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Remediation of ^{137}Cs-contaminated concrete rubble by supercritical CO_2 extraction

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Highlights

- Supercritical CO_2 was used as solvent to extract ^{137}Cs from concrete rubble.
- The best extractant system was found to be CalixOctyl/HPFOA.
- Extraction is hindered by carbonation reducing the porosity of the cement.
- Poor Cs desorption also explained by formation of insoluble Cs-concrete complexes.
- Preceding extraction with HNO_3 leaching increased the extraction yield up to 55%.

Abstract

The removal of cesium contamination is a critical issue for the recycling of concrete rubble in most decommissioning operations. The high solvent strength and diffusivity of supercritical CO_2 make it an attractive choice as vector for extractant system in this context. Experimental extraction runs have been carried out in a radioactive environment on rubble contaminated with ^{137}Cs. The best extraction system was found to be CalixOctyl (25,27-Bis(1-octyloxy)calix[4]arene-crown-6, 1,3-alternate) with pentadecafluorooctanoic acid as a

modifier. The effects of various operating parameters were investigated, namely the coarseness of rubble, the temperature of supercritical CO_2, the residual water and initial cesium concentrations, and the amounts of extractant and modifier used. The yields from direct extraction were low (< 30%), because of the virtually irreversible sorption of Cs in concrete. The best extraction yield of ~55% was achieved by leaching concrete rubble with nitric acid prior to supercritical CO_2 extraction.

Keywords: supercritical CO_2, metal extraction, calixarene, concrete rubble

1. Introduction

Concern has been growing worldwide about the presence of contamination from years of industrial activities during which toxic substances were improperly handled, stored and disposed. In March 2011, the Fukushima Daiichi nuclear accident led to the release of large quantities of radionuclides, with the total amounts of ^{137}Cs and ^{131}I released estimated to be approximately $1.5 \cdot 10^{17}$ Bq and $1.3 \cdot 10^{16}$ Bq, respectively (Kato et al., 2012). The presence of these elements in the natural environment is concerning as they present both external and internal exposure risks. In this context, the DEMETERRES project was set up to develop innovative and environmentally-friendly processes for ex situ and in situ treatments to extract radionuclides and especially Cs.

Most decommissioning projects involve the treatment of contaminated concrete rubble. The total amounts of primary and secondary waste generated vary greatly between decontamination processes (Kaminski et al., 2015) and the best choice depends on what the final objectives are: reducing the dose rate before another treatment or declassification for surface storage or suppressing any trace of contamination for rehabilitation and reuse. The choice of a decontamination process depends essentially on the nature of the matrix to be treated and on the nature of different radionuclides to extract. Cesium for example is very difficult to desorb from concrete rubble because sorption inside the concrete structure is virtually irreversible and because it forms insoluble complexes with calcium silicate hydrate gels (Real et al., 2002). Mechanical, thermal and chemical (such as gel (Castellani et al., 2014) and foam (Dame et al.,2005)) processes can be used to remove surface contamination to a certain depth but the main drawback of these techniques is that they destroy a part of the concrete matrix.

Concrete can also be decontaminated using physicochemical processes such as leaching or hydrothermal treatments, whose main advantage is that they preserve the rubble matrix. There have been a number of studies on this topic regarding the treatment of

construction materials (Samuleev et al., 2013), granite (Wang et al., 2010), dredged sediments, shales (Sandalls, 1987), ashes (Parajuli et al., 2013) and cemented waste (Reynier et al., 2015).

Supercritical CO_2 treatments are a promising alternative that also preserve the structure of the concrete. Supercritical CO_2 is used in a wide range of extraction processes because it is nontoxic, inexpensive, environmentally friendly, and has a low critical temperature and pressure (McHugh and Krukonis, 1994). Supercritical CO_2 exhibits both high solvent strength and diffusivity, which facilitate extraction in porous structures. Supercritical CO_2 has already been investigated for the extraction of metals (Lin et al., 2014). However, a crucial issue for these processes is the availability of an efficient and selective extractant that is soluble in supercritical CO_2.

The three classes of chemicals that are generally used for cesium removal by liquid-liquid extraction are dicarbollides, crown ethers and calixarenes (Dozol et al., 2000). Dicarbollides have a good extraction capacity for cesium, but their selectivity for cesium over other alkali elements is low. In the same way, crown ethers, whose selectivity is based on cation size (macrocycle cavity size complementarity), are poorly selective in the presence of other alkali species. Crown ethers with modifiers (such as di-(2-ethylhexyl) phosphoric acid (HDEHP), pentadecafluorooctanoic acid (HPFOA) or tetraethylammonium perfluoroctane sulfonate ($PFOSANEt_4$)) have been evaluated for the recovery of cesium from aqueous solutions containing other alkali ions such as Na^+ or K^+ (Lee et al., 1986) and from synthetic soil samples using supercritical CO_2 (Park et al., 2015). Elsewhere, Lamare et al. (1997) used calixarenes functionalized with crown ethers to extract cesium from a sodium nitrate solution. They found that the selectivity of these compounds for cesium was highly dependent on the conformation of the calixarenes. Indeed, CalixOctyl (25,27-Bis(1-octyloxy)calix[4]arene-crown-6, 1,3-alternate) is remarkably selective in forming complexes with cesium rather than other alkali species in acidic environments (Rais et al., 2015).In the other hand, the solubility of calixarenes in supercritical CO_2 has been measured at 60°C and 20 MPa to be between 0.1

and 120 mmol·L^{-1} depending on their functionalization (Glennon et al., 1997). These properties have led to their use for the supercritical CO_2 extraction of Cs (Kanekar et al., 2014), Cd (Rathod et al., 2015), Pb (Rathod et al., 2014) and U (Rao et al., 2013).

As extractant/Cs complexes are almost completely insoluble in supercritical CO_2, an organic modifier is required to neutralize the charge of the complex and increase its solubility. The importance of interfacial phenomena between the supercritical CO_2 phase and the aqueous phase for CalixOctyl/modifier/Cs has been highlighted by molecular dynamics simulations (Schurhammer et al., 2001; Sieffert et al., 2006). The organic modifier used in most cases is HPFOA with macrocyclic polyethers. Extraction yields up to 60% have been obtained with a good selectivity for cesium over potassium cations (Mochizuki et al., 1999; Wai et al., 1999).

Cesium decontamination studies have been carried out previously using supercritical CO_2 from silica soil (Leybros et al., 2016). Satisfactory yields of between 70 and 95% were achieved with (non-radioactive) cesium ^{133}Cs concentrations much greater (1–14 mg/g) than observed in practice for ^{137}Cs contaminations. This paper reports experimental extraction runs with realistic ^{137}Cs activities (~800 Bq/g) performed in a nuclear laboratory on concrete rubble. The extractant considered was CalixOctyl with an organic modifier. The first step of the study consisted in determining the most suitable modifier. The influence of various operating parameters was investigated before the efficiency of supercritical CO_2 extraction was compared for this application with leaching using water and nitric acid. Supercritical extraction complemented by acid leaching was also considered.

