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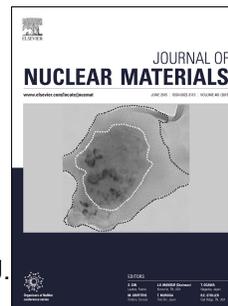


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Short communication: The dissolution of UK simulant vitrified high-level-waste in groundwater solutions

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Abstract

Dissolution of a simulant UK nuclear waste glass containing Mg, Ca and Zn was investigated over 35 d at 50 °C in water and simulant groundwater solutions. The dissolution rates were influenced subtly by the groundwater composition, following the trend, from least to most durable: clay > water > granite \approx saline. Solutions were rapidly silica saturated but boron dissolution rates continued to increase. This is hypothesised to be due to the formation of secondary Mg-silicate precipitates, preventing the formation of a passivating silica gel layer and allowing glass dissolution to proceed at close to the maximum rate.

Key words: aluminoborosilicate glass, nuclear waste, chemical durability, corrosion, zinc, magnesium, calcium, groundwater.

34 Some reprocessed high-level-waste (HLW) in the United Kingdom will be immobilised in a Ca and Zn
35 oxide modified Mixed Windscale (MW) base glass with a nominal composition of
36 $4.2\text{Li}_2\text{O}\cdot 8.6\text{Na}_2\text{O}\cdot 6.0\text{CaO}\cdot 6.0\text{ZnO}\cdot 4.2\text{Al}_2\text{O}_3\cdot 23.4\text{B}_2\text{O}_3\cdot 47.6\text{SiO}_2$ wt.%, referred to as CaZn MW. The
37 transition from regular MW to the CaZn MW base glass has been made to enhance the incorporation
38 of high Mo-content Post-Operational-Clean-Out (POCO) waste from the decommissioning of the
39 highly-active-storage tanks [1, 2]. At present, this glass is being used to immobilise reprocessing
40 wastes only. Investigation of the short-term durability of the CaZn MW glass [3-5], compared with
41 regular MW glass (both incorporating reprocessing waste), shows that the addition of CaO and ZnO
42 improves durability in the short-term [3, 4]. However, there remains uncertainty with regard to the
43 chemical durability of CaZn-glass, especially under conditions representative of geological disposal,
44 including in groundwater and at expected temperatures. The presence of Mg, as both a glass
45 component and a key constituent of groundwater, is known to trigger the formation of secondary
46 phases, which accelerate glass corrosion [6-11]. Furthermore, similar effects have been observed for
47 glasses incorporating even small quantities of Zn [5, 12].

48

49 This study aims to evaluate the influence of different simulant groundwater solution compositions,
50 compared with pure water, on the dissolution rates of the CaZn MW28 glass (28 wt.% waste loading)
51 in a short-term accelerated leaching experiment, and to identify the role of secondary phases in the
52 dissolution mechanism.

53

54 CaZn MW28 was fabricated from a selection of oxide precursors and 28 wt.% of an inactive HLW
55 calcine obtained from the National Nuclear Laboratory (NNL-UK) from the reprocessing of Oxide (o)
56 and Magnox (m) spent nuclear fuel at a ratio of 75o:25m. The batch was melted at 1060 °C for 5
57 hours (including 4 hours stirring) and annealed at 500 °C for 1 hour. The measured composition,
58 ascertained by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) analysis after
59 total digest of the glass in hydrofluoric acid was (in wt.% (± 3 % uncertainty)): 3.2 Al_2O_3 , 20.5 B_2O_3 ,
60 0.8 BaO, 4.9 CaO, 1.2 CeO_2 , 0.4 Cr_2O_3 , 1.4 Cs_2O , 1.8 Fe_2O_3 , 3.3 Gd_2O_3 , 0.1 HfO_2 , 0.6 La_2O_3 , 2.6 Li_2O , 1.5
61 MgO, 1.9 MoO_3 , 6.9 Na_2O , 1.9 Nd_2O_3 , 0.3 NiO, 0.6 Pr_2O_3 , 0.3 RuO_2 , 37.7 SiO_2 , 0.4 Sm_2O_3 , 0.3 SrO, 0.3
62 TeO_3 , 0.2 Y_2O_3 , 4.7 ZnO and 2.0 ZrO wt.%. The measured density obtained by helium pycnometry
63 was $2.894 \pm 0.003 \text{ g cm}^{-3}$ (uncertainty calculated from the standard deviation of ten measurements).

64

65 Crushed glass particles (75 – 150 μm diameter) were prepared and Product-Consistency-Test-B (PCT-
66 B) experiments, according to ASTM standard C1285-14 [13], were conducted at 50 °C in Ultra-High-
67 Quality (UHQ) water (18.2 $\text{M}\Omega \text{ cm}$) (initial pH(RT) 7.2) and in three simulant groundwater solutions

68 (Table 1). The surface area to volume ratio was $2,000 \text{ m}^{-1}$, and duplicate experiments were
 69 performed for 1, 3, 7, 14, 28 and 35 days under oxic conditions. Synthetic groundwater solutions
 70 were prepared by addition of chemical reagents added to 1 L of distilled water [14], as shown in
 71 Table 1. A total of 1.08 g of glass and 10 mL of solution was used. The amount of glass dissolved was
 72 measured from the normalised mass of elements (i) (g m^{-2}) (NL_i), according to:

$$73$$

$$74 \text{NL}_i = (C_i - C_{i,b}) / (f_i \times (SA/V)) \quad (1)$$

75
 76 where C_i and $C_{i,b}$ are the average concentration of element, i , in the leachate and blank tests
 77 (solution only, no glass), respectively (mg L^{-1}), measured using ICP-OES (ThermoScientific
 78 iCAPDuo6300); f_i is the mass fraction of i in the glass (unitless) and SA/V is the surface area to
 79 volume ratio of the total particles (m^{-1}), based on the geometric surface area. Uncertainty in NL_i was
 80 calculated by the standard deviation of the sum of uncorrelated random errors (see supplementary
 81 data).

