

Dissolution kinetics of high-FeO Olivine rock under anoxic conditions at 25°C

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The high-FeO olivine-bearing rock from Lavasjärvi intrusion (SE-Finland) has been suggested as redox-active backfill-additive in deep high level nuclear waste repositories. The performance assessment of a deep repository has to be based on both natural and laboratory studies. In this sense, a natural analogue study on the long-term behaviour of this olivine rock has been published [1]. Laboratory studies have been focused on the sorption of redox sensitive radionuclides onto the olivine-rock. However, the dissolution kinetics of the olivine rock is necessary in order to assess its behaviour in the near field.

We present here data on the olivine rock dissolution under anoxic conditions using a thin layer flow-through reactor. This methodology allows to determine directly the dissolution rate law avoiding secondary phase formation. Complementary batch reactor and column experiments were performed in order to test the behaviour of the obtained rate law in different conditions.

Dissolution rate law

The normative mineral content of the high-FeO rock was: olivine (65%; $X_{\text{fayalite}} = 0.39-0.58$), plagioclase (20%), magnetite (8%), pyroxene (4%) and serpentine (3%). The total FeO content was 28 wt.%. Crushed samples of particle size between 120-160 microns were used in this work. The specific surface area was determined by the BET method using a gas mixture of 30% N₂/Ar. The value obtained was 0.173 m² g⁻¹.

The experimental flow system used is based on a thin layer reactor [2]. The use of this reactor minimizes the effect of diffusion through the solid as well as the possibility of secondary phase formation. Our reactor consists in a Flex-column with a jacket to control temperature inside the

reactor. The column has a cylindrical shape with an interior diameter of 10 mm and two adapters which permit an adjustable height. The solid layer thickness was restricted to a maximum of 2 mm. The total solid was 0.3 g. Leaching solution was distilled water at different pH (2–3.6), anoxic conditions were achieved by bubbling nitrogen through the solution. Samples were taken of the effluent and filtered through a 0.22 microns MILLIPORE membrane filter and acidified prior to be analysed by means of an ICP-AES spectrophotometer.

Magnesium, iron and silicon concentrations were determined as a function of time. When steady state was achieved, dissolution rates were calculated by applying the following equation:

$$r = q [M]/S$$

where q (L s⁻¹) is the flow rate, $[M]$ (mol L⁻¹) is the concentration of Mg, Fe or Si in the effluent and S (m²) is the total surface area corresponding to the olivine enclosed in the flow reactor. Steady state concentrations were achieved in a few hours. These concentrations are more than one order of magnitude lower than equilibrium concentrations. The amount of Ca and Na from plagioclase dissolution is one order of magnitude lower than those of Mg and Fe. Therefore, the amount of SiO₂(aq) from plagioclase dissolution was assumed included in the analytical uncertainty and was not considered.

The dissolution law resulting from the experiments carried out at far-from-equilibrium conditions can be expressed as:

$$\log r = -7.21 (\pm 0.4) + 0.47 (\pm 0.03) \text{ pH}$$

These values have been compared to those reported in the literature. The rate constants for minerals of pure compositions, Mg₂SiO₄ and Fe₂SiO₄, were calculated from the experiments at

TABLE 1. Olivine dissolution rates at different pH

pH	Rate (mol m ⁻² s ⁻¹)
2.1	5.49(±0.27) 10 ⁻⁹
3.0	2.69(±0.13) 10 ⁻⁹
3.6	1.28(±0.06)10 ⁻⁹

constant pH performed by Wogelius and Walther [3] for Mg₂SiO₄, and Westrich *et al.* [4] for Fe₂SiO₄. The latter authors show that the log of the dissolution rates for mixed-cation orthosilicate minerals show a linear ratio from the log of the rates of the pure composition phases. Therefore, the rate constant k_0 for the olivine was calculated according to:

$$\log k_0 = 0.55 \log k_0^{\text{Mg}_2\text{SiO}_4} + 0.45 \log k_0^{\text{Fe}_2\text{SiO}_4}$$

The calculated value of $\log k_0 = -6.89$, agrees with our experimental value. Proton dependence is also close to the value reported by Blum and Lasaga [5].

Applications to batch and column experiments

The olivine dissolution rate law described above has been used to predict the behaviour of the olivine barrier in different conditions. The predictions have been compared, so far, with the results of batch and column experiments.

Calculations of the time and space evolution of solute concentration are based on the continuity equation:

$$\phi \frac{\partial c_i}{\partial t} = q \frac{\partial c_i}{\partial x} - \phi v_i r \sigma (\Omega^\theta - 1)^\eta$$

where ϕ is the porosity, c_i the concentration of the i -th solute (kmol m⁻³), q the darcian flow (m³ m⁻² s⁻¹), v_i is the stoichiometric coefficient of the i -th solute in the FeO-olivine, r is the dissolution rate at the pH of interest, σ is its reactive surface area, and Ω the olivine saturation index of the solution. In absence of experimental values for θ and η , the unity has been assumed as expected from Transition State Theory.

Batch experiments were performed in methacrylate vessels to avoid cation sorption on the walls. Two grams of olivine were used as starting material. The dissolution of olivine was studied at pH = 3. Anoxic conditions were achieved by bubbling nitrogen continuously into the vessel. The pH and the redox potential were monitored by means of a glass electrode and a platinum electrode, respectively.