2. Materials and methods

2.1. Reagents

Calixarenes are macrocyclic compounds formed by the condensation of a phenol and an aldehyde. They have hydrophobic cavities which can accommodate small molecules or ions. The selectivity of calixarenes stems from the size of their cavities and the nature of their functionalization. Crown calixarenes have a much higher selectivity for cesium over other alkali cations than crown ethers do (Danil de Namor et al., 1998), the most selective calixarenes being CalixOctyl (25,27-Bis(1-octyloxy)calix[4]arene-crown-6, 1,3-alternate), shown in **Fig. 1**. The calixarene structure stiffens the whole molecule through steric effects that fix the size of the crown ether's cavity. CalixOctyl was synthesized following Casnati et al. (1995) and its purity (> 95%) was verified by ^{1}H and ^{13}C NMR and IR spectroscopy. The solubility of this calixarene in CO_2 is about 0.64 kg·m^{-3} at 27 MPa and 40 °C (Dartiguelongue et al., 2017).

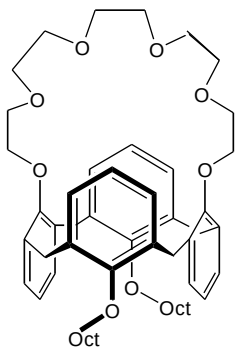


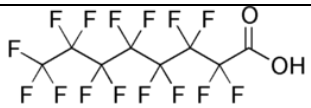
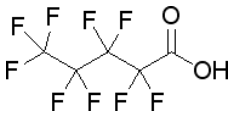
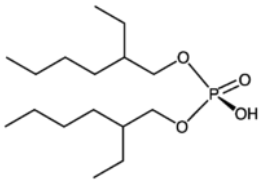
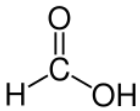
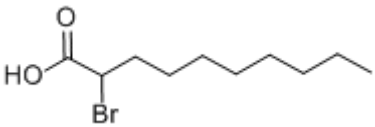
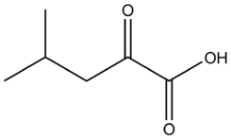
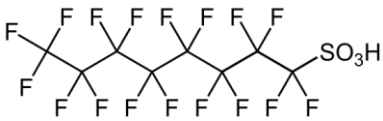
Fig. 1. Chemical structure of CalixOctyl (25,27-Bis(1-octyloxy)calix[4]arene-crown-6, 1,3-alternate).

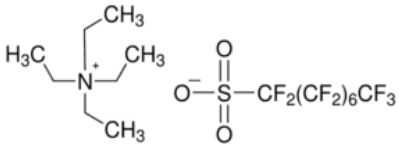
The organic modifiers considered in this study were HDEHP, bromocapric acid, HPFOA, formic acid, perfluoropentanoic acid (PFPEA), methyloxovaleric acid, heptadecafluorooctanesulfonic acid (PFOS) and $PFOSANEt_4$. The characteristics of these chemicals are summarized in **Table 1**. No further purification was performed. These modifiers are generally highly soluble in supercritical CO_2 under the conditions used here (Byun et al., 2000; Dartiguelongue et al., 2016; Meguro et al., 1998; Shimizu et al., 2006).

Carbon dioxide (> 99.99% purity) was obtained from Air Liquide and used without further purification.

Table 1

Chemical structure and purity of the modifiers used in this study.

Chemical name	CAS N°	Source	Chemical formula/structure	Purity (wt%)
HPFOA	335-67-1	Aldrich		0.96
PFPEA	2706-90-3	Aldrich		0.97
HDEHP	298-07-7	Aldrich		0.97
Formic acid	64-18-6	Aldrich		0.96
2-bromodecanoic acid	2623-95-2	Aldrich		0.96
4-methyl-2-oxovaleric acid	816-66-0	Aldrich		0.98
PFOS	1726-23-1	Aldrich		0.40 in water

PFOSA-NEt4	56773-42-3	Aldrich		0.98

HPFOA, pentadecafluorooctanoic acid; PFPEA, perfluoropentanoic acid; HDEHP, bis(2-ethylhexyl)phosphate; PFOS, heptadecafluorooctanesulfonic acid; PFOSA-NEt4, tetraethylammonium heptadecafluorooctanesulfonate

Different types of (uncontaminated) concrete rubble from peeling operations were obtained from decommissioning sites. The rubble were sieved and crushed. The rubble samples contained particles of 2–5 mm in diameter (for Run 9 the particles were smaller: 1–2 mm in diameter). The rubble samples were artificially contaminated by impregnation with diluted solutions (45 mL, 780 Bq·mL^{-1}) of ^{137}Cs + ^{137}Ba^{m} in HCl (0.1 mol·L^{-1}), prepared from sealed 5 mL, 40 kBq·g^{-1} standard solutions (AREVA CERCA LEA, > 97.5%). Nitric acid samples (3 mol·L^{-1}) were prepared by dilution from commercial HNO_3 (Aldrich, 65 wt%).

2.2. Extraction experiments

The setup used for the extraction experiments is shown in **Fig. 2** and has been described previously (Leybros et al., 2017). Briefly nonetheless, the device was operated in dynamic mode. A high pressure pump (Jasco HPLC PU-2080-CO2) was used to supply CO_2 allowing to reach operating pressure of 30MPa at a maximum flow rate of 10 mL·min^{-1}. The CO_2 flow rate was measured using a mass flowmeter (FT1, Brooks). The heat exchanger and stove were used to heat the feed up to the operating temperature (typically 40–60 °C).

