Remediation of ^{137}Cs-contaminated concrete gravels by supercritical CO$\_2$ extraction

A. Leybros, N. Segond, Agnès Grandjean

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

2 # extraction

3

4 Antoine Leybros[a]*, Nathalie Segond[b], Agnès Grandjean[a]

5

6 *[a] CEA, DEN, DE2D, SEAD, LPSD, F30207 Bagnols sur Cèze, France*

7 *[b] AREVA Back-end BG- D&S BU, F92084 la Defense, France*

8

9 ** Corresp. author.;Tel: +(33) 04 66 79 16 41; E-mail:* antoine.leybros@cea.fr

10

Highlights

12

13 • Supercritical CO_2 was used as solvent to extract ^{137}Cs from concrete rubble.

14 • The best extractant system was found to be CalixOctyl/HPFOA.

15 • Extraction is hindered by carbonation reducing the porosity of the cement.

16 • Poor Cs desorption also explained by formation of insoluble Cs-concrete complexes.

17 • Preceding extraction with HNO_3 leaching increased the extraction yield up to 55%.

18

Abstract

20 The removal of cesium contamination is a critical issue for the recycling of concrete rubble in

21 most decommissioning operations. The high solvent strength and diffusivity of supercritical

22 CO_2 make it an attractive choice as vector for extractant system in this context. Experimental

23 extraction runs have been carried out in a radioactive environment on rubble contaminated

24 with ^{137}Cs. The best extraction system was found to be CalixOctyl (25,27-Bis(1-

25 octyloxy)calix[4]arene-crown-6, 1,3-alternate) with pentadecafluorooctanoic acid as a

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

32

33 **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

60   construction materials (Samuleev et al., 2013), granite (Wang et al., 2010), dredged sediments,

61   shales (Sandalls, 1987), ashes (Parajuli et al., 2013) and cemented waste (Reynier et al., 2015).

62   Supercritical CO_2 treatments are a promising alternative that also preserve the

63   structure of the concrete. Supercritical CO_2 is used in a wide range of extraction processes

64   because it is nontoxic, inexpensive, environmentally friendly, and has a low critical

65   temperature and pressure (McHugh and Krukonis, 1994). Supercritical CO_2 exhibits both high

66   solvent strength and diffusivity, which facilitate extraction in porous structures. Supercritical

67   CO_2 has already been investigated for the extraction of metals (Lin et al., 2014). However, a

68   crucial issue for these processes is the availability of an efficient and selective extractant that

69   is soluble in supercritical CO_2.

70   The three classes of chemicals that are generally used for cesium removal by liquid-

71   liquid extraction are dicarbollides, crown ethers and calixarenes (Dozol et al., 2000).

72   Dicarbollides have a good extraction capacity for cesium, but their selectivity for cesium over

73   other alkali elements is low. In the same way, crown ethers, whose selectivity is based on

74   cation size (macrocycle cavity size complementarity), are poorly selective in the presence of

75   other alkali species. Crown ethers with modifiers (such as di-(2-ethylhexyl) phosphoric acid

76   (HDEHP), pentadecafluorooctanoic acid (HPFOA) or tetraethylammonium perfluoroctane

77   sulfonate (PFOSANEt$_4$)) have been evaluated for the recovery of cesium from aqueous

78   solutions containing other alkali ions such as Na^+ or K^+ (Lee et al., 1986) and from synthetic

79   soil samples using supercritical CO_2 (Park et al., 2015). Elsewhere, Lamare et al. (1997) used

80   calixarenes functionalized with crown ethers to extract cesium from a sodium nitrate solution.

81   They found that the selectivity of these compounds for cesium was highly dependent on the

82   conformation of the calixarenes. Indeed, CalixOctyl (25,27-Bis(1-octyloxy)calix[4]arene-

83   crown-6, 1,3-alternate) is remarkably selective in forming complexes with cesium rather than

84   other alkali species in acidic environments (Rais et al., 2015).In the other hand, the solubility

85   of calixarenes in supercritical CO_2 has been measured at 60°C and 20 MPa to be between 0.1

4

86   and 120 mmol·L^{-1} depending on their functionalization (Glennon et al., 1997). These

87   properties have led to their use for the supercritical CO_2 extraction of Cs (Kanekar et al.,

88   2014), Cd (Rathod et al., 2015), Pb (Rathod et al., 2014) and U (Rao et al., 2013).

89   As extractant/Cs complexes are almost completely insoluble in supercritical CO_2, an

90   organic modifier is required to neutralize the charge of the complex and increase its solubility.

91   The importance of interfacial phenomena between the supercritical CO_2 phase and the

92   aqueous phase for CalixOctyl/modifier/Cs has been highlighted by molecular dynamics

93   simulations (Schurhammer et al., 2001; Sieffert et al., 2006). The organic modifier used in

94   most cases is HPFOA with macrocyclic polyethers. Extraction yields up to 60% have been

95   obtained with a good selectivity for cesium over potassium cations (Mochizuki et al., 1999;

96   Wai et al., 1999).

97   Cesium decontamination studies have been carried out previously using supercritical

98   CO_2 from silica soil (Leybros et al., 2016). Satisfactory yields of between 70 and 95% were

99   achieved with (non-radioactive) cesium ^{133}Cs concentrations much greater (1–14 mg/g) than

100 observed in practice for ^{137}Cs contaminations. This paper reports experimental extraction runs

101 with realistic ^{137}Cs activities (~800 Bq/g) performed in a nuclear laboratory on concrete

102 rubble. The extractant considered was CalixOctyl with an organic modifier. The first step of

103 the study consisted in determining the most suitable modifier. The influence of various

104 operating parameters was investigated before the efficiency of supercritical CO_2 extraction

105 was compared for this application with leaching using water and nitric acid. Supercritical

106 extraction complemented by acid leaching was also considered.

