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4 Title: Analysis of ³H, ³⁶Cl, ¹³³Ba, ¹³⁴Cs and ²²Na from synthetic granitic groundwater: an
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11 **Analysis of ^3H , ^{36}Cl , ^{133}Ba , ^{134}Cs and ^{22}Na from synthetic**
12 **granitic groundwater: an in-situ through diffusion**
13 **experiment at ONKALO**

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19 **Abstract**

20 A method for analyzing ^3H , ^{36}Cl , ^{22}Na , ^{133}Ba and ^{134}Cs from simulated groundwater
21 (SGW) samples was introduced. Gamma emitting radionuclides ^{22}Na , ^{133}Ba and ^{134}Cs
22 were measured by using an HPGe-detector. Beta emitting ^3H and ^{36}Cl were separated
23 from gamma emitting ^{22}Na , ^{133}Ba and ^{134}Cs . AgCl precipitation was used for the
24 separation of ^{36}Cl from SGW samples with yields of $98 \pm 2\%$. ^3H was separated by
25 distillation with recoveries of $97 \pm 3\%$. This method was used for the determination of
26 activity concentrations of ^3H , ^{36}Cl , ^{22}Na , ^{133}Ba and ^{134}Cs in SGW samples collected from
27 an in-situ through diffusion experiment (TDE).

28 **Keywords**

29 ^3H , ^{36}Cl , ^{133}Ba , ^{134}Cs , ^{22}Na , distillation, AgCl precipitation, gamma spectroscopy, liquid
30 scintillation counting

31 **Introduction**

32 The final disposal of spent nuclear fuel (SNF) from present nuclear power plants in
33 Finland (Olkiluoto and Loviisa) is planned to take place in a crystalline granitic rock at
34 Olkiluoto island (Eurajoki, Finland) [1]. The SNF will be protected by multiple barrier
35 system. The fuel elements are placed into iron canisters with an outer layer of copper.
36 The canisters are sealed and placed in vertical holes drilled in tunnels around 420 meters
37 below ground, in Olkiluoto island. In the vertical holes, the canisters are embedded in
38 compacted bentonite clay. The tunnels will be backfilled and the last barrier will be the
39 bedrock itself. Behavior of radionuclides in fractured crystalline rock has been studied for
40 the safety assessment calculations [2, 3]. The evaluation of the safety is done for
41 hundreds of thousands of years in the final disposal site [4]. If released into the bedrock,
42 radionuclides will be transported by advection along water conducting fractures and their
43 retardation may occur by molecular diffusion from the fractures into the stagnant pore
44 water and/or by sorption onto mineral surfaces in the adjacent rock matrix [5].

45 In-situ diffusion experiments in crystalline rock have been performed in several countries
46 e.g. Sweden [6, 7, 8], Switzerland [9, 10] and Canada [11, 12] to demonstrate the
47 behavior of radionuclides which might be released from the canisters into the bedrock in
48 the disposal site of spent nuclear fuel. In 1996, in Canada series of in-situ experiments
49 with iodide were conducted to study diffusion in sparsely fractured rock (SFR) [11, 12].
50 In Switzerland, the retention of several radionuclides was studied in-situ in Grimsel
51 granodiorite via a long-term diffusion (LTD) experiment [9, 10]. In Sweden at the Äspö
52 Hard Rock Laboratory, a Long Term Diffusion Experiment (LTDE) studied retention of
53 22 radionuclides in granodiorite [7, 8]. The focus in the Swedish experiment was more
54 directed towards sorption rather than diffusion due to the relatively short experimental
55 time of about six months.

56 The laboratory data of rock porosity and diffusion might be overestimated because of
57 drilling artefacts caused by stress release and/or prehandling the rock core samples by
58 sawing. The data that is used in safety case calculations is conservative and performed
59 mostly in laboratory conditions. The in-situ experiments are performed to increase
60 understanding and realism of diffusion data. This is the first time that diffusion of
61 radionuclides is studied in-situ in Olkiluoto. In addition, this is one of the first through
62 diffusion experiments in-situ in the world.

63 A project “rock matrix REtention PROPERTIES” (REPRO) at ONKALO, which is the
64 underground rock characterization facility in Olkiluoto, Finland, consists of extensive
65 series of in-situ sorption and diffusion experiments that are supplemented by laboratory
66 work [13, 14]. One of these in-situ experiments is a Through Diffusion Experiment
67 (TDE) launched in autumn 2015 for studying the diffusion and sorption of ^3H , ^{36}Cl , ^{22}Na ,
68 ^{133}Ba and ^{134}Cs in the Olkiluoto bedrock. The bedrock in the experimental site is mainly
69 veined gneiss with veins of coarse-grained pegmatitic granite. The veined gneiss shows a
70 weak to moderate banded foliation but locally also irregular foliation [15].

71 The radionuclides were chosen to cover different types of elements existing in the spent
72 nuclear fuel. We decided to avoid radionuclides having several oxidation states because
73 we wanted to “keep it simple”. ^3H is a conservative tracer, ^{36}Cl might show anion
74 exclusion properties of rocks. ^3H (HTO) and ^{36}Cl are not assumed to have chemical
75 reaction on the mineral surfaces in granitic rock. The scoping calculations done before
76 the experiment showed that ^3H and ^{36}Cl could have a breakthrough from the injection
77 borehole into the observation boreholes in a few years’ time during the in-situ experiment
78 and possible anion exclusion could be seen as well [16]. For the sorbing tracers, it is
79 likely that only slightly sorbing ^{22}Na could be seen from the observation boreholes in
80 reasonable timescales. Distribution coefficient of ^{22}Na varied between 1×10^{-4} and 1×10^{-2}
81 m^3/kg in the granitic rock and its main minerals [14, 17]. ^{22}Na is often used in in-situ
82 experiments because it can be measured with online gamma measurements contrary to
83 the beta emitters ^3H and ^{36}Cl . Besides these above mentioned three radionuclides,
84 strongly sorbing elements ^{133}Ba and ^{134}Cs were added. Both cesium and barium are
85 known to sorb by ion exchange mechanism having distribution coefficients between

86 $1 \times 10^{-1} \text{ m}^3/\text{kg}$ and $1 \times 10^{-3} \text{ m}^3/\text{kg}$ [3, 18-21]. ^{134}Cs was chosen as an analogue for another
87 cesium isotope, ^{135}Cs , which is one of the most important radionuclides after 100 000
88 years of deposition and might find its way into the biosphere [22]. ^{133}Ba is a chemical
89 analogue of ^{226}Ra which is safety relevant radionuclide in the spent fuel deposition
90 because of the ingrowth of ^{226}Ra from uranium [23].