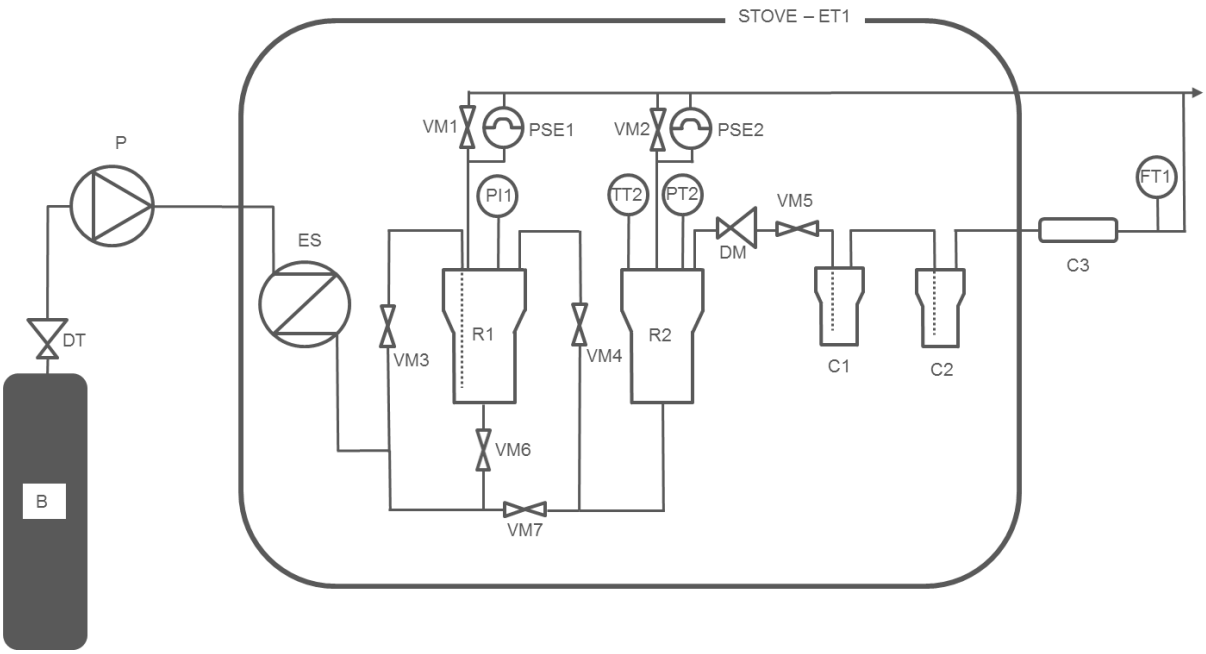


Fig. 2. Schematic diagram of the setup used for the extraction of cesium using supercritical CO_2. VM: stop valve; P: pump; ES: heat exchanger; R1: solubilization reactor; R2: extraction reactor; DM: back-pressure regulator; C1, C2 and C3: collectors.

The extractant and modifier were loaded in advance into reactor R1, in which they were solubilized in supercritical CO_2. The reactions with and extraction of Cs occurred in reactor R2, which contained one of the samples of contaminated concrete rubble in an extraction basket. For the extraction step, the supercritical CO_2 was fed from the bottom of this basket. The dynamic extraction processes lasted up to 6 h. The CO_2 flow rate from the feed pump was 10 mL·min^{-1}. A back pressure regulation device (Tescom) was used to set the operating pressure in the R1 extraction reactor to 27 MPa.

This device and procedure are designed to extract cesium in reactor R2 as an organometallic complex (Cs/extractant/modifier). The Cs was then recovered in the separators (C1 and C2) held at a lower pressure (0.1 MPa) to reduce the solvating power of the CO_2. The C3 collector trapped any trace amounts of cesium complex that remained in the gas stream after depressurization.

2.3. Leaching experiments

Leaching experiments were performed at ambient temperature using 45 mL of either water or 3 mol·L^{-1} HNO_3. The rubble samples were leached for 3 h.

2.4. Protocol for the preparation of cesium-contaminated concrete rubble

The samples of contaminated rubble (initial mass, 45 g) were impregnated (fully soaked) with 45 mL of an aqueous solution of ^{137}Cs with an activity equal 780 Bq·mL^{-1} and then dried in a stove until the desired water content (3 wt%) was achieved (**Fig. 3**). The targeted initial activity was 35 kBq. For run 10, in which a cesium activity in the contaminating solution of ~7.8·10^{5} Bq·mL^{-1} was simulated, an aqueous solution of 3.1·10^{-4} g·L^{-1} ^{133}Cs was doped with a 780 Bq·mL^{-1} ^{137}Cs solution. To guarantee the reproducibility of each experiment, the residual water content of the rubble samples was measured as a function of the drying time. Here, the target of residual water contents of around 3 wt% were obtained after 40 h drying at 40 °C.

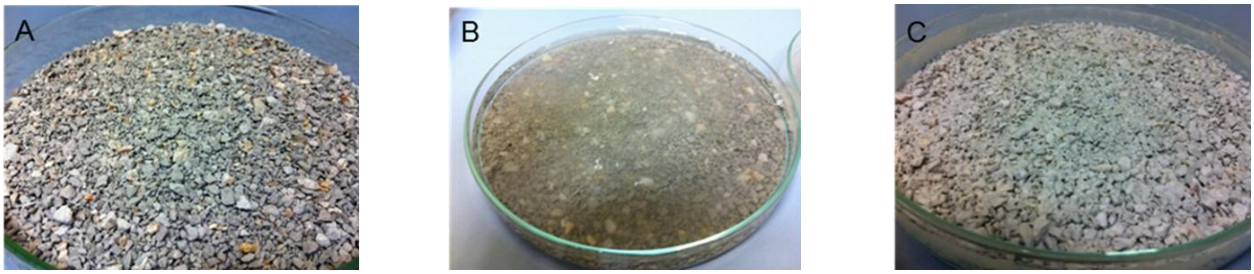


Fig. 3. Preparation of cesium-contaminated rubble. Photographs of (A) their initial state; (B) during impregnation with a ^{137}Cs solution and (C) after drying.

2.4. Analysis

The rubble samples were analyzed by γ–ray spectrometry before and after supercritical CO_2 extraction, as were the extracts collected in the three collectors. The presence (absence) of ^{137}Cs in the extracts reveals the presence (absence) of back-extraction. The extraction yield of the decontamination process was calculated using **Eq. (1)**,

$$E(\%) = \frac{a_{initial} - a_{final}}{a_{initial}} \quad (1)$$

where $a_{initial}$ and a_{final} are respectively the activity of the sample (in Bq) before and after the extraction run.

These γ–ray spectrometry measurements were performed using a Tennelec series 5 γ-ray spectrometer (Canberra, USA) equipped with a high-purity germanium detector and a Tennelec TC242 amplifier. The acquisition software was Interwinner 6.

One of the main limitations of this approach is the possible attenuation of the γ radiation in case of measurement in the solid sample. A calibration curve was therefore established for the activity of the rubble samples to determine a valid working range. The rubble samples used as standards were prepared as described above for the extraction samples, with the same mass, but with targeted activities of 35, 15, 3 and 0.5 kBq. The results presented in **Table 2** show that γ–ray spectrometry is accurate enough to quantify cesium extraction efficiencies under these working conditions.

Table 2

Nominal versus measured ^{137}Cs activity of the standard samples used to validate the radioactivity measurements performed by γ–ray spectrometry.

	Nominal activity (kBq)	Measured activity (kBq)	Deviation (%)
Sample n°1	35	32.652	7.2

Sample n°2	15	14.202	5.6
Sample n°3	3	2.896	3.6
Sample n°4	0.5	0.421	18.7

3. Results and discussion

Table 3 summarizes all the results obtained for each supercritical CO_2 extraction run. We describe first how the best modifier was selected, and then the influence of different operating parameters (particle size, temperature, CalixOctyl/modifier ratio, and residual water content).

Table 3

Extraction of cesium from concrete rubble using supercritical CO_2: operating conditions and results.

