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1 **Desorption of Cs from vermiculite by ultrasound assisted ion exchange**

2 Sophie Herr^a, Antoine Leybros^b, Yves Barre^b, Sergueï Nikitenko^a, Rachel Pflieger^a

3

4 ^a*ICSM, Univ Montpellier, UMR 5257, CEA, CNRS, ENSCM, Marcoule, France*

5 ^b*CEA, DES, ISEC, DMRC, Univ Montpellier, Marcoule, France*

6

7 **Abstract**

8 Nuclear power plant accidents typically lead to the contamination of large volumes of soils
9 with radioactive cesium. This element is hard to desorb from soil, especially when it is bound
10 to mica minerals, and aggressive and energy-consuming techniques are often required. In this
11 study, we investigated the use of ultrasound with Mg²⁺ cation exchange for the removal of a
12 ¹³³Cs-contaminated vermiculite over a wide range of temperatures (20-200 °C). At room
13 temperature, ultrasound was found to significantly accelerate Cs desorption but only
14 reversibly adsorbed Cs species were removed. Under hydrothermal conditions and ultrasonic
15 irradiation in contrast, the removal efficiency after 1 h was 50 % at 100 °C and more than
16 95 % at 200 °C, compared with only 50 % without ultrasonication at 200 °C. Cs
17 contamination can therefore be nearly totally removed, even from collapsed vermiculite sites
18 where sorption is considered irreversible. Ultrasound waves and high temperatures both make
19 trapped Cs more accessible by spreading the sheets and improving mass transfer. Acoustic
20 noise spectra show that even at high pressure and temperature, cavitation bubbles form,
21 oscillate and collapse, with the desired physical effects. These results demonstrate the
22 potential of synergistic ultrasound and hydrothermal treatment for soil remediation.

23 **Highlights**

- 24 • Cs desorption from vermiculite is studied at 20-200 °C using Mg²⁺ ion exchange
- 25 • At 20 °C, adding ultrasounds accelerates kinetics by a factor of 20
- 26 • Ultrasound and hydrothermal treatment demonstrate synergy
- 27 • Desorption yields reach 98 % at 200 °C under ultrasound
- 28 • Acoustic spectra demonstrate the occurrence of active cavitation even at 200 °C

29 *Keywords*

30 Cesium ion, Vermiculite, Desorption, Decontamination, Ultrasound, Sonohydrothermal
31 treatment

32 **1. Introduction**

33 Nuclear power plant accidents lead to significant releases of radioactive cesium (¹³⁷Cs)
34 into the environment. In the vicinity of Fukushima Dai-ichi (Japan, 2011) for instance, 10.527
35 million m³ of contaminated soil with radioactivity exceeding 8,000 Bq·kg⁻¹ had already been
36 stored as of March 2021, with 50 million more expected by 2045 [1]. Serious concerns have
37 been raised about the decontamination of these soils ever since the disaster [2].

38 Severe accidents lead to the formation of Cs-rich microparticles but Cs is mostly released
39 in the form of highly soluble ionic species such as CsI or CsOH. Studies [3,4] have suggested
40 that Cs⁺ ions are retained in soil by clay minerals because of their high cation exchange
41 capacity (CEC) and surface area. The soils surrounding the Fukushima site consist mainly of
42 micaceous weathered biotite (WB) and vermiculite-biotite (VB), minerals that are highly
43 selective for Cs⁺ [4]. Cs is adsorbed at different sites on the surface, edges and in the
44 interlayer space (the “wedge zones” [5]) of the clay. Interactions between clays and Cs⁺ ions

45 may lead to the partial collapse of the interlayer space and subsequent ion fixation, making
46 desorption more difficult [3].

47 A range of separation and extraction methods have been developed for the reduction and
48 decontamination of solid waste, including sieving and magnetic separation [6,7],
49 electrokinetic remediation [8], chemical leaching [9–11], supercritical CO₂ extraction [12]
50 and heat and/or subcritical water treatment [13–15]. Soil washing is a well-known chemical
51 method, and several studies have investigated Cs extraction by ion exchange [16]. The release
52 of metals into the liquid phase can be promoted using acids [17,18], polymers [11], ligands
53 [10] or surfactants [19]. It is generally assumed that monovalent cations such as K⁺, Na⁺ or
54 NH₄⁺, are better suited to access external and interlayer sites because of their small radii, but
55 have limited diffusivity [20]. Moreover, their low hydration energy means they tend to
56 dehydrate and collapse the interlayer sheets, hindering desorption [4,21]. Divalent cations on
57 the other hand, Mg²⁺ in particular, slightly expand the interlayer [4,22], preventing its
58 collapse, and remain somewhat mobile within the layer with a low but non-zero diffusion rate
59 [20]. Effective room-temperature Mg²⁺ extraction has indeed been demonstrated, albeit at
60 high salt concentrations ([Mg²⁺] = 1-3.5 M) and over long time periods (up to 48 h) [14–16].
61 Again using high Mg²⁺ concentrations (at least 3 M), Tamura et al. achieved desorption rates
62 above 50 % in weakly contaminated vermiculite, with treatments of at least 24 h required to
63 exceed 80 % [10]. The desorption process can however be made more efficient by increasing
64 the temperature. Yin et al. achieved complete desorption after four 30 min-cycles at 250 °C
65 with a 1 M Mg²⁺ solution [26]. Higher temperatures allow the energy barrier formed by the
66 collapsed sheets to be overcome, to some extent, by expanding the interlayer, but at the cost
67 of greater energy consumption [14,17,25].

68 The present study investigated the use of ultrasound to facilitate the process and avoid the
69 harsh conditions used previously to achieve optimal Cs extraction yields. The propagation of

70 ultrasound waves in a liquid leads to the nucleation, growth and violent implosion of gas
71 bubbles, a phenomenon known as cavitation. The temperature and pressure as the bubbles
72 collapse can reach several thousands of Kelvin and hundreds of bars. Sonochemical reactions
73 (the formation and reaction of radicals) predominate at high ultrasound frequencies (0.1–
74 1 MHz), while at low ultrasound frequencies (20–100 kHz), the main effects are physical,
75 through the strong self-agitation of the solution. Working in a heterogeneous medium favors
76 asymmetric bubble collapse, leading to the emission of micro-jets, surface erosion, and local
77 turbulence, which all improve intraparticle diffusion. Ultrasound is therefore widely used for
78 surface cleaning [27] as well as for stripping, delamination or to reduce particle sizes in
79 materials [28,29]. The use of ultrasound to increase heavy metal leaching yields from soils
80 and sediments has not been widely studied, but the results of the few studies published in the
81 past decade suggest that the method is promising. For example, Park et al. used a 28 kHz
82 sonoreactor to extract heavy metals (Cu, Pb, Zn) from soil samples from of an abandoned
83 railway station in Korea [30]. In keeping with previous studies [31], they found that the
84 desorption rates were higher when mechanical stirring was supplemented with ultrasonication
85 [30]. Ultrasound has also been used to accelerate the kinetics of soil washing [32] or reduce
86 chemical usage or the concentration of saline solutions in desorption processes [31,33].