82
 83 Two different approaches were used to assess the normalised dissolution rate of boron (NR_B , $\text{g m}^{-2} \text{d}^{-1}$)
 84 1). In the first case, the 1 – 35 d NL_B data were fitted using linear regression, and the uncertainty in
 85 NR_B was calculated from a chi-squared fit. In the second the data was fitted using:

$$86$$

$$87 \text{NL}_B = A \tan^{-1}(t/B) \quad (2)$$

88
 89 where A and B are fitting constants and t is time; an inverse tan fit has previously been found to
 90 provide a good empirical fit to the normalised mass loss data for a number of glasses, including the
 91 International Simple Glass (ISG) [15, 16]. In this case an “initial” dissolution rate, often defined as the
 92 maximum rate of glass dissolution controlled by hydrolysis of the silicate network [17], was
 93 calculated by evaluating the slope at $t = 0$:

$$94$$

$$95 \text{dNL}_i / \text{dt}_{(t=0)} \quad (3)$$

96
 97 The experiments performed here do not involve infinitely dilute conditions, therefore, the “forward”
 98 rate, where $Q = 0$, is not calculated (noting that Q refers to the ion activity product in Transition
 99 State Theory applied to glass corrosion [18 - 20]). Thus the rates calculated in Eqn (3) are the
 100 inferred rates at $t = 0$ and are termed “initial” rates for these experiments. After dissolution, dried
 101 particles (dried for 14h at $50 \text{ }^\circ\text{C}$) were adhered to carbon tabs or mounted in epoxy and ground to

102 reveal a cross-section. Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy
 103 (EDS) were performed using a Hitachi TM3030 SEM (operating at an accelerating voltage of 15 kV)
 104 and a Bruker Quantax 70, respectively. X-ray diffraction (XRD) was performed on pristine and 35 d
 105 altered particles using a Bruker D2 Phaser X-ray diffractometer. An angular range of $10 < 2\theta < 70$
 106 with a 0.02° step size of $0.17^\circ \text{ min}^{-1}$ was used, with a total scan time of 110 minutes. The
 107 geochemical modelling package PHREEQ-C version 3 was used to calculate the saturation indices of
 108 various secondary phases in the leachates at all time points. The concentration of elements in the
 109 leachate and the leachate pH(RT) were used as input to calculate a range of possible phases
 110 saturated in solution according to the Lawrence Livermore National Laboratory (LLNL) database.

111

112 **Table 1.** Composition of three synthetic solutions representative of generic repository groundwaters (GW) [14].

113

Element	Concentration (mmol L^{-1})		
	Granitic GW [21]	Saline GW [21]	Clay GW [22]
Na	2.8	140	55
K	0.1	2.1	1.1
Ca	0.5	19.9	7.5
Mg	0.2	0.4	5.7
Cl	2.1	173	52.5
HCO ₃	2.0	2.0	-
SO ₄ ²⁻	0.1	4.0	15
SiO ₂	0.2	-	-
pH(RT)	8.2	7.7	6.5

114

115 The measured NL_B (commonly used as an indicator for glass corrosion since boron does not
 116 participate in alteration layer formation), showed that dissolution of CaZn MW28 glass followed the
 117 trend, from the least to the most durable after 35 d: clay > UHQ > granite \approx saline (Fig. 1a). The
 118 dissolution rate of boron, NR_B , calculated using the two fitting methods described above are given in
 119 Table 2 and Fig. S1a. For all solutions except for the saline groundwater, the dissolution rate of
 120 boron calculated using the linear regression method between 1 and 35 d was approximately the
 121 same (within error) as that calculated at $t = 0$ using the inverse tan fit (Table 2). The similarity in the
 122 calculated rates suggests that for the granite, clay and UHQ solutions, the NR_B for the 35 d duration
 123 of the experiment was similar to the inferred initial rate (at $t = 0$), i.e. close to the maximum
 124 dissolution rate of the glass [12].

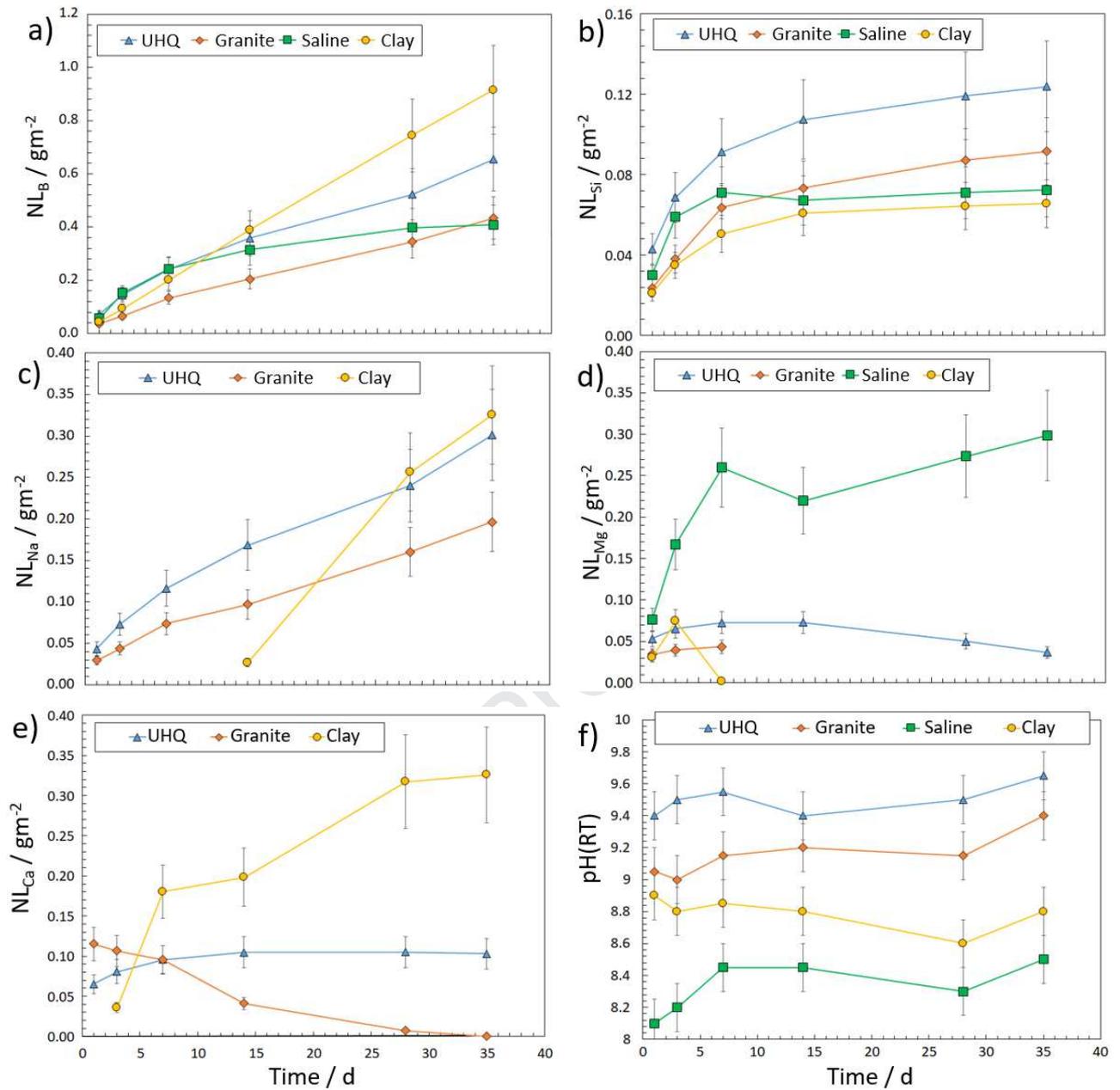
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126 The NL_{Si} (Fig. 1b and S1b) increased rapidly before slowing; this is typically observed when glass
 127 undergoes the “rate drop” caused by the formation of a passivating silica gel layer before transition