Run	Modifier	P (MPa)	T (°C)	Molar ratio Cs/Extractant/Modifier	Initial activity (Bq)	Final activity (Bq)	Activity of extracts (Bq)	Extraction yield (%)
1	HDEHP	27.3	43	$1/3.4\cdot10^6/1.0\cdot10^7$	33 541 ± 2 415	30 465 ± 2 193	126 + 24	9.2 ± 7.2
2	Bromocapric acid	27.0	41	$1/2.5\cdot10^6/1.7\cdot10^7$	33 525 ± 2 414	32 791 ± 2 361	224 ± 42	2.2 ± 7.2
3	HPFOA	27.3	41	$1/3.3\cdot10^6/1.5\cdot10^7$	32 653 ± 2 351	28 650 ± 2 063	448 ± 84	12.3 ± 7.2
4	Formic acid	27.2	41	$1/2.9\cdot10^6/1.5\cdot10^7$	33 640 ± 2 422	32 832 ± 2 364	29 ± 5	2.4 ± 7.2
5	PFPEA	27.4	40	$1/2.4\cdot10^6/1.6\cdot10^7$	31 649 ± 2 279	29 673 ± 2 136	408 ± 76	6.2 ± 7.2
6	Methyl oxovaleric acid	26.9	41	$1/2.5\cdot10^6/1.2\cdot10^7$	32 751 ± 2 358	30 591 ± 2 202	191 ± 36	6.6 ± 7.2
7	PFOS	27.2	42	$1/2.0\cdot10^6/1.0\cdot10^7$	32 564 ± 2 345	30 455 ± 2 193	1 143 ± 214	6.5 ± 7.2
8	PFOSA-N(Et)4	27.1	43	$1/2.1\cdot10^6/1.3\cdot10^7$	32 970 ± 2 374	31 534 ± 2 270	249 ± 47	5.9 ± 7.2
9[a]	HPFOA	27.2	43	$1/3.1\cdot10^6/1.1\cdot10^7$	33 181 ± 2 389	26 971 ± 1 942	138 ± 26	18.7 ± 7.2
10[b]	HPFOA	27.5	42	$1/2.5\cdot10^3/1.1\cdot10^4$	32 139 ± 2 314	25 081 ± 1 806	1 225 ± 229	22.0 ± 7.2
11	HPFOA	27.3	57	$1/2.4\cdot10^6/1.1\cdot10^7$	33 041 ± 2 379	28 177 ± 2 029	996 ± 186	14.7 ± 7.2
12[c]	HPFOA	27.1	42	$1/2.7\cdot10^6/1.0\cdot10^7$	29 232 ± 2 105	23 536 ± 1 695	1 511 ± 283	19.5 ± 7.2

13	HPFOA	26.6	101	$1/2.1\cdot10^{6}/1.0\cdot10^{7}$	33 399 ± 2 405	27 563 ± 1 985	414 ± 77	17.5 ± 7.2
14[d]	HPFOA	27.0	40	$1/2.0,10^{6}/1.0\cdot10^{7}$	33 031 ± 2 378	25 678 ± 1 849	184 ± 34	22.3 ± 7.2
15[c]	HPFOA	26.4	64	$1/2.2\cdot10^{6}/1.1\cdot10^{7}$	33 038 ± 2 378	24 261 ± 1 747	63 ± 12	26.5 ± 7.2
16	HPFOA	27.1	43	$1/6.6\cdot10^{6}/3.0\cdot10^{7}$	32 981 ± 2 375	27 277 ± 1 964	1 325 ± 248	17.3 ± 7.2
17	HPFOA	26.8	58	$1/2.8\cdot10^{6}/2.0\cdot10^{7}$	32 648 ± 2 351	28 372 ± 2 043	261 ± 49	13.1 ± 7.2

HDEHP, bis(2-ethylhexyl)phosphate; HPFOA, pentadecafluorooctanoic acid; PFPEA, perfluoropentanoic acid; PFOS, heptadecafluorooctanesulfonic acid; PFOSA-NEt4, tetraethylammonium heptadecafluorooctanesulfonate.

Unless otherwise specified, the samples contained particles 2–5 mm in diameter, with an initial ^{137}Cs concentration of $2.7\cdot10^{-7}$ $mg\cdot g^{-1}$ and a residual water content of 3 wt%.

[a]The particles in this sample were between 1 and 2 mm in diameter.

[b]The initial cesium concentration in this sample was $2.7\cdot10^{-4}$ $mg\cdot g^{-1}$.

[c] The residual water content of this sample was 2 wt%.

[d] The residual water content of this sample was 1 wt%.

3.1. Determining the most suitable extractant/modifier system

CalixOctyl was combined with different modifiers in supercritical CO_2 (at 27 MPa, 40 °C; Runs 1–8 in **Table 2**).Indeed, CalixOctyl is little soluble in our working conditions and the most suitable modifier has to be identified to enhance both extractant system and organometallic complexes solubilities. As shown in **Table 2**, these runs were performed with a high stoichiometric excess of the extractant, given the very small amount of ^{137}Cs present in the samples. The extraction yields were low, between 2 and 12%. The extracts in the collectors were found to have a low activity (between 10 and 500 Bq), whatever the modifier. The modifier that gave the highest extraction yield was HPFOA (12.3%, Run 3). This can be explained by the high solubility of fluorinated compounds in supercritical CO_2, which stems from the presence of fluorine substituents and the length of the fluorinated chain (Smart et al., 1997). Furthermore, the low pKa of fluorinated compounds (Goss, 2008) facilitates ion exchange with cesium inside the concrete.

Low extraction yields are expected for concrete rubble because of their chemical structure: cesium cations are strongly adsorbed on their calcium silicate hydrate structure (Evans, 2008). This virtually irreversible ion exchange process and the formation of insoluble complexes with calcium silicate hydrate make cesium desorption (and therefore extraction) very difficult. Moreover, the concentration of alkali ions (Na^+; K^+) was significantly higher (a few mmol per gram of concrete as determined by inductively coupled plasma atomic emission spectroscopy) than the Cs^+ concentration in the samples (a few pmol per gram), which makes strong competition between Cs and other alkali cations.

Another factor that may contribute to the low extraction yields is accelerated carbonation, which reduces the size of the pores inside the concrete structure (Garcia-Gonzalez et al., 2008). The rubble samples were found to be between 0.5 and 2.3 g heavier after extraction. **Fig. 4** shows the thermogravimetric analysis of a rubble sample treated by

supercritical CO_2 for 4 h at 27 MPa and 40 °C. The presence of a calcite peak (at 760–770 °C) confirms that carbonation has occurred (Villagran-Zaccardi et al., 2017). This suggest that the pores inside the concrete do indeed shrink, trapping the organometallic CalixOctyl/modifier/Cs complexes formed therein. CO_2–philic extractants, more soluble in supercritical CO_2, may therefore be a more suitable choice to extract cesium from the concrete matrix before carbonation.

