shown in Fig. 2 for the cationic IER (IRN77, experiments B1–B6) by itself and in Fig. 3 for mixtures with the anionic IER (IRN78; experiments B7–B10).

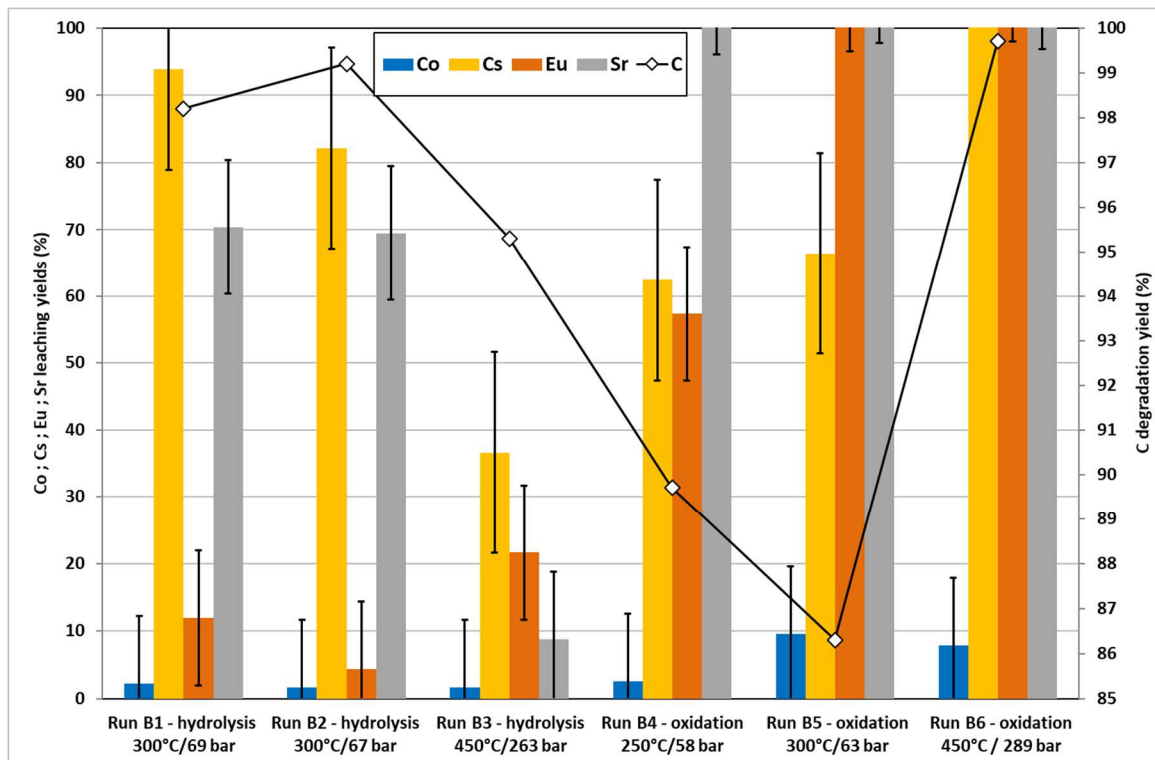


Fig. 2. Extraction yields for Cs, Co, Eu, Sr and carbon degradation yields for batch hydrothermal treatments of the cationic IER Amberlite® IRN77 under different operating conditions.

When IRN77 was treated alone, the carbon degradation yields were higher than 85% under all operating conditions (Fig. 3). A few residual particles were observed for the hydrolysis runs (B1–

B3), suggesting that the yields measured for these experiments may be slight overestimates. As expected, the highest degradation yield (around 99.7%) was obtained for experiment B6 performed under supercritical conditions (450°C, 290 bar). These yields are in the same range as those reported by Dubois et al. [3]. The similarity of the measurements obtained for experiments B1 and B2 indicates that these results are reproducible.

Regarding the metal leaching yields, Fig. 3 shows that in the absence of oxidant, the leaching yields for Cs, Sr decreased from 93.9% and 70.3%, respectively, under subcritical conditions (experiment B1) to 36.6% and 8.8%, respectively, under subcritical conditions (experiment B3), while the Eu leaching yield increased from 11.9 to 21.6 %. The Co leaching yield was below 10% in all six experiments, which is less than the measurement uncertainty. The Cs; Eu and Sr yields were significantly higher in the presence of hydrogen peroxide (experiments B4–B6) and increased with the temperature and pressure of the process up to ~100% under supercritical conditions (experiment B6). Subcritical oxidation at 300°C, 63 bar (B5) may be sufficient to treat IERs in practice, with leaching yields of 100% for Sr and Eu and 66.4% for Cs.