128 into the residual rate (Stage II) of dissolution [23]. However, the NL_B data indicated that there was no
129 rate drop. Considering that the glass dissolved at the “initial” rate (as at $t = 0$), this behaviour can be
130 attributed to rapid saturation of the solutions with respect to silica, and the almost immediate
131 precipitation of secondary silicate phases, thus preventing the formation of a passivating silica gel
132 layer and allowing dissolution to proceed at a rapid rate. In previous studies, the drop in NL_{Si} was
133 attributed to the formation of Mg-silicate phases [10, 11]. Indeed, there was a decrease in the NL_{Mg}
134 for clay, UHQ and granite solutions. It seems reasonable to suggest that the formation of secondary
135 Mg-silicate phases may, therefore, drive enhanced glass dissolution, at a relatively rapid rate (similar
136 in magnitude to the “initial” rate, governed by silicate network hydrolysis), with the source of the
137 Mg from both the solution and the glass (since this behaviour was also observed in UHQ where the
138 only source of Mg was the glass).

139
140 In contrast, for the saline groundwater, the NR_B calculated using the linear regression method was
141 considerably lower than the inverse tan fit, suggesting that the dissolution reaction of the glass in
142 this solution was passivated by the formation of a silica gel layer, as typically observed in borosilicate
143 glass dissolution. This was confirmed by the NL_{Si} data (Fig. 1b), which reached a residual rate at ~ 7 d.
144 It is interesting to note that in this solution, the NL_{Mg} *increased*, rather than decreased. This is
145 discussed further below.

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154 **Fig. 1.** (a – e) Normalized mass loss (NL) of elements, i , from CaZn MW28 particles during 35 d PCT-B leaching at 50°C in
 155 various groundwater compositions (errors bars are calculated from the sum of uncorrelated random errors); and f) pH(RT)
 156 measurements of the leachate. ($\text{pH(RT)}_{t=0}$: UHQ 7.2, granite 8.2, saline 7.7, clay 6.5).
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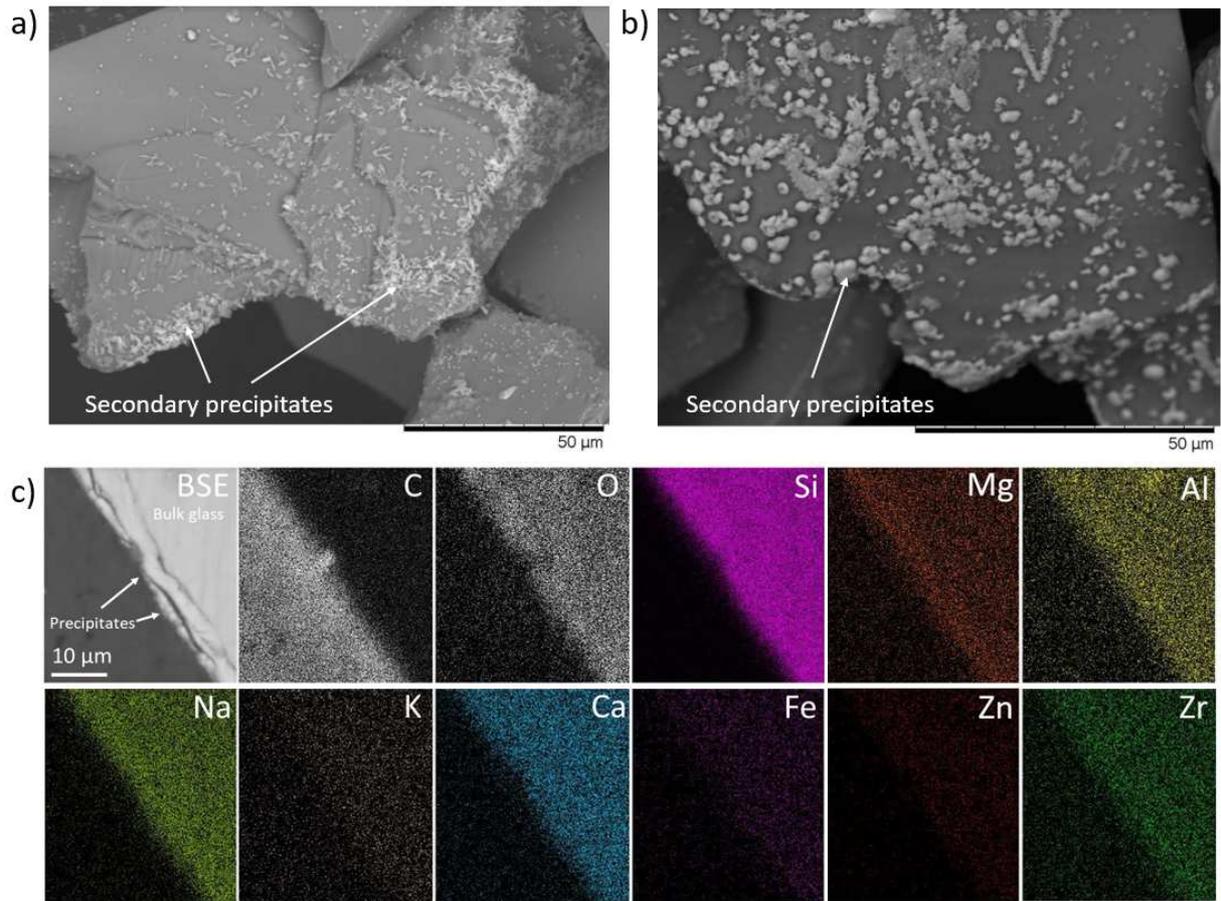
168 **Table 2.** Normalised dissolution rate of boron (NR_B) calculated between 1 and 35 d for all experiments using a chi-square fit
 169 and between 14 and 35 d for the saline groundwater solution (since this was the linear part of the dissolution reaction) and
 170 the $NR_{B \& Si}$ "initial rate" as calculated at $t=0$ using an inverse tan fit.
 171