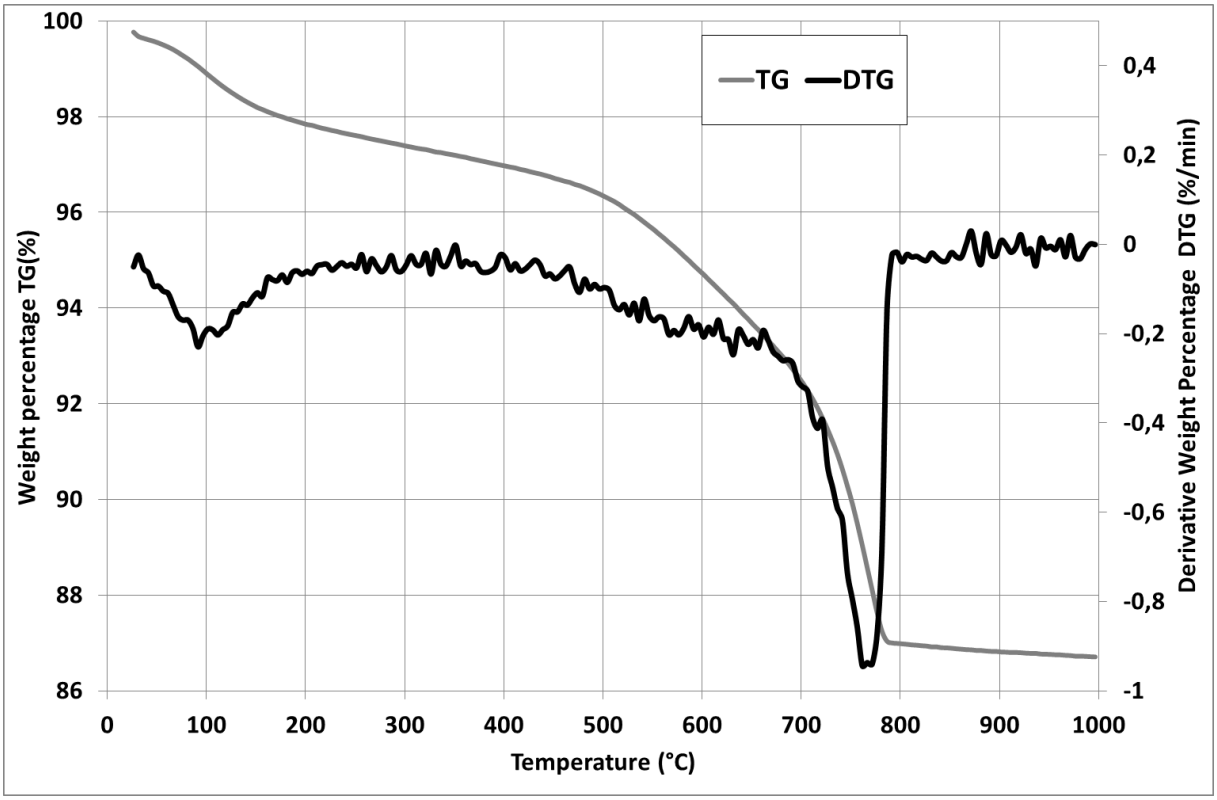


Fig. 4. Demonstration of the formation of calcite in a sample of concrete rubble. Thermogravimetric analysis of a sample of concrete rubble after treatment using supercritical CO_2 (P = 27 MPa; T = 40°C; CO_2 flow = 10 g·min^{-1}, treatment time = 4 h).

Our results are similar to those of Kanekar et al. (2014), who extracted cesium from soils using supercritical CO_2 and calixarene mixed with methanol. The efficiency of extraction

processes such as these can be improved by tuning the operating parameters to find the best compromise between thermodynamic and kinetic limiting factors.

3.2. Optimizing the operating parameters

Having identified CalixOctyl/HPFOA as the most suitable extractant system, the following paragraphs describe the effects on the process efficiency of the particle size in the samples (section 3.2.1), of the initial cesium concentration and the Cs/extractant stoichiometric ratio (section 3.2.2) and of the temperature and residual water content (section 3.2.3).

3.2.1. Role of rubble particle size

Comparing the results obtained for Runs 3 and 9 (**Table 3**) shows that reducing the rubble particle size from 2–5 mm to 1–2 mm (all other parameters being identical) leads to a modest increase in the extraction yield from 12.3 ± 7.2% to 18.7 ± 7.2%. This effect is expected because smaller particles have a larger specific surface area, making the cesium binding sites in the concrete pores more accessible. The energetic cost of crushing the rubble should be considered however in choosing the best particle size in view of industrialization of the process.

3.2.2. Cesium content and amounts of extractant and modifier

Run 3 was repeated in Run 10 but with a much higher cesium concentration initially present in the concrete rubble sample ($2.7 \cdot 10^{-4}$ mg·g^{-1} versus $2.7 \cdot 10^{-7}$ mg·g^{-1}, **Table 3**). In the latter case, $^{133}CsNO_3$ was added to simulate a rubble radioactivity of 10^6 Bq·mL^{-1}, which is in the range of the levels of contamination observed in practice. The extraction efficiency measured for Run 10 was 22.0 ± 7.2% compared with 12.3 ± 7.2% for Run 3. This suggests that the selectivity of the process for Cs over other alkali metal ions is not perfect.

The influence on the extraction yield of the amounts of extractant/modifier (CalixOctyl/HPFOA) used was investigated in Run 16, performed with twice the amount of extractant as Run 3 (all other parameters being equal, including the CalixOctyl/HPFOA molar ratio at 1/5). **Table 3** shows that this has little effect on the extraction yield (17.3 ± 7.2% for Run 16 versus 12.3 ± 7.2% for Run 3). The extraction capacity (the ratio of the amount of Cs extracted from the sample over the amount of extractant (CalixOctyl) used) was higher for Run 3 (5.5 10^{-8} versus 3.3 10^{-8} for Run 16). This suggests that the limiting factor here is the low Cs concentration in the rubble, which makes the probability of Cs–extractant interactions very low even when the amount of extractant used is increased.

The results for Run 17 show that increasing the ratio between extractant and modifier from 1/5 (Run 11) to 1/7 (Run 17) had little effect on the extraction yield (13.1 ± 7.2% for Run 17 versus 14.7 ± 7.2% for Run 11). This may be because the HPFOA molecules self-associate in supercritical CO_2, which limits their solubility. This effect has been observed previously for fluorocarboxylic acids in supercritical CO_2 (Dartiguelongue et al., 2016). Further investigations are in progress to determine whether the structure of the complexes formed by the extractant system may involve a molecule of calixarene and fluorocarboxylic acid monomers or dimers.

3.2.3. Operating temperature and rubble water content

Previous studies on supercritical CO_2 extraction in porous media have demonstrated that the solvent strength and diffusivity of CO_2 are strongly dependent on its density (Anitescu and Tavlarides, 2006). In Runs 3 and 11–15 (**Table 3**), the operating temperature was varied between 40 and 100 °C with a rubble water content of either 1 wt% (Run 14) 2 wt% (Runs 12 and 15) or 3 wt% (Runs 3 and 11–13) (**Fig.5**). Note that calixarene was found to be chemically stable at temperatures up to 150 °C. Increasing the temperature up to 100 °C did not significantly affect the extraction yield (which varied from 12.3 ± 7.2% to 17.5 ±

7.2%, see **Table 3**). The solvent strength of CO_2 is lower at higher temperatures but this decrease may have been offset by an increase in the extraction kinetics and reduced concrete carbonation.