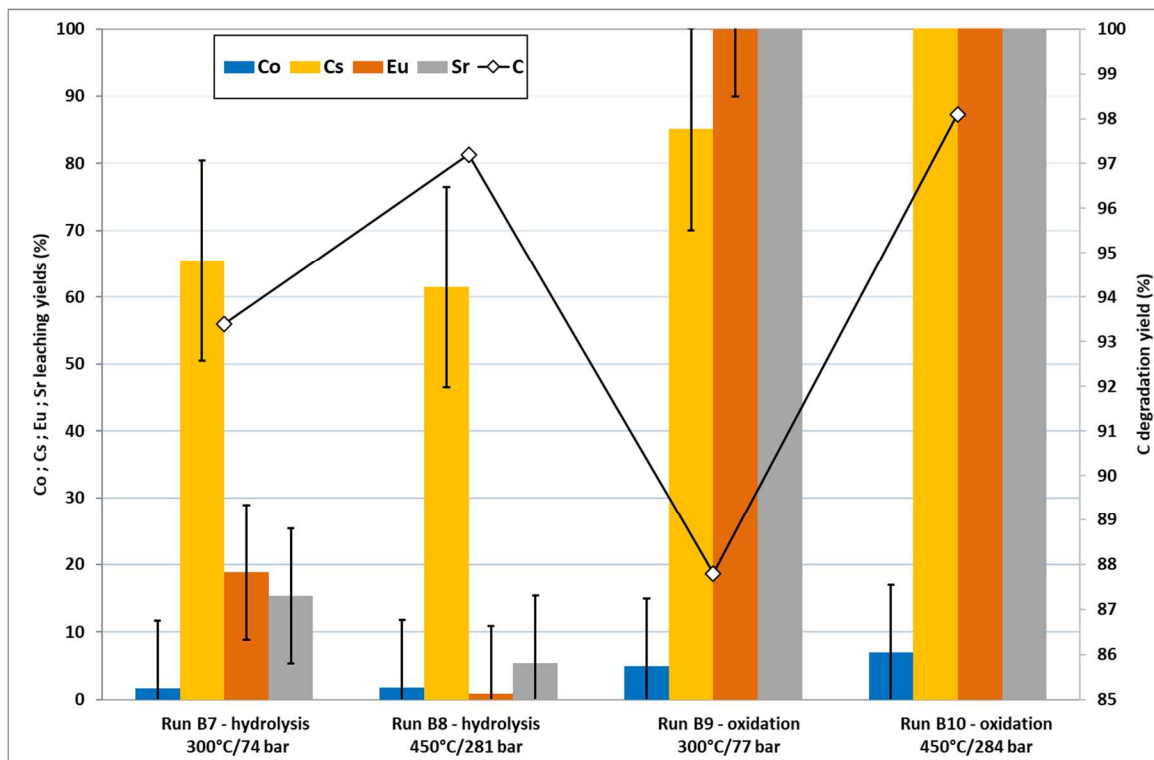


Fig. 3. Extraction yields for Cs, Co, Eu, Sr and carbon degradation yields for batch hydrothermal treatments of mixtures of the cationic and anionic IERs Amberlite® IRN77 and IRN78 under different operating conditions.