107

108 **2. Materials and methods**

109

110 *2.1. Reagents*

5

111   Calixarenes are macrocyclic compounds formed by the condensation of a phenol

112   and an aldehyde. They have hydrophobic cavities which can accommodate small molecules or

113   ions. The selectivity of calixarenes stems from the size of their cavities and the nature of their

114   functionalization. Crown calixarenes have a much higher selectivity for cesium over other

115   alkali cations than crown ethers do (Danil de Namor et al., 1998), the most selective

116   calixarenes being CalixOctyl (25,27-Bis(1-octyloxy)calix[4]arene-crown-6, 1,3-alternate),

117   shown in **Fig. 1**. The calixarene structure stiffens the whole molecule through steric effects

118   that fix the size of the crown ether's cavity. CalixOctyl was synthesized following Casnati et

119   al. (1995) and its purity (> 95%) was verified by ^{1}H and ^{13}C NMR and IR spectroscopy. The

120   solubility of this calixarene in CO_2 is about 0.64 $kg \cdot m^{-3}$ at 27 MPa and 40 °C (Dartiguelongue

121   et al., 2017).
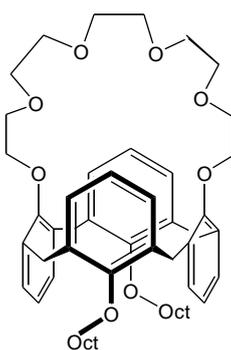
122

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

124   alternate).

125

126   The organic modifiers considered in this study were HDEHP, bromocapric acid,

127   HPFOA, formic acid, perfluoropentanoic acid (PFPEA), methyloxovaleric acid,

128   heptadecafluorooctanesulfonic acid (PFOS) and PFOSANEt4. The characteristics of these

129   chemicals are summarized in **Table 1**. No further purification was performed. These

130   modifiers are generally highly soluble in supercritical CO_2 under the conditions used here

131   (Byun et al., 2000; Dartiguelongue et al., 2016; Meguro et al., 1998; Shimizu et al., 2006).

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

133 purification.

134

135 **Table 1**

136 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
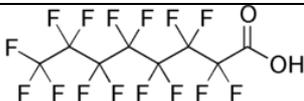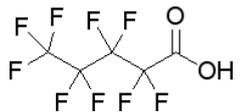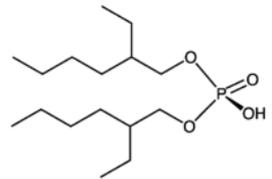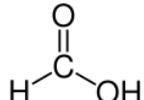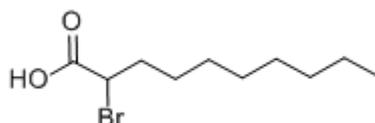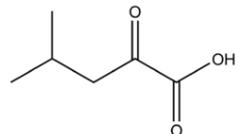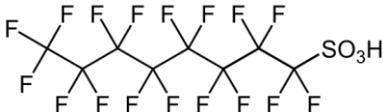
PFOSA-NEt4	56773-42-3	Aldrich	(structure: tetraethylammonium heptadecafluorooctanesulfonate)	0.98
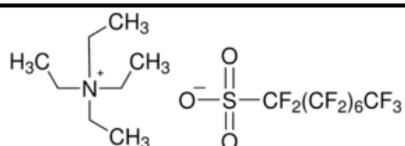
Different types of (uncontaminated) concrete rubble from peeling operations were obtained from decommissioning sites. The rubble were sieved and crushed. The rubble samples contained particles of 2–5 mm in diameter (for Run 9 the particles were smaller: 1–2 mm in diameter). The rubble samples were artificially 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).
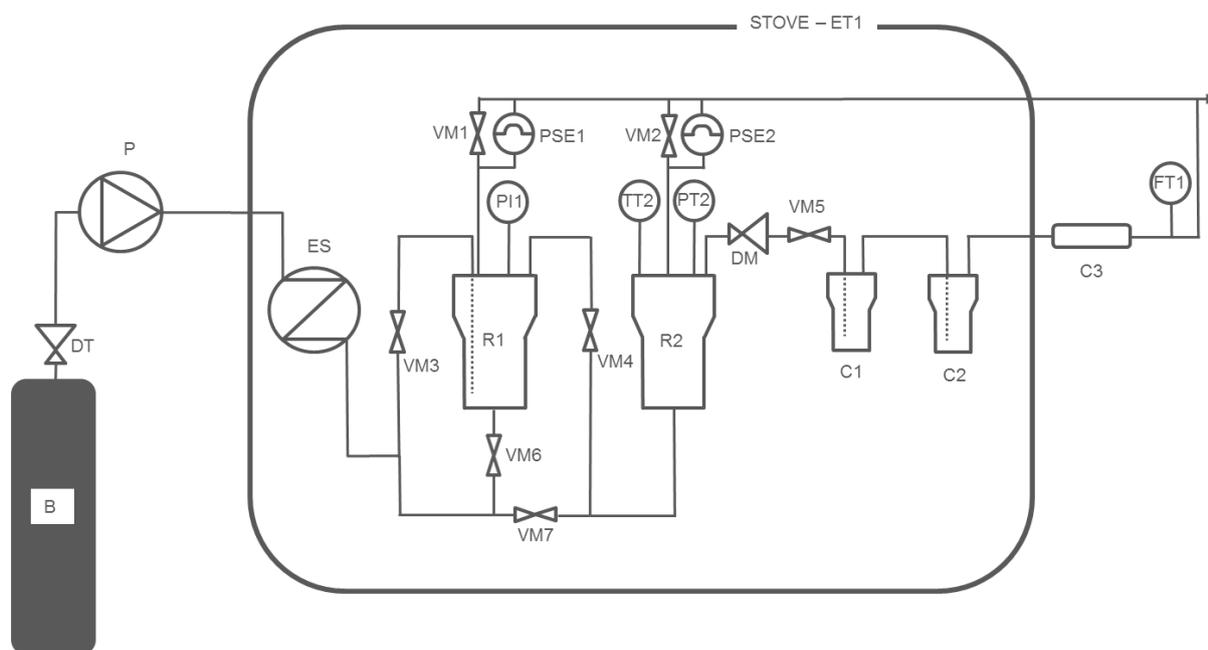
Fig. 2. Schematic diagram of the setup used for the extraction of cesium using supercritical CO_2. VM: stop valve; P: pump; ES: heat exchanger; R1: solubilization reactor; R2: extraction reactor; DM: back-pressure regulator; C1, C2 and C3: collectors.

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.