Solution	B dissolution rate 1 - 35 d ($NR_B / g m^{-2} d^{-1}$)	R^2	B initial rate ($NR_B / g m^{-2} d^{-1}$)	R^2	Si initial rate ($NR_{Si} / g m^{-2} d^{-1}$)	R^2
Clay	$(2.82 \pm 0.23) \times 10^{-2}$	0.999	$(2.8 \pm 0.7) \times 10^{-2}$	1.000	$(1.4 \pm 0.3) \times 10^{-2}$	0.975
UHQ	$(2.43 \pm 0.32) \times 10^{-2}$	0.882	$(2.0 \pm 0.5) \times 10^{-2}$	0.986	$(3.0 \pm 0.5) \times 10^{-2}$	0.975
Granite	$(1.54 \pm 0.12) \times 10^{-2}$	0.994	$(1.6 \pm 0.5) \times 10^{-2}$	0.988	$(1.5 \pm 0.2) \times 10^{-2}$	0.983
Saline	$(1.67 \pm 0.14) \times 10^{-2}$	0.421	$(4.8 \pm 0.5) \times 10^{-2}$	0.995	$(4.0 \pm 0.5) \times 10^{-2}$	0.989
Saline 14-35 d	$(0.46 \pm 0.42) \times 10^{-2}$	0.947	n/a	n/a	n/a	n/a

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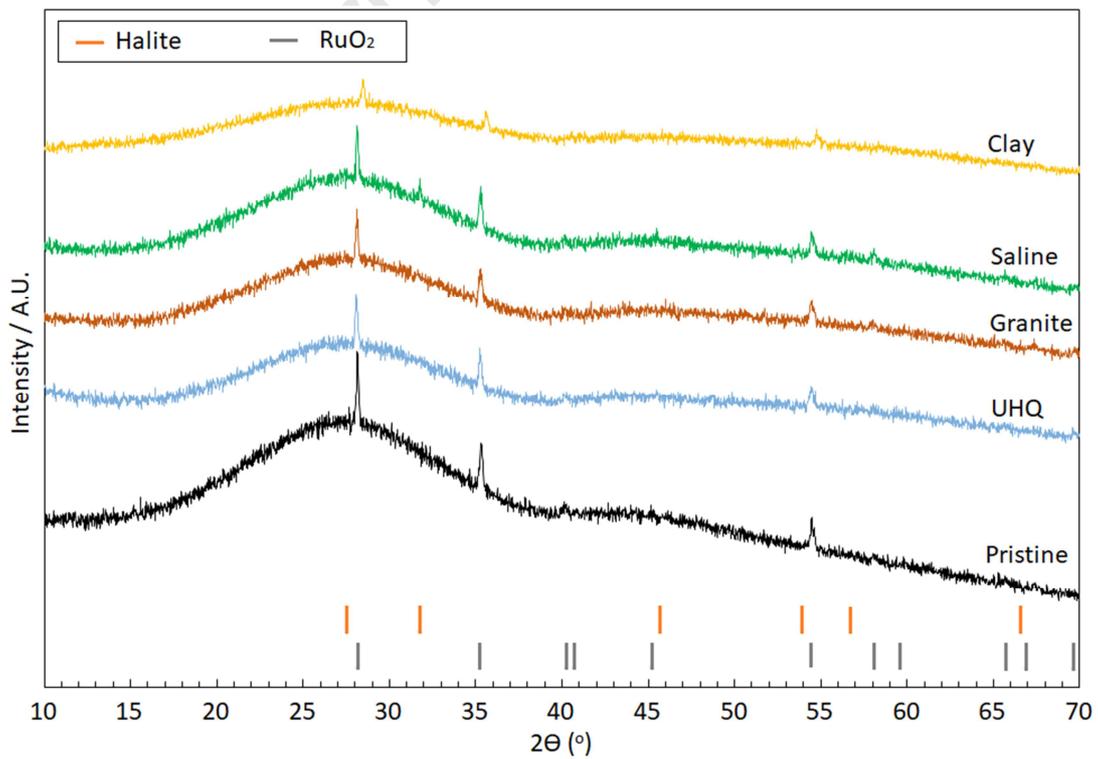
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174 Analysis of the glass surface after dissolution by SEM / EDS (Fig. 2, Supplementary Figure 2)
 175 confirmed the enrichment of Mg (and Al) at the surface of the glass leached in clay groundwater,
 176 and a series of precipitates, approximately 2 – 5 μm in size, with a clay-like morphology, were first
 177 observed after 28 d of dissolution (Fig. 2b). X-ray diffraction (Fig. 3) analysis of glass dissolved for 35
 178 d in each of the solutions did not reveal distinct crystalline phases (except for halite (NaCl), PDF 02-
 179 0818, in the saline groundwater), which is unsurprising given the low quantity of surface
 180 precipitates. Crystalline RuO_2 (PDF 21-1172) was observed in the pristine glass and in all glasses after
 181 35 d of leaching; this is an expected feature of the waste glass being studied. It was not possible to
 182 observe a silica gel layer on the surface of the glass samples at the resolution employed, with the
 183 possible exception of the glass corroded in the saline solution which, after 35 d, appeared to show a
 184 "peeled" dehydrated gel layer with the glass surface underneath (Fig. S2d).



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Fig. 2. BSE-SEM image and elemental mapping of CaZn MW28 after 35 d of leaching at 50 °C in clay groundwater.