87 The aim of this study was to develop a new method to efficiently desorb Cs^+ under milder
88 operating conditions by combining ion exchange with ultrasonication. Some of the
89 contaminated clay was washed with ammonium acetate to collapse some of the adsorption
90 sites and make the samples realistically difficult to decontaminate [34]. This effect was
91 evaluated at high and low Cs loads with respectively about 30 and 90 % of the Cs^+ ions
92 adsorbed on irreversible sites [35]. The desorption of Cs by ion exchange with a divalent
93 cation (Mg^{2+}) was first evaluated at atmospheric pressure and then under hydrothermal
94 conditions.

95 **2. Materials and methods**

96 *2.1. Materials*

97 Vermiculite (Sigma-Aldrich) was crushed and sieved through a 100 µm mesh. This mesh
98 size was chosen to maximize adsorption and obtain suitable proportions of surface and
99 internal sites [14,36]. The chemical composition of the raw vermiculite was measured to be
100 $(\text{Si}_{2.66}\text{Al}_{0.94}\text{Fe}_{0.06})\cdot(\text{Fe}_{0.24}\text{Mg}_{2.35}\text{Ti}_{0.02})\cdot\text{O}_{10}\cdot(\text{OH})_2 \text{K}_{0.46}\text{Ca}_{0.35}\text{Na}_{0.20}\text{Mg}_{0.18}$. All experiments were
101 performed using milli-Q-grade ultrapure water (18.2 MΩ·cm at 25 °C), pure Ar (purity
102 >99.9 %, Air Liquide) and analytical-grade reagents: cesium nitrate (CsNO_3), magnesium
103 chloride (MgCl_2), sodium nitrate (NaNO_3) purchased from Sigma-Aldrich and ammonium
104 acetate ($\text{CH}_3\text{COONH}_4$), purchased from Thermo Fisher Scientific.

105 *2.2. Sample analysis and characterization*

106 The mixtures obtained at the end of the experiments were filtered using a Büchner funnel
107 and 0.45 µm filter paper and the residue was dried in an oven before X-ray analysis. The
108 filtered supernatant was analyzed by atomic absorption spectroscopy (AAS, A Analyst 400,
109 Perkin Elmer) to measure the remaining Cs concentration. X-ray diffraction patterns were
110 recorded using a Panalytical X'Pert MPD Pro device equipped with a Cu source ($\lambda\text{K}\alpha_1 =$
111 1.5406 \AA) in Bragg-Brentano geometry with a step of 0.013° and a counting time of 0.34 s.
112 The 2θ range was $5\text{--}70^\circ$ and the measurement time was 42 min. The evolution of the
113 morphology of the clay was observed by scanning electron microscopy (SEM, VEGA3,
114 Tescan). Particle size distributions were measured by laser granulometry using a CILAS 1090
115 particle size analyzer. The mean chemical composition of the samples was measured energy
116 dispersive X-ray spectroscopy (EDX, Bruker XFlash® 5010 SDD) and wavelength-dispersive
117 X-ray fluorescence spectroscopy (WDXRF, Bruker S8 TIGER).

118 2.3. Adsorption and desorption isotherms

119 Cs adsorption isotherms were measured over a Cs⁺ concentration range of 2.5·10⁻² to
120 10⁵ mg·L⁻¹ in polyethylene tubes containing 1 g/L clay mineral suspensions, with 0.01 M
121 NaNO₃ as background electrolyte. The suspensions were mechanically shaken for 1 h, the
122 time required to reach thermodynamic equilibrium (see section 3.1.1), and the Cs-
123 contaminated solids were then separated from the solution. The particles were resuspended in
124 equal volumes of the same electrolyte solution, without Cs, to investigate the desorption
125 process under the same conditions as the adsorption experiments. Distribution coefficients,
126 K_d, were calculated as follows: $K_d = ([Cs]_i - [Cs]_f) \times v / (m \times [Cs]_f)$, where [Cs]_i and [Cs]_f
127 (mg·L⁻¹) are the initial and final concentrations of Cs in solution before and after adsorption,
128 and v/m (L·kg⁻¹) is the liquid to solid ratio used for the adsorption tests.

129 2.4. Preparation of Cs-loaded vermiculite

130 Samples of Cs-loaded vermiculite were prepared with high and low Cs concentrations
131 (batch 1 and batch 2, respectively, shown as squares in Figure S1) to study the desorption
132 process in the two reversibility regimes identified by the adsorption and desorption isotherms
133 (sections 2.3 and 3.1.2). Some of these samples were further mixed with 1 L of 1 M
134 CH₃COONH₄ for a week to partially collapse the interlayers in the structure, and then washed
135 with 1 L of water to remove the CH₃COONH₄. The resulting vermiculite samples are referred
136 to as “washed” and are labeled with a subscript NH₄⁺ in Table S1. The Cs loads were
137 calculated using the following equation: $Q = ([Cs]_i - [Cs]_f) \times v / m$, where Q (mg·g⁻¹) is the Cs
138 concentration per unit mass of vermiculite; [Cs]_i and [Cs]_f (mg·L⁻¹) are the initial and final
139 concentrations of Cs⁺ in solution before and after adsorption, and v/m (L·g⁻¹) is the liquid to
140 solid ratio used for the adsorption tests. The concentrations of adsorbed Cs⁺ were estimated to
141 be 7.5 and 7.4 mg·g⁻¹ in the unwashed and washed samples of batch 1; and 26.3 and
142 24.0 mg·g⁻¹ in the unwashed and washed samples of batch 2 respectively.

143 2.5. *Desorption experiments*

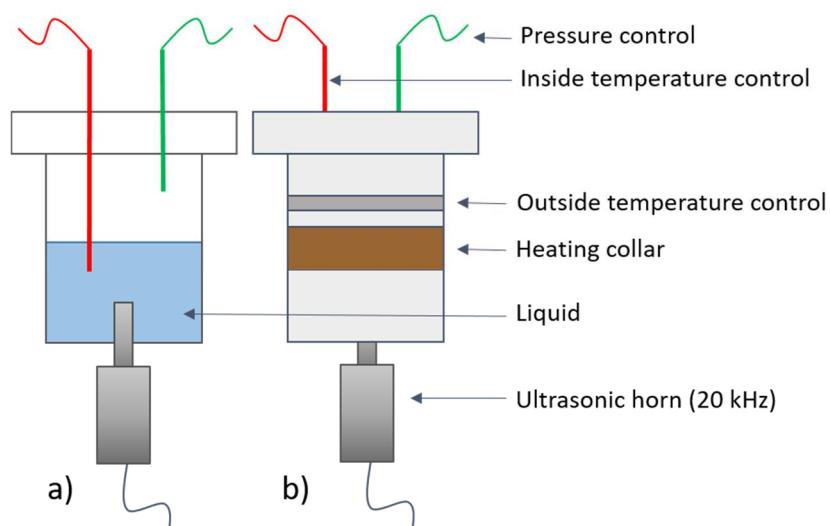
144 Desorption experiments were performed under ambient and hydrothermal conditions, with
145 and without ultrasonication. The vermiculite samples were in each case contacted with a 1 M
146 aqueous solution of MgCl_2 for 1 h and samples (about 1 mL) were extracted every 10 min.
147 The Cs desorption rate was calculated as $[\text{Cs}]_e \times v \times 100 / m \times Q$, with Q ($\text{mg}\cdot\text{g}^{-1}$) the Cs load per
148 unit mass of vermiculite, $[\text{Cs}]_e$ ($\text{mg}\cdot\text{L}^{-1}$) the Cs^+ concentration in the extraction solution, and $v/$
149 m ($\text{L}\cdot\text{g}^{-1}$) the liquid-to-solid ratio used for the desorption tests.