174 *2.3. Leaching experiments*

175   Leaching experiments were performed at ambient temperature using 45 mL of either

176 water or 3 mol·L^{-1} HNO$_3$. The rubble samples were leached for 3 h.

177

178 *2.4. Protocol for the preparation of cesium-contaminated concrete rubble*

179   The samples of contaminated rubble (initial mass, 45 g) were impregnated (fully

180 soaked) with 45 mL of an aqueous solution of ^{137}Cs with an activity equal 780 Bq·mL^{-1} and

181 then dried in a stove until the desired water content (3 wt%) was achieved (**Fig. 3**). The

182 targeted initial activity was 35 kBq. For run 10, in which a cesium activity in the

183 contaminating solution of ~7.8·10^5 Bq·mL^{-1} was simulated, an aqueous solution of 3.1·10^{-4}

184 g·L^{-1} ^{133}Cs was doped with a 780 Bq·mL^{-1} ^{137}Cs solution. To guarantee the reproducibility of

185 each experiment, the residual water content of the rubble samples was measured as a function

186 of the drying time. Here, the target of residual water contents of around 3 wt% were obtained

187 after 40 h drying at 40 °C.

188
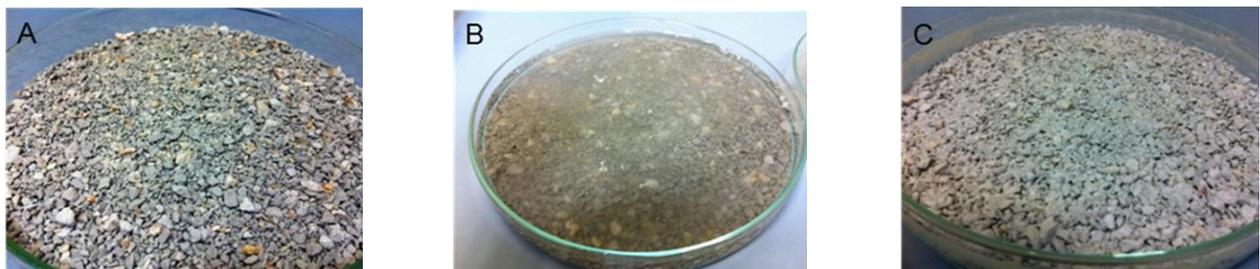
189

190 **Fig. 3.** Preparation of cesium-contaminated rubble. Photographs of (A) their initial state; (B)

191 during impregnation with a ^{137}Cs solution and (C) after drying.

192

193 *2.4. Analysis*

194   The rubble samples were analyzed by γ–ray spectrometry before and after

195 supercritical CO_2 extraction, as were the extracts collected in the three collectors. The

196 presence (absence) of ^{137}Cs in the extracts reveals the presence (absence) of back-extraction.

197 The extraction yield of the decontamination process was calculated using **Eq. (1)**,

198 $$E(\%) = \frac{a_{initial} - a_{final}}{a_{initial}}$$ (1)

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

200 extraction run.

201   These γ–ray spectrometry measurements were performed using a Tennelec series 5

202 γ-ray spectrometer (Canberra, USA) equipped with a high-purity germanium detector and a

203 Tennelec TC242 amplifier. The acquisition software was Interwinner 6.

204   One of the main limitations of this approach is the possible attenuation of the γ

205 radiation in case of measurement in the solid sample. A calibration curve was therefore

206 established for the activity of the rubble samples to determine a valid working range. The

207 rubble samples used as standards were prepared as described above for the extraction

208 samples, with the same mass, but with targeted activities of 35, 15, 3 and 0.5 kBq. The results

209 presented in **Table 2** show that γ–ray spectrometry is accurate enough to quantify cesium

210 extraction efficiencies under these working conditions.

211

212 **Table 2**

213 Nominal versus measured ^{137}Cs activity of the standard samples used to validate the

214 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

215

216

217

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).

223 **Table 3**

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

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

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

226 tetraethylammonium heptadecafluorooctanesulfonate.

227 Unless otherwise specified, the samples contained particles 2–5 mm in diameter, with an initial ^{137}Cs concentration of $2.7 \cdot 10^{-7}$ mg·g^{-1} and a residual water content of 3 wt%.

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

229 [b]The initial cesium concentration in this sample was $2.7 \cdot 10^{-4}$ mg·g^{-1}.

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

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

232

233

234

3.1. Determining the most suitable extractant/modifier system

236   CalixOctyl was combined with different modifiers in supercritical CO_2 (at 27 MPa,

237   40 °C; Runs 1–8 in **Table 2**).Indeed, CalixOctyl is little soluble in our working conditions and

238   the most suitable modifier has to be identified to enhance both extractant system and

239   organometallic complexes solubilities. As shown in **Table 2**, these runs were performed with

240   a high stoichiometric excess of the extractant, given the very small amount of ^{137}Cs present in

241   the samples. The extraction yields were low, between 2 and 12%. The extracts in the

242   collectors were found to have a low activity (between 10 and 500 Bq), whatever the modifier.

243   The modifier that gave the highest extraction yield was HPFOA (12.3%, Run 3). This can be

244   explained by the high solubility of fluorinated compounds in supercritical CO_2, which stems

245   from the presence of fluorine substituents and the length of the fluorinated chain (Smart et al.,

246   1997). Furthermore, the low pKa of fluorinated compounds (Goss, 2008) facilitates ion

247   exchange with cesium inside the concrete.

248   Low extraction yields are expected for concrete rubble because of their chemical

249   structure: cesium cations are strongly adsorbed on their calcium silicate hydrate structure

250   (Evans, 2008). This virtually irreversible ion exchange process and the formation of insoluble

251   complexes with calcium silicate hydrate make cesium desorption (and therefore extraction)

252   very difficult. Moreover, the concentration of alkali ions (Na^+; K^+) was significantly higher (a

253   few mmol per gram of concrete as determined by inductively coupled plasma atomic emission

254   spectroscopy) than the Cs^+ concentration in the samples (a few pmol per gram), which makes

255   strong competition between Cs and other alkali cations.

