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SON68 glass alteration enhanced by magnetite

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Abstract

This paper reports experimental and modeling results of SON68 glass / magnetite interactions while in contact with synthetic groundwater from a clay environment. It is shown that magnetite enhances glass alteration, first by the sorption of Si released from the glass onto magnetite surfaces, then by a second process that could be the precipitation of an iron silicate mineral or the transformation of magnetite into a more reactive phase like hematite or goethite. This study globally suggests a detrimental effect of magnetite on the long-term durability of nuclear glass in geological disposal conditions.

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Introduction

Reliable prediction of material durability on the very long term is one of the most challenging issues in the material, earth, and environmental sciences. The ultimate goal of the present study is to quantitatively evaluate the impact of magnetite on the long-term durability of borosilicate glass. Some countries (e.g., France, Japan) intend to pack high-level radioactive waste in thick carbon steel overpacks and dispose of the packages in a deep geological repository [1,2]. Different corrosion products are likely to form in repository conditions: iron oxides, carbonates, hydroxycarbonates, silicates, etc. Here, we have chosen to perform glass alteration experiments in synthetic groundwater in equilibrium with the Callovo-Oxfordian clay (considered as a potential host rock for radioactive waste disposal in France), in contact with magnetite. Geochemical modeling, including the GRAAL model for glass dissolution [3] is used to help interpret the experimental data.

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1. Materials and Methods

SON68 glass has been altered in static mode at 50°C in a synthetic clay-based groundwater, in contact with commercial magnetite (Puratronic, Alfa Aesar). A blank test without magnetite was also run (Table 1). The glass composition and preparation methods are given in [4]. Glass powder (63-125 µm) was mixed with magnetite and placed together with synthetic groundwater in stainless steel vessels equipped with two valves for solution sampling. Eh, pH and carbonate concentration were adjusted by bubbling 0.9 Ar/0.05 H2/0.05 CO2 gas before closing the reactor.

The sorption capacity of magnetite for Si is 19 ± 14 µmolSi.g-1 at room temperature and pH 8.5 [5]. The groundwater composition was (mmol.L⁻¹)[6]: Cl: 40.99 ; S: 14 ; Na: 42.02 ; K: 1 ; Ca: 9.91 ; Mg: 4.1 ; Sr : 0.2 ; Si 0.35 ; HCO₃⁻; 3.8. The resulting pH and Eh are 6.7 and around -200 mV/SHE, respectively.

During the tests, samples of about 1 mL were taken at different times and analyzed by ICP-AES after filtration and acidification. The pH was measured at 50 °C just after sampling.

Table 1. Experimental matrix. SSA corresponds to the specific surface area determined using the BET method.

<table>
<thead>
<tr>
<th></th>
<th>Blank</th>
<th>G+M</th>
<th>G+2M</th>
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<tbody>
<tr>
<td>Mglass (g) – SSA = 0.55 m².g⁻¹</td>
<td>6</td>
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</tr>
<tr>
<td>Mmagnetite (g) – SSA = 1.8 m².g⁻¹</td>
<td>-</td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>Vsolution (mL)</td>
<td>45</td>
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The system was modeled with the geochemical code Hytec [7] using the glass dissolution model GRAAL[3] which calculates the amount of dissolved glass according to the reactivity of a reactive interphase (PRI). This layer (a Si-Al phase in the current version of the model) forms by diffusion and dissolves following a classical TST type rate law. The gel is simulated via 5 simple end-members. For this study, the GRAAL equations were parameterized at 50°C from independent leaching tests as previously done at 90°C [3,4], resulting in the following parameter values: k⁺ = 4.4 10⁻⁷ g.m⁻².d⁻¹, n = 0.4, Ea = 76 kJ.mol⁻¹, D₀ = 9.3 10⁻²⁴ m².s⁻¹, n' = -0.65, Ea' = 94.7 kJ.mol⁻¹, LogK₅₆₅PRI = 2.73, LogK₅₆₅⁻ < -9.18, LogK₅₆₅Ca = -28, LogK₅₆₅AlNa = -8.5, LogK₅₆₅CaAl = 1.68, LogK₅₆₅Na = -2.64. Note that the composition of the 6 end-members is the same as those for 90°C, and their solubilities were derived from experiments on simple glasses leached at 50°C and different pHs (the experimental approach is described in [8]). In the simulations, the following minerals were allowed to precipitate (at thermodynamic equilibrium): portlandite, brucite, amorphous aluminium hydroxide, hydroxylapatite, pimelite, zinsilite, calcite, magnesite, and siderite. Note that talc was also added to the list to simulate a Mg-silicate phase, but its logK was modified in order to fit the Mg concentrations measured in the blank test (LogK₅₀°C = -23.11).

Silicon sorption onto magnetite was implemented in Hytec according to previous work [9]. The corresponding diffuse double layer model takes into account two surface complexes (Mag-FeH₃SiO₄ and Mag-FeH₂SiO₄⁻) and neglects the potential competition between Si and other cations.

2. Results and discussion

Figure 1 shows the evolution of pH, Si, B and Mg in the Blank and G+M tests. A higher pH is observed in the presence of magnetite that can result either from a greater alteration as shown by boron concentrations used as glass alteration tracer (alteration is increased by a factor 3) or from a specific reaction with magnetite. Silicon and Mg are respectively partly and totally consumed within 200 days in the presence of magnetite whereas Si concentrations are more or less constant and Mg concentration
drops slowly in the blank test. The behavior of Mg is likely related to the precipitation of a Mg-rich silicate phase as previously shown in other studies [4] and also confirmed by modeling (see below). Note that Fe concentrations are systematically below the detection limit.

Note that when the amount of magnetite is doubled (G+2M), the glass dissolution rate beyond 100 days is twice that in the test G+M (Figure 3). This strongly suggests a long-term effect of the magnetite.

Modeling is compared to experimental data, first in the case of the blank test (Fig 2). Globally, it can be seen that the trends are correctly reproduced even though some discrepancies appear. The main difference concerns the parabolic trend of boron suggested by the model whereas glass seems to dissolve more linearly especially when Mg is dropping, i.e. after 200 days. The two stages (parabolic release of boron before 200 days and linear thereafter) could certainly be better reproduced if we had considered a kinetic constraint for the precipitation of the Mg silicate phase, but this was not the purpose of the study.

With magnetite, two cases have been considered: one with silica sorption onto magnetite only (magnetite is not allowed to dissolve in this case) and the other including sorption and precipitation of an iron silicate mineral (magnetite can dissolve, its dissolution rate is tailored to fit the experimental data, and the Na-nontronite is added as a potential iron silicate phase). Figure 3 shows that sorption is able to fit glass behavior until around hundred days but cannot simulate the following trend. When precipitation of Na-nontronite is allowed (it can precipitate once thermodynamic equilibrium is achieved and without kinetic limitation), it precipitates at a rate controlled by magnetite dissolution and the long-term trend of glass alteration is reproduced more accurately. This result is consistent with the conclusions of a Japanese team that proposes amorphous silica precipitation on magnetite surfaces to explain their results [10]. In the case of magnetite dissolution, the corresponding dissolution rate would be $2 \times 10^{-13} \text{ mol.m}^{-2}.\text{s}^{-1}$, leading to an equivalent corroded thickness of about 1 nm after 800 days. Characterization of the samples is in
progress as well as investigations into other hypotheses like the transformation of magnetite into more oxidized phases like hematite or goethite that present higher silica sorption capacities. At this stage one can conclude that magnetite, which is one of the iron corrosion products expected in geological disposal conditions, is actually potentially reactive with respect to glass and could enhance its alteration over long period of time, contrary to what was anticipated before [1,11]. However, an accurate evaluation of this effect on the glass package lifetime will require more data (including the effects of other expected corrosion products) and modeling work taking into account the physical geometry of the system.

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References


Figure 3 Comparison between experimental results (diamonds) and modelling with sorption of Si only (dashed lines) and with sorption of Si + precipitation of iron silicate phase (solid lines).