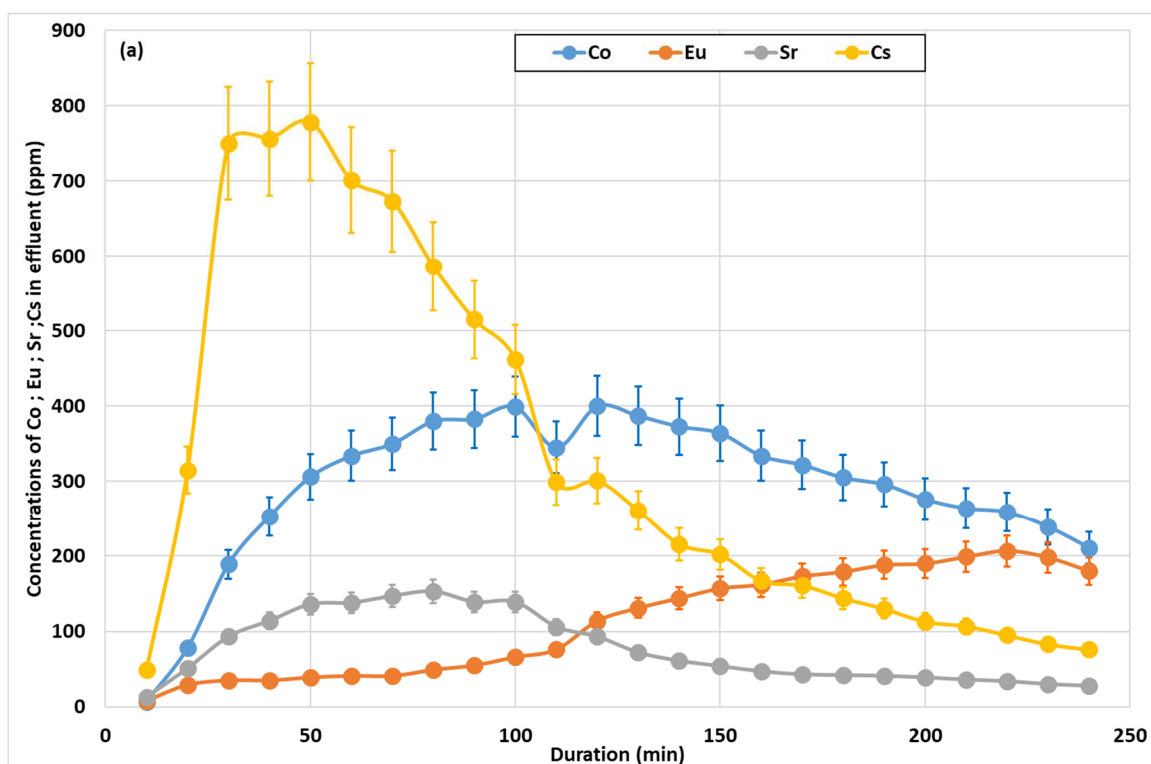
Fig. 3 shows similar trends in the results for the IER mixtures. The carbon degradation yields varied between 87.8 and 98.1% (experiments B7–B10), similar to the values obtained for IRN77 by itself (experiments B1–B6; Fig. 3). The highest carbon degradation yield was once again obtained under supercritical conditions in the presence of oxidant (experiment B10; 450°C 284 bar). It can be assumed that the IERs disintegrate completely under these conditions. The Cs leaching yield increased from 61.5–65.5% in the hydrolysis experiments (B7 and B8), to 85.1 and 100% in the presence of H₂O₂ under sub- and supercritical conditions, respectively (experiments B9 and B10). The increase is even more striking for Eu and Sr, with the leaching yield jumping from below 20% in experiments B7 and B8 to almost total mineralization in experiments B9 and B10. For Co on the other hand, no significant leaching was observed in any of the experiments. Any Co species released into the aqueous phase must presumably have precipitated because of the pH of the solution.

These results demonstrate the feasibility of extracting radioactive cationic contaminants using hydrothermal oxidation. A compromise may have to be drawn between the leaching efficiency and the structural integrity of the IER, since the supercritical conditions required for complete extraction of the target species also lead to the destruction of the IER and the release of all contaminants into the aqueous phase. Hydrothermal oxidation under subcritical conditions may thus be an interesting lower-cost alternative to treat high-level IER waste with more basic high-pressure equipment constraints.

3.2. *Semi-dynamic hydrothermal treatments*

The results for the dynamic hydrothermal experiments D1 and D2 are shown in Figs. 4 and 5. The two experiments had similar outcomes, with the same trends observed for the time evolutions of the solution concentrations (Figs. 4a and 5a) and cumulative extraction yields (Fig. 4b and 5b). A