256   Another factor that may contribute to the low extraction yields is accelerated

257   carbonation, which reduces the size of the pores inside the concrete structure (Garcia-

258   Gonzalez et al., 2008). The rubble samples were found to be between 0.5 and 2.3 g heavier

259   after extraction. **Fig. 4** shows the thermogravimetric analysis of a rubble sample treated by

260 supercritical CO_2 for 4 h at 27 MPa and 40 °C. The presence of a calcite peak (at 760–770 °C)

261 confirms that carbonation has occurred (Villagran-Zaccardi et al., 2017). This suggest that the

262 pores inside the concrete do indeed shrink, trapping the organometallic

263 CalixOctyl/modifier/Cs complexes formed therein. CO_2–philic extractants, more soluble in

264 supercritical CO_2, may therefore be a more suitable choice to extract cesium from the concrete

265 matrix before carbonation.

266
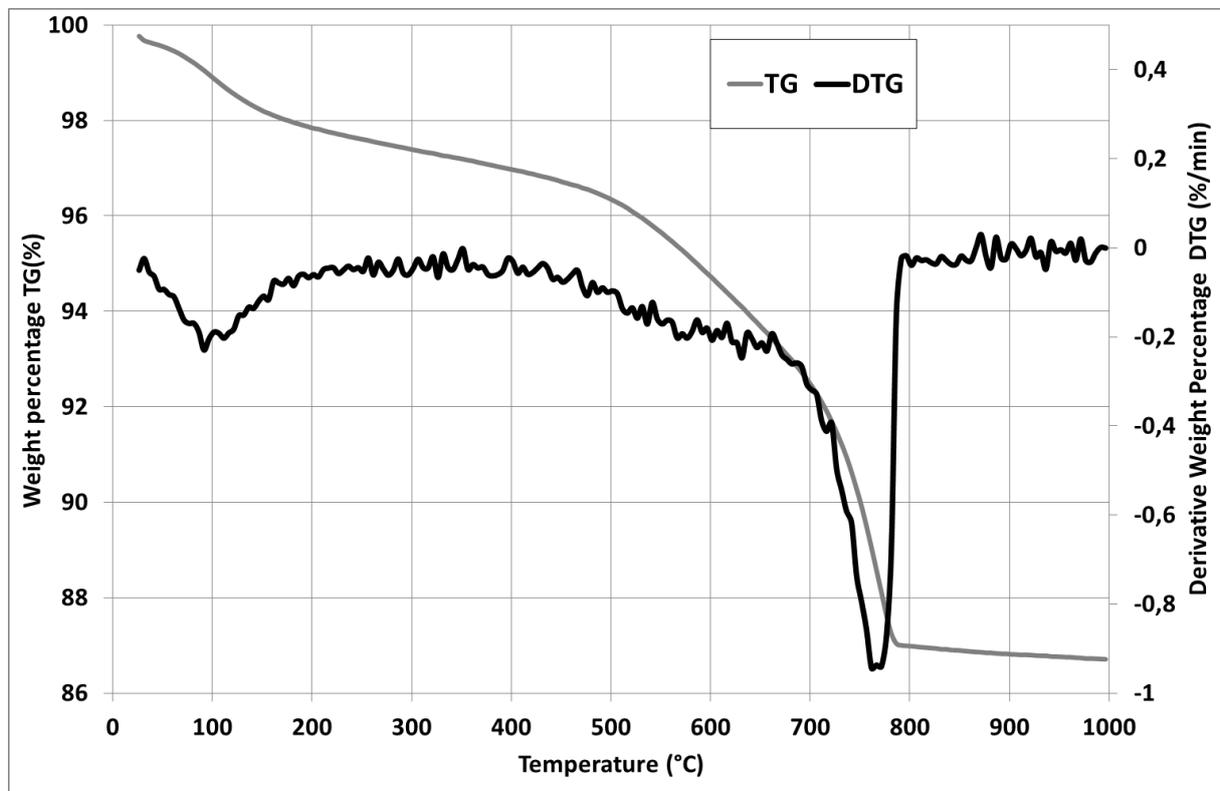
267

268 **Fig. 4.** Demonstration of the formation of calcite in a sample of concrete rubble.

269 Thermogravimetric analysis of a sample of concrete rubble after treatment using supercritical

270 CO_2 (P = 27 MPa; T = 40°C; CO_2 flow = 10 g·min^{-1}, treatment time = 4 h).

271

272 Our results are similar to those of Kanekar et al. (2014), who extracted cesium from

273 soils using supercritical CO_2 and calixarene mixed with methanol. The efficiency of extraction

16

274 processes such as these can be improved by tuning the operating parameters to find the best

275 compromise between thermodynamic and kinetic limiting factors.

276

277 *3.2. Optimizing the operating parameters*

278   Having identified CalixOctyl/HPFOA as the most suitable extractant system, the

279 following paragraphs describe the effects on the process efficiency of the particle size in the

280 samples (section 3.2.1), of the initial cesium concentration and the Cs/extractant

281 stoichiometric ratio (section 3.2.2) and of the temperature and residual water content (section

282 3.2.3).

283

284 *3.2.1. Role of rubble particle size*

285   Comparing the results obtained for Runs 3 and 9 (**Table 3**) shows that reducing the

286 rubble particle size from 2–5 mm to 1–2 mm (all other parameters being identical) leads to a

287 modest increase in the extraction yield from 12.3 ± 7.2% to 18.7 ± 7.2%. This effect is

288 expected because smaller particles have a larger specific surface area, making the cesium

289 binding sites in the concrete pores more accessible. The energetic cost of crushing the rubble

290 should be considered however in choosing the best particle size in view of industrialization of

291 the process.

292

293 *3.2.2. Cesium content and amounts of extractant and modifier*

294   Run 3 was repeated in Run 10 but with a much higher cesium concentration initially

295 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

296 the latter case, ^{133}CsNO$_3$ was added to simulate a rubble radioactivity of 10^6 Bq·mL^{-1}, which

297 is in the range of the levels of contamination observed in practice. The extraction efficiency

298 measured for Run 10 was 22.0 ± 7.2% compared with 12.3 ± 7.2% for Run 3. This suggests

299 that the selectivity of the process for Cs over other alkali metal ions is not perfect.