91 In TDE, concentrated mixture of non-sorbing and sorbing radionuclides ^3H , ^{36}Cl , ^{22}Na ,
92 ^{133}Ba and ^{134}Cs was injected to a meter long packed-off section of a drill hole filled with
93 simulated groundwater (SGW) at a depth of 11–12 m from the niche wall. Some of the
94 tracers used in the TDE experiment occur naturally in trace amounts in the groundwater.
95 For example, 1.2 Bq/L ^3H has been measured [24] in the Olkiluoto groundwater.
96 $^{36}\text{Cl}/\text{total Cl}$ ratio has been examined from 34 samples from the Olkiluoto groundwater
97 taken from different depths (from ground level down to -819 m) and different locations in
98 the Olkiluoto island, and the values of $(3-123) \times 10^{-15}$ were found [25]. Thus it is not
99 possible that the background level of ^{36}Cl disturbs the measurement of it in the in-situ
100 experiment. Concentrations of 6.8×10^{-9} to $8.3 \times 10^{-6} \text{ mol/L}$ of stable natural cesium and
101 5.9×10^{-7} to $1.9 \times 10^{-5} \text{ mol/L}$ of stable natural barium has been measured from Olkiluoto
102 groundwater in previous studies [26]. Breakthrough of the radionuclides is followed from
103 the circulation SGW into two observation drill holes which are at a depth of about 10
104 centimeters from the injection borehole. In addition, the activity variation of the
105 radioactive tracers is followed from the injection drill hole. In this work the activity of
106 radionuclides in the injection hole was followed for 440 days.

107 The radionuclides ^3H , ^{36}Cl , ^{22}Na , ^{133}Ba and ^{134}Cs cannot be measured straight from the
108 TDE tracer cocktail because some of them are disturbing each other in the radioanalytical
109 determination. ^{22}Na , ^{133}Ba and ^{134}Cs are gamma emitting radionuclides, but they have
110 also beta/electron emissions that will interfere the measurements of purely beta emitting
111 ^3H and ^{36}Cl . Therefore, to measure beta emitting ^3H and ^{36}Cl from the SGW, ^{22}Na , ^{133}Ba
112 and ^{134}Cs need to be separated from the sample. ^{36}Cl can be separated by AgCl
113 precipitation which is a well-known method to separate chloride from solutions [27, 28].
114 ^{133}Ba could be moved out from the SGW by precipitation as well and precipitation of
115 barium as sulfates or carbonates [29, 30] is widely used procedure. ^{134}Cs could be

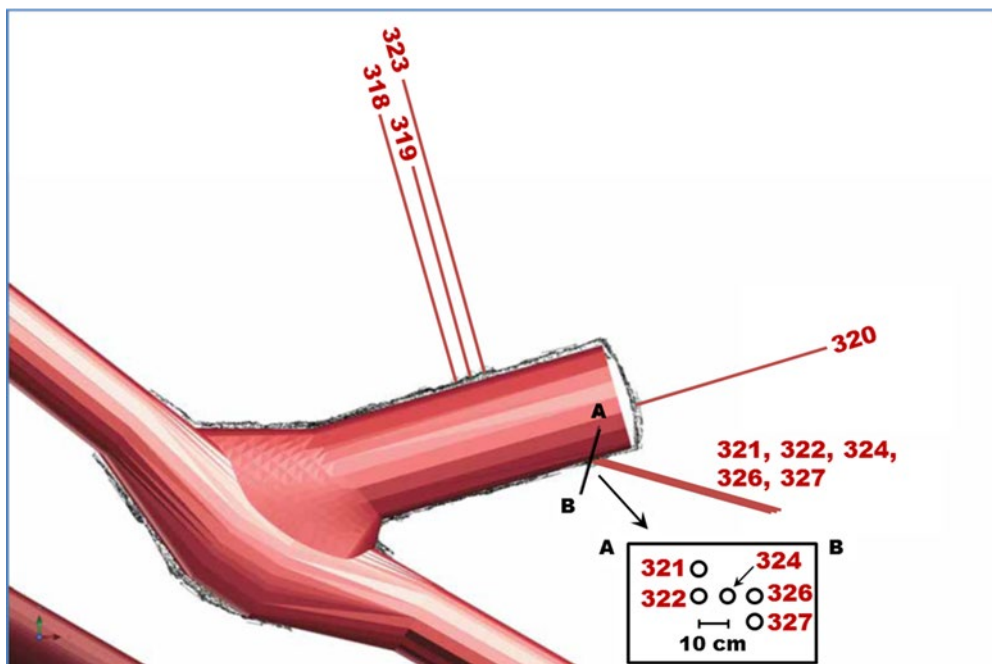
116 separated from the SGW by ion exchange method, e.g. with cation exchange resin
117 CsTreat[®] (Fortum, Espoo, Finland) [31, 32]. After the above-mentioned separation
118 procedures, ³H could be measured together with ²²Na by liquid scintillation counting
119 (LSC) because ²²Na interference is known to be low; only about 3-4 % of ²²Na betas are
120 shown in the energy window of ³H [28]. The ²²Na activity (after gamma measurement)
121 was subtracted from the LSC measurement results in the previous WPDE1&2 work [14,
122 28]. In this work, we decided to use another approach to separate ³H from the three
123 gamma emitting radionuclides as well as from ³⁶Cl. A distillation procedure, which is
124 widely used for measuring ³H in natural waters, was introduced for analyzing the TDE
125 tracers from the SGW solutions.

126 The aim of this work was to optimize the analysis procedure of the five radionuclides in
127 the TDE tracer mixture, and to quantify the possible losses and interferences in the
128 chemical separations. This procedure provides then analytically accurate data for the in-
129 situ TDE experiment.

130 **Materials and methods**

131 *The REPRO site*

132 Fig. 1 presents the drill holes in the Rebro niche where the in-situ experiments for
133 studying radionuclides migration in Olkiluoto bedrock are done [14, 33]. Injection drill
134 holes ONK-PP324, ONK-PP326 and ONK-PP327 were used in the TDE. ONK-PP326 is
135 the injection drill hole and the observation drill holes are ONK-PP324 and ONK-PP327.
136 The experiments are conducted at a depth of about 420 m in the REPRO-niche [33]. The
137 bedrock of Olkiluoto is crystalline rock that is mainly composed of veined gneiss,
138 diatexite and granitic pegmatoids [15]. In the REPRO niche at the depth where long term
139 experiments are being performed, the main rock types are veined gneiss, pegmatitic
140 granite, quartz gneiss and diatexitic gneiss [33].