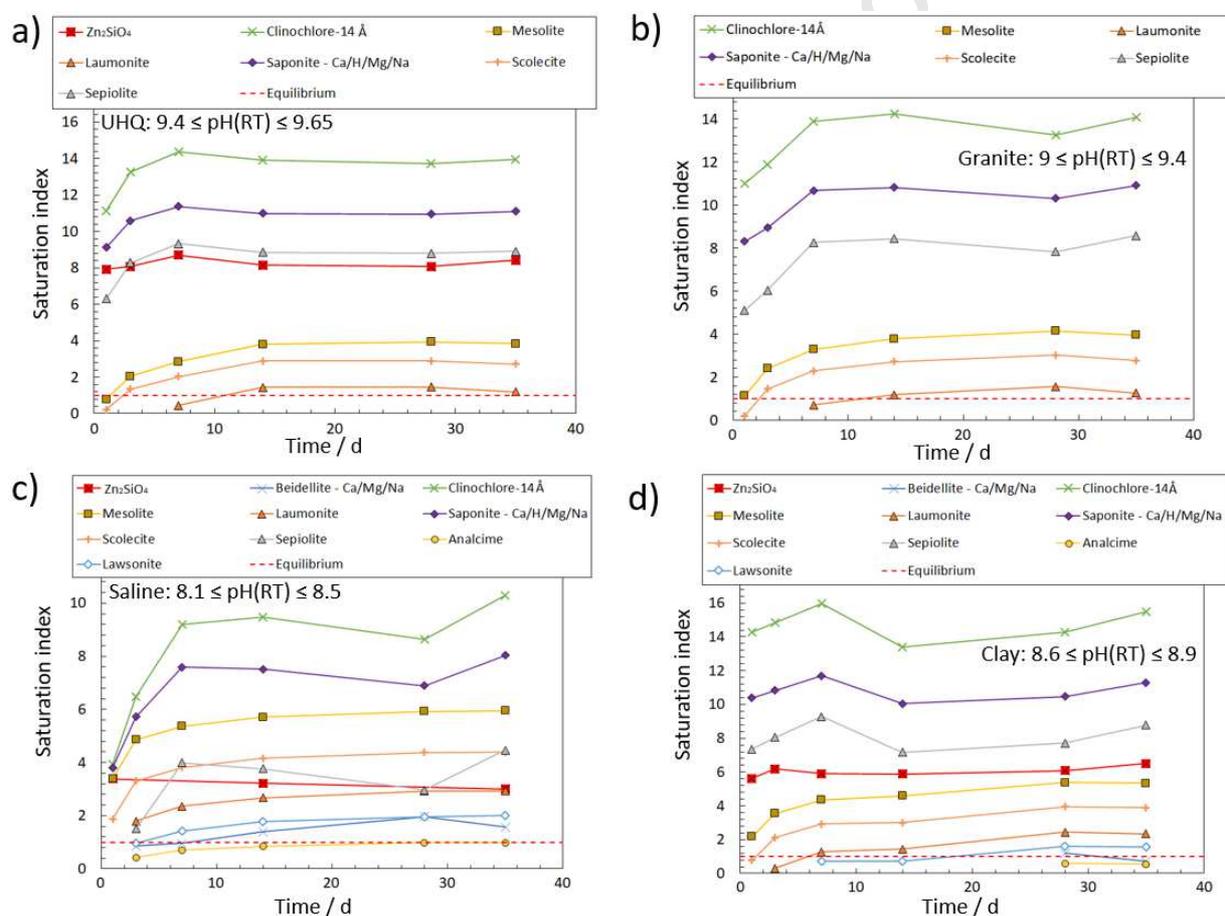


188

189 **Fig. 3.** XRD traces of CaZn MW28 particles pre- and post-35 d PCT-B leaching at 50 °C in UHQ and groundwater
190 compositions.

191 Further indication that there was rapid onset of silica saturation in all solutions, and that Mg-silicate
192 phases may have precipitated, is given by PHREEQ-C geochemical modelling of the solution
193 leachates. Figure 4 shows that the solutions of all experiments were predicted to be saturated with
194 respect to a number of phyllosilicate phases, rich in Mg, including saponite ($\text{Mg}_{3.165}\text{Al}_{.33}\text{Si}_{3.67}\text{O}_{10}(\text{OH})_2$)
195 and sepiolite ($\text{Mg}_4\text{Si}_6\text{O}_{15}(\text{OH})_2 \cdot 6\text{H}_2\text{O}$). Additionally, they were saturated with respect to a range of Ca-
196 bearing zeolites including mesolite ($\text{Na}_2\text{Ca}_2(\text{Al}_2\text{Si}_3\text{O}_{10})_3 \cdot 8\text{H}_2\text{O}$), scolecite ($\text{CaAl}_2\text{Si}_3\text{O}_{10} \cdot 3\text{H}_2\text{O}$) and
197 laumontite ($\text{CaAl}_2\text{Si}_4\text{O}_{12} \cdot 4\text{H}_2\text{O}$) at every time point, in accordance with the observed reduction in the
198 NL_{Ca} , which was particularly evident for the granite and saline groundwaters.

199



200 **Fig. 4.** PHREEQ-C geochemical modelling of the leachate from CaZn MW28 post 35 d PCT-B tests at 50 °C in (a) UHQ water;
201 (b) granite; (c) saline and; (d) clay groundwater solutions. The measured input pH(RT) range of each data set is provided.
202 Chemical formulae for each phase is provided in Table S1.
203
204

205 It is widely understood that Ca can be readily incorporated into silica gel layers, which has the effect
206 of strengthening the gel layer and making it more resistant to dissolution in the short-term [11, 24–
207 29]. The only experiment in which a silica gel layer was observed (and inferred from NL_{Ca} data) was
208 that performed in the saline solution, which had an initial Ca concentration of 19.9 mmol L^{-1} (Table

209 1). Unlike the other groundwaters, the NL_{Ca} was negative in the saline solution; since NL_i values are
 210 calculated by subtracting the concentration of Ca in the blank solution (Eqn. 1), this indicates that
 211 there was significant removal of Ca from the solution, either into the silica gel layer (Fig. S2d) or
 212 secondary precipitates. Furthermore, in contrast to all of the other solutions, the NL_{Mg} in the saline
 213 solution appeared to increase rather than decrease (Fig. 1d), suggesting that Mg leached from the
 214 glass and remained in solution rather than participating in silica gel charge compensation or
 215 secondary precipitate formation. This is in agreement with Aréna *et al.* [26] who reported that Ca
 216 incorporation into the gel layer of the ISG dissolved in Mg-rich clay groundwater was favoured over
 217 Mg incorporation.