17

300   The influence on the extraction yield of the amounts of extractant/modifier

301   (CalixOctyl/HPFOA) used was investigated in Run 16, performed with twice the amount of

302   extractant as Run 3 (all other parameters being equal, including the CalixOctyl/HPFOA molar

303   ratio at 1/5). **Table 3** shows that this has little effect on the extraction yield ($17.3 \pm 7.2\%$ for

304   Run 16 versus $12.3 \pm 7.2\%$ for Run 3). The extraction capacity (the ratio of the amount of Cs

305   extracted from the sample over the amount of extractant (CalixOctyl) used) was higher for

306   Run 3 ($5.5 \ 10^{-8}$ versus $3.3 \ 10^{-8}$ for Run 16). This suggests that the limiting factor here is the

307   low Cs concentration in the rubble, which makes the probability of Cs–extractant interactions

308   very low even when the amount of extractant used is increased.

309   The results for Run 17 show that increasing the ratio between extractant and

310   modifier from 1/5 (Run 11) to 1/7 (Run 17) had little effect on the extraction yield ($13.1 \pm$

311   7.2% for Run 17 versus $14.7 \pm 7.2\%$ for Run 11). This may be because the HPFOA molecules

312   self-associate in supercritical CO_2, which limits their solubility. This effect has been observed

313   previously for fluorocarboxylic acids in supercritical CO_2 (Dartiguelongue et al., 2016).

314   Further investigations are in progress to determine whether the structure of the complexes

315   formed by the extractant system may involve a molecule of calixarene and fluorocarboxylic

316   acid monomers or dimers.

317

318   *3.2.3. Operating temperature and rubble water content*

319   Previous studies on supercritical CO_2 extraction in porous media have demonstrated

320   that the solvent strength and diffusivity of CO_2 are strongly dependent on its density

321   (Anitescu and Tavlarides, 2006). In Runs 3 and 11–15 (**Table 3**), the operating temperature

322   was varied between 40 and 100 °C with a rubble water content of either 1 wt% (Run 14) 2

323   wt% (Runs 12 and 15) or 3 wt% (Runs 3 and 11–13) (**Fig.5**). Note that calixarene was found

324   to be chemically stable at temperatures up to 150 °C. Increasing the temperature up to 100 °C

325   did not significantly affect the extraction yield (which varied from $12.3 \pm 7.2\%$ to $17.5 \pm$

326 7.2%, see **Table 3**). The solvent strength of CO_2 is lower at higher temperatures but this

327 decrease may have been offset by an increase in the extraction kinetics and reduced concrete

328 carbonation.

329
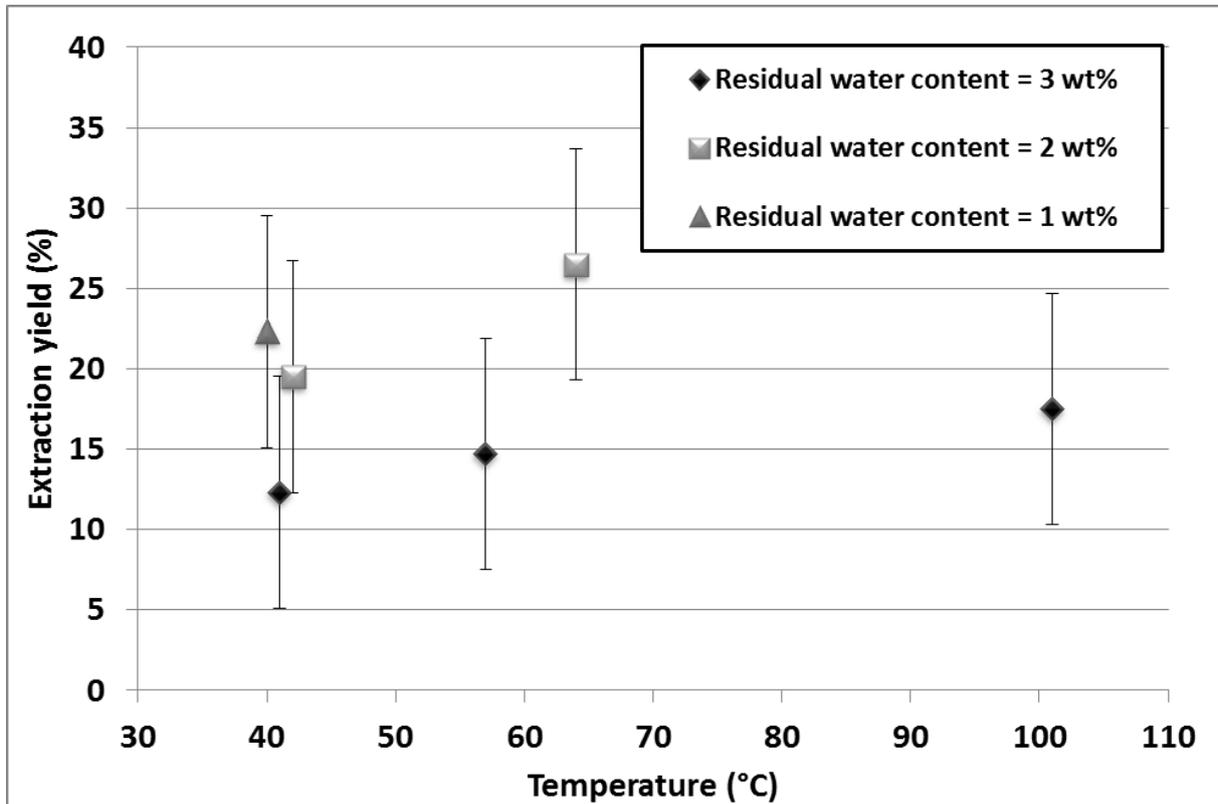
331 **Fig. 5.** Influence of residual water content and temperature on extraction yield.

332

333 Reducing the water content of the rubble was found to have a favorable effect on the

334 extraction yield, which was 22.3 ± 7.2% for Run 14 with 1 wt% water (**Table 3**). It is

335 therefore important to properly dry rubble before proceeding with supercritical CO_2 extraction.

336 These results are in keeping with the literature. Wang et al. (1995) suggest that low water

337 concentrations may promote extraction because this allows hydrogen ions from the modifier

338 to be exchanged with cesium adsorbed in the solid matrix. On the other hand, higher water

339 contents limit extraction because the formation of a water films in the pores may block the

340 supercritical CO_2 and thus limit interactions with the extractant system (Smyth et al., 1999).