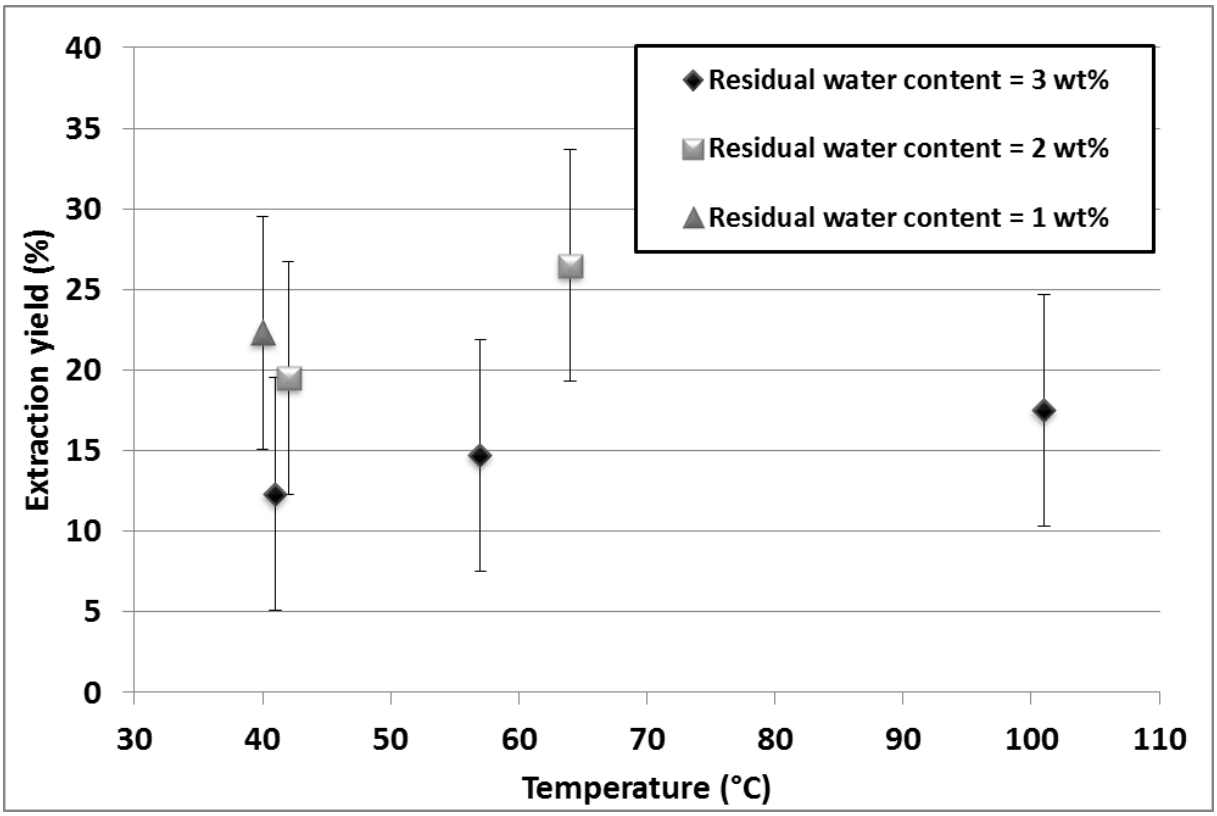


Fig. 5. Influence of residual water content and temperature on extraction yield.

Reducing the water content of the rubble was found to have a favorable effect on the extraction yield, which was 22.3 ± 7.2% for Run 14 with 1 wt% water (**Table 3**). It is therefore important to properly dry rubble before proceeding with supercritical CO_2 extraction. These results are in keeping with the literature. Wang et al. (1995) suggest that low water concentrations may promote extraction because this allows hydrogen ions from the modifier to be exchanged with cesium adsorbed in the solid matrix. On the other hand, higher water contents limit extraction because the formation of a water films in the pores may block the supercritical CO_2 and thus limit interactions with the extractant system (Smyth et al., 1999).

Moreover, increasing the water content promotes carbonation and therefore reduces the porosity of the concrete (Vance et al., 2015).

The best extraction yield of all these runs was 26.5 ± 7.2% for Run 15, performed at an intermediate temperature (65 °C) and water content (2 wt%). In line with the mechanisms described above, these conditions offer the optimal balance between faster extraction or back-extraction kinetics and slower carbonation on the one hand, and a lower CO_2 solvent strength on the other.

3.3. Combining supercritical CO_2 extraction with leaching

Table 4 compares the effects of leaching (with water or HNO_3) with the results obtained using HNO_3 leaching followed by supercritical CO_2 extraction to extract Cs from concrete rubble.

Table 4.

Extraction of cesium from concrete rubble by leaching and by leaching followed by supercritical CO_2 extraction: operating conditions and results.

Run		P (bar)	T (°C)	Molar ratio Cs/Extractant/Modifier	Initial activity (Bq)	Activity of leaching solution (Bq)	Final activity (Bq)	Activity of extracts (Bq)	Extraction yield (%)
18	Water leaching	_	ambient	_	33 152 ± 2 387	4 471 ± 161	26 461 ± 1 905		20.2 ± 7.2
19	HNO_3 leaching	_	ambient	_	32 482 ± 2 339	17 627 ± 952	16 944 ± 915		47.8 ± 6.3
20	HNO_3 leaching followed by $SCCO_2$ extraction	27.4	40	$1/ 2.0.10^6/1.0.10^7$	32 765 ± 2 359	14 074 ± 760	14 861 ± 802	494 ± 92	54.6 ± 6.3

$SCCO_2$, supercritical CO_2

The extraction efficiency of the water leaching run was almost as high as the best supercritical CO_2 extraction (Run 18, 20.2 ± 7.2% and Run 15, 26.5 ± 7.2% respectively). With HNO_3 leaching (Run 19), the extraction yield was much higher (47.8 ± 6.3%). These yields are similar to those of previous studies of the acidic leaching of soil and/or concrete samples (Kim et al., 2007; Samuleev et al., 2013) and show that HNO_3 efficiently desorbs ^{137}Cs from otherwise irreversible sorption sites in the concrete pores.

A further increase in the extraction yield was obtained by performing supercritical CO_2 extraction after HNO_3 leaching (Run 20, 54.6 ± 6.3%). These results suggest coupling between leaching and supercritical CO_2 extraction by cumulating steps up to reach targeted threshold for rubble activity for reuse or storage. It would be interesting to perform the HNO_3 leaching in situ in supercritical CO_2, which may reduce the amount of HNO_3 required and allow the procedure to be performed in a single step. The benefits would be substantial on an industrial scale. The influence of the HNO_3 concentration may also be worth investigating, to find the optimal balance between extraction yields and the corrosion of the pipes and internal walls.