218
 219 Interestingly, the clay groundwater contained significantly more Ca than the UHQ and granite
 220 solutions, yet the NL_{Ca} did not decrease, indicating that it was not removed from solution. This
 221 highlights the competition for Ca^{2+} and Mg^{2+} to form secondary silicate precipitates [16, 29–30], that
 222 favour Mg over Ca. This can be attributed to the more negative Gibbs Free Energy of hydration for
 223 Mg ($\Delta G_{Hyd}(Mg^{2+})$ -1830 kJ mol⁻¹, compared with ($\Delta G_{Hyd}(Ca^{2+})$ of -1505 kJ mol⁻¹ for Ca) [31], which
 224 shows that Mg-silicates are thermodynamically more likely to form. Although Ca has a more
 225 favourable adsorption constant than Mg ($K_{ads} = 10^{-5.9}$ for Ca compared with $10^{-6.2}$ for Mg) and a
 226 higher ligand exchange rate ($K_{ex} = 10^{8.5}$ for Ca and $10^{5.2}$ for Mg), both of which favour the
 227 incorporation of Ca within the silica gel layer of corroding glass [29, 32], if Mg ions react with
 228 dissolving silica from the glass before a gel layer can form, there can be no Ca-silica gel layer.

229
 230 The observation that the NL_{Mg} was significantly greater in the saline groundwater compared to all
 231 other solutions investigated may also be explained by the lower pH imposed by the saline system
 232 (Fig. 1f), inhibiting the formation of Mg-silicate phases [26]. This is consistent with the study by Thien
 233 *et al.* [8], who found that the precipitation of saponite ($Ca_{0.25}(Mg,Fe)_3((Si,Al)_4O_{10})(OH)_2 \cdot nH_2O$), was
 234 more efficient at pH 9, while at pH < 9, Mg was partially incorporated into the gel in a charge
 235 compensating role.

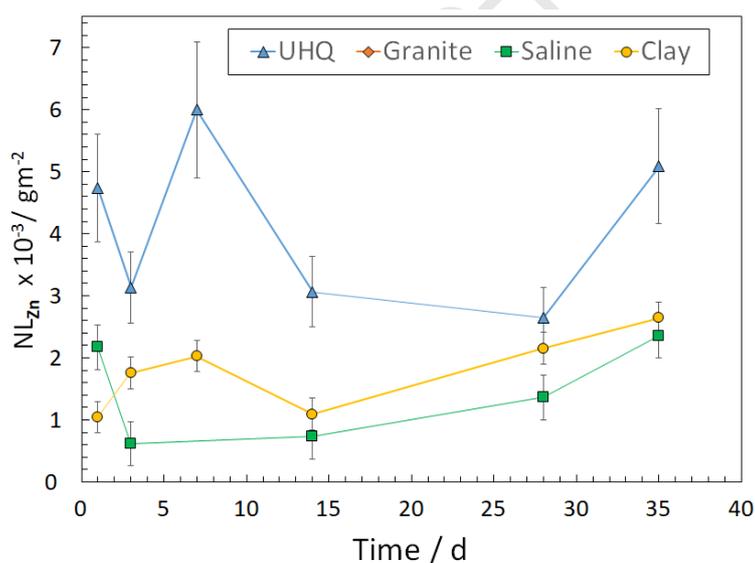
236
 237 Previous studies have shown the propensity for the precipitation of Zn-silicate phases, such as
 238 hemimorphite ($Zn_2(SiO_4) \cdot H_2O$), upon the dissolution of Zn-containing MW glasses [33-34].
 239 Furthermore, the hydrated zinc silicate phase, zincsilite ($Zn_3Si_4O_{10}(OH)_2 \cdot 4(H_2O)$), was proposed to
 240 form upon SON68 dissolution [35]. The Gibbs Free Energy of hydration of Zn^{2+} is more negative than
 241 that of Mg^{2+} ($\Delta G_{Hyd}(Zn^{2+})$ is -1955 kJ mol⁻¹ and $\Delta G_{Hyd}(Mg^{2+})$ is -1830 kJ mol⁻¹), indicating that if Mg-
 242 silicates are capable of forming, then it is highly likely that Zn-silicates will also form, should Zn be

243 dissolved from the glass. In a simple ternary borosilicate glass composition containing Zn, it was
 244 hypothesised that the precipitation of Zn-silicate prevents the re-condensation of silica to form a gel
 245 layer, sustaining glass dissolution [12], which agrees well with the behaviour observed in the present
 246 study.

247

248 In the granite groundwater solution there was no Zn detected, suggesting that Zn was not released
 249 to solution (Fig. 5). In the UHQ, saline and clay groundwater solutions, however, it was possible to
 250 measure Zn in solution but the concentrations were close to the detection limit of the instrument
 251 (approx. 0.01 ppm) and, as such, had large errors associated with their values. Despite the absence
 252 of evidence for Zn-silicates in SEM/EDS and XRD analyses in this short duration study, geochemical
 253 modelling of all solutions showed that Zn_2SiO_4 was predicted to be stable. While it is highly unlikely
 254 that this phase would form under the hydrothermal conditions of the dissolution experiments
 255 performed here, it shows that Zn-silicate phases could be stable.

256



257

258 **Fig. 5.** Normalised mass loss of Zn (NL_{Zn}) from CaZn MW28 particles during 35 d PCT-B leaching at 50°C in various
 259 groundwater compositions calculated from elemental concentration values (ppm) at the limits of instrument detection.

260

261 This study highlights the fact that different groundwaters exert a subtle influence on the short-term
 262 dissolution rate of CaZn MW28 glass. Rapid onset of silica saturation and Mg-silicate precipitation
 263 [9], as predicted by geochemical modelling of the solutions and tentatively identified by SEM/EDS, is
 264 the postulated reason for elevated dissolution rates, where Mg from both the glass and the solution
 265 likely prevents the re-condensation of silica to form a gel layer, sustaining glass dissolution at a rate
 266 similar in magnitude to the “initial” rate. The same solubility limiting phases were predicted to form
 267 in all solutions (Fig. 4), therefore, the differences in dissolution rate may be attributed to the kinetics
 268 of formation and the quantity of the elements in each solution. The exception is saline groundwater,

269 which may have promoted the formation of a passivating silica gel layer (Fig. S2d), did not show a
270 propensity for Mg-silicate formation and had amongst the lowest dissolution rates.

271

272 The dissolution behaviour observed here is not well described by any of the accepted dissolution
273 rate definitions: the initial rate is widely defined as the congruent, linear release of elements at the
274 maximum rate controlled by hydrolysis of the silica network [17]; the residual rate occurs once the
275 solution is saturated with respect to silica and glass dissolution is no longer driven by silicate
276 hydrolysis but by diffusion processes (of ions through the silica gel layer) [17], while the massive
277 precipitation of secondary silicates (almost exclusively zeolite phases) and rapid dissolution of the
278 glass is known as “rate resumption”, which is typically associated with a significant pH increase [36].
279 In contrast, in the groundwater solutions of the present study, the CaZn MW28 glass apparently
280 underwent “initial” rate dissolution while under conditions of silica saturation, promoted by
281 aggressive precipitation of secondary Mg-phylosilicate phases, with no change in pH. Seemingly all
282 of the currently defined stages of dissolution occurred simultaneously, thus an alternative definition
283 for such behaviour is required.