341 Moreover, increasing the water content promotes carbonation and therefore reduces the

342 porosity of the concrete (Vance et al., 2015).

343   The best extraction yield of all these runs was $26.5 \pm 7.2\%$ for Run 15, performed at

344 an intermediate temperature (65 °C) and water content (2 wt%). In line with the mechanisms

345 described above, these conditions offer the optimal balance between faster extraction or back-

346 extraction kinetics and slower carbonation on the one hand, and a lower CO_2 solvent strength

347 on the other.

348

349 *3.3. Combining supercritical CO_2 extraction with leaching*

350   Table 4 compares the effects of leaching (with water or HNO_3) with the results

351 obtained using HNO_3 leaching followed by supercritical CO_2 extraction to extract Cs from

352 concrete rubble.

353 **Table 4.**

354 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	HNO₃ leaching	–	ambient	–	32 482 ± 2 339	17 627 ± 952	16 944 ± 915		47.8 ± 6.3
20	HNO₃ leaching followed by SCCO₂ 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

355 SCCO₂, supercritical CO_2

356

21

357

358   The extraction efficiency of the water leaching run was almost as high as the best

359   supercritical CO_2 extraction (Run 18, 20.2 ± 7.2% and Run 15, 26.5 ± 7.2% respectively).

360   With HNO_3 leaching (Run 19), the extraction yield was much higher (47.8 ± 6.3%). These

361   yields are similar to those of previous studies of the acidic leaching of soil and/or concrete

362   samples (Kim et al., 2007; Samuleev et al., 2013) and show that HNO_3 efficiently desorbs

363   ^{137}Cs from otherwise irreversible sorption sites in the concrete pores.

364   A further increase in the extraction yield was obtained by performing supercritical

365   CO_2 extraction after HNO_3 leaching (Run 20, 54.6 ± 6.3%). These results suggest coupling

366   between leaching and supercritical CO_2 extraction by cumulating steps up to reach targeted

367   threshold for rubble activity for reuse or storage. It would be interesting to perform the HNO_3

368   leaching in situ in supercritical CO_2, which may reduce the amount of HNO_3 required and

369   allow the procedure to be performed in a single step. The benefits would be substantial on an

370   industrial scale. The influence of the HNO_3 concentration may also be worth investigating, to

371   find the optimal balance between extraction yields and the corrosion of the pipes and internal

372   walls.

373

374   **4. Conclusion**

375   Supercritical CO_2 extraction runs have been performed on samples of cesium-

376   contaminated concrete rubble, with an extractant system composed of a cesium-selective

377   crown calixarene and a modifier. These experiments were carried out in a radioactive

378   environment with realistic levels of ^{137}Cs contamination. Preliminary tests identified the most

379   suitable modifier (HPFOA) to be used in this context with CalixOctyl (the crown calixarene).

380   Experiments performed on rubble with different particle sizes and residual water contents, at

381   different temperatures and with different amounts of cesium and extractant showed that the

382   most important factors were the temperature of the process and the water content of the

383   samples. In choosing the operating conditions, a compromise has to be found between kinetic

384   (for extraction, back-extraction and the carbonation of the concrete), thermodynamic (the

385   solubility of the extractant system and the resulting organometallic compounds) and

386   diffusivity effects. The best cesium extraction yield obtained here using supercritical CO_2

387   extraction alone was $26.5 \pm 7.2\%$. Similar results were obtained by Kanekar et al. (2014) for

388   soil samples using supercritical CO_2 and three calix-crown derivatives in methanol or

389   acetonitrile. An extraction yield of $54.6 \pm 6.3\%$ was obtained by leaching the concrete rubble

390   with nitric acid before the supercritical CO_2 extraction step. Leaching makes the cesium more

391   labile and thus more easily extractable. Our results show furthermore that the benefits of

392   leaching and supercritical CO_2 extraction are cumulative. Further studies are ongoing to

393   synthesize a CO_2-phile and Cs-selective extractant and compare its performance with the

394   CalixOctyl/HPFOA system. Thermodynamic studies of CalixOctyl/HPFOA/CO_2 mixtures

395   may also facilitate the optimization of the operating conditions in view of scaling up the

396   process.

397

402

403   **References**

404

405   Anitescu, G., Tavlarides, L., 2006. Supercritical extraction of contaminants from soils and

406   sediments. J. Supercrit. Fluids. 38, 167–180. https://doi.org/10.1016/j.supflu.2006.03.024

407   Byun, H.S., Kim, K., McHugh, M.A., 2000. Phase behavior and modeling of supercritical

408   carbon dioxide-organic acid mixtures. Ind. Eng. Chem. Res. 39, 4580–4587.

409   http://dx.doi.org/10.1021/ie0001164

410   Castellani, R., Poulesquen, A., Goettmann, F., Marchal, P., Choplin, L., 2014. A topping gel

411   for the treatment of nuclear contaminated small items. Nucl. Eng. Des. 278, 481-490.

412   http://dx.doi.org/10.1016/j.nucengdes.2014.07.043

413   Casnati, A., Pochini, A., Ungaro, R., Ugozzoli, F., Arnaud, F., Fanni, S., Schwing, M.-J.,

414   Egberink, R., de Jong, F.,Reinhoudt, D. N., 1995. Synthesis, complexation, and membrane

415   transport studies of 1,3-alternate calix[4]arene-crown-6 conformers: a new class of cesium

416   selective ionophores. J. Am. Chem. Soc. 117, 2767–2777.

417   http://dx.doi.org/10.1021/ja00115a012

418   Dame, C., Fritz, C., Pitois, O., Faure, S., 2005. Relations between physicochemical properties

419   and instability of decontamination foams. Colloids and Surfaces A: Physicochem. Eng.

420   Aspects. 263, 210-218. http://dx.doi.org/10.1016/j.colsurfa.2004.12.053

421   Danil de Namor A., Cleverley, R., Zapata-Ormachea, M., 1998. Thermodynamics of

422   calixarene chemistry. Chem. Rev. 98, 2495–2525. http://dx.doi.org/10.1021/cr970095w

423   Dartiguelongue, A., Leybros, A., Grandjean, A., 2016. Solubility of perfluoropentanoic acid

424   in supercritical carbon dioxide: Measurements and modeling. J. Chem. Eng. Data. 61, 3902–

425   3907. http://dx.doi.org/10.1021/acs.jced.6b00649

426   Dartiguelongue, A., Leybros, A., Grandjean, A., 2017. Solubility and solution enthalpy of a

427   cesium-selective calixarene in supercritical carbon dioxide. J. Supercrit. Fluids. 125, 42–49.

428   http://dx.doi.org/10.1016/j.supflu.2017.01.017

429   Dozol, J.F., Dozol, M., Macias, R., 2000. Extraction of strontium and cesium by dicarbollides,

430   crown ethers and functionalized calixarenes. J. Incl. Phenom. Macrocycl. Chem. 38, 1–22.

431   http://dx.doi.org/10.1023/A:1008145814521

432   Evans, N., 2008. Binding mechanisms of radionuclides to cement. Cem. Concr. Res. 38, 545–

433   553. http://dx.doi.org/10.1016/j.cemconres.2007.11.004

434

435   Garcia-Gonzalez, C., El Grouh, N., Hidalgo, A., Fraile, J., Lopez-Periago, A., Andrade, C.,

436   Domingo, C., 2008. New insights on the use of supercritical carbon dioxide for the

437   accelerated carbonation of cement pastes. J. Supercrit. Fluids 43, 500–509.

438   http://dx.doi.org/10.1016/j.supflu.2007.07.018

439   Glennon, J. Hutchinson, S., Harris, S., Walker, A., McKervey, A., McSweeney, C., 1997.

440   Molecular baskets in supercritical CO_2. Anal. Chem. 69, 2207–2212.

441   http://dx.doi.org/10.1021/ac960850q

442   Goss K., 2008. The pKa values of PFOA and other highly fluorinated carboxylic acids.

443   Environ. Sci. Technol. 42, 456–458. http://dx.doi.org/10.1021/es702192c

444   Jokic S., Nagy, B., Zekovic, Z., Vidovic, S., Bilic, M., Velic, D., Simandi, B., 2012. Effects

445   of supercritical CO_2 extraction parameters on soybean oil yield. Food Bioprod. Process. 90,

446   693–699. http://dx.doi.org/10.1016/j.fbp.2012.03.003

447   Kaminski, M., Lee, S., Magnuson, M., 2016. Wide-area decontamination in an urban

448   environment after radiological dispersion: A review and perspectives. J. Hazard. Mater. 305,

449   67–86. http://dx.doi.org/10.1016/j.jhazmat.2015.11.014

450   Kanekar, A.S., Pathak, P.N., Mohapatra, P.K., 2014. Online recovery of radiocesium from

451   soil, cellulose and plant samples by supercritical fluid extraction employing crown ethers and

452   calix-crown derivatives as extractants. J. Radioanal. Nucl. Chem. 300, 1281–1289.

453   http://dx.doi.org/10.1007/s10967-014-3034-0

454   Kato, H., Onda, Y., Teremage, M., 2012. Depth distribution of ^{137}Cs, ^{134}Cs and ^{131}I in soil

455   profile after Fukushima Dai-ichi nuclear power plant accident. J. Environ. Radioact. 111, 59–

456   64. http://dx.doi.org/10.1016/j.jenvrad.2011.10.003

457   Kim, G., Choi, W., Jung, C., Moon, J., 2007. Development of a washing system for soil

458   contaminated with radionuclides around TRIGA reactors. J. Ind. Eng. Chem. 13, 406–413.

459

460   Lamare, V., Bressot, C., Dozol, J.F., Vicens, J., Asfari, Z., Ungaro, R., Casnati, A., 1997.

461   Selective extraction of cesium at tracer level concentration from a sodium nitrate solution

462   with calix-crowns. Molecular modeling study of the Cs^+/Na^+ selectivity. Sep. Sci. Technol.

463   32, 175–191. http://dx.doi.org/10.1080/01496399708003193

464   Lee, I.C., Kim, S. J., Lee, C., 1986. Extraction of alkali metal cation with crown ethers and

465   HDEHP. J. Korean Chem. Soc. 30, 359–368.

466   Leybros, A., Grandjean, A., Segond, N., Messalier, M., Boutin, O., 2016. Cesium removal

467   from contaminated sand by supercritical CO_2 extraction. J. Environ. Chem. Eng. 4, 1076–

468   1080. http://dx.doi.org/10.1016/j.jece.2016.01.009

469   Leybros, A., Hung, L., Hertz, A., Hartmann, D., Grandjean, A., Boutin, O., 2017.

470   Supercritical CO_2 extraction of uranium from natural ore using organophosphorus extractants.

471   Chem. Eng. J. 316, 196–203. http://dx.doi.org/10.1016/j.cej.2017.01.101

472   Lin, F., Liu, D., Das, S. M., Prempeh, N., Hua, Y., Lu, J., 2014. Recent progress in heavy

473   metals extraction by supercritical CO_2 fluids. Ind. Eng. Chem. Res. 53, 1866–1877.

474   http://dx.doi.org/10.1021/ie4035708

475   McHugh, M.A., Krukonis, V. J., 1994. Supercritical fluid extraction: Principles and Practice,

476   second ed., Butterworth-Heinemann, Boston.

477   Meguro, Y., Iso, S., Sasaki, T., Yoshida, Z., 1998. Solubility of organophosphorus metal

478   extractants in supercritical carbon dioxide. Anal. Chem. 70, 774–779.

479   http://dx.doi.org/10.1021/ac9707390

480   Mochizuki, S., Wada, N., Smith Jr., R., Inomata, H., 1999. Perfluorocarboxylic acid counter

481   ion enhanced extraction of aqueous alkali metal ions with supercritical carbon dioxide.

482   Analyst. 124, 1507–1511. http://dx.doi.org/10.1039/A904873A

483   Parajuli, D., Tanaka, H., Hakuta, Y., Minami, S., Fukuda, K., Umeoka, R., Kamimura, Y.,

484   Hayashi, Y., Ouchi, M., Kawamoto, T., 2013. Dealing with the aftermath of Fukushima

485   Daiichi nuclear accident: decontamination of radioactive cesium enriched ash. Environ. Sci.

486   Technol. 47, 3800–3806. http://dx.doi.org/10.1021/es303467n

487   Park, J., Park, K., Kim, H., 2015. Decontamination techniques of metal ions in soil by

488   supercritical fluid with synthetic ligands in: Proceedings of Global 2015, Paris, pp.2114-2121.

489   Rao, A., Rathod, N., Malkhede, D., Raut, V., Ramakumar, K., 2013. Supercritical carbon

490   dioxide extraction of uranium from acidic medium employing calixarenes. Sep. Sci. Technol.

491   48, 644–651. http://dx.doi.org/10.1080/01496395.2012.707731

492   Rathod, N., Rao, A., Kumar, P., Ramakumar, K, Malkhede, D., 2014. Complexation with

493   calixarenes and efficient supercritical CO_2 extraction of Pb(II) from acidic medium. New J.

494   Chem. 38, 5331–5340. http://dx.doi.org/10.1039/C4NJ00927D

495   Rathod, N., Rao, A., Kumar, P., Ramakumar, K., Malkhede, D., 2015. Studies on

496   complexation and supercritical fluid extraction of Cd^{2+} with calixarenes. Ind. Eng. Chem. Res.

497   54, 3933–3941. http://dx.doi.org/10.1021/ie5045583

498   Rais, J., Tachimori, S., Yoo, E., Alexova, J., Bubenikova, M., 2015. Extraction of radioactive

499   Cs and Sr from nitric acid solutions with 25,27-Bis(1-octyloxy)calix[4]-26,28-Crown-6 and

500   Dicyclohexyl-18-Crown-6: Effect of nature of the organic solvent. Sep. Sci. Technol. 20,

501   1202–1212. http://dx.doi.org/10.1080/01496395.2014.978464

502   Real, J., Persin, F., Camaras-Claret, C., 2002. Mechanisms of desorption of [134]Cs and [85]Sr

503   aerosols deposited on urban surfaces. J. Environ. Radioact. 62, 1–15.

504   http://dx.doi.org/10.1016/S0265-931X(01)00136-9

505 Reynier, N., Lastra, R., Laviolette, C., Fiset, J., Bouzoubaa, N., Chapman, M., 2015.

506 Uranium, cesium and mercury leaching and recovery from cemented radioactive wastes in

507 sulfuric acid and iodide media. Minerals. 5, 744–757. http://dx.doi.org/10.3390/min5040522

508 Samuleev, P., Andrews, W., Creber, K., Azmi, P., Velicogna, D., Kuang, W., Volchek, K.,

509 2013. Decontamination of radionuclides on construction materials. J. Radioanal. Nucl. Chem.

510 296, 811–815. http://dx.doi.org/10.1007/s10967-012-2146-7

511 Sandalls, F., 1987. Removal of radiocaesium from urban surfaces. Radiat. Prot. Dosimetry.

512 21, 137–140. http://dx.doi.org/10.1093/oxfordjournals.rpd.a080066

513 Schurhammer, R., Berny, F., Wipff, G., 2001. Importance of interfacial phenomena in

514 assisted ion extraction by supercritical CO_2: a molecular dynamics investigation. Phys. Chem.

515 Chem. Phys. 3, 647–656. http://dx.doi.org/10.1039/B007238I

516 Shimizu, R., Sawada, K., Enokida, Y., Yamamoto, I., 2006, Decontamination of radioactive

517 contaminants from iron pipes using reactive microemulsion of organic acid in supercritical

518 carbon dioxide. J. Nucl. Sci. Technol. 43, 694–698.

519 http://dx.doi.org/10.1080/18811248.2006.9711150

520 Sieffert, N., Wipff, G., 2006. Alkali cation extraction by calix[4]crown-6 to room-temperature

521 ionic liquids. The effect of solvent anion and humidity investigated by Molecular Dynamics

522 Simulations. J. Phys. Chem. A. 110, 1106–1117. http://dx.doi.org/10.1021/jp054990s

523 Smart, N., Carleson, T., Kast, T., Clifford, A., Burford, M., Wai, C, 1997. Solubility of

524 chelating agents and metal containing compounds in supercritical fluid carbon dioxide.

525 Talanta. 44, 137–150. http://dx.doi.org/10.1016/S0039-9140(96)02008-5

526 Smyth, T., Zytner, R., Stiver, W., 1999. Influence of water on the supercritical fluid extraction

527 of naphthalene from soil. J. Hazard. Mater. 67, 183–196. http://dx.doi.org/10.1016/S0304-

528 3894(99)00043-6

529 Vance, K., Falzone, G., Pignatelli, I., Bauchy, M., Balonis, M., Sant, G., 2015. Direct

530 carbonation of $Ca(OH)_2$ using liquid and supercritical CO_2: Implication for carbon-neutral

531   cementation. Ind. Eng. Chem. Res. 54, 8908–

532   8918. http://dx.doi.org/10.1021/acs.iecr.5b02356

533   Villagran-Zaccardi, Y., Eguez-Alava, H., De Buysser, K., Gruyaert, E., De Belie, N., 2017.

534   Calibrated quantitative thermogravimetric analysis for the determination of portlandite and

535   calcite content in hydrated cementitious systems. Mater. Struct. 50, 179-189.

536   https://dx.doi.org/10.1617/s11527-017-1046-2

537   Wai, C., Kulyako, Y., Myasoedov, B., 1999. Supercritical carbon dioxide extraction of

538   caesium from aqueous solutions in the presence of macrocyclic and fluorinated compounds.

539   Mendeleev Commun. 9, 80–81. https://doi.org/10.1070/MC1999v009n05ABEH001117

540   Wang, S., Elshani, J., Wai, C., 1995. Selective extraction of mercury with ionizable crown

541   ethers in supercritical carbon dioxide. Anal. Chem. 67, 919–923.

542   http://dx.doi.org/10.1021/ac00101a019

543   Wang, T., Li, M., Teng, S., 2010. Desorption of cesium from granite under various aqueous

544   conditions. Appl. Radiat. Isot. 68, 2140–2146.

545   http://dx.doi.org/10.1016/j.apradiso.2010.07.005

546