141

142 **Fig. 1** The experimental drill holes in REPRO niche Onkalo, Olkiluoto, Finland where
143 the various in-situ experiments for studying radionuclides retention in Olkiluoto bedrock
144 were performed. The locations of REPRO drill holes in the investigation niche ONK-
145 TKU-4219 [14, 33]

146 *Ground water*

147 Before the TDE in-situ experiment, the groundwater sample was taken from the drill hole
148 ONK-PP319 at Repro niche and it was analysed for chemical composition in the
149 laboratory of TVO nuclear power company at Olkiluoto island. The SGW for the TDE
150 was made to resemble this water. 260 mL of SGW was circulated in the injection drill
151 hole and in the two observation drill holes each for 6 months before the experiment
152 started and the radioactive tracers were injected into the SGW circulation. Circulation
153 pumps with PEEK material in contact with the water were used for water circulation in
154 all the three drill holes. The pumps ran continuously with a flow rate of 2 mL/min - 4
155 mL/min. During the 6 months equilibration period, four water samples from the
156 circulated SGW were taken and the analysis of chemical composition were performed in
157 Labtium Oy (Espoo, Finland). pH of the SGW was 7.9 ± 0.1 and the average chemical
158 composition of the initial SGW and the one after the equilibration period are presented in

159 Table 1. It can be seen from the Table 1 that the concentrations of all components of the
160 SGW decreased slightly during equilibration period. This is due to minor chemical
161 processes between the elements of rock minerals and the synthetic ground water.

162 **Table 1** The chemical composition of ONK-PP319 water and that of the SGW after six
163 months equilibration period in the TDE in-situ injection drill hole

Element	Concentration in ONK-PP319 water ¹ (mg/L)	Concentration in SGW after equilibration period of 6 months ² (mg/L)
Br	34 ± 0.4%	33.8 ± 1.3
Ca	690 ± 0.3%	472 ± 6
K	14 ± 0.7%	10.7 ± 1.1
Sr	5.7 ± 0.6%	4.20 ± 0.04
Mg	34 ± 0.5%	28.2 ± 0.4
SiO ₂	5.4 ± 0.5%	4.9 ± 0.3
Na	2 840 ± 0.9%	2 560 ± 20
Cl	5 890 ± 0.3%	5 310 ± 70

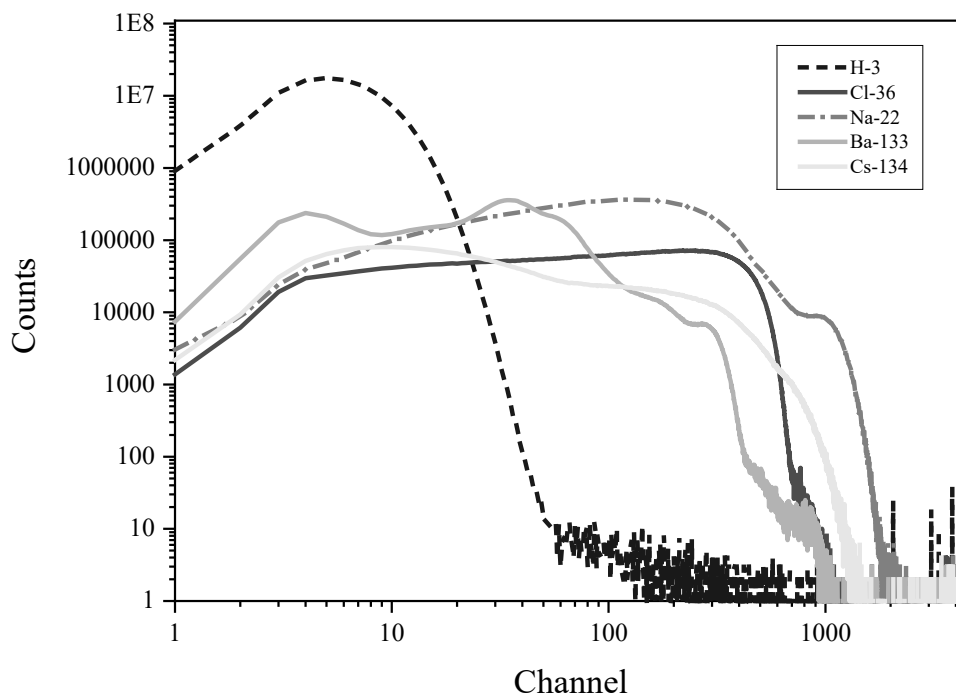
164 ¹TVO laboratory

165 ²Labtium Oy, Espoo, Finland

166 *Radionuclides*

167 The rough activities of radionuclides that were injected into the TDE injection drill hole
168 circulation in a 10 mL volume, were 200 MBq of ³H as tritiated water (HTO), 7 MBq of
169 ³⁶Cl as NaCl, 10 MBq of ²²Na as NaCl, 1 MBq of ¹³³Ba as BaCl₂ and 1 MBq of ¹³⁴Cs as
170 CsCl [34]. Initially 11 mL of tracer solution was prepared, and 1 mL sample was saved
171 for the accurate radioactivity analysis as well as this surplus solution was used to test the
172 analysis methods.

173 Fig. 2 shows the beta/electron spectra of ^3H , ^{36}Cl , ^{22}Na , ^{133}Ba and ^{134}Cs measured with
174 LSC. As can be seen from the Fig. 2, the beta/electron emissions of ^{22}Na , ^{133}Ba and ^{134}Cs
175 are interfering with the ^{36}Cl spectrum. They all are also interfering somewhat the ^3H
176 measurement and therefore it was decided that tritium will be separated from the sample
177 solution by distillation [35] and measured with LSC alone. LSC measurements of ^3H are
178 sensitive to quenching effects as well as to other radionuclide's interference. Distillation
179 is a good method to separate ^3H from other radionuclides since most of the impurities
180 vaporize poorly at the boiling point of water [36]. Possible radionuclides that would
181 vaporize are iodine isotopes as iodine gas and ^{14}C as carbon dioxide but these were not
182 used in this experiment ^{36}Cl has been separated from a weakly acidic water solution by
183 AgCl precipitation in previous experiments [27, 35]. The same method was used also in
184 this work. After precipitation, the AgCl precipitate was separated from the liquid phase
185 and dissolved to ammonia and the solution was measured by LSC.