150 2.5.1. *Ambient conditions*

151 The experiments at ambient conditions were performed in two different sonoreactors with
152 connectors for temperature control, gas bubbling, and sampling. Experiments with low
153 frequency ultrasound (20 kHz) were performed in a glass reactor with a Ti-6Al-4V horn
154 (irradiating surface area, 1 cm^2) immersed in the suspension, powered by a 750 W generator
155 (Sonics & Materials Vibracell VCX 750). High frequency studies (362 kHz) were performed
156 in the same reactor installed on top of a 25 cm^2 high-frequency transducer (L3
157 communications ELAC Nautik) connected to a 125 W generator (LVG 60 RF-generator) [37].
158 The volumes of solution treated were respectively 300 mL for 20 kHz and 200 mL for 362
159 kHz, with solid to liquid ratio kept at 100, for both 20 and 60 °C conditions. The absorbed
160 acoustic power measured using the thermal probe method was 25 W at 20 kHz and 43 W at
161 362 kHz. Argon gas was bubbled throughout the experiments at $100\text{ mL}\cdot\text{min}^{-1}$ and for 20 min
162 beforehand to avoid interfering reactions with air and to enhance sonochemical activity [38].
163 At 20 kHz, the physical effect of the ultrasound waves was sufficient to maintain a
164 homogeneous suspension but at 362 kHz, the solution was mechanically stirred at 250 rpm
165 during sonication to prevent the clay from settling. The experiments were repeated without
166 continuous Ar flow to evaluate the feasibility of treatment in an air-equilibrated atmosphere.

167 2.5.2. Hydrothermal conditions

168 The experiments under hydrothermal conditions were performed in the homemade reactor
169 shown in Figure 1 and described in detail elsewhere [39]. The reactor consists of a Ti-6Al-4V
170 vessel with a total volume of 80 mL equipped with a commercial ultrasonic probe (diameter,
171 1.9 cm) made from the same alloy and powered by a 20 kHz transducer connected to a 130 W
172 electric generator with a frequency self-adjustment system fixed at 19.5–20.5 kHz (Sonics).
173 The samples (50 ml) were introduced and equilibrated at the autogenous pressure
174 corresponding to the chosen temperature. The temperature was controlled using a removable
175 heater attached to the external surface of the reactor and two thermocouples placed inside and
176 outside the reactor. The pressure inside the reactor was measured using a calibrated digital
177 manometer. To prevent overheating, the ultrasonic transducer was cooled by air flow during
178 sonohydrothermal treatment. The solid to liquid ratio was 100. The system was heated up to
179 the chosen temperature in the presence of ultrasound and kept at this temperature for 1 h.
180 Ultrasonication was performed at an electric power of 25 W and bulk temperatures of 100 (P
181 = 1.3 bar), 150 (P = 7 bar) and 200 °C (P = 20 bar).



182
183 **Figure 1.** Schematic diagrams of (a) the inside and (b) the outside of the hydrothermal
184 sonochemical reactor used in the study.

185 2.6. *Acoustic spectra*

186 Acoustic spectra were recorded using a hydrophone (Brüel & Kjær, model 8103, 0.1-
187 180 kHz) placed close to the outer wall of the reactor and connected to an amplifier (Brüel &
188 Kjær measuring amplifier Type 2525) and an oscilloscope (PicoScope 3424, 10 mHz;
189 resolution, 1 mV; input signal, ± 2 V). The incoming signal was converted into an acoustic
190 spectrum by fast Fourier transform. For each experimental condition, 32 spectra were
191 recorded, converted into volts and averaged before converting back to dB.

192 **3. Results and discussion**

193 3.1. *Desorption in ambient conditions*

194 3.1.1. *Kinetic study*

195 Figure S2 shows the Cs⁺ desorption ratios measured as a function of time under 20 and
196 362 kHz ultrasonication in ambient conditions in soil samples mixed in a 1 M MgCl₂ solution
197 with either Ar or air bubbling at 20 °C. In all cases, the Cs⁺ ions were released rapidly within
198 the first 10 min and then more gradually before a plateau corresponding to
199 adsorption/desorption equilibrium was reached after 1 h, which was therefore the length of
200 time chosen for the desorption experiments.

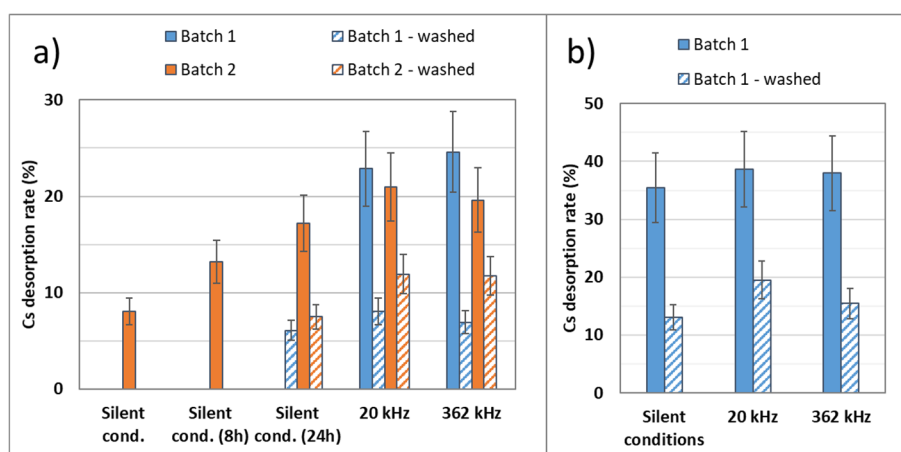
201 3.1.2. *Adsorption/desorption isotherms*

202 The adsorption and desorption isotherms (Figure S1) were found to overlap for filtrate
203 concentrations below roughly 3×10^{-6} M ($\log [\text{Cs}^+] \leq -5.5$), implying that at these
204 concentrations the interactions of Cs⁺ with the vermiculite are completely reversible. The
205 hysteresis observed at higher concentrations suggests however that the adsorption process
206 ceases to be reversible above this threshold. This is in keeping with the results of a previous
207 study carried out under similar conditions where a transition between “partial reversibility”

208 and "total reversibility" was observed at 6×10^{-6} M [35]. These results were interpreted using
209 a thermodynamic model involving multiple ion exchange sites and partial reversibility was
210 attributed to the collapse of some of the sites after the adsorption of Cs^+ ions.

211 3.1.3. Cs-desorption experiment

212 The results obtained for the different desorption runs are summarized in Table S1. **Figure**
213 **2** shows the results obtained at 20 and 60 °C.