284

285 As radioactive waste geological disposal programmes mature, and dissolution rates are determined
286 in increasingly complex groundwater solutions, this study serves to highlight the need for further
287 investigation of systems containing divalent cations and their influence on glass dissolution
288 behaviour. This is also important for new glass compositions developed to progress the
289 decommissioning of nuclear facilities, such as the incorporation of Zn in POCO glass compositions. In
290 particular, further detailed studies of the role of Mg and Zn-silicate precipitation in glass dissolution,
291 in conjunction with appropriate thermodynamic databases, are required to understand whether Zn-
292 silicate influences glass dissolution by the same mechanism, and to the same magnitude, as Mg-
293 silicate precipitation, and to determine if there is an additive [37] or competitive effect when both
294 Mg and Zn are present.

295

296

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298

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306

307 Data availability

308

309 The raw data required to reproduce these findings are available upon request.

310

311

312 References

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Appendix. Supplementary data

Uncertainty in NL_i was calculated by the standard deviation of the sum of uncorrelated random errors [16] according to:

$$\sigma_f = \sqrt{\sum_{i=1}^n \left(\frac{\partial f}{\partial x_i}\right)^2 \sigma_i^2} \quad [S1]$$

where σ_f is the standard deviation of $f(x_i)$, where x_i is the parameter pertaining to element i and σ_i is the standard deviation of parameter x_i . Substituting Equation 1 (main text) into Equation S1, and using a relative error, $\hat{\sigma}_{NL_i} = \frac{\sigma_{NL_i}}{NL_i}$ gives:

$$\hat{\sigma}_{NL_i} = \sqrt{\frac{(\hat{\sigma}_{C_{i,S}C_{i,S}})^2 + (\hat{\sigma}_{C_{i,b}C_{i,0}})^2}{(C_{i,S} - C_{i,0})^2} + \hat{\sigma}_{f_i}^2 + \hat{\sigma}_{SA/V}^2} \quad [S2]$$

from which the experimental uncertainty on r_i can be derived. Relative errors of 10%, 10%, 3% and 15% were ascribed to C_i , $C_{i,0}$, f_i and SA/V respectively.

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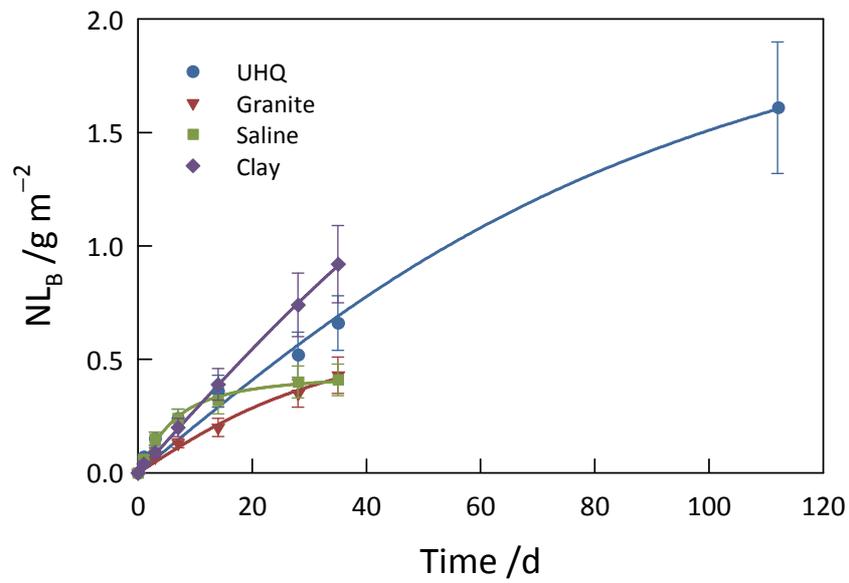
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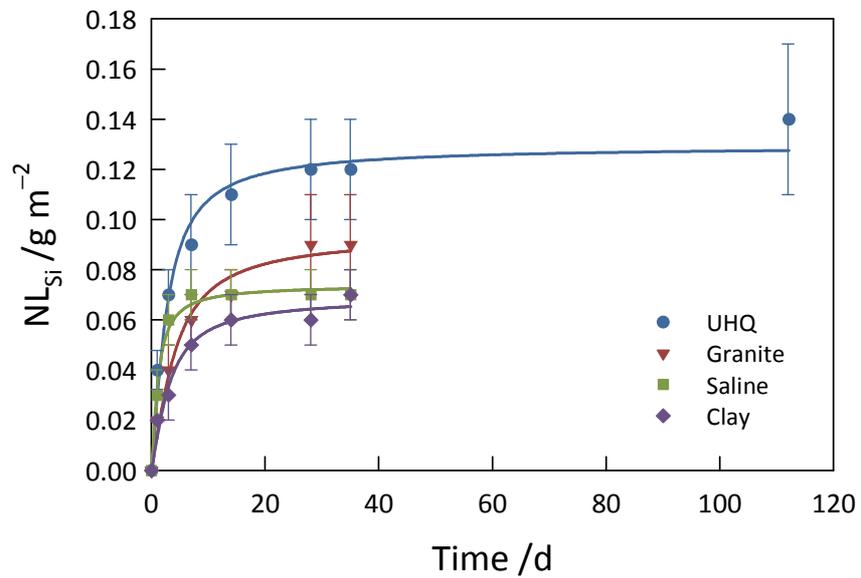
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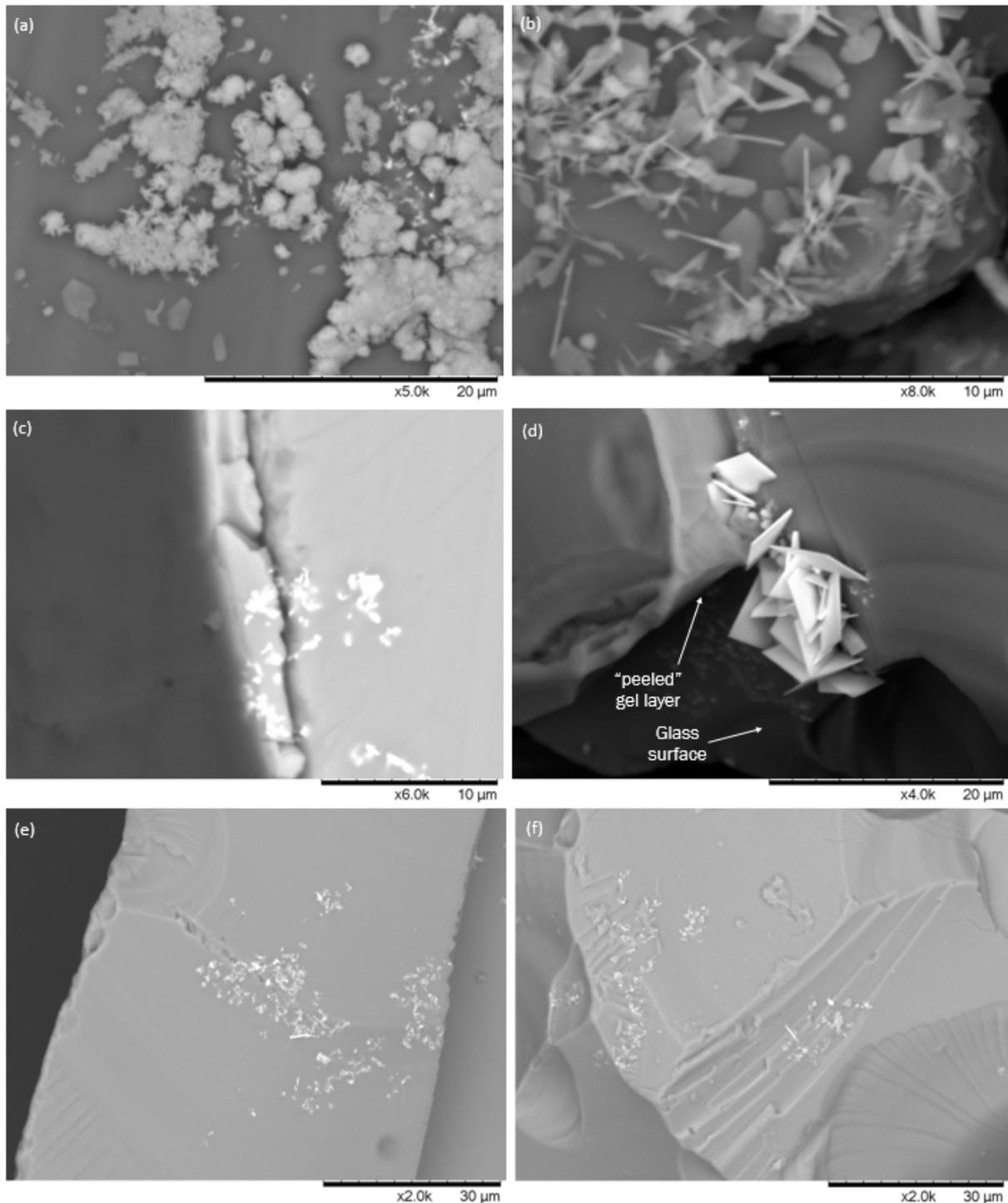
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449 **Figure S1.** (a) Inverse tan empirical fit to the normalised mass loss (B & Si) data; and (b) PCT-B tests for CaZn
 450 MW28 at 50°C, SA/V = 2,000 m⁻¹, in various groundwater solutions and UHQ water. Note the additional data
 451 point at 112 d for the UHQ test only. Uncertainty in NL_i was calculated by the standard deviation of the sum of
 452 uncorrelated random errors (Eqns. 1, S1 & S2).