186
187

188 **Fig. 2** Beta/electron spectra of ^3H , ^{36}Cl , ^{22}Na , ^{133}Ba and ^{134}Cs measured with Tri-Carb
189 2910 TR liquid scintillation counter (Perkin Elmer)

190 The radionuclides ^3H (37 MBq/g 29.7.2015) and ^{22}Na (7.609 MBq/g 15.11.2012) were
 191 purchased from Perkin Elmer (Boston, USA). The producer gives 10% uncertainty for the
 192 product; these are not precision calibrated solutions. ^{36}Cl (9.612 ± 0.106 MBq/g
 193 20.12.2013), ^{133}Ba (5.00 ± 0.12 MBq/g 1.3.2008) and ^{134}Cs (35.22 ± 0.35 MBq/g
 194 25.9.2014) were purchased from EuroStandard CZ (Prague, Czech Republic). Table 2
 195 shows the decay-modes, energy information and half-lives of the radionuclides used in
 196 this work. Activities of gamma emitting radionuclides ^{22}Na , ^{133}Ba and ^{134}Cs were
 197 measured directly from the subsamples taken from the ONK-PP326 circulation water by
 198 using a HPGe-detector (Canberra XtRa; Extended Range Coaxial HPGe Detector with
 199 spectral analysis program Gamma Acquisition & Analysis Genie/Canberra). ^3H and ^{36}Cl
 200 were measured with LSC (Perkin Elmer Tri-Carb 2910 TR, spectrum analyzer
 201 SpectraWorks). Liquid scintillation cocktail used in this work was OptiPhase HiSafe 3
 202 (Perkin Elmer) that is capable of handling a broad range of solutes, particularly high ionic
 203 strength ones.

204 **Table 2** Radionuclides used in the TDE and their main decay-modes, energies and half-
 205 lives [37]

Nuclide	Main decay-mode/intensity (%)	Energies of γ and β emissions used in analyses (keV)	Half-life (years)
^3H	$\beta^-/100$	β 18.591 ± 0.003	12.32 ± 0.02
^{22}Na	$\beta^+/90.38 \pm 0.03$	γ $1\ 274.537 \pm 0.007$	2.602 ± 0.002
^{36}Cl	$\beta^-/98.10 \pm 0.14$	β 709.55 ± 0.05	$301\ 000 \pm 2\ 000$
^{133}Ba	$\varepsilon/100\%$	γ 356.0129 ± 0.0007	10.551 ± 0.011
^{134}Cs	$\beta^-/99.9997 \pm 0.0001$	γ 604.721 ± 0.002	2.0652 ± 0.0004

206

207 AgCl precipitation for ^{36}Cl measurement and ^3H distillation were tested with two sets of
 208 samples. One set (four samples) included only radioactive ^{36}Cl (1 400-2 400 Bq) in 5 mL
 209 of SGW for testing AgCl precipitation. Another set (ten samples) included only ^3H (240 –
 210 36 000 Bq) in 10 mL SGW for testing of the distillation. The three gamma emitting

211 radionuclides were not included into the test samples because by this way the recoveries
212 of beta emitting radionuclides could be determined accurately without interferences.

213 *AgCl precipitation tests*

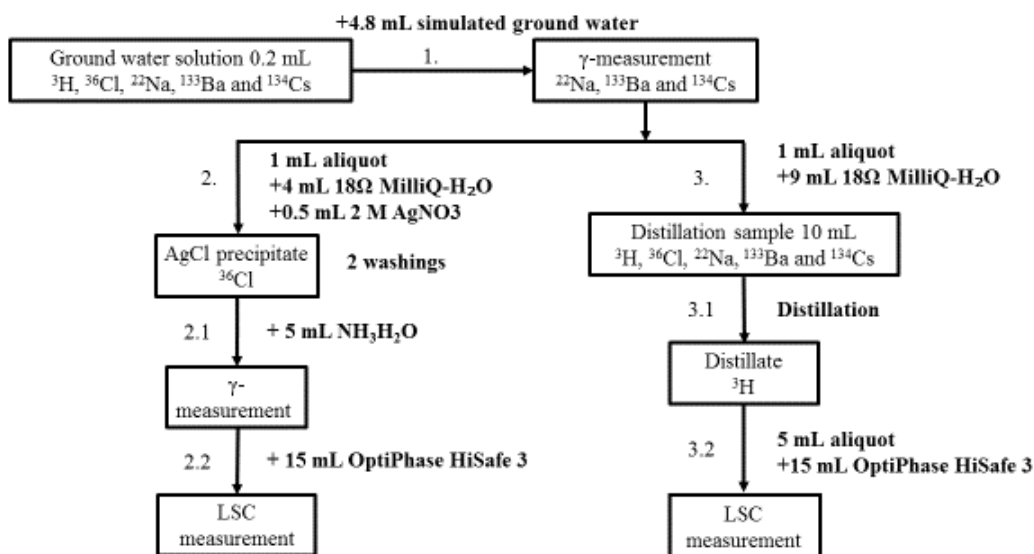
214 The testing of the separation of ^{36}Cl by AgCl precipitation was performed adding 0.5 mL
215 of 2 mol/L AgNO_3 to 5 mL SGW which chloride concentration was about 5 g/L. SGW
216 contains 5310 mg/L of chloride (see Table 1) and no additional carrier for ^{36}Cl was
217 needed because in 5 mL of SGW there is 26.55 mg of chloride which is equivalent for
218 0.15 mol/L and thus the AgNO_3 concentration ($0.0005 \text{ L} \times 2 \text{ mol/L} / 0.005 \text{ L} = 0.2 \text{ mol/L}$)
219 was sufficient to precipitate all chloride from the solution. After mixing the solutions
220 together, the mixture was stirred vigorously to ensure precipitation of all ^{36}Cl . AgCl
221 precipitate was separated from supernatant by centrifugation (4500 rpm for 15 minutes,
222 Sigma centrifuge 3-16KL, Rotor 1180). Then the precipitate was washed twice with 5
223 mL of 18 Ω MilliQ- H_2O and dissolved into 5 mL of 17% NH_3 solution. The dissolved
224 precipitate was first measured with HPGe detector to check if there is any leak of
225 gamma-emitting nuclides into the precipitate. After that, the dissolved chloride solution
226 was mixed with 15 mL of liquid scintillation cocktail and beta activity of ^{36}Cl was
227 measured by LSC. The quenching curve for ^{36}Cl was determined with 800 Bq ^{36}Cl in 5
228 mL of SGW, 15 mL OptiPhase HiSafe 3 liquid scintillation cocktail and CCl_4 as a
229 quenching substance.

230 *Distillation tests for separating ^3H*

231 In the distillation procedure for determining ^3H , the 10 mL SGW samples with known
232 amount of ^3H was heated with thermophore and the vapor was condensed in the water
233 circulation condenser. The distillate that contained ^3H as tritiated water was collected into
234 a round-bottomed glass flask. These samples were distilled to near dryness to ensure
235 good recovery for ^3H . After that 5 mL aliquots were taken from the distillates (Fig. 3 step
236 3.2) and the ^3H activity was measured with LSC. The quenching curve for ^3H was
237 determined with ^3H internal standard capsules (Perkin Elmer, Boston, USA) with activity
238 of $3\ 100 \pm 40$ Bq dissolved in 5 mL of SGW, 15 mL OptiPhase HiSafe 3 and CCl_4 as a
239 quenching substance.

240 *Final procedure for water sample analysis*

241 The activities of radionuclides in the TDE injection solution were analysed with the
 242 developed procedure. In addition, the TDE water samples from the injection drill hole
 243 for following the variation of tracer activities were measured. Fig. 3 shows the
 244 schematics used for the accurate activity analysis of the TDE injection tracer solution (1
 245 mL) and the TDE water samples (0.2 mL).



246 **Fig. 3** Analysis scheme for activity measurements of water samples taken from the
 247 injection drill hole of the TDE. Separation of ^{36}Cl is done by AgNO_3 precipitation and ^3H
 248 by distillation
 249

250 *The tracer activities of the TDE injection solution*

251 The activities of the tracers in the TDE injection solution were analysed from a 1 mL
 252 surplus tracer solution (called now-on S1) that was made at the same time as the initial
 253 tracer solution. The S1 solution had to be diluted before analysis and first it was diluted
 254 to 10 mL with SGW (called now-on S2 dilution). Secondly 0.5 mL of the S2 dilution was
 255 diluted to 100 mL with MilliQ-H₂O (called now-on S3 dilution). From this S3 dilution
 256 two about 0.2 mL samples were taken for the activity analysis of ^3H , ^{36}Cl , ^{22}Na , ^{133}Ba and
 257 ^{134}Cs . One of these 0.2 mL samples was further diluted with SGW to 5 mL for AgCl
 258 precipitation (called now-on S4a dilution) (marked to Fig. 3 as step 2) and the other

259 sample was diluted to 10 mL for distillation (called now-on S4b dilution) (marked to Fig.
260 3 as step 3). The S4a dilution has a chloride content of 25.48 mg and concentration of
261 0.14 mol/L so the 0.2 mol/L AgNO₃ concentration in the solution is sufficient for
262 precipitate all chloride in the sample. Every dilution was weighed for the accurate
263 calculation of injected tracer activities. Gamma activities of ²²Na, ¹³³Ba and ¹³⁴Cs were
264 first measured from the S4a dilution (Fig. 3 step 1) by using HPGe-detector with
265 measurement time of 4.4 hours. In long measurements with Ge-detector the background
266 activities consist mainly of daughters of ^{238,235}U and ²³²Th and of ⁴⁰K, from the
267 surrounding building materials and of daughters of ²²²Rn. No background gamma peaks
268 were overlapping with the energies of gamma-emitting radionuclides analysed in this
269 work.

270 After gamma measurement, 0.5 mL of 2 M AgNO₃ was added (Fig. 3 step 2) to the 5 mL
271 S4a dilution sample to precipitate AgCl. The AgCl precipitate was diluted to 5 mL of
272 17% NH₃ solution and the dilution was measured with Ge-detector (5 mL measurement
273 geometry) for any gamma-active residue that could have been left to the sample despite
274 the washing of the precipitate. After the gamma measurement, 15 mL of liquid
275 scintillation cocktail was added (Fig. 3 step 2.2) and the sample was measured for ³⁶Cl
276 activity with LSC.

277 The 10 mL S4b dilution sample was distilled to near dryness and the distillate was
278 measured with HPGe-detector for any gamma active residue. 15 mL of liquid scintillation
279 cocktail was added and the ³H activity of injection tracer solution was measured from 7
280 mL distillate sample with LSC.

281 *Analysis of the water samples from TDE injection drill hole ONK-PP326*

282 The decrease of the activities of tracers were followed by taking about 0.2 mL water
283 samples from the injection drill hole ONK-PP326. Water samples were weighed for
284 accurate mass. The first groundwater samples from the TDE injection drill hole was taken
285 6 hours after the experiment started in November 2015. Groundwater samples from the
286 drill hole ONK-PP326 were taken frequently in the first week of the experiment. In total,
287 7 samples were collected in the first week. After that samples were taken every two
288 weeks and after three months of the experiment samples were taken once a month. From

289 nine months on samples were taken once per every two months. Total amount of 23
 290 samples (until spring 2017) have been collected in 440 days.

291 Before measurements, the 0.2 mL TDE groundwater samples were diluted to 5 mL with
 292 SGW (Fig. 3 step 1) and activities of ^{22}Na , ^{133}Ba and ^{134}Cs were measured by HPGe-
 293 detector. The separations of ^{36}Cl and ^3H were performed as described in Fig. 3. All
 294 samples were weighed before and after dilutions and distillations and all the results were
 295 corrected to the initial 0.2 mL sample.

296 **Results and discussion**

297 *AgCl precipitation tests*

298 Table 3 shows the results of AgCl precipitation tests. ^{36}Cl from the supernatant,
 299 precipitate dissolved in NH_3 and two washing solutions was measured by LSC with a
 300 measurement efficiency of $89 \pm 1\%$. The average yield of AgCl precipitation was $98 \pm$
 301 2% in the four measured test samples.

302 When ^{36}Cl was analyzed from the water samples with all five tracer radionuclides, no
 303 gamma emitting radionuclides were present in the AgCl precipitate. A disturbance from
 304 ^3H possibly staying in sample is ruled out by setting the lower level of the ^{36}Cl counting
 305 window to exceed the maximum energy of ^3H betas. A detection limit of 0.15 Bq/g with a
 306 measurement time of 2 h was obtained for ^{36}Cl . The yield results are in good agreement
 307 with results of Hou et al. [26] and Qian et al. [27].

308 **Table 3** The separation of ^{36}Cl by AgCl precipitation. Activity of ^{36}Cl in different
 309 solutions and the yield of AgCl precipitation are given

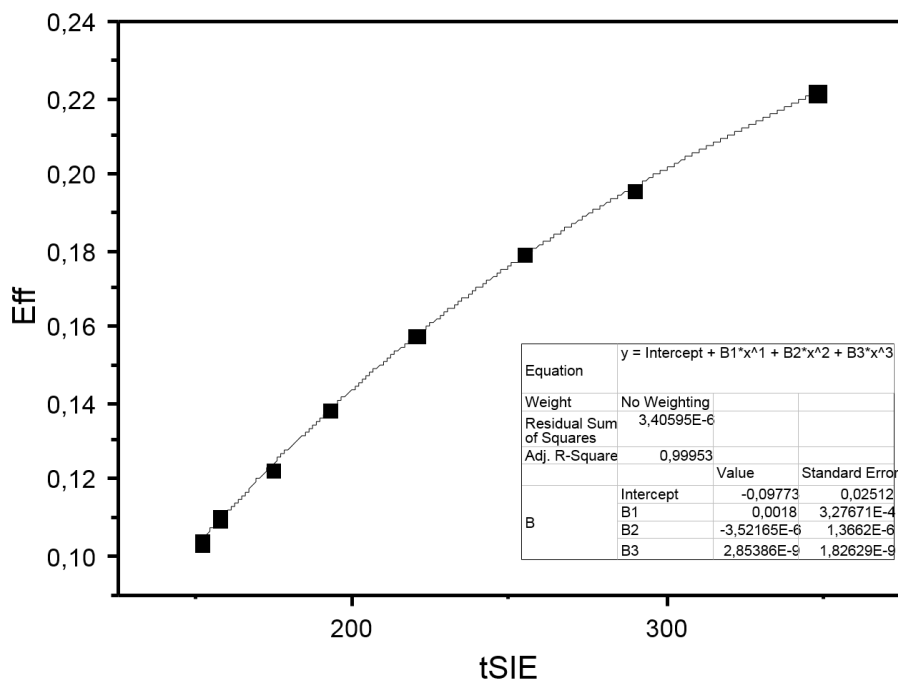
Sam ple	Initial ^{36}Cl activity (Bq)	^{36}Cl activity in supernatant (Bq)	^{36}Cl activity in wash 1 (Bq)	^{36}Cl activity in wash 2 (Bq)	^{36}Cl activity in AgCl precipitate (Bq)	^{36}Cl yield (%)
1	$1\ 380 \pm 15$	64 ± 1	$0.289 \pm$	0.30 ± 0.01	$1\ 340 \pm 15$	97 ± 1

			0.014			
2	1 380 ± 15	63 ± 1	0.283 ± 0.014	0.55 ± 0.02	1 320 ± 14	96 ± 1
3	2 380 ± 30	0.32 ± 0.01	0.309 ± 0.014	0.44 ± 0.02	2 390 ± 90	100 ± 4
4	2 380 ± 30	0.47 ± 0.02	0.317 ± 0.014	0.37 ± 0.02	2 370 ± 90	100 ± 4

310

311 *Distillation tests for separating ³H*

312 Fig. 4 shows the quench correction curve for ³H. The recovery of ³H was calculated by
 313 comparing the known activity concentration of the 10 mL distillation sample to the
 314 measured activity concentration in the distillate. An average recovery of 97 ± 3 % was
 315 obtained, that is in good agreement with Atkinson et al. [38], who have reported
 316 distillation recoveries of >98% for ³H from environmental water samples. No gamma
 317 emitting radionuclides nor ³⁶Cl were observed to leak to the distillate. Therefore ³H could
 318 be measured clean from disturbing spectral components with low detection limit of 0.4
 319 Bq/g (measurement time 2 h).



321
 322 **Fig. 4** Quench correction curve for ^3H . 5 mL SGW sample mixed with 15 mL of
 323 OptiPhase HiSafe 3 liquid scintillation cocktail. Samples measured with TriCarb 2910
 324 TR (Perkin Elmer)

325 *Activity of the TDE injection tracer solution*

326 Activity of the injection tracer solution was analysed from the S4a and S4b dilutions.
 327 Gamma emitting radionuclides ^{22}Na , ^{133}Ba and ^{134}Cs were measured from the S4a
 328 dilution by Ge-detector with detection limits of 0.45 Bq/g for ^{22}Na (1275 keV), 0.65 Bq/g
 329 for ^{133}Ba (365 keV) and 0.50 Bq/g for ^{134}Cs (604 keV) with a measurement time of 4.4 h.
 330 Beta emitting radionuclide ^{36}Cl was separated from S4a dilution and ^3H was distilled
 331 from S4b dilution. Results of the TDE tracer solution analysis are shown in Table 4. The
 332 total amount of injected tracer activities of gamma emitting nuclides ^{22}Na , ^{133}Ba and
 333 ^{134}Cs as well as beta emitting radionuclides ^3H and ^{36}Cl were corrected to the injected
 334 tracer volume which was 9.7 g.

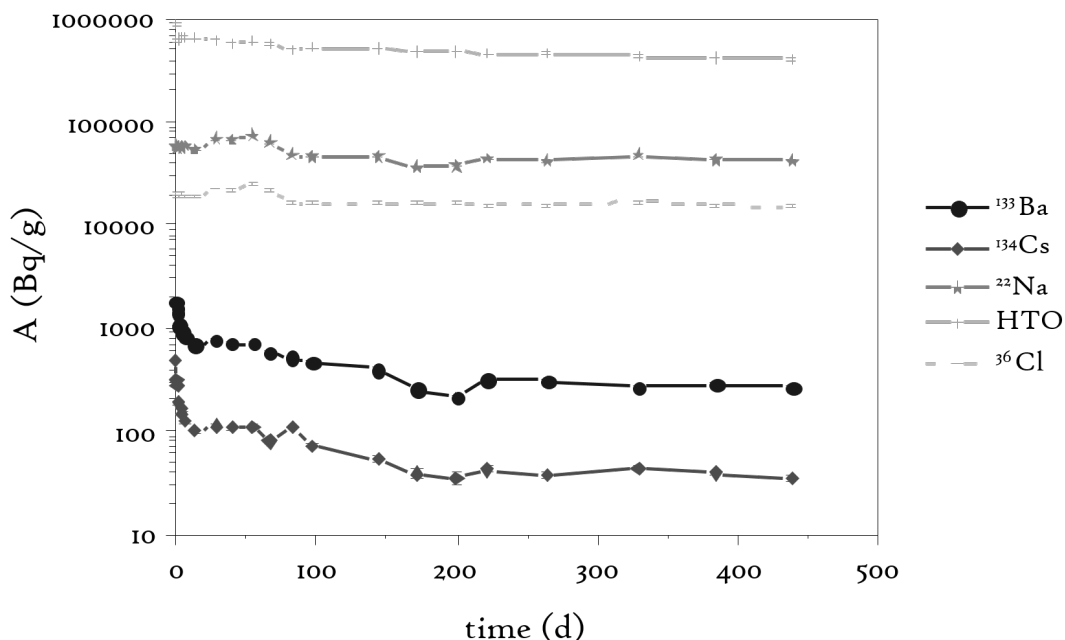
335 **Table 4** Injected tracer solution activities in TDE

Radionuclide	Injected activity (MBq)
^3H	198 ± 3
^{36}Cl	5.5 ± 0.2
^{22}Na	22.4 ± 0.2
^{133}Ba	2.09 ± 0.04
^{134}Cs	1.92 ± 0.06

336

337 *Analysis of the water samples from the TDE injection drill hole ONK-PP326*

338 The variation of radionuclide activities (Bq/g of ^3H , ^{36}Cl , ^{22}Na , ^{133}Ba and ^{134}Cs) in the
339 TDE injection drill hole as a function of time are shown in Fig. 5. All activities are half-
340 life corrected to the start of the experiment (19.11.2015). The general trend in all
341 activities is falling; ^{133}Ba and ^{134}Cs the most and ^{36}Cl the least. After 440 days from the
342 start of the experiment, about 69% of the initial ^{36}Cl concentration and about 52% of the
343 initial ^3H concentration is still present, whereas only 3% of initial ^{133}Ba and 0.4% of the
344 initial ^{134}Cs is left in the injection drill hole circulation SGW. This is explained by the
345 non-sorbing nature of ^3H and ^{36}Cl which decrease in the system only by diffusion into the
346 pores of surrounding rock whereas the sorbing ^{133}Ba and ^{134}Cs activity decrease fast in
347 the SGW due to the chemical reactions with the mineral surfaces of the rock. ^{133}Ba and
348 ^{134}Cs distribution coefficients ($K_d = 1 \times 10^{-1} - 1 \times 10^{-3} \text{ m}^3/\text{kg}$) [3, 26] are found to be large on
349 veined gneiss which is the dominant rock type in the TDE area. Approximately 47% of
350 ^{22}Na is present in the injection drill hole circulation SGW after 440 days of the
351 experiment. No radionuclides migration into the two observation drill holes ONK-PP324
352 and ONK-PP327 were observed during the 440 days of the experiment. Not even the
353 non-sorbing radionuclides ^3H and ^{36}Cl had diffused through the 10 cm distance in the
354 rock.



355
 356 **Fig. 5** Activities (Bq/g) of ^3H (plus), ^{36}Cl (minus), ^{22}Na (star), ^{133}Ba (dot) and ^{134}Cs
 357 (squares) in the TDE injection drill hole as a function of time (in days)

358 Conclusions

359 Analysis method for ^3H , ^{36}Cl , ^{133}Ba , ^{134}Cs and ^{22}Na from synthetic groundwater solution
 360 was introduced. It includes separation of ^{36}Cl by AgCl precipitation and ^3H separation by
 361 distillation. Gamma emitting nuclides are measured precisely from the groundwater
 362 samples without any sample treatment. The developed separation procedure for analysis
 363 of ^3H , ^{36}Cl , ^{133}Ba , ^{134}Cs and ^{22}Na for the TDE in-situ experiment at ONKALO was found
 364 to be effective and simple, with detection limits for all the nuclides close to 0.5 Bq/g.

365 The radionuclide analyses show that the activities of ^3H , ^{36}Cl , ^{22}Na , ^{133}Ba and ^{134}Cs in
 366 TDE injection hole are decreasing during the observation period of 440 days. Anyhow
 367 there were anomalies in the decreasing trend. These are most probably originated from
 368 strong pressure changes in the packed off drill hole sections in the early part of the
 369 experiment.

370 ^{133}Ba and ^{134}Cs have adsorbed strongly onto the rock matrix which is shown in fast
371 decrease of their activity concentrations in the beginning of the experiment. 96% of the
372 initial ^{133}Ba and >99% of ^{134}Cs has been retained to the surroundings after 440 days
373 experiment. From the weakly sorbing ^{22}Na and non-sorbing ^3H and ^{36}Cl app. 31-53% of
374 the activity is retained in the rock matrix of the injection drill hole surface and its
375 surroundings, but no activity has migrated to the observation holes at the time of this
376 analysis. All activities in the injection drill hole are still well above the detection limits.

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379 **References**

- 380 1. Posiva (2009) Olkiluoto site description 2008 – Part 1. Posiva Report 2009-01
- 381 2. Hakanen M, Ervanne H, Puukko E (2012) Safety case for the disposal of spent nuclear
382 fuel at Olkiluoto – Radionuclide migration parameters for the geosphere. Posiva Report
383 2012-41
- 384 3. Muuri E, Siitari-Kauppi M, Matara-aho M, Ikonen J, Lindberg A, Qian L, Koskinen L
385 (2017) Cesium sorption and diffusion on crystalline rock: Olkiluoto case study. J
386 Radioanal Nucl Chem 311: 439-446
- 387 4. Pastina B and Hellä P (2006) Expected evolution of spent nuclear fuel repository at
388 Olkiluoto (revised). Posiva report 2006-5
- 389 5. Kekäläinen P, Voutilainen M, Poteri A, Hölttä P, Hautojärvi A, Timonen J (2011)
390 Solutions to and validation of matrix-diffusion models. Transport Porous Med 87(1):125-
391 149
- 392 6. Andersson P, Byegård J, Tullborg E-L, Doe T, Hermanson J, Winberg A (2004) In situ
393 tracer tests to determine retention properties of a block scale fracture network in granitic
394 rock at the Äspö Hard Rock Laboratory, Sweden. J Cont Hyd 70:271-297

- 395 7. Nilsson K, Byegård J, Selnert E, Widestrand H, Höglund S, Gustafsson E (2010) Äspö
396 hard rock laboratory: Long term sorption diffusion experiment (LTDE-SD), Results from
397 rock sample analyses and modelling. SKB report R-10-68
- 398 8. Widestrand H, Byegård J, Nilsson K, Höglund S, Gustafsson E (2010) Long term
399 sorption diffusion experiment (LTDE-SD), Performance of main in situ experiment and
400 results from water phase measurements. SKB report R-10-67
- 401 9. Ikonen J, Sardini P, Jokelainen L, Siitari-Kauppi M, Martin A, Eikenberg J (2016) The
402 tritiated water and iodine migration in situ in Grimsel granodiorite. Part I: determination
403 of the diffusion profiles. *J Radioanal Nucl Chem* 310:1041-1048
- 404 10. Soler J M, Kanda J, Havlova V, Tachi Y, Ebina T, Sardini P, Siitari-Kauppi M,
405 Eikenberg J, Martin A J (2015) Comparative modeling of an in situ diffusion experiment
406 in granite at the Grimsel Test Site. *J Con Hyd* 179:89-101
- 407 11. Vilks P, Cramer J J, Jensen M, Miller N H, Miller H G, Stanchell F W (2003) In situ
408 diffusion experiment in granite: Phase I. *J Con Hyd* 61:191-202
- 409 12. Vilks P, Miller N H (2007) Evaluation of experimental protocols for characterizing
410 diffusion in sedimentary rocks. NWMO TR-2007-11
- 411 13. Aalto P, Aaltonen I, Ahokas H, Andersson J, Hakala M, Hellä P, Hudson J,
412 Johansson E, Kemppainen K, Koskinen L, Laaksoharju M, Lahti M, Lindgren S,
413 Mustonen A, Pedersen K, Pitkänen P, Poteri A, Snellman M, Ylä-Mella M (2009)
414 Program for repository host rock characterisation in the ONKALO (ReRoC). Posiva
415 Working Report 2009-31
- 416 14. Voutilainen M, Poteri A, Helariutta K, Siitari-Kauppi M, Nilsson K, Andersson P,
417 Byegård J, Skålberg M, Kekäläinen P, Timonen J, Lindberg A, Pitkänen P, Kemppainen
418 K, Liimatainen J, Hautojärvi A, Koskinen L (2014) In-situ experiments for investigating
419 the retention properties of rock matrix in ONKALO, Olkiluoto, Finland – 14258
420 WM2014 Conference, March 2-6, Phoenix, Arizona, USA
- 421 15. Aaltonen I, Engström J, Front K, Gehör S, Kosunen P, Kärki A, Paananen M,
422 Paulamäki S, Mattila J (2016) Geology of Olkiluoto. Posiva Report 2016-16

- 423 16. Valkiainen M, Aalto, H, Lindberg A, Olin M, Siitari-Kauppi M (1995) Diffusion in
424 the matrix of rocks from Olkiluoto-The effect of anion exclusion. YJT-95-20
- 425 17. Hölttä P, Poteri A, Siitari-Kauppi M, Huittinen N (2008) Retardation of mobile
426 radionuclides in granitic rock fractures by matrix diffusion. Phys Chem Earth 33:983-990
- 427 18. Jokelainen L, Meski T, Lindberg A, Soler J M, Siitari-Kauppi M, Martin A,
428 Eikenberg J (2013) The determination of ^{134}Cs and ^{22}Na diffusion profiles in granodiorite
429 using gamma spectroscopy. J Radioanal Nucl Chem 295:2153-2161
- 430 19. Muuri E, Ikonen J, Matara-aho M, Lindberg A, Holgersson S, Voutilainen M, Siitari-
431 Kauppi M, Martin A (2016) Behavior of Cs in Grimsel granodiorite: sorption on main
432 minerals and crushed rock. Radiochim Acta 104(8):575–582
- 433 20. Hakem N L, Al Mahamid I, Apps J A, Moridis G J (2000) Sorption of cesium and
434 strontium on Hanford soil. J Radioanal Nucl Chem 246(2):275-278
- 435 21. Molinero J, Samper J (2006) Large-scale modeling of reactive solute transport in
436 fracture zones of granitic bedrocks. J Con Hyd 82:293-318
- 437 22. Haapanen R, Aro L, Helin J, Hjerpe T, Ikonen A T K, Kirkkala T, Koivunen S,
438 Lahdenperä A-M, Puhakka L, Rinne M, Salo T (2009) Posiva Biosphere Description
439 2009, 424
- 440 23. Nilsson B, Papp T (1980) Feasibility of safe terminal disposal of spent nuclear fuel.
441 IAEA Pulletin, 22(3):63-72
- 442 24. Kortelainen N (2009) Isotopic composition of atmospheric precipitation and shallow
443 groundwater in Olkiluoto: O-18, H-2 and H-3. Posiva Working Report 2009-06
- 444 25. Gascoyne M (2014) Chlorine isotopes and their application to groundwater dating at
445 Olkiluoto. Posiva Working Report 2014-38
- 446 26. Hellä P, Pitkänen P, Löfman J, Partamies S, Vuorinen U, Wersin P (2014) Safety case
447 for the disposal of spent nuclear fuel at Olkiluoto: definition of reference and bounding
448 groundwaters, buffer and backfill porewaters. POSIVA 2014-04

- 449 27. Hou X, Ostergaard L F, Nielsen S P (2007) Determination of ^{36}Cl in nuclear waste
450 from reactor decommissioning. *Anal Chem* 79:3126-3134
- 451 28. Qian L, Helariutta K, Ikonen J, Siitari-Kauppi M, Voutilainen M, Koskinen L (2015)
452 Measurement of ^3H , ^{36}Cl , ^{22}Na , ^{85}Sr and ^{133}Ba activities from synthetic groundwater. *J*
453 *Radioanal Nucl Chem* 306:131-137
- 454 29. Symeopoulos B D, Koutsoukos P G (1992) Spontaneous precipitation of barium
455 sulfate in aqueous solution. *J Chem Soc Faraday Trans* 88(20):3063-3066
- 456 30. Chen Q, Hou X, Yu Y, Dahlgard H, Nielsen S P (2002) Separation of Sr from Ca,
457 Ba and Ra by means of $\text{Ca}(\text{OH})_2$ and $\text{Ba}(\text{Ra})\text{Cl}_2$ or $\text{Ba}(\text{Ra})\text{SO}_4$ for the determination of
458 radiostrontium. *Anal Chim Acta* 466:109-116
- 459 31. Möller T, Harjula R, Lehto J (2002) Ion exchange of ^{85}Sr , ^{134}Cs and ^{57}Co in sodium
460 titosilicate and the effect of crystallinity on selectivity. *Sep Pur Tech* 28:13-23
- 461 32. Harjula R., Lehto J., Paajanen A., Tusa E., Yarnell P. (2004). Use of inorganic ion
462 exchange materials as precoat filters for nuclear waste effluent treatment. *Reac Func Pol*
463 60:85-95
- 464 33. Toropainen V, 2012 Core drilling of REPRO drillholes in ONKALO at Olkiluoto
465 2010-2011. POSIVA Working Report 2012-26
- 466 34. Andersson P., Byegård J., Nilsson K., Skålberg M., Voutilainen M., Kekäläinen P.,
467 Siitari-Kauppi M., Helariutta K., Ikonen J., Sammaljärvi J., Kuva J., Timonen J., Poteri
468 A, Yli-Kaila M. (2018). Through Diffusion Experiment (TDE) of the REPRO project,
469 Experimental Plan and Scoping Calculations, Posiva Working Report. Unpublished.
- 470 35. Lehto J, Hou X (2007) *Chemistry and analysis of radionuclides*. Wiley-VCH
- 471 36. Vasaru G (1993) *Tritium isotope separation*. CRC Press, Inc. 0-8493-4322-4
- 472 37. <http://www.nndc.bnl.gov/nudat2>. Accessed 9 Jun 2017
- 473 38. Atkinson R, Eddy T, Kuhne W, Jannik T, Brandl A (2014) Measurement of the
474 tritium concentration in the fractionated distillate from environmental water samples. *J*
475 *Env Rad* 135:113-119