214 **Figure 2.** Cs^+ desorption yields after 1 h (or the specified duration) in 1 M MgCl_2 as a
215 function of the presence and frequency of ultrasonic irradiation at (a) 20 °C and (b) 60 °C.
216 “Washed” means washed with ammonium acetate to collapse some of the adsorption sites and
217 make the samples realistically difficult to decontaminate.

218
219
220 Figure 2a shows that at 20 °C the desorption rates after 1 h of ultrasonication at 20 and
221 362 kHz were similar for both low and high initial Cs loads (for all four samples), and
222 significantly higher than after silent treatment for the same duration or longer. The fact that
223 equilibrium was not reached after 24 h without ultrasonication indicates that, at room
224 temperature, ultrasound mainly increases the kinetics of the process by ensuring better
225 mixing. The slightly higher desorption rate under ultrasonication for all four batches, may also
226 be due to a decrease in particle size induced by the ultrasound waves (Figure S3), and the

227 corresponding increase in specific surface area [28]. At 60 °C however (Figure 2b), the
228 desorption rates measured with and without ultrasonication for both washed or not samples,
229 were within the respective error margins, and roughly twice as high as the values measured at
230 20 °C, indicating that, as expected, increasing the treatment temperature increases the kinetics
231 of the reaction, and that at 60 °C, the accelerating effect of ultrasonication is much weaker.

232 As expected, the desorption rates measured for the washed samples (i.e. after NH_4^+ ion
233 exchange) were lower, for all treatment conditions. The initial Cs^+ loads were similar (Table
234 S1), meaning that only a small fraction of Cs^+ ions were replaced by NH_4 ions. On the other
235 hand, these lower desorption yields are in line with the collapse of some of the interlayer
236 spaces (caused by the washing with ammonium acetate) and the subsequent increase in the
237 number of Cs^+ ions trapped in difficult to access sites [20,40,41]. The desorption rates
238 measured for the NH_4^+ -washed samples were nevertheless higher at 60 °C than at 20 °C
239 (Figure 2b vs Figure 2a), possibly because of a slight expansion of the sheets [26], allowing
240 more Cs^+ ions to be released.

241 Figure 2a also shows that for equivalent treatment conditions, the measured desorption
242 rates were lower with batch 2 (high initial Cs load) than with batch 1 (low initial Cs load). In
243 their study, Latrille and Bildstein calculated the proportions of irreversibly and reversibly
244 adsorbed Cs^+ ions and the “remaining part of reversibly adsorbed Cs after desorption” over a
245 wide range of Cs^+ concentrations [35]. Based on these calculations, batches 1 and 2 contain
246 30 % and 80–90 % of irreversibly sorbed Cs^+ ions, respectively, and 24 % and 10–15 % of
247 remaining reversibly adsorbed Cs. Our results (runs 3, 5 and 8, 8^{air}, 9, 9^{air}, Table S1) are in
248 keeping with these values. Furthermore, since the irreversibly sorbed cesium is not affected
249 by exchange with ammonium acetate, this explains why washing led to a smaller decrease in
250 the Cs desorption yield for batch 2 than for batch 1 (Figure 2a).

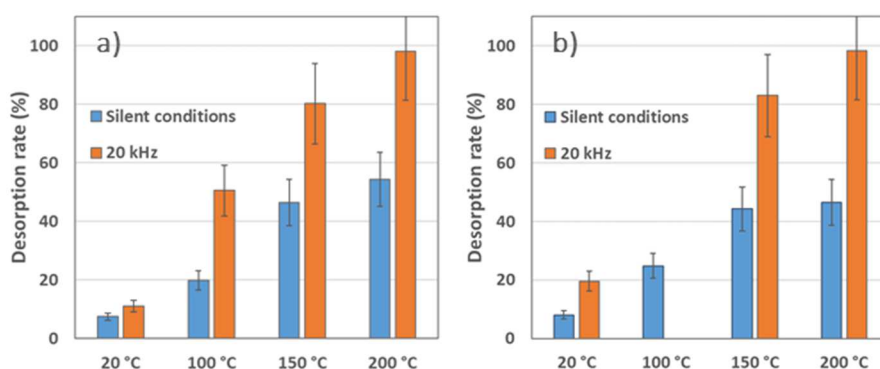
251 3.2. *Particle size distributions and morphology*

252 Figure S3 compares the particle size distributions of vermiculite samples before and after
253 ion exchange with $MgCl_2$ (1 M) with and without 20 kHz ultrasonication. Raw vermiculite
254 has a broad particle size distribution (between 10 and 100 μm) with a mean particle size of
255 around 80 μm . The shift to lower values after ultrasound irradiation can be attributed to the
256 mechanical effect of the ultrasound waves [28,29] as no such shift was observed for the clay
257 treated without ultrasonication. The SEM images in Figure S4 show that the morphology of
258 the samples treated with ultrasonication is more heterogenous, with the presence of smaller
259 particles, in agreement with the granulometry results. The particles in the ultrasonicated
260 samples also appear smoother, with more rounded edges.

261 3.3. *Hydrothermal treatment*

262 Figure 3 shows that when treated without ultrasonication, the percentage of desorbed Cs
263 increased with the treatment temperature for both natural (Figure 3a) and washed (Figure 3b)
264 vermiculite samples. The increase is pronounced between 20 and 150 $^{\circ}C$, presumably because
265 of the corresponding increase in the saturated vapor pressure, but the desorption rates are not
266 significantly higher at 200 than at 150 $^{\circ}C$. Even at the highest temperatures however, the
267 extraction efficiency was limited (e.g. no higher than 47 % and 55 % for runs 12 and 12_{NH4+},
268 respectively; Table S1).

269



270

271 **Figure 3.** Cs⁺ desorption yields after 1 h of hydrothermal or sonohydrothermal treatment in
272 1 M MgCl₂ at different temperatures for (a) natural and (b) NH₄⁺-washed Cs-loaded
273 vermiculite samples.