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Figure S2. BSE-SEM images of the CaZn MW28 glass surface after 35 d of dissolution in groundwater at 50°C showing (a) and (b) the range of crystalline phases precipitated on the surface of glass dissolved in clay groundwater; (c) the absence of a distinct gel layer at the surface of the glass dissolved in clay groundwater (cross section image); (d) possible evidence for a dehydrated silica gel layer peeled back from the glass surface, in addition to halite crystallites for glass dissolved in saline groundwater; (e) glass surface from the UHQ water and (f) granite tests, which did not show any surface precipitation or gel layers (the bright phases are crystallites of RuO₂).

468 **Table S1.** Chemical formulae for all predicted phases from PHREEQ-C geochemical modelling
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Mineral phase	Chemical formula
Analcime	$\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$
Beidellite - (Ca,Mg)	$(\text{Ca},\text{Mg})_{0.165}\text{Al}_{2.33}\text{Si}_{3.67}\text{O}_{10}(\text{OH})_2$
Beidellite - Na	$\text{Na}_{0.61}\text{Al}_{4.7}\text{Si}_{7.32}\text{O}_{20}(\text{OH})_4$
Clinochlore - 14 Å	$\text{Mg}_5\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_8$
Laumontite	$\text{CaAl}_2\text{Si}_4\text{O}_{12} \cdot 4\text{H}_2\text{O}$
Lawsonite	$\text{CaAl}_2\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$
Mesolite	$\text{Na}_{0.676}\text{Ca}_{0.657}\text{Al}_{1.99}\text{Si}_{3.01}\text{O}_{10} \cdot 2.647\text{H}_2\text{O}$
Saponite – Ca	$\text{Ca}_{0.165}\text{Mg}_3\text{Al}_{0.33}\text{Si}_{3.67}\text{O}_{10}(\text{OH})_2$
Saponite – H	$\text{H}_{0.33}\text{Mg}_3\text{Al}_{0.33}\text{Si}_{3.67}\text{O}_{10}(\text{OH})_2$
Saponite – Mg	$\text{Mg}_{3.165}\text{Al}_{0.33}\text{Si}_{3.67}\text{O}_{10}(\text{OH})_2$
Saponite – Na	$\text{Na}_{0.33}\text{Mg}_3\text{Al}_{0.33}\text{Si}_{3.67}\text{O}_{10}(\text{OH})_2$
Scolecite	$\text{CaAl}_2\text{Si}_3\text{O}_{10} \cdot 3\text{H}_2\text{O}$
Sepiolite	$\text{Mg}_4\text{Si}_6\text{O}_{15}(\text{OH})_2 \cdot 6\text{H}_2\text{O}$
Zinc silicate	Zn_2SiO_4

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Short communication: The dissolution of UK simulant vitrified high-level-waste in groundwater solutions

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: