Kinetic feedback effects induced by dissolution/precipitation processes in a geothermal context

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ABSTRACT

The relative intensities of primary mineral leaching and secondary phase formation may significantly affect porosity and permeability of the reservoir of a given geothermal site, thereby influencing its hydraulic performance and the efficiency of the geothermal power plant. In the present study, we estimated the impact of secondary coating formation on K-feldspar dissolution kinetics at conditions relevant for the context of Soultz-sous-Forêts (Alsace, France). Our results demonstrate that µm-thick coatings formed on K-feldspar surface negligibly impact its dissolution rate, because of the porous texture of the coatings. Ongoing efforts are directed to ascertaining the critical size of fracture filling which has to be reached prior to preventing a continuous supply of dissolved cations from the fracture walls.

1. INTRODUCTION

In the context of the enhanced geothermal system at Soultz-sous-Forêts (Alsace, France), the pumping of hot water and the re-injection of cooled water at depth may favor the dissolution of the main rock-forming minerals of the reservoir, such as K-spar and plagioclase, while promoting the precipitation of secondary phases, such as calcite and/or Al-(hydr)oxides (Fritz et al., 2010). The relative intensities of primary mineral leaching and secondary phase formation may significantly affect porosity and permeability of the reservoir, thereby influencing its hydraulic performance and the efficiency of the geothermal site.

Therefore, the prediction of the kinetics of dissolution and precipitation reactions at play during fluid/rock interactions, their coupling and their temporal evolution represent a critical issue for evaluating the efficiency of a geothermal site, as well as the prediction of its long-term evolution.

Heterogeneous precipitation of secondary phases may prevent a direct contact between the bulk fluid and the surface of the dissolving minerals, thereby limiting their dissolution (e.g. Velbel, 1993; Daval et al., 2009). Up to now, a substantial body of classical experimental works dedicated to determining the kinetics of fluid/mineral interactions were run on crushed single mineral powders, either monitoring dissolution or precipitation, without investigating the coupling between these reactions. Moreover, the decrease of the reactive surface of the primary phases is not accounted for in most of the geochemical codes that we are aware of. However, it is noteworthy that in geothermal contexts, fluid circulation occurs in fractures where primary silicates are covered with secondary coatings, raising the question as to what the actual "reactive surface" is.

The present ongoing work aims at providing new insights on the effect of secondary coatings on the dissolution kinetics of K-feldspar, which is one of the prevalent minerals of the granitic reservoir of Soultz-sous-Forêts. To reach this goal, coated and uncoated K-feldspar powders were subjected to dissolution experiments to estimate the difference of powder reactivity. These results were coupled together with physical characterizations of the secondary coatings to estimate their diffusivity. Diffusion modelling was carried out to assess the compositional gradients that may develop in the secondary coating pore water. Our results demonstrate that secondary coatings do not represent a diffusion barrier and have only a modest effect on K-feldspar reactivity. Our ongoing efforts are directed to upscaling these results to the context of Soultz-sous-Forêts.

2. METHODS

Our experimental strategy consists in dissolving freshly crushed K-spar powders, and comparing their dissolution rates with those of powders previously coated with secondary minerals. First of all, we designed an experimental protocol allowing the development of various K-spar powders artificially coated with a layer of secondary phases. The powders were prepared in a continuously stirred titanium reactor at 180 °C in a flow-through system. The second step was to characterize the proportion of coated K-spar (using SEM image processing), as well as the mineralogical composition, the thickness or the diffusivity of the coating (using SEM methods and image processing to determine the coating porosity). The final step consisted in comparing the dissolution rates of coated and uncoated K-spar powders. More details about the experimental set-up can be found in e.g. Daval et al. (2010).

3. RESULTS AND DISCUSSION

The reactivity of 15 different batches of powders (5 uncoated, and 10 coated) has been investigated in the present study, with the main results summarized below:

3.1 Experiments run on uncoated powders

A typical example of dissolution experiments is shown in Fig. 1.

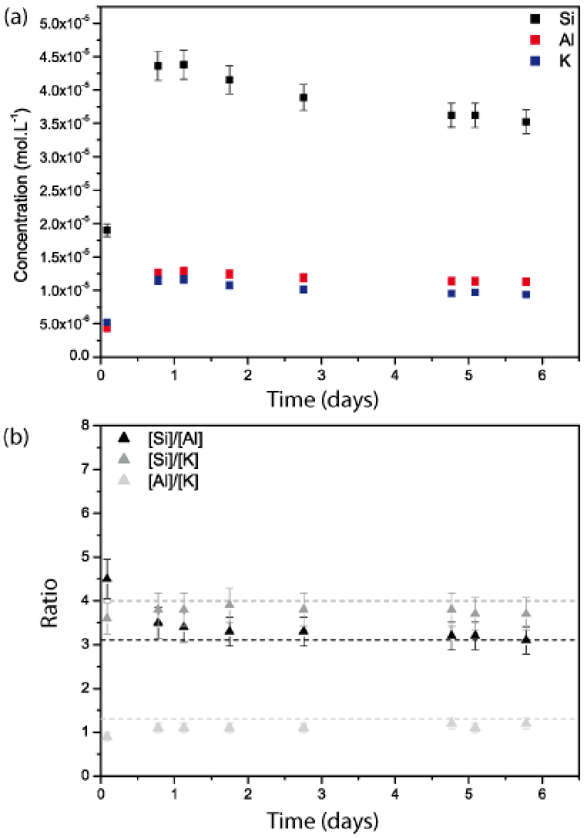

Figure 1: Outlet concentration of released cations in an experiment run on uncoated powders (a), and corresponding elemental ratios (b). These results illustrate that the dissolution is stoichiometric, and the dissolution rate quickly reaches a steady-state.

All experiments were run at far-from-equilibrium conditions ($\Delta G \leq$ -110 kJ/mol), where a dissolution rate plateau is expected (Pollet-Villard et al., submitted). Overall, the 5 reacted batches of powders have a similar reactivity, with an average dissolution rate of 1.2 ± 0.2 mol/m²/s. The absence of secondary coatings was revealed by 3 independent methods: (1) thermodynamic calculations, which showed that the solutions were undersaturted with respect to any secondary phases; (2) the stoichiometric release of elements to the solution (Fig. 1b), which indicates that secondary precipitation was unlikely and (3) direct SEM observations, which confirmed the absence of secondary crystals at the surface of the reacted powders.

3.2 Experiments run on coated powders

A typical example of dissolution experiments is shown in Fig. 2.

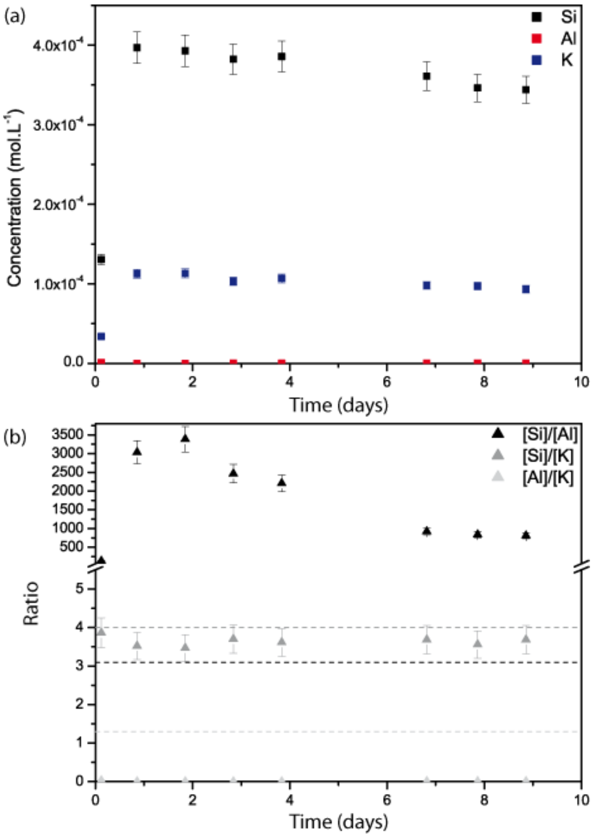

Figure 2: Outlet concentration of released cations in an experiment run on coated powders (a), and corresponding elemental ratios (b). These results illustrate that the dissolution is non-stoichiometric, while the dissolution rate quickly reaches a steady-state.

These experiments can be characterized by the following observations:

(1) The starting powders were systematically covered with boehmite coatings, whose thickness varied between 0.8 and 5.2 µm;

(2) The porosity of a typical coating as characterized by combining focused ion beam (FIB) milling with SEM observations decreased from the outer coating/solution interface to the inner coating/K-spar interface (Fig. 3);

(3) From a thermodynamic standpoint, all experiments were run on the dissolution rate plateau ($\Delta G \leq$ -69 kJ/mol). The dissolution of the various batches was

strongly non-stoichiometric, with aqueous Al concentration close to the detection limit (Fig. 2), and the dissolution rate was slightly lower than that observed on the uncoated powders, ranging between 0.36 and 0.70 mol/m²/s.

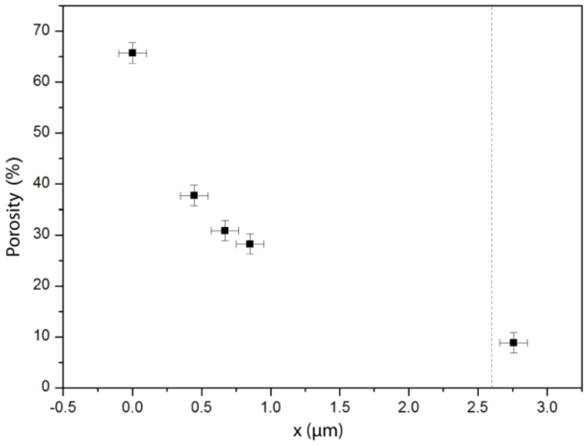

Figure 3: Porosity evolution of the coating from the outer fluid/coating interface ($x = 0$) onwards. The porosity was measured by FIB-SEM to decrease from ~65% to ~8%.

3.3 Diffusion modeling

To assess whether or not the coatings developed on the various batch powders could have represented a diffusion barrier, diffusion simulations were performed. If one assumes that the transport of dissolved species inside the coating was ensured by diffusion only, then it should verify the 2nd Fick's law:

$$\varphi \frac{\partial C}{\partial t} = -\frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right) \quad [1]$$

where φ is the porosity of the coating at a given distance x from the outer fluid/coating interface, C is the concentration of the reactive species (e.g. H+) and D is the apparent diffusion coefficient of the species. The apparent diffusion coefficient can related to the porosity of the coating following Archie's law (Archie 1942):

$$D = \varphi^m D_0 \quad [2]$$

where D_0 is the absolute diffusion coefficient and m is an empirical parameter often referred to as "cementation factor". Practically, D_0 was taken from Oelkers and Helgeson (1988), and the cementation factor was varied between 1.5 and 2.0, which is supposedly consistent with the texture of the coatings, as compared to the values suggested in e.g. Bruggeman (1935).

The diffusion equation was numerically solved with the boundary conditions set as follows:

$$\begin{cases} C_i^0 = 0 & \text{pour } 1 \leq i \leq N \\ C_0^t = C_0 & \text{pour } t > 0 \end{cases} \quad [3]$$

In addition, the continuous consumption of reactive species (H^+) due to the dissolution of the K-spar was accounted for by the following sink term (P):

$$P = 4k\sqrt{C_N^t} \quad [4]$$

where k stands for the dissolution rate constant of K-spar, determined from the experiments run on powders devoid of secondary coatings.

The results of the diffusion simulations are reported in Fig. 4. Arguably, a steady-state profile is quickly reached, showing that the concentration of the reactive species remains very close to that set the outer fluid/coating boundary, indicating that the coatings do not represent a diffusion barriers for the transport of reactants. As a consequence, the discrepancies observed between the reactivity of the coated and uncoated powders cannot be ascribed to the formation of secondary coatings. In the next section, we discuss a possible mechanism which could account for the observed differences in terms of K-spar reactivity.

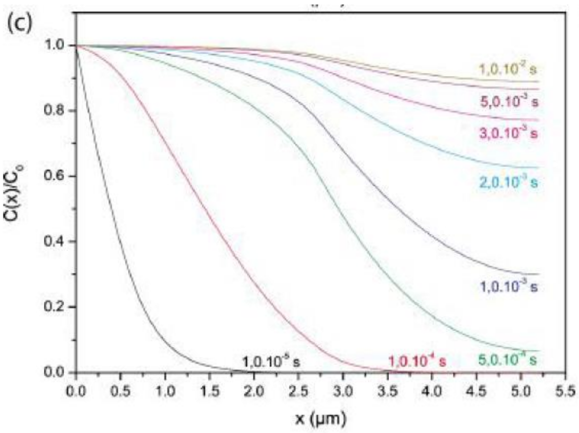

Figure 4: Concentration profiles resulted from our diffusion modelling efforts. A steady-state profile is obtained after 10^{-2} s, and the concentration of H^+ in the immediate vicinity of the feldspar surface differs from the concentration at the outer fluid/coating interface by less than 10%.

3.4 Evidence for an inhibiting effect of Al

In previous studies (e.g. Gautier et al., 1994), it was suggested that Al may play an inhibiting role on the dissolution kinetics of feldspars, and in particular, of K-spar. To test this model, the dissolution rates were reported as a function of the Al concentration in Fig. 5. Overall, the data may indicate that the decrease of K-spar dissolution rate of is correlated with Al concentration. The slope of the regression line is -0.31, which is close to the theoretical value suggested by Gautier et al. (1994) of 0.33.

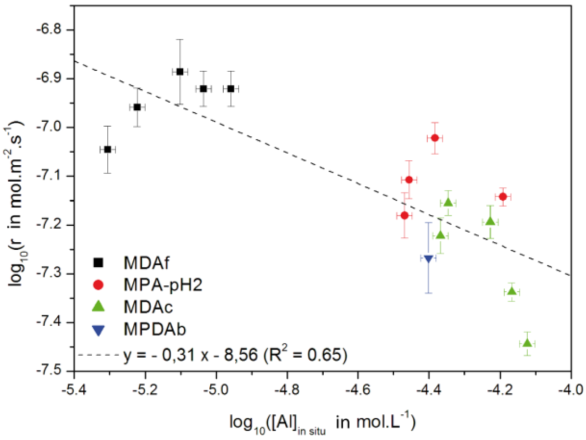

Figure 5: Dissolution rates measured for all powders reacted in this study (uncoated: black squares; coated: red, green and blue symbols) reported as a function of the Al concentration. The correlation is consistent with an inhibiting effect of Al.

4. CONCLUSIONS

Our study demonstrated that the formation of µm-thick secondary coatings negligibly affects the dissolution rate of K-spar. The slight reactivity discrepancies observed between the uncoated and coated powders (never exceeding a four-fold factor) may be explained by the inhibiting role of dissolved Al on feldspar dissolution rate. Our current efforts are directed to estimating whether such results still hold true when coatings with thickness closer to that found in real fractures (on the mm-cm range) are considered.

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