274

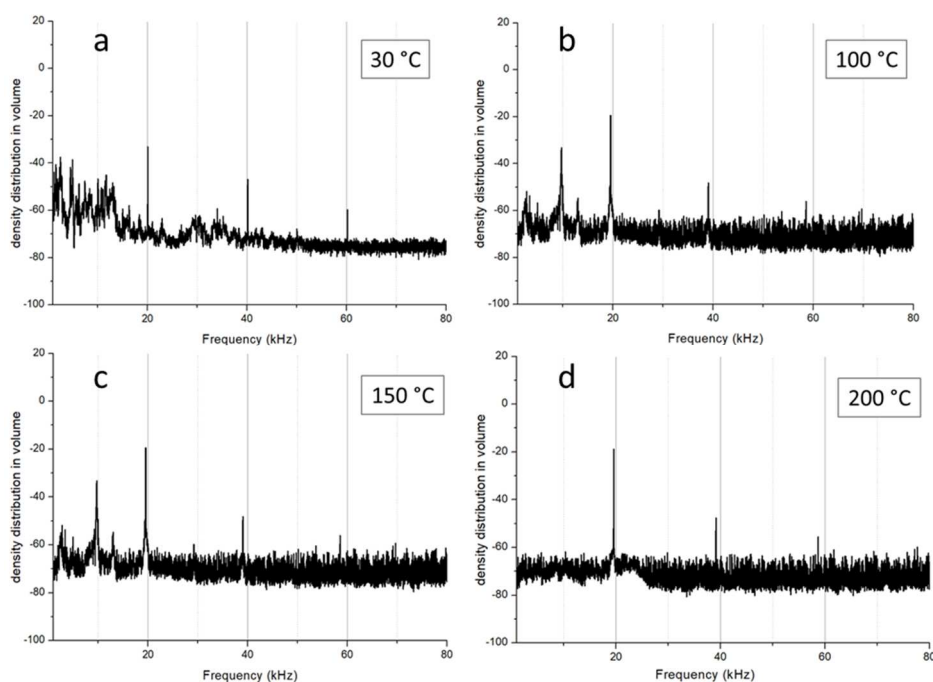
275 For the samples that were sonicated under hydrothermal conditions (sonohydrothermal
276 treatment), the desorption yields also increased significantly with the temperature between 20
277 and 150 °C, but in this case the gain between 150 and 200 °C was more significant, both for
278 the natural and washed vermiculite. In absolute terms moreover, the desorption yields were
279 much higher than without ultrasonication. For instance, the desorption rate measured for
280 natural vermiculite after 1 h at 100 °C under 20 kHz irradiation was similar to the value
281 measured after treatment at 200 °C without ultrasonication (Figure 3a). In other words, adding
282 ultrasound allows the same extraction efficiency to be achieved at a much lower treatment
283 temperature. The temperature of the sonohydrothermal treatment can nevertheless be
284 increased to maximize the yields, up to 98 % in this case at 200 °C, within an hour. The 2 %
285 of Cs⁺ ions still in the vermiculite at the end of the treatment may come from the readsorption
286 of some of the ions as the sample cooled down [25].

287 When comparing Figures 3.a and 3.b, the difference in yield for washed and non-washed
288 clays is insignificant at temperatures above 100 °C for each condition. This may be explained
289 by the fact that the high temperatures allow to overcome the potential collapse induced by the
290 washing with ammonium acetate.

291 3.4. *High pressure acoustic spectra*

292 While the characteristics and effects of acoustic cavitation are widely documented around
293 room temperature and ambient pressure, very few studies have been conducted at high
294 temperatures and pressures and to the best of our knowledge, none of these concern
295 suspensions of micron-sized particles. High pressures should limit the formation of bubbles

296 while high temperatures should promote bubble nucleation [42]. Cau et al. evidenced
297 cavitation and sonochemical activity at 200 °C (13 bar) by measuring hydrogen gas released
298 during water sonolysis [39]. Nikitenko et al. compared the acoustic spectra of water under
299 hydrothermal conditions over a wide range of temperatures (20–200 °C) [43]. Up to 100 °C,
300 the number of harmonic (nf_0) peaks increased, an effect that was attributed to an increase in
301 the number of bubbles and more intense stable cavitation. When the temperature was further
302 increased up to 200 °C, additional sub- and ultraharmonics (f_0/n and harmonics thereof) were
303 observed that were tentatively ascribed to the presence of non-spherical bubbles undergoing
304 surface oscillations. Interestingly, these sub- and ultraharmonics disappeared when TiO₂
305 nanoparticles were added. This disappearance was attributed to the stabilizing effect on the
306 bubbles of the accumulation of these particles on the gas/liquid interface. Acoustic spectra are
307 therefore one of the only means of studying cavitation at high pressure and temperature.
308 **Figure 4** presents the cavitation noise spectra recorded at 30, 100, 150 and 200 °C for
309 vermiculite suspensions in 1 M MgCl₂. The presence of harmonic peaks in each case
310 demonstrates the presence of cavitation bubbles and the broadband white noise is a sign of
311 transient cavitation.



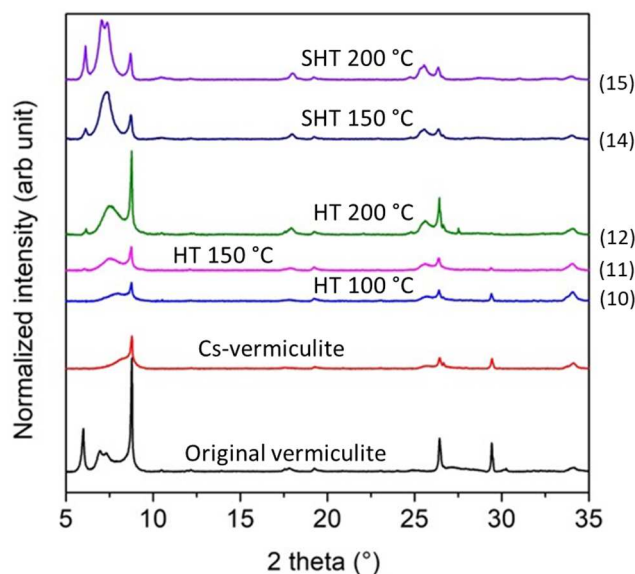
312

313 **Figure 4.** Acoustic noise spectra from ultrasonicated ($f_0 = 20$ kHz) suspensions of vermiculite
314 in 1 M $MgCl_2$ at (a) 30 °C, (b) 100 °C, (c) 150 °C, and (d) 200 °C.

315

316 At 100 and 150 °C moreover, strong subharmonics were observed that are absent from
317 Nikitenko et al.'s spectra of sonicated water below 200 °C (reproduced in Figure S5) [43].
318 These subharmonics have previously been attributed to chaotic bubble oscillations or to
319 surface oscillations of non-spherical bubbles [44]. The latter effect should indeed be promoted
320 by the presence of particles and by an increased number of bubbles [45], leading to
321 interactions. Meanwhile, the peak broadening and shift in frequency observed at 100 °C and
322 above, can be attributed to fast random bubble motion and chaotic oscillations [44].
323 Interestingly, the harmonics and white noise are both less intense in these spectra recorded in
324 the presence of particles, than in those recorded pure water by Nikitenko et al. (Figure S5)
325 [43]. In contrast, Tuziuti et al. observed that the acoustic spectra of water at atmospheric
326 pressure under 42 kHz ultrasonication were more intense when silica particles (10 μm) were
327 added [46]. These opposite effects are probably due to the different particle sizes, the larger
328 particles in the present study (up to 100 μm) likely having a greater damping effect on the
329 ultrasound waves and slightly altering the viscosity of the solution.

330 3.5. XRD spectra of natural, Cs-loaded and decontaminated vermiculite



331
332 **Figure 5.** X-ray diffractograms of vermiculite samples, as received, after loading with Cs, and
333 after hydrothermal or sonohydrothermal treatment (HT or SHT) for 1 h in 1 M MgCl₂ at 100–
334 200 °C, with 20 kHz ultrasound for the SHT. The numbers in brackets correspond to the run
335 numbers in Table S1.

