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1 **Assessing the durability of nuclear glass with respect to silica controlling**
2 **processes in a clayey underground disposal**

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7

8 **ABSTRACT**

9 The long-term behaviour of vitrified high-level waste in an underground clay repository was
10 assessed by using the reactive transport model HYTEC with respect to silica diffusion, sorption
11 and precipitation processes. Special attention was given to the chemical interactions between
12 glass, corroded steel and the host-rock considering realistic time scale and repository design. A
13 kinetic and congruent dissolution law of R7T7 nuclear glass was used assuming a first-order
14 dissolution rate, which is chemistry dependent, as well as a long-term residual rate. Without
15 silica sorption and precipitation, glass dissolution is diffusion-driven and the fraction of altered
16 glass after 100,000 years ranges from 5% to 50% depending on the fracturation degree of the
17 glass block. Corrosion products may limit glass dissolution by controlling silica diffusion,
18 whereas silica sorption on such products has almost no effect on glass durability. Within the
19 clayey host-rock, precipitation of silicate minerals such as chalcedony may affect glass durability
20 much more significantly than sorption. In that case, however, a concomitant porosity drop is
21 predicted that could progressively reduce silica diffusion and subsequent glass alteration.

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24 **INTRODUCTION**

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26 The alteration or dissolution rate of borosilicate glasses depends on the dissolved silica
27 concentration in the bulk solution. As the aqueous concentration rises, the rate decreases down to
28 a long-term value that is many orders of magnitude lower than the initial rate. In addition to a
29 control by chemical affinity, this significant decrease results from the formation of a dense
30 protective gel acting as a diffusive barrier at the glass/solution interface [1]. Whatever the
31 underlying processes, several lab experiments have proved that glass dissolution is clearly
32 enhanced by the presence of clay minerals, and to a lesser extent, of steel corrosion products [2-
33 4]. Silica diffusion followed by sorption and/or precipitation are potential underlying
34 mechanisms, albeit their long-term relevance is still a debated question.

35 Previous studies have addressed the lifetime of nuclear glass under clayey disposal
36 conditions according to analytical models [5,6]. In the present study, the durability of vitrified
37 high-level waste (HLW) is assessed by using a reactive transport code – i.e., a numerical code
38 coupling chemistry and hydrodynamics – with respect to silica diffusion, sorption and
39 precipitation processes. Numerical modelling provides not only means to extrapolate glass
40 dissolution data to long periods of time and to representative repository designs in terms of
41 geometry and material masses, but also to consider detailed chemical processes at a mechanistic
42 level for a full set of interacting chemical elements. A special attention is given to the chemical
43 interactions between glass, corroded steel and the clayey host-rock in the near-field.

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47 **DISPOSAL AND MODELLING FEATURES**

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49 **Disposal concept and materials**

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51 The host-rock formation properties are those of stiff clays such as can be found in France: an
52 indurated claystone with low water content and diffusion as the predominant transport process.

53 A common effective diffusive coefficient, $D_{\text{eff-HR}}$, of $2 \times 10^{-11} \text{ m}^2/\text{s}$ was considered for all the
54 dissolved species. The mineralogy is characterized by a high content in clay minerals, quartz,
55 calcite, dolomite and pyrite for a cation exchange capacity (CEC) of 20 meq/100g of rock.

56 The disposal concept consists of horizontal tunnels of small diameters consolidated by
57 linings of steel but without backfill materials. The excavated damaged zones ($D_{\text{eff-EDZ}} = 1 \times 10^{-10}$
58 m^2/s) are thus restricted to a dozen of centimetres only. The waste package consists of a nuclear
59 glass zone with a diameter of 0.44 m (glass block + interstices), and a low alloyed steel canister,
60 0.055 m thick. The liner is also made of low alloyed steel and has a thickness of 0.025 m. An
61 average temperature of 50°C was considered in the calculations.

62 The steel waste canister and the tunnel lining were both assumed to be corroded after 1,000
63 years allowing for water to saturate the medium and diffusive transfers to occur in the waste
64 zone. Magnetite was introduced as the main corrosion product, but steel corrosion mechanisms
65 were not explicitly taken into account in the modelling. Magnetite, which has a higher molar
66 volume than metallic iron, was assumed to fill the interstice voids. It is not obvious to attribute
67 an effective diffusion coefficient to this magnetite-enriched zone. A relatively high $D_{\text{eff-mag}}$ value
68 of $1 \times 10^{-10} \text{ m}^2/\text{s}$ was considered in the present calculations, though a less conservative value of
69 $1 \times 10^{-11} \text{ m}^2/\text{s}$ was also selected in test-case III for sensitivity analysis as explained below.

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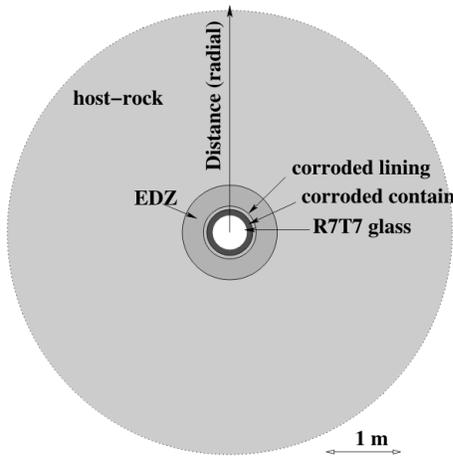


Figure 1. Simplified disposal configuration considered in the calculations (assuming radial symmetry).

71 **Modelling approach and data**

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73 The calculations presented herein were carried out with the reactive transport code
74 HYTEC[7] in radial symmetry, i.e. equivalently to a 2-D transversal cross-section of the disposal
75 tunnel (see Figure 1). All simulations were based on the local equilibrium assumption, except for
76 glass dissolution. The thermodynamic data were compiled from the EQ3/6-LLNL database.
77 Silica sorption was simulated according to the double layer surface complexation theory. A data
78 set has been obtained experimentally for magnetite [8,9], but derived from a distribution
79 coefficient ($K_d = 0.05 \text{ kg/m}^3$) for the host-rock [3,10]. The sorption data (ionic exchange and
80 surface complexation) were taken from literature [11,12]. Sorption was only taken into account
81 for Ca-H-K-Na-Si, and not for the other glass constituents, in a first approximation. Precipitation

82 of neoformed silicate phases was not allowed in the entire system, neither in the waste zone nor
83 in the host-rock, except for test-case IV as explained in the results section.

84 A simplified R7T7 glass composition was considered including the glass network formers
85 B-Si-O, the modifiers Na-Ca and two radioactive elements Cs-I. Glass alteration kinetics start
86 with fast interdiffusion and network hydrolysis reactions to become controlled by the formation
87 of a gel layer in a second step. These processes can be explicitly simulated in very small-scale
88 models [13]. Lumping these small-scale processes together in terms of a global parametric kinetic
89 rate-law, however, has the advantage of being operational for models at the scale of a waste-
90 disposal. Assuming congruent dissolution of the glass matrix, the kinetic process was described
91 by the combination of a first-order dissolution rate R [3], dependent of the bulk solution
92 chemistry (pH, orthosilicic acid activity),

$$R = k S \left(H^+ \right)^{-0.4} \left(1 - \frac{(H_4SiO_4)}{C^*} \right) \quad (1)$$

94 and a long-term residual dissolution rate, R_r , which is chemistry independent [14],

$$R_r = k_r S \quad (2)$$

96 The parenthesis stands for the species activity in the bulk solution, k and k_r are dissolution rate
97 constants, C^* is a saturation threshold for which the first-order dissolution stops, and the total
98 surface S depends on the degree of fracturation of the vitrified waste. The dissolution rate terms
99 are both temperature-dependent. Table I gives the parameter values used throughout this paper.

100 The approach followed here is similar, though simplified, compared to the LIXIVER-2
101 model [3]. Silica diffusion and sorption within the gel layer are not explicitly taken into account
102 in our model and, consequently, there is no incongruent leaching of silica and boron/alkalis from
103 the glass. Furthermore, an Elementary Representative Volume (ERV) approach was used for

104 spatial discretization. Water intrusion and glass dissolution were allowed within the whole glass
 105 zone, due to the cracking of the R7T7 block, and not at the glass/canister boundaries only.
 106 With this respect, the effective diffusion coefficient, $D_{\text{eff-glass}}$, assumed for silica and the other
 107 glass elements inside the (fractured) glass zone was $5 \times 10^{-10} \text{ m}^2/\text{s}$. The common parameter S of
 108 Eqs (1) and (2) corresponds – conservatively - to the entire available surface, including the outer
 109 cylindrical surface and the internal fracture surfaces. It is worth mentioning that, for most of the
 110 calculations presented here, the silica saturation threshold was reached inside the glass fractured
 111 zone and the glass matrix dissolved in these inner zones according to the residual rate only.

112

113 **Table I.** Kinetic parameters related to R7T7 glass dissolution, Eqs 1 and 2.

T	50° C	
k	$1.50 \cdot 10^{-5} \text{ g/m}^2/\text{d}$	e.g. $k(\text{H}^+)^{-0.4} = 10^{-2} \text{ g/m}^2/\text{d}$ at pH = 7
k_r	$5.00 \cdot 10^{-5} \text{ g/m}^2/\text{d}$	
C^*	$2.50 \cdot 10^{-3} \text{ mol/L}$	
Total surface S (per glass block)	10 m^2	Fracturation ratio ^(*) = 5
	110 m^2	Fracturation ratio = 60

114 (*) Fracturation ratio FR = total surface/surface of the unfractured glass block.

115 **Table II.** Altered fraction (%) of the vitrified waste with respect to silica controlling processes.

	2,000 years	10,000 years	100,000 years
Test-case I (diffusion driven only)			
fracturation rate = 5	0.2	1.1	7.0
fracturation rate = 60	0.5	5.0	50.2

Test-case II (Si sorption on corroded steel)

fracturation rate = 5	0.2 - 0.45 ^(*)	1.1 - 1.35 ^(*)	7.0 - 7.25 ^(*)
fracturation rate = 60	0.5 - 0.75 ^(*)	5.0 - 5.25 ^(*)	50.2 - 50.45 ^(*)

Test-case III (Si sorption on corroded steel
and clayey host-rock)

fracturation rate = 5	1.0	3.5	19.5
fracturation rate = 60	1.0	5.5	50.7

Test-case IV (Si precipitation in the clayey
host-rock)

fracturation rate = 60,

$D_{\text{eff-magnetite}} = 1 \times 10^{-10} \text{ m}^2/\text{s}$	1.9	65.0 ^(**)	-
$D_{\text{eff-magnetite}} = 1 \times 10^{-11} \text{ m}^2/\text{s}$	0.5	3.1	-

116 (*) Without considering pre-equilibrium of magnetite sorption site with host-rock dissolved silica.

117 (**) In the penalizing assumption of no feedback of mineral precipitation on diffusive transfers.

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120 **RESULTS AND DISCUSSION**

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122 **Diffusion-driven base test-case**

123

124 Four test-cases are considered introducing step by step the complexity of the chemical near-field

125 interactions. Test-case I focuses on silica diffusion through the corroded steel components and

126 within the host-rock without silica sorption and precipitation. For a minor fracturation ratio, the

127 global proportion of altered glass remains low (~ 7% after 100,000 years, see Table II) in

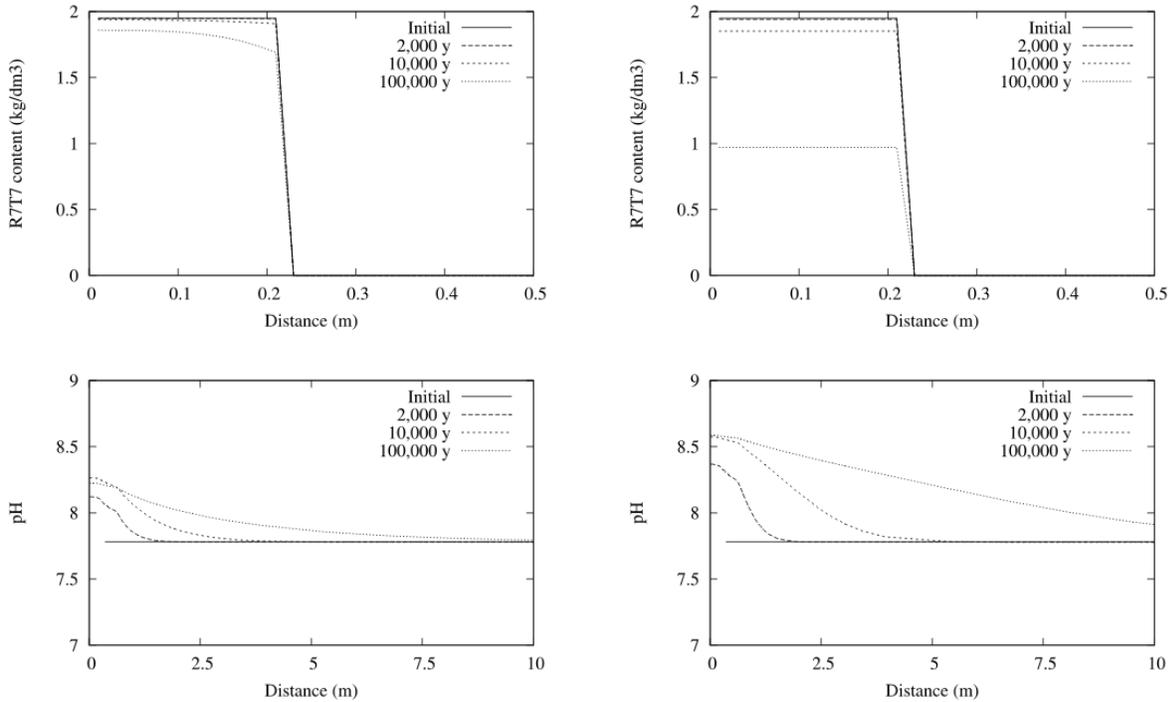
128 agreement with glass lifetimes published in previous analytical studies [5,6]. Alteration is driven
129 by silica diffusion, i.e. relatively fast at the beginning then followed by a gradual decrease. The
130 diffusion process is mainly active at the outer parts of the vitrified waste zone open to the near-
131 field environment (see Figure 2). The dissolved silica activity in solution remains slightly below
132 the saturation term C^* in such zones corresponding to a very weak first-order dissolution rate. In
133 contrast, saturation is reached in the inner volumes of the fractured glass, i.e. $(\text{H}_4\text{SiO}_4) \geq C^*$,
134 preventing any R-type dissolution. The residual rate R_r which is independent on aqueous silica
135 activities is nevertheless active in such inner zones. Calculations indicate a more pronounced
136 effect when the fracturation state raises from 5 to 60, with a total altered fraction close to 50% in
137 100,000 years. Alteration remains, however, moderate over the first 10,000 years as reported in
138 Table II, a time period corresponding to the highest radionuclide activity. A higher total surface
139 S speeds up glass dissolution leading to a rapid saturation with respect to C^* and, consequently,
140 to a residual dissolution and flat decrease in R7T7 content in the entire glass zone (Figure 2).

141 The R7T7 glass behaves like an alkaline mineral, leading to an increase of pH in the bulk
142 solution with dissolution. Figure 2, however, shows almost no modification of the near-field pH
143 for test-case I whatever the fracturation ratio. This is due to a dilution effect as well as buffering
144 capacities of the host-rock through proton exchange with surface sites of the clay-minerals.

145

Fracturation ratio = 5

Fracturation ratio = 60



146

147 **Figure 2.** Evolution with time of R7T7 content (top) and pH profiles (bottom) for the diffusion-
 148 driven base case (test-case I) as a function of the fracturation ratio of the glass block.

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150 **Effects of steel corrosion products**

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152 The corroded container and liner, located at the vicinity of the vitrified waste, are the first
 153 materials that can control dissolved silica and glass alteration. Silica sorption on magnetite was
 154 therefore introduced in test-case II. At disposal time scales, sorption on magnetite has almost no
 155 effect on glass dissolution. The surface sites of silica are saturated by glass dissolution in one
 156 hundred years after canister failure. In comparison with test-case I, the total altered fraction is
 157 incremented by 0.25% only (Table II). Furthermore, the corrosion of the steel materials will most
 158 probably progress from the host-rock side. Hence, silica and others elements will migrate from

159 the host-rock and saturate the magnetite sorption sites before glass dissolution. For this reason,
 160 the results are found almost identical to those of the first test-case, if considering pre-saturation
 161 of the magnetite sorption sites. The role of magnetite on glass alteration enhancement could be
 162 neglected provided that precipitation of iron silicate minerals, in addition to sorption processes,
 163 does not take place. Silica precipitation may indeed amplify glass dissolution. Another point,
 164 positive this time, is that long-term expansion of corrosion product and subsequent porosity drop
 165 may generate a more efficient barrier against silica diffusion than assumed in the present
 166 calculations. This point is examined in the next section.

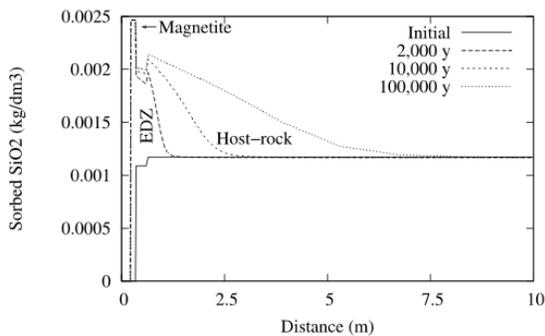
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168 **Silica controlling processes by the clayey host-rock**

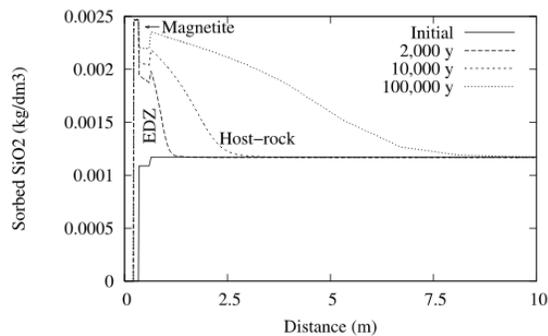
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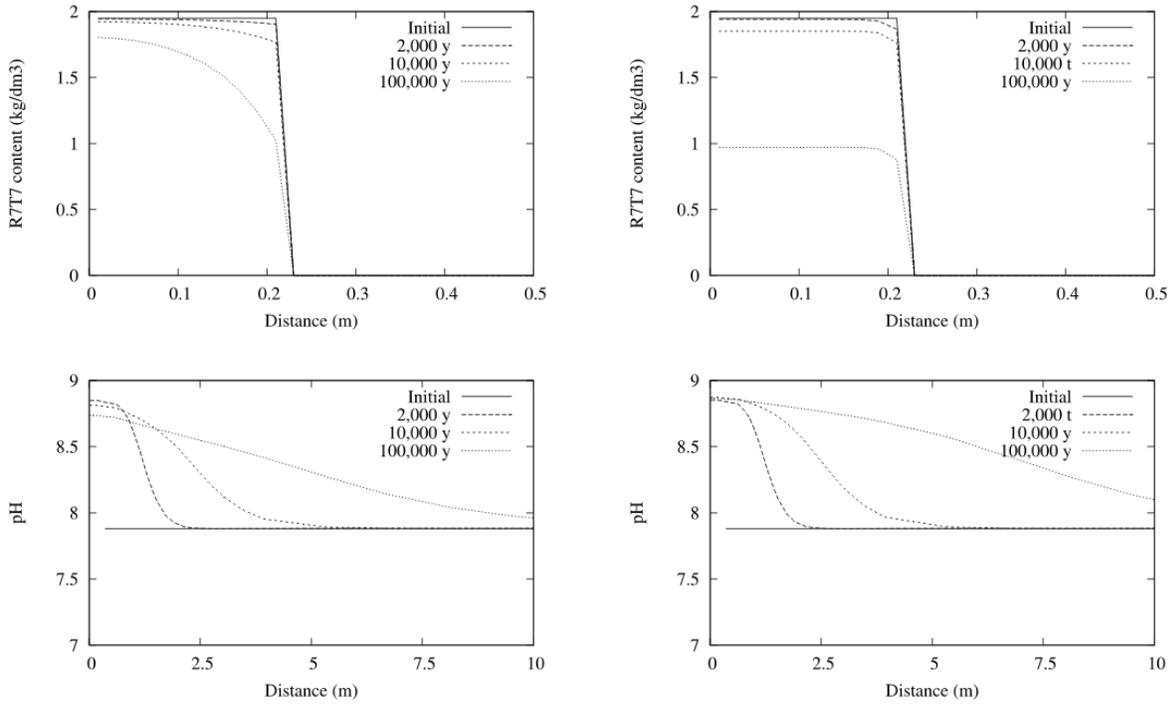
170 The third and fourth test-cases aim at investigating the possibility of a host-rock behaving
 171 like a silica sink by sorption and precipitation of new phases respectively, thus increasing the
 172 glass dissolution rate. Figure 3 clearly indicates that the profile of silica sorbed on host-rock

Fracturation ratio = 5



Fracturation ratio = 60





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174 **Figure 3.** Evolution with time of silica sorption on corroded steel and the host-rock clay
 175 minerals, R7T7 contents and pH profiles for test-case III.

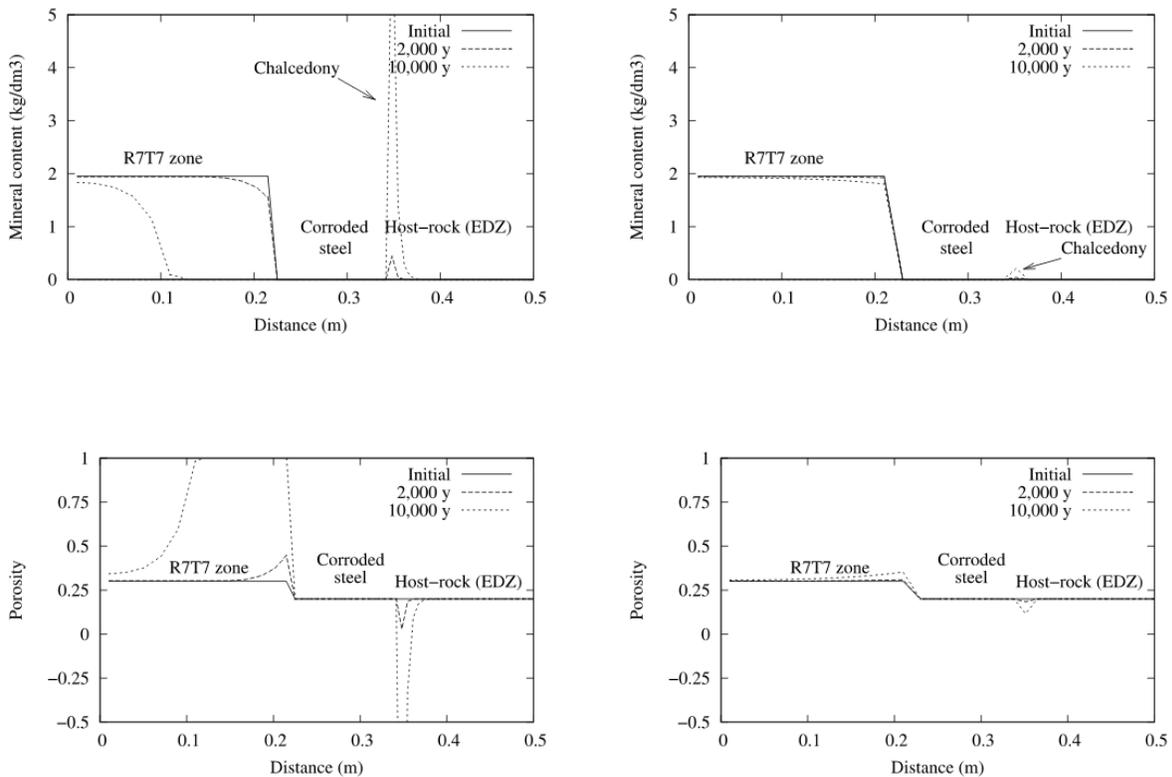
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177 increases with time contrarily to the magnetite one. However, the overall process of silica
 178 migration and sorption is still diffusion-controlled. Migration is particularly well-restrained due
 179 to the low effective diffusion coefficient of the host-rock. The total altered glass fraction only
 180 reaches approximately 10% after 100,000 years for the lowest fracturation ratio (see Table II).
 181 The dissolution process is more active at the boundary of the vitrified waste zone open to the
 182 near-field environment than in the inner zones, likewise test-case I, but in a more accentuated
 183 manner (Figure 3). Glass dissolution is essentially driven by the residual rate in the highest
 184 fracturation case. As a result, silica sorption has only a slight effect on dissolution as discussed

185 above. The pH is still buffered by the host-rock minerals, albeit slightly higher compared with
 186 test-case I (Figure 3).
 187 These findings are not significantly changed while fitting the surface complexation constant of
 188 silica on a Kd value one order of magnitude higher. On the other hand, the results seemed to be
 189 more sensitive to the specific surface of clay minerals (20 m²/g was assumed in the present
 190 calculations), i.e. their total number of sorption sites. On the long-term, sorption processes in the

$D_{\text{eff}}(\text{magnetite}) = 1 \times 10^{-10} \text{ m}^2/\text{s}$

$D_{\text{eff}}(\text{magnetite}) = 1 \times 10^{-11} \text{ m}^2/\text{s}$



191
 192 **Figure 4.** *Top:* progressive alteration of the vitrified waste driven by silicate mineral
 193 precipitation in the host-rock (fracturation ratio = 60, test-case IV) with respect to the value
 194 assigned to the effective diffusion coefficient of elements in the corrosion products; *bottom:*
 195 evolution of the porosity calculated according to the mineral contents but without feedback on
 196 diffusion parameters (which can lead to unrealistic negative values for porosity).

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host-rock may act as precursors for precipitating silicate minerals such as chalcedony at 50° C [2,4]. As shown in Figure 4, precipitation may affect glass durability much more than sorption in agreement with conclusions drawn in previous modelling studies [5,6]. However, the intensity of glass alteration is dependent on the effective diffusion coefficient $D_{\text{eff-mag}}$ considered for corrosion products. For the lowest $D_{\text{eff-mag}}$, the altered glass fraction remains low. For the highest $D_{\text{eff-mag}}$, the altered glass fraction already approaches 65% after 10,000 years when chalcedony can precipitate. The pH simultaneously increases to a value close to 10, which further catalyses glass dissolution according to Eq 1. At the same time, the precipitation of chalcedony, which is restricted to a narrow zone in the host-rock, leads to a significant drop of porosity (Figure 4). Calculations indicate that a porosity drop reduces diffusive transfer and glass alteration after a few thousand years already. The feedback of mineral precipitation on diffusive transfers was not explicitly taken into account in this first modelling work. At last, Figure 4 also shows that, depending on the assumed effective diffusion coefficient, corrosion products may limit glass dissolution by controlling silica diffusion.

CONCLUSIONS

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Sensitivity calculations have been performed according to a modelling study based on a coupled chemistry transport code to assess of the effect of sorption and precipitation processes on R7T7 glass durability. An operational kinetic law was used to describe glass dissolution at realistic time scales and conforming the repository design. The related parametric rate-law

220 should be updated with respect to new experimental data, since the model is unable to provide by
221 itself for an accurate chemical description of the gel evolution in near-field disposal conditions.
222 This paper focused on silica processes involved in the near-field of the disposal, but other major
223 glass constituents such as aluminium, characterized by a low solubility, should be considered in
224 further calculations. Without silica sorption and precipitation, glass dissolution is diffusion-
225 driven and the fraction of altered glass after 100,000 years ranges from 5% to 50% depending on
226 the fracturation degree of the glass block. Steel corrosion products limit glass dissolution by
227 controlling silica diffusion, whereas silica sorption on magnetite has almost no effect on glass
228 durability. Within the host-rock, precipitation of silicate minerals such as chalcedony may affect
229 glass durability more considerably than sorption. In that case, however, a concomitant porosity
230 drop is predicted that could progressively reduce diffusion and subsequent glass alteration.

231

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235

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