key difference with the batch experiments is that significant amounts of Co were extracted ($85.7 \pm 10\%$ and $98.7 \pm 10\%$ of the initial mass at the end of experiments D1 and D2, respectively), which suggests that the residence time in these experiments was short enough for the cobalt species (presumably Co^{2+} or Co^{3+}) to be evacuated from the reactor before they precipitated. Here, the semi-dynamic approach allows better control of contaminant speciation through the renewal of the oxidant solution. For the other elements, while the extraction rates for Cs were similar to those for Co (about $90 \pm 10\%$), those for Sr and Eu were much lower ($35\text{--}53 \pm 10\%$ and $15\text{--}22 \pm 10\%$, respectively). Cs was also released faster into solution than the other elements were (Figs. 4a and 5a). This may be because IRN77 has a higher affinity for Sr and Eu than for Cs and Co. Indeed, IERs have a stronger affinity for ions with higher valences and smaller solvated volumes, and those that interact with functional groups and do not form complexes with other ions. This selectivity becomes more apparent at low concentrations in the extraction solution.



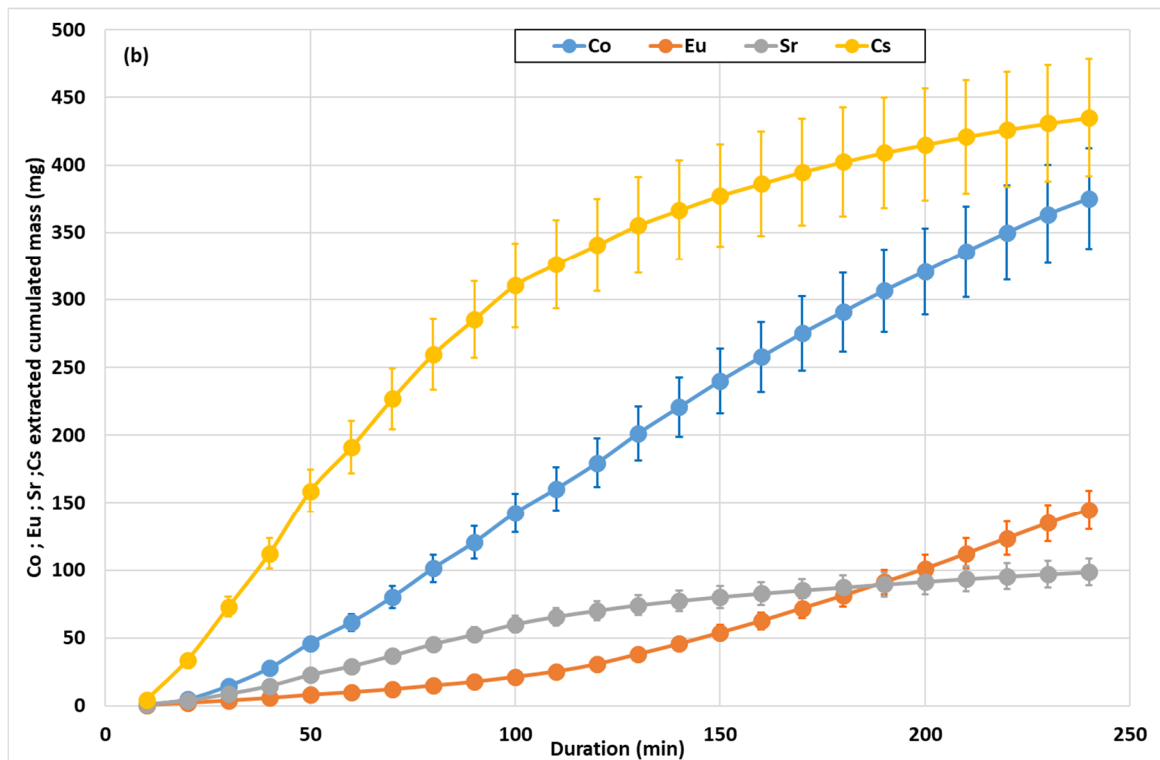
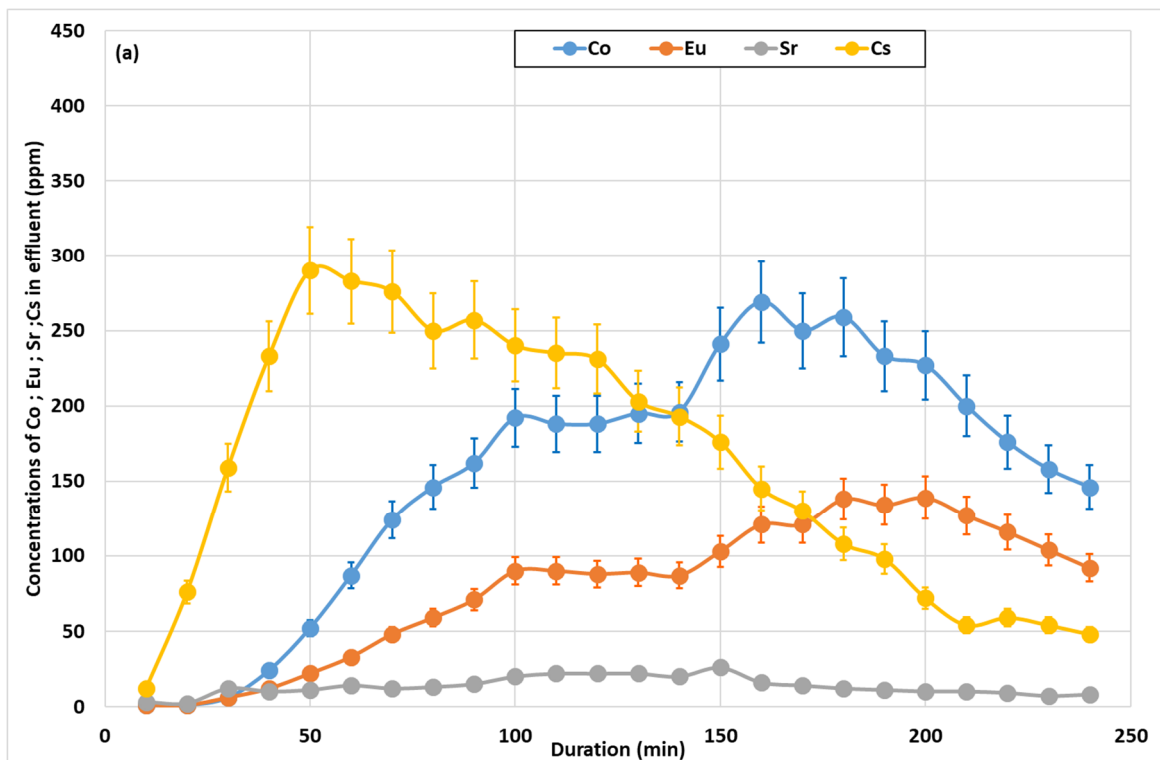


Fig. 4. (a) Concentrations of Cs, Co, Eu, Sr in the collected effluents and (b) cumulative extraction yields as a function of experiment time during semi-dynamic hydrothermal treatment of the cationic IER Amberlite® IRN77 (experiment D1).



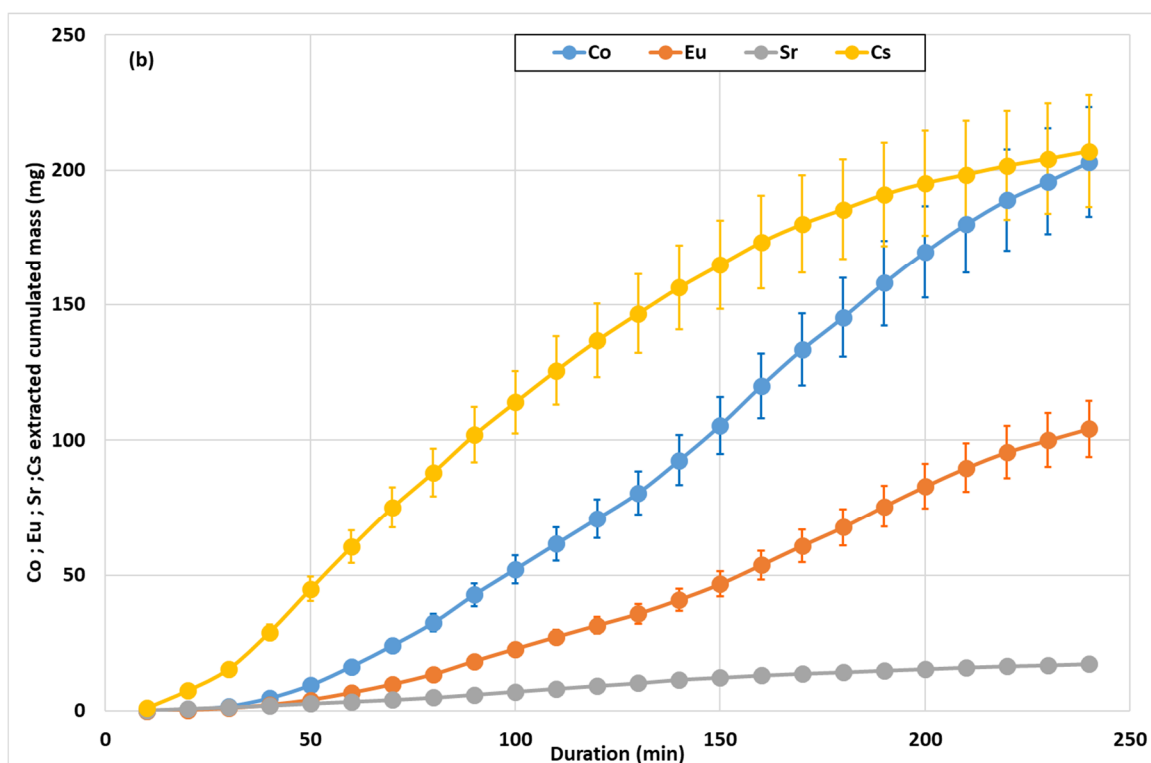


Fig. 5. (a) Concentrations of Cs, Co, Eu, Sr in the collected effluents and (b) cumulative extraction yields as a function of experiment time during semi-dynamic hydrothermal treatment of a mixture of the cationic and anionic IERs Amberlite® IRN77 and IRN78 (experiment D2).

These results show how much time is required in this semi-dynamic setup to decontaminate IERs containing roughly 10 mg/g Cs, Co, Eu and Sr. The Co and Cs in these IER samples was fully extracted in 4 h at 200°C and 50 bar. This needs to be confirmed for trace contaminations and further experiments are also required on IERs exposed to γ radiation to investigate the effects of radiolysis on their organic backbone.

3.3. Leaching at ambient temperature and pressure

The main results of the leaching experiments are compared in Fig. 6. There was no metal extraction when the leaching solution was oxalic acid (experiment L8; see Table 4), ascorbic acid (L9), mixtures of citric acid and ammonium sulfate mixture (L3 and L4), or low concentration (0.1 mol·L⁻¹) nitric acid (L1). Fig. 6 highlights differences in the selectivity of the other leaching solutions

for different cations. While in contrast with the batch hydrothermal runs, Co was well extracted by all five of these solutions (yields of $64\text{--}100 \pm 10\%$), Eu was poorly extracted in $1\text{ mol}\cdot\text{L}^{-1}\text{ HNO}_3$ and good ($> 60\%$) extraction yields for Sr were only achieved with EDTA at $1\text{ mol}\cdot\text{L}^{-1}$ and mixed at $0.05/0.3\text{ mol}\cdot\text{L}^{-1}$ with sodium carbonate (experiment L7). The type and concentration of acid and of counterion are therefore all important in order to optimize the treatment process.