336
337 **Figure 5** compares the XRD patterns of natural, Cs-contaminated and
338 (sono)hydrothermally treated vermiculite samples. (The equivalent spectra for washed
339 vermiculite are shown in Figure S6.) For natural vermiculite, the peaks in the low-angle
340 region at $2\theta = 6.0^\circ$, 6.9° , 7.3° and 8.7° , corresponding to interlayer spacings of 14.7, 12.6,
341 12.1 and 10.1 Å, respectively, indicate the presence of different interlayer structures. The
342 sharp peaks at 6.0° (14.7 Å) and 8.7° (10.1 Å) correspond respectively to interlayers filled
343 with hydrous Mg²⁺ in a Mg²⁺ vermiculite phase and to interlayers containing anhydrous K⁺ in
344 a K⁺-mica phase [47]. The two peaks at 6.9° and 7.3° (12.6 Å and 12.1 Å) can be attributed to
345 regular and irregular interstratifications of these two layers [25]. Upon contamination with
346 Cs⁺, the peaks at 6.0° (14.7 Å), 6.9° (12.6 Å) and 7.3° (12.1 Å) disappear, suggesting that
347 during the adsorption process, Cs⁺ progressively replaces hydrous Mg²⁺ rather than anhydrous

348 K^+ because the Mg^{2+} interlayer space is larger and easier to access. The peak at 8.7° is slightly
349 broader in the NH_4^+ -washed samples (Figure S7), possibly because of the insertion of some
350 NH_4^+ cations with a basal spacing of 10.1–10.4 Å ($2\theta = 8.7$ – 8.5°). No differences are visible
351 in the XRD spectra of Cs-loaded samples recorded before and after room temperature
352 treatment (Figure S7), indicating that little Cs^+ to Mg^{2+} substitution occurred.

353 In contrast, the spectra of hydrothermally and sonohydrothermally treated samples differ
354 significantly from those of natural and Cs-loaded vermiculite (Figures 5 and S5). In the
355 spectra of the hydrothermally treated samples, the two peaks at $2\theta = 6.9$ and 7.3° (12.6 and
356 12.1 Å) corresponding to interstratified layers reappear, pointing to Mg^{2+} substitution in the
357 Cs^+ loaded layers (but not in the K^+ layers since the peak at 8.7 Å remains). The same trends
358 are observed in the spectra from washed samples (Figure S6) and in a more pronounced
359 manner in the XRD patterns of the sonohydrothermally treated samples. Indeed, the peak
360 from hydrous Mg^{2+} layers at 6.0° (14.7 Å) is as strong after sonohydrothermal treatment at
361 $200^\circ C$ as in natural vermiculite, indicating the complete replacement of Cs^+ by Mg^{2+} cations.
362 This is consistent with the nearly complete desorption of Cs^+ from these clays after
363 sonohydrothermal treatment at $200^\circ C$ (Figure 3). These results show that sonohydrothermal
364 conditions are required for Cs^+ ions to be replaced by Mg ions in such a way as to recreate the
365 monoionic Mg layers found in natural vermiculite.

366 **4. Conclusion**

367 This study investigated the desorption of Cs^+ from vermiculite through a combination of
368 ion exchange and ultrasonication at treatment temperatures of up to $200^\circ C$, for different Cs
369 loads and ultrasonication parameters. Two types of vermiculite were studied: the first simply
370 contaminated with Cs^+ , the second, washed with ammonium acetate after contamination, to
371 partially collapse the interlayers in the structure and trap a greater proportion of the adsorbed

372 Cs, mimicking the effect of Cs interactions with clays in the environment. At room
373 temperature, sonication was found to greatly accelerate the desorption process, by more than a
374 factor of 20, but the desorption yield remained limited. Increasing the temperature to 60 °C
375 increased the desorption yield up to 40 % for the untreated vermiculite and to 20 % for NH₄⁺-
376 treated vermiculite. In contrast with the limited efficiency of treatments at atmospheric
377 pressure, the elevated temperature and autogenic pressure under hydrothermal treatment
378 contributed to Cs desorption rates of up to 55 % at 200 °C and almost complete desorption
379 was achieved under sonohydrothermal treatment at 200 °C, highlighting the potential of this
380 process for the remediation of Cs contaminated soils. Sonohydrothermal treatment at 100 °C
381 was found to be as efficient as hydrothermal treatment at 200 °C, suggesting that
382 ultrasonication can also be used to minimize energy consumption while maintaining the same
383 operating efficiency.

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386 5. References

- 387 [1] S. Yamasaki, S. Utsunomiya, A review of efforts for volume reduction of contaminated
388 soil in the ten years after the accident at the Fukushima Daiichi Nuclear Power Plant, J.
389 Nucl. Sci. Technol. 59 (2022) 135–147.
390 <https://doi.org/10.1080/00223131.2021.1974596>.
- 391 [2] Environmental Remediation in Affected Areas in Japan, (n.d.) 30.
- 392 [3] B.L. Sawhney, Selective Sorption and Fixation of Cations by Clay Minerals: A Review,
393 Clays Clay Miner. 20 (1972) 93–100. <https://doi.org/10.1346/CCMN.1972.0200208>.
- 394 [4] H. Mukai, K. Tamura, R. Kikuchi, Y. Takahashi, T. Yaita, T. Kogure, Cesium
395 desorption behavior of weathered biotite in Fukushima considering the actual radioactive
396 contamination level of soils, J. Environ. Radioact. 190–191 (2018) 81–88.
397 <https://doi.org/10.1016/j.jenvrad.2018.05.006>.
- 398 [5] J.M. Wampler, E.J. Krogstad, W.C. Elliott, B. Kahn, D.I. Kaplan, Long-Term Selective
399 Retention of Natural Cs and Rb by Highly Weathered Coastal Plain Soils, Environ. Sci.
400 Technol. 46 (2012) 3837–3843. <https://doi.org/10.1021/es2035834>.
- 401 [6] Y. Yoshida, K. Sekiya, N. Nomura, F. Mishima, Y. Akiyama, S. Nishijima, Study on
402 volume reduction of contaminated soil by radioactive cesium using magnetic separation,
403 IEEE Transactions on Applied Superconductivity. 25 (2014) 1–5.
- 404 [7] I. Kim, J.-H. Kim, S.-M. Kim, C.W. Park, I.-H. Yoon, H.-M. Yang, Y. Sihn, Enhanced
405 selective separation of fine particles from Cs-contaminated soil using magnetic
406 nanoparticles, Journal of Soils and Sediments. 21 (2021) 346–354.
- 407 [8] C. Kim, S. Choi, M. Shin, Review—Electro-Kinetic Decontamination of Radioactive
408 Concrete Waste from Nuclear Power Plants, Journal of The Electrochemical Society.
409 165 (2018) E330.

- 410 [9] D. Parajuli, A. Takahashi, H. Tanaka, M. Sato, S. Fukuda, R. Kamimura, T. Kawamoto,
411 Variation in available cesium concentration with parameters during temperature induced
412 extraction of cesium from soil, *Journal of Environmental Radioactivity*. 140 (2015) 78–
413 83. <https://doi.org/10.1016/j.jenvrad.2014.11.005>.
- 414 [10] K. Tamura, H. Sato, A. Yamagishi, Desorption of Cs⁺ ions from a vermiculite by
415 exchanging with Mg²⁺ ions: effects of Cs⁺-capturing ligand, *J. Radioanal. Nucl. Chem.*
416 303 (2015) 2205–2210.
- 417 [11] C.W. Park, B.H. Kim, H.-M. Yang, B.-K. Seo, K.-W. Lee, Enhanced desorption of Cs
418 from clays by a polymeric cation-exchange agent, *J. Hazard. Mater.* 327 (2017) 127–
419 134. <https://doi.org/10.1016/j.jhazmat.2016.12.037>.
- 420 [12] A. Leybros, N. Segond, A. Grandjean, Remediation of ¹³⁷Cs-contaminated concrete
421 rubble by supercritical CO₂ extraction, *Chemosphere*. 208 (2018) 838–845.
422 <https://doi.org/10.1016/j.chemosphere.2018.06.051>.
- 423 [13] S.-M. Kim, I.-H. Yoon, I. Kim, J.-H. Kim, S.-J. Park, Hydrothermal Desorption of Cs
424 with Oxalic Acid from Hydrobiotite and Wastewater Treatment by Chemical
425 Precipitation, *Energies*. 13 (2020) 3284. <https://doi.org/10.3390/en13123284>.
- 426 [14] X. Yin, L. Zhang, M. Harigai, X. Wang, S. Ning, M. Nakase, Y. Koma, Y. Inaba, K.
427 Takeshita, Hydrothermal-treatment desorption of cesium from clay minerals: The roles
428 of organic acids and implications for soil decontamination, *Water Res.* 177 (2020)
429 115804. <https://doi.org/10.1016/j.watres.2020.115804>.
- 430 [15] X. Yin, L. Zhang, C. Meng, Y. Inaba, X. Wang, A. Nitta, Y. Koma, K. Takeshita,
431 Selective removal of radiocesium from micaceous clay for post-accident soil
432 decontamination by temperature-controlled Mg-leaching in a column, *Journal of*
433 *Hazardous Materials*. 387 (2020) 121677.
434 <https://doi.org/10.1016/j.jhazmat.2019.121677>.

- 435 [16] D. Ding, Z. Zhang, Z. Lei, Y. Yang, T. Cai, Remediation of radiocesium-contaminated
436 liquid waste, soil, and ash: a mini review since the Fukushima Daiichi Nuclear Power
437 Plant accident, *Environ. Sci. Pollut. Res. Int.* 23 (2016) 2249–2263.
438 <https://doi.org/10.1007/s11356-015-5825-4>.
- 439 [17] S.-M. Kim, I.-H. Yoon, I.-G. Kim, C.W. Park, Y. Sihm, J.-H. Kim, S.-J. Park, Cs
440 desorption behavior during hydrothermal treatment of illite with oxalic acid, *Environ.*
441 *Sci. Pollut. Res. Int.* 27 (2020) 35580–35590. [https://doi.org/10.1007/s11356-020-](https://doi.org/10.1007/s11356-020-09675-3)
442 [09675-3](https://doi.org/10.1007/s11356-020-09675-3).
- 443 [18] Y. Akemoto, T. Iwamura, S. Takahashi, M. Kan, S. Tanaka, Desorption of Cs⁺ from
444 contaminated biotite with a low molecular mass organic acid, *J. Environ. Chem. Eng.* 9
445 (2021) 106101. <https://doi.org/10.1016/j.jece.2021.106101>.
- 446 [19] C.W. Park, B.H. Kim, H.-M. Yang, B.-K. Seo, J.-K. Moon, K.-W. Lee, Removal of
447 cesium ions from clays by cationic surfactant intercalation, *Chemosphere.* 168 (2017)
448 1068–1074. <https://doi.org/10.1016/j.chemosphere.2016.10.102>.
- 449 [20] X. Yin, X. Wang, H. Wu, H. Takahashi, Y. Inaba, T. Ohnuki, K. Takeshita, Effects of
450 NH₄⁺, K⁺, Mg²⁺, and Ca²⁺ on the Cesium Adsorption/Desorption in Binding Sites of
451 Vermiculitized Biotite, *Environ. Sci. Technol.* 51 (2017) 13886–13894.
452 <https://doi.org/10.1021/acs.est.7b04922>.
- 453 [21] Q.H. Fan, M. Tanaka, K. Tanaka, A. Sakaguchi, Y. Takahashi, An EXAFS study on the
454 effects of natural organic matter and the expandability of clay minerals on cesium
455 adsorption and mobility, *Geochim. Cosmochim. Acta.* 135 (2014) 49–65.
456 <https://doi.org/10.1016/j.gca.2014.02.049>.
- 457 [22] S.-M. Park, D.S. Alessi, K. Baek, Selective adsorption and irreversible fixation behavior
458 of cesium onto 2:1 layered clay mineral: A mini review, *Journal of Hazardous Materials.*
459 369 (2019) 569–576. <https://doi.org/10.1016/j.jhazmat.2019.02.061>.

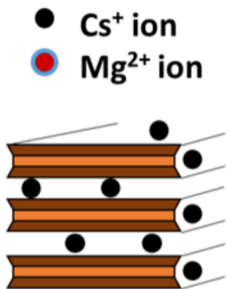
- 460 [23] K. Morimoto, T. Kogure, K. Tamura, S. Tomofuji, A. Yamagishi, H. Sato, Desorption of
461 Cs⁺ Ions Intercalated in Vermiculite Clay through Cation Exchange with Mg²⁺ Ions,
462 Chem. Lett. 41 (2012) 1715–1717. <https://doi.org/10.1246/cl.2012.1715>.
- 463 [24] H. Mukai, A. Hirose, S. Motai, R. Kikuchi, K. Tanoi, T.M. Nakanishi, T. Yaita, T.
464 Kogure, Cesium adsorption/desorption behavior of clay minerals considering actual
465 contamination conditions in Fukushima, Sci Rep. 6 (2016) 21543.
466 <https://doi.org/10.1038/srep21543>.
- 467 [25] X. Yin, N. Horiuchi, S. Utsunomiya, A. Ochiai, H. Takahashi, Y. Inaba, X. Wang, T.
468 Ohnuki, K. Takeshita, Effective and efficient desorption of Cs from hydrothermal-
469 treated clay minerals for the decontamination of Fukushima radioactive soil, Chem. Eng.
470 J. 333 (2018) 392–401. <https://doi.org/10.1016/j.cej.2017.09.199>.
- 471 [26] X. Yin, X. Wang, H. Wu, T. Ohnuki, K. Takeshita, Enhanced desorption of cesium from
472 collapsed interlayer regions in vermiculite by hydrothermal treatment with divalent
473 cations, J. Hazard. Mater. 326 (2017) 47–53.
474 <https://doi.org/10.1016/j.jhazmat.2016.12.017>.
- 475 [27] F.A. D, C.A. F, J.G. J, Effect of ultrasound on surface cleaning of silica particles., Int. J.
476 Miner. Process. 60 (2000) 101–113.
- 477 [28] F. Ali, L. Reinert, J.-M. Levêque, L. Duclaux, F. Muller, S. Saeed, S.S. Shah, Effect of
478 sonication conditions: solvent, time, temperature and reactor type on the preparation of
479 micron sized vermiculite particles, Ultrason. Sonochem. 21 (2014) 1002–1009.
480 <https://doi.org/10.1016/j.ultsonch.2013.10.010>.
- 481 [29] L. Novikova, P. Ayrault, C. Fontaine, G. Chatel, F. Jérôme, L. Belchinskaya, Effect of
482 low frequency ultrasound on the surface properties of natural aluminosilicates, Ultrason.
483 Sonochem. 31 (2016) 598–609. <https://doi.org/10.1016/j.ultsonch.2016.02.014>.

- 484 [30] B. Park, Y. Son, Ultrasonic and mechanical soil washing processes for the removal of
485 heavy metals from soils, *Ultrason. Sonochem.* 35 (2017) 640–645.
486 <https://doi.org/10.1016/j.ultsonch.2016.02.002>.
- 487 [31] Y. Son, S. Nam, M. Ashokkumar, J. Khim, Comparison of energy consumptions
488 between ultrasonic, mechanical, and combined soil washing processes, *Ultrason.*
489 *Sonochem.* 19 (2012) 395–398. <https://doi.org/10.1016/j.ultsonch.2011.11.002>.
- 490 [32] S. Kim, W. Lee, Y. Son, Ultrasonic and mechanical soil washing processes for the
491 remediation of heavy-metal-contaminated soil, *Jpn. J. Appl. Phys.* 55 (2016) 07KE04.
492 <https://doi.org/10.7567/JJAP.55.07KE04>.
- 493 [33] A. Fraiese, A. Cesaro, V. Belgiorno, M.A. Sanromán, M. Pazos, V. Naddeo, Ultrasonic
494 processes for the advanced remediation of contaminated sediments, *Ultrason. Sonochem.*
495 67 (2020) 105171. <https://doi.org/10.1016/j.ultsonch.2020.105171>.
- 496 [34] J.H. Kim, H. Anwer, Y.S. Kim, J.-W. Park, Decontamination of radioactive cesium-
497 contaminated soil/concrete with washing and washing supernatant- critical review,
498 *Chemosphere.* 280 (2021) 130419. <https://doi.org/10.1016/j.chemosphere.2021.130419>.
- 499 [35] C. Latrille, O. Bildstein, Cs selectivity and adsorption reversibility on Ca-illite and Ca-
500 vermiculite, *Chemosphere.* 288 (2022) 132582.
501 <https://doi.org/10.1016/j.chemosphere.2021.132582>.
- 502 [36] L. Dzene, E. Tertre, F. Hubert, E. Ferrage, Nature of the sites involved in the process of
503 cesium desorption from vermiculite, *J. Colloid. Interface Sci.* 455 (2015) 254–260.
504 <https://doi.org/10.1016/j.jcis.2015.05.053>.
- 505 [37] R. Pflieger, A.A. Ndiaye, T. Chave, S.I. Nikitenko, Influence of ultrasonic frequency on
506 Swan band sonoluminescence and sonochemical activity in aqueous tert-butyl alcohol
507 solutions, *J. Phys. Chem. B.* 119 (2015) 284–290. <https://doi.org/10.1021/jp509898p>.

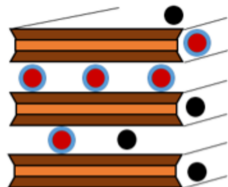
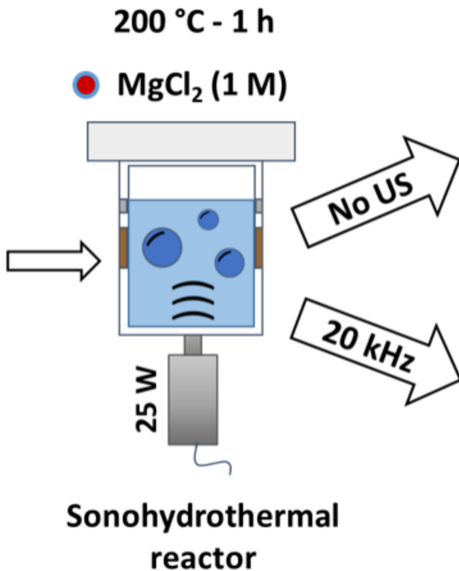
- 508 [38] F.R. Young, Sonoluminescence, CRC Press, Boca Raton, 2004.
509 <https://doi.org/10.1201/9780203491959>.
- 510 [39] C. Cau, Y. Guari, T. Chave, J. Larionova, P. Pochon, S.I. Nikitenko, Sonohydrothermal
511 Synthesis of Nanostructured (Ce,Zr)O₂ Mixed Oxides with Enhanced Catalytic
512 Performance, *J. Phys. Chem. C.* 117 (2013) 22827–22833.
513 <https://doi.org/10.1021/jp407096p>.
- 514 [40] M. Nakano, K. Kawamura, S. Emura, Local Structural Information from Exafs Analyses
515 and Adsorption Mode of Strontium on Smectite, *Clay Sci.* 12 (2004) 311–319.
516 <https://doi.org/10.11362/jcssjclayscience1960.12.311>.
- 517 [41] T. Missana, A. Benedicto, M. García-Gutiérrez, U. Alonso, Modeling cesium retention
518 onto Na-, K- and Ca-smectite: Effects of ionic strength, exchange and competing cations
519 on the determination of selectivity coefficients, *Geochim. Cosmochim. Acta.* 128 (2014)
520 266–277. <https://doi.org/10.1016/j.gca.2013.10.007>.
- 521 [42] M.M. van Iersel, J.-P.A.J. van den Manacker, N.E. Benes, J.T.F. Keurentjes, Pressure-
522 induced reduction of shielding for improving sonochemical activity, *J. Phys. Chem. B.*
523 111 (2007) 3081–3084. <https://doi.org/10.1021/jp070635l>.
- 524 [43] S.I. Nikitenko, M. Brau, R. Pflieger, Acoustic noise spectra under hydrothermal
525 conditions, *Ultrasonics Sonochemistry.* 67 (2020) 105189.
526 <https://doi.org/10.1016/j.ultsonch.2020.105189>.
- 527 [44] W. Lauterborn, T. Kurz, Physics of bubble oscillations, *Rep. Prog. Phys.* 73 (2010)
528 106501. <https://doi.org/10.1088/0034-4885/73/10/106501>.
- 529 [45] K. Yasui, Acoustic cavitation and bubble dynamics, Springer, 2018.
- 530 [46] T. Tuziuti, K. Yasui, M. Sivakumar, Y. Iida, N. Miyoshi, Correlation between acoustic
531 cavitation noise and yield enhancement of sonochemical reaction by particle addition, *J.*
532 *Phys. Chem. A.* 109 (2005) 4869–4872. <https://doi.org/10.1021/jp0503516>.

533 [47] T. Kogure, K. Morimoto, K. Tamura, H. Sato, A. Yamagishi, XRD and HRTEM
534 Evidence for Fixation of Cesium Ions in Vermiculite Clay, Chem. Lett. 41 (2012) 380–
535 382. <https://doi.org/10.1246/cl.2012.380>.

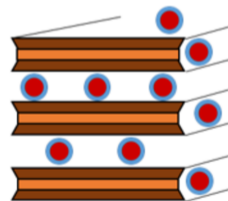
536



Cs-Vermiculite
(26 mg_{Cs+}/g)



47 %
of desorption



98 %
of desorption