4. Conclusion

Supercritical CO_2 extraction runs have been performed on samples of cesium-contaminated concrete rubble, with an extractant system composed of a cesium-selective crown calixarene and a modifier. These experiments were carried out in a radioactive environment with realistic levels of ^{137}Cs contamination. Preliminary tests identified the most suitable modifier (HPFOA) to be used in this context with CalixOctyl (the crown calixarene). Experiments performed on rubble with different particle sizes and residual water contents, at different temperatures and with different amounts of cesium and extractant showed that the most important factors were the temperature of the process and the water content of the

samples. In choosing the operating conditions, a compromise has to be found between kinetic (for extraction, back-extraction and the carbonation of the concrete), thermodynamic (the solubility of the extractant system and the resulting organometallic compounds) and diffusivity effects. The best cesium extraction yield obtained here using supercritical CO_2 extraction alone was 26.5 ± 7.2%. Similar results were obtained by Kanekar et al. (2014) for soil samples using supercritical CO_2 and three calix-crown derivatives in methanol or acetonitrile. An extraction yield of 54.6 ± 6.3% was obtained by leaching the concrete rubble with nitric acid before the supercritical CO_2 extraction step. Leaching makes the cesium more labile and thus more easily extractable. Our results show furthermore that the benefits of leaching and supercritical CO_2 extraction are cumulative. Further studies are ongoing to synthesize a CO_2-phile and Cs-selective extractant and compare its performance with the CalixOctyl/HPFOA system. Thermodynamic studies of CalixOctyl/HPFOA/CO_2 mixtures may also facilitate the optimization of the operating conditions in view of scaling up the process.

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References

Anitescu, G., Tavlarides, L., 2006. Supercritical extraction of contaminants from soils and sediments. J. Supercrit. Fluids. 38, 167–180. https://doi.org/10.1016/j.supflu.2006.03.024

Byun, H.S., Kim, K., McHugh, M.A., 2000. Phase behavior and modeling of supercritical carbon dioxide-organic acid mixtures. Ind. Eng. Chem. Res. 39, 4580–4587. http://dx.doi.org/10.1021/ie0001164

Castellani, R., Poulesquen, A., Goettmann, F., Marchal, P., Choplin, L., 2014. A topping gel for the treatment of nuclear contaminated small items. Nucl. Eng. Des. 278, 481-490. http://dx.doi.org/10.1016/j.nucengdes.2014.07.043

Casnati, A., Pochini, A., Ungaro, R., Ugozzoli, F., Arnaud, F., Fanni, S., Schwing, M.-J., Egberink, R., de Jong, F.,Reinhoudt, D. N., 1995. Synthesis, complexation, and membrane transport studies of 1,3-alternate calix[4]arene-crown-6 conformers: a new class of cesium selective ionophores. J. Am. Chem. Soc. 117, 2767–2777. http://dx.doi.org/10.1021/ja00115a012

Dame, C., Fritz, C., Pitois, O., Faure, S., 2005. Relations between physicochemical properties and instability of decontamination foams. Colloids and Surfaces A: Physicochem. Eng. Aspects. 263, 210-218. http://dx.doi.org/10.1016/j.colsurfa.2004.12.053

Danil de Namor A., Cleverley, R., Zapata-Ormachea, M., 1998. Thermodynamics of calixarene chemistry. Chem. Rev. 98, 2495–2525. http://dx.doi.org/10.1021/cr970095w

Dartiguelongue, A., Leybros, A., Grandjean, A., 2016. Solubility of perfluoropentanoic acid in supercritical carbon dioxide: Measurements and modeling. J. Chem. Eng. Data. 61, 3902–3907. http://dx.doi.org/10.1021/acs.jced.6b00649

Dartiguelongue, A., Leybros, A., Grandjean, A., 2017. Solubility and solution enthalpy of a cesium-selective calixarene in supercritical carbon dioxide. J. Supercrit. Fluids. 125, 42–49. http://dx.doi.org/10.1016/j.supflu.2017.01.017

Dozol, J.F., Dozol, M., Macias, R., 2000. Extraction of strontium and cesium by dicarbollides, crown ethers and functionalized calixarenes. J. Incl. Phenom. Macrocycl. Chem. 38, 1–22. http://dx.doi.org/10.1023/A:1008145814521

Evans, N., 2008. Binding mechanisms of radionuclides to cement. Cem. Concr. Res. 38, 545–553. http://dx.doi.org/10.1016/j.cemconres.2007.11.004

Garcia-Gonzalez, C., El Grouh, N., Hidalgo, A., Fraile, J., Lopez-Periago, A., Andrade, C., Domingo, C., 2008. New insights on the use of supercritical carbon dioxide for the accelerated carbonation of cement pastes. J. Supercrit. Fluids 43, 500–509. http://dx.doi.org/10.1016/j.supflu.2007.07.018

Glennon, J. Hutchinson, S., Harris, S., Walker, A., McKervey, A., McSweeney, C., 1997. Molecular baskets in supercritical CO_2. Anal. Chem. 69, 2207–2212. http://dx.doi.org/10.1021/ac960850q

Goss K., 2008. The pKa values of PFOA and other highly fluorinated carboxylic acids. Environ. Sci. Technol. 42, 456–458. http://dx.doi.org/10.1021/es702192c

Jokic S., Nagy, B., Zekovic, Z., Vidovic, S., Bilic, M., Velic, D., Simandi, B., 2012. Effects of supercritical CO_2 extraction parameters on soybean oil yield. Food Bioprod. Process. 90, 693–699. http://dx.doi.org/10.1016/j.fbp.2012.03.003

Kaminski, M., Lee, S., Magnuson, M., 2016. Wide-area decontamination in an urban environment after radiological dispersion: A review and perspectives. J. Hazard. Mater. 305, 67–86. http://dx.doi.org/10.1016/j.jhazmat.2015.11.014

Kanekar, A.S., Pathak, P.N., Mohapatra, P.K., 2014. Online recovery of radiocesium from soil, cellulose and plant samples by supercritical fluid extraction employing crown ethers and calix-crown derivatives as extractants. J. Radioanal. Nucl. Chem. 300, 1281–1289. http://dx.doi.org/10.1007/s10967-014-3034-0

Kato, H., Onda, Y., Teremage, M., 2012. Depth distribution of ^{137}Cs, ^{134}Cs and ^{131}I in soil profile after Fukushima Dai-ichi nuclear power plant accident. J. Environ. Radioact. 111, 59–64. http://dx.doi.org/10.1016/j.jenvrad.2011.10.003

Kim, G., Choi, W., Jung, C., Moon, J., 2007. Development of a washing system for soil contaminated with radionuclides around TRIGA reactors. J. Ind. Eng. Chem. 13, 406–413.

Lamare, V., Bressot, C., Dozol, J.F., Vicens, J., Asfari, Z., Ungaro, R., Casnati, A., 1997. Selective extraction of cesium at tracer level concentration from a sodium nitrate solution with calix-crowns. Molecular modeling study of the Cs^+/Na^+ selectivity. Sep. Sci. Technol. 32, 175–191. http://dx.doi.org/10.1080/01496399708003193

Lee, I.C., Kim, S. J., Lee, C., 1986. Extraction of alkali metal cation with crown ethers and HDEHP. J. Korean Chem. Soc. 30, 359–368.

Leybros, A., Grandjean, A., Segond, N., Messalier, M., Boutin, O., 2016. Cesium removal from contaminated sand by supercritical CO_2 extraction. J. Environ. Chem. Eng. 4, 1076–1080. http://dx.doi.org/10.1016/j.jece.2016.01.009

Leybros, A., Hung, L., Hertz, A., Hartmann, D., Grandjean, A., Boutin, O., 2017. Supercritical CO_2 extraction of uranium from natural ore using organophosphorus extractants. Chem. Eng. J. 316, 196–203. http://dx.doi.org/10.1016/j.cej.2017.01.101

Lin, F., Liu, D., Das, S. M., Prempeh, N., Hua, Y., Lu, J., 2014. Recent progress in heavy metals extraction by supercritical CO_2 fluids. Ind. Eng. Chem. Res. 53, 1866–1877. http://dx.doi.org/10.1021/ie4035708

McHugh, M.A., Krukonis, V. J., 1994. Supercritical fluid extraction: Principles and Practice, second ed., Butterworth-Heinemann, Boston.