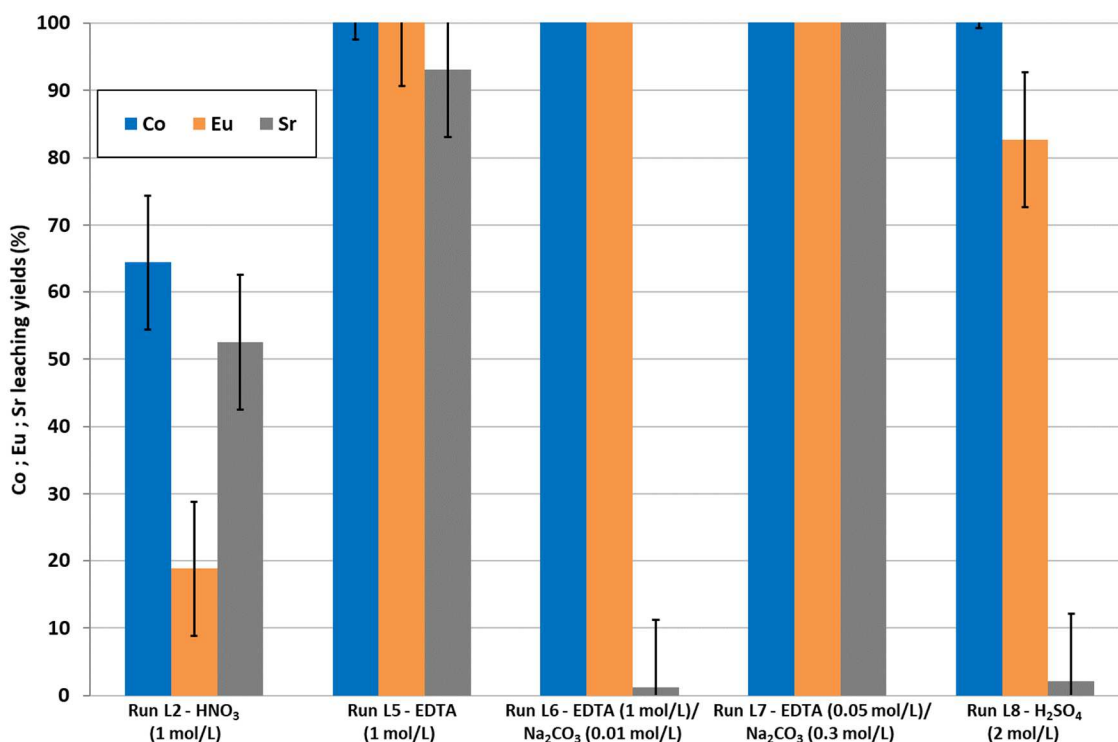


Fig. 6. Extraction yields for Co, Eu, Sr for acid leaching treatments of the cationic IER Amberlite® IRN77 at ambient temperature and pressure.

While these results are promising, it should be kept in mind that leaching solutions may complicate the treatment process downstream. EDTA for example cannot be handled by current effluent treatment plants and an additional treatment stage after leaching would have to be included to mineralize it.

3.4. Interpretation: speciation of metal contaminants in sub and supercritical hydrothermal media

Comparing the results obtained for hydrothermal (hydrolysis or oxidation) and leaching treatments highlights the importance of understanding the speciation of the metals under different operating conditions: Co, Cs, Eu or Sr may be present in ionic, oxide or complexed forms and may interact with organic IER degradation products. The speciation of each element as a function of the water density and molar concentration can be predicted using Pourbaix diagrams [18], but few are available for hydrothermal conditions.

There have nonetheless been several studies of the speciation of certain metals and of the fate of sulfur and nitrogen in sub- and supercritical hydrothermal media in the context of IER treatment. Ragnasdottir et al. [19] found ionic forms of Cs and Sr under all conditions but could not exclude complexation with IER degradation products. Liu et al. [20] analyzed the speciation of Eu in hydrothermal media and predicted a predominance of Eu (III) ions up to 100 °C, mainly Eu (II) species between 100 °C and 200 °C, and mostly Eu (III) hydroxides above 200 °C. Note that they did not include pressure in their analysis. Jocz et al. [21] built Co speciation diagrams at temperatures and pressures ranging from 150 to 550 °C and 220 to 500 bar, with ionic forms (Co^{2+} , Co^{3+} , CoOH^{2+} and CoOH^+) predominating at 370 °C and Co_3O_4 appearing at between 380 and 550 °C. The authors state however that other species must also be taken into account such as functional groups from the degradation of the IER containing sulfur or nitrogen. In hydrothermal media, sulfur can appear mainly as sulfides (H_2S , HS^- , S^{2-} and S_3^-), sulfites (SO_2 , HSO_3^- , SO_3^{2-}) and sulfates (HSO_4^- , SO_4^{2-}) depending on the temperature and O_2 fugacity [22]. This can lead to the formation and precipitation of insoluble cobalt sulfate, sulfide or sulfite species. These variations in Co speciation may explain why no Co was detected by ICP-AES in the batch hydrothermal experiments (B1–B10). For nitrogen finally, Li & Oshima [23] elucidated the oxidation mechanism of the trimethylammonium functional group from IRN78 in supercritical water, identifying a range of degradation products such as nitric oxide, nitrates, nitrites and nitrous oxide, with the probable presence of ammonium ions during

hydrolysis. The content of nitrogenous species in gaseous and liquid effluents may vary substantially with the operating temperature [24].

