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

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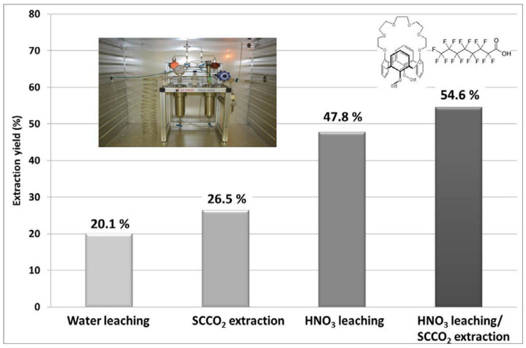
HIGHLIGHTS

- 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%.

GRAPHICAL ABSTRACT



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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.

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

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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., 2016) 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 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 higher solvent strength and diffusivity than liquids, which facilitate extraction in porous structures. Supercritical CO_2 has already been investigated for the extraction of metals in neutral or ionic form (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 $6.0 \cdot 10^{-6}$ and $7.2 \cdot 10^{-3}$ $mol \cdot mol_{CO2}$ 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 highly acid with affinity for supercritical CO_2 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 and Wipff, 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 ions 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 ^1H and ^{13}C NMR and IR spectroscopy. The solubility of this calixarene in CO_2 is about $3.7 \cdot 10^{-5}$ $mol \cdot mol_{CO2}$ at 27 MPa and 40 °C (Dartiguelongue et al., 2017).

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.

Different types of (uncontaminated) concrete rubble from peeling operations were obtained from decommissioning sites. The rubble were crushed and sieved. 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 $Bq \cdot mL^{-1}$) of $^{137}Cs + {}^{137}Ba^m$ in HCl (0.1 $mol\,L^{-1}$), prepared from sealed 5 mL, 40 $kBq \cdot g^{-1}$ standard solutions (ORANO CERCA LEA, > 97.5%). Nitric acid samples (3 $mol\,L^{-1}$) were prepared by dilution from commercial HNO_3 (Aldrich, 65 wt%).