Meguro, Y., Iso, S., Sasaki, T., Yoshida, Z., 1998. Solubility of organophosphorus metal extractants in supercritical carbon dioxide. Anal. Chem. 70, 774–779. http://dx.doi.org/10.1021/ac9707390

Mochizuki, S., Wada, N., Smith Jr., R., Inomata, H., 1999. Perfluorocarboxylic acid counter ion enhanced extraction of aqueous alkali metal ions with supercritical carbon dioxide. Analyst. 124, 1507–1511. http://dx.doi.org/10.1039/A904873A

Parajuli, D., Tanaka, H., Hakuta, Y., Minami, S., Fukuda, K., Umeoka, R., Kamimura, Y., Hayashi, Y., Ouchi, M., Kawamoto, T., 2013. Dealing with the aftermath of Fukushima Daiichi nuclear accident: decontamination of radioactive cesium enriched ash. Environ. Sci. Technol. 47, 3800–3806. http://dx.doi.org/10.1021/es303467n

Park, J., Park, K., Kim, H., 2015. Decontamination techniques of metal ions in soil by supercritical fluid with synthetic ligands in: Proceedings of Global 2015, Paris, pp.2114-2121.

Rao, A., Rathod, N., Malkhede, D., Raut, V., Ramakumar, K., 2013. Supercritical carbon dioxide extraction of uranium from acidic medium employing calixarenes. Sep. Sci. Technol. 48, 644–651. http://dx.doi.org/10.1080/01496395.2012.707731

Rathod, N., Rao, A., Kumar, P., Ramakumar, K, Malkhede, D., 2014. Complexation with calixarenes and efficient supercritical CO_2 extraction of Pb(II) from acidic medium. New J. Chem. 38, 5331–5340. http://dx.doi.org/10.1039/C4NJ00927D

Rathod, N., Rao, A., Kumar, P., Ramakumar, K., Malkhede, D., 2015. Studies on complexation and supercritical fluid extraction of Cd^{2+} with calixarenes. Ind. Eng. Chem. Res. 54, 3933–3941. http://dx.doi.org/10.1021/ie5045583

Rais, J., Tachimori, S., Yoo, E., Alexova, J., Bubenikova, M., 2015. Extraction of radioactive Cs and Sr from nitric acid solutions with 25,27-Bis(1-octyloxy)calix[4]-26,28-Crown-6 and Dicyclohexyl-18-Crown-6: Effect of nature of the organic solvent. Sep. Sci. Technol. 20, 1202–1212. http://dx.doi.org/10.1080/01496395.2014.978464

Real, J., Persin, F., Camaras-Claret, C., 2002. Mechanisms of desorption of ^{134}Cs and ^{85}Sr aerosols deposited on urban surfaces. J. Environ. Radioact. 62, 1–15. http://dx.doi.org/10.1016/S0265-931X(01)00136-9

Reynier, N., Lastra, R., Laviolette, C., Fiset, J., Bouzoubaa, N., Chapman, M., 2015. Uranium, cesium and mercury leaching and recovery from cemented radioactive wastes in sulfuric acid and iodide media. Minerals. 5, 744–757. http://dx.doi.org/10.3390/min5040522

Samuleev, P., Andrews, W., Creber, K., Azmi, P., Velicogna, D., Kuang, W., Volchek, K., 2013. Decontamination of radionuclides on construction materials. J. Radioanal. Nucl. Chem. 296, 811–815. http://dx.doi.org/10.1007/s10967-012-2146-7

Sandalls, F., 1987. Removal of radiocaesium from urban surfaces. Radiat. Prot. Dosimetry. 21, 137–140. http://dx.doi.org/10.1093/oxfordjournals.rpd.a080066

Schurhammer, R., Berny, F., Wipff, G., 2001. Importance of interfacial phenomena in assisted ion extraction by supercritical CO_2: a molecular dynamics investigation. Phys. Chem. Chem. Phys. 3, 647–656. http://dx.doi.org/10.1039/B007238I

Shimizu, R., Sawada, K., Enokida, Y., Yamamoto, I., 2006, Decontamination of radioactive contaminants from iron pipes using reactive microemulsion of organic acid in supercritical carbon dioxide. J. Nucl. Sci. Technol. 43, 694–698. http://dx.doi.org/10.1080/18811248.2006.9711150

Sieffert, N., Wipff, G., 2006. Alkali cation extraction by calix[4]crown-6 to room-temperature ionic liquids. The effect of solvent anion and humidity investigated by Molecular Dynamics Simulations. J. Phys. Chem. A. 110, 1106–1117. http://dx.doi.org/10.1021/jp054990s

Smart, N., Carleson, T., Kast, T., Clifford, A., Burford, M., Wai, C, 1997. Solubility of chelating agents and metal containing compounds in supercritical fluid carbon dioxide. Talanta. 44, 137–150. http://dx.doi.org/10.1016/S0039-9140(96)02008-5

Smyth, T., Zytner, R., Stiver, W., 1999. Influence of water on the supercritical fluid extraction of naphthalene from soil. J. Hazard. Mater. 67, 183–196. http://dx.doi.org/10.1016/S0304-3894(99)00043-6

Vance, K., Falzone, G., Pignatelli, I., Bauchy, M., Balonis, M., Sant, G., 2015. Direct carbonation of $Ca(OH)_2$ using liquid and supercritical CO_2: Implication for carbon-neutral

cementation. Ind. Eng. Chem. Res. 54, 8908–8918. http://dx.doi.org/10.1021/acs.iecr.5b02356

Villagran-Zaccardi, Y., Eguez-Alava, H., De Buysser, K., Gruyaert, E., De Belie, N., 2017. Calibrated quantitative thermogravimetric analysis for the determination of portlandite and calcite content in hydrated cementitious systems. Mater. Struct. 50, 179-189. https://dx.doi.org/10.1617/s11527-017-1046-2

Wai, C., Kulyako, Y., Myasoedov, B., 1999. Supercritical carbon dioxide extraction of caesium from aqueous solutions in the presence of macrocyclic and fluorinated compounds. Mendeleev Commun. 9, 80–81. https://doi.org/10.1070/MC1999v009n05ABEH001117

Wang, S., Elshani, J., Wai, C., 1995. Selective extraction of mercury with ionizable crown ethers in supercritical carbon dioxide. Anal. Chem. 67, 919–923. http://dx.doi.org/10.1021/ac00101a019

Wang, T., Li, M., Teng, S., 2010. Desorption of cesium from granite under various aqueous conditions. Appl. Radiat. Isot. 68, 2140–2146. http://dx.doi.org/10.1016/j.apradiso.2010.07.005