The complicated picture outlined by these results (Table 5) suggests that modeling studies should be considered to predict the speciation of radionuclides at different water densities and the interactions between these species and IER degradation products. Indeed, chemical equilibria in considered sub/supercritical water medium will be calculated by Gibbs energy minimization using CHESS software [25] with extended SUPCRT92 database [26].

Table 5

Speciation of metal contaminants in sub and supercritical hydrothermal media.

	<i>Extraction yields</i>		<i>Bibliography</i>		
	Batch	Semi-dynamic	Subcritical water	Supercritical water	
Co	< 10% whatever conditions	85.7 - 98.7 %	Predominance of Co^{2+} , Co^{3+} , CoOH^{2+} , CoOH^+ as a function of pH and O_2 fugacity.	Predominance of Co_3O_4 , Co^{2+} , CoOH^+ as a function of pH and O_2 fugacity.	[21]
Cs	Hydrolysis 36.6 - 95.9% (Higher yields in subcritical medium) Oxidation 62.4 - 100% (Higher yields in supercritical medium)	89.1- 89.8 %	Predominance of Cs^+ .		[19]
Sr	Hydrolysis 5.4 - 70.3 % (Higher yields in subcritical medium) Oxidation 100%	15.3 - 21.9%	Predominance of Sr^{2+} .		[19]

Eu	Hydrolysis < 21.6% Oxidation 57.4 – 100% (Higher yields in supercritical medium)	34.9 - 52.8 %	Predominance of Eu(III) ions up to 100°C. Predominance of Eu (II) ions between 100 and 200°C. Predominance of Eu (III) hydroxides above 200°C.	Predominance of Eu (III) hydroxides.	[20]
Sulfonated species (degradation products of cationic IER IRN77)			As a function of pH and O ₂ fugacity : Presence of SO ₄ ²⁻ , HSO ₄ ⁻ , SO ₂ at ambient temperature ; Presence of HSO ₄ ⁻ , SO ₂ at 200°C ; Presence of SO ₄ ²⁻ , HSO ₄ ⁻ , S ₃ ²⁻ , S ²⁻ , HS ⁻ , H ₂ S at 300°C.	As a function of pH and O ₂ fugacity : Presence of H ₂ SO ₄ , SO ₂ , S ²⁻ , S ₃ ⁻ , HS ⁻ , H ₂ S above 400°C.	[22]
Nitrogenous species (degradation products of anionic IER IRN78)			Formation of NO, NO ₃ ⁻ , NO ₂ ⁻ and N ₂ O as a function of temperature, pH and O ₂ fugacity.	[23, 24]	

4. Conclusion

Batch and semi-dynamic sub- and supercritical hydrothermal processes have been compared with acid leaching at ambient temperature for the treatment of cationic and anionic IERs contaminated with Cs, Sr, Co and Eu, as representative surrogates of the radionuclides found in spent IERs from the nuclear industry. The results of the batch experiments show that while supercritical conditions are optimal in terms of extraction efficiencies, simpler and less energy-intensive subcritical hydrothermal treatments may offer sufficient reductions in radioactivity for the IERs to be stored. A similar conclusion can be drawn from the semi-dynamic experiments carried out in a laboratory-scale reactor under mild conditions (200°C, 50 bar), in which 50 g samples of IER were successfully treated in 4 h. Extraction yields close to 100% were also obtained at ambient pressure and temperature using a 0.05/0.3 mol·L⁻¹ EDTA/Na₂CO₃ mixture as the leaching solution.

These results are promising for the development of pilot or industrial scale processes for the treatment of spent nuclear IERs. Which of hydrothermal oxidation or ambient leaching is the most appropriate will depend on the expected extraction yields and the cost of the processes, but also on how easy the final waste is to manage. Hydrothermal processes would be easier to implement under milder conditions but would produce two final waste streams: solid residues from the partially decontaminated IERs, and effluents containing radionuclides and organic carbon species, whose compatibility with nuclear effluent treatment plants remains to be studied. Supercritical hydrothermal treatments would be more demanding and expensive to implement but the final waste would be easier to manage. In both cases, an additional precipitation step would be required to reduce the high sulfate concentration of the waste and make it compatible with current effluent treatment plants. The EDTA-based leaching process proposed here would likewise require a post-treatment step (e.g. advanced oxidation [27]) to mineralize the ~10 g/L EDTA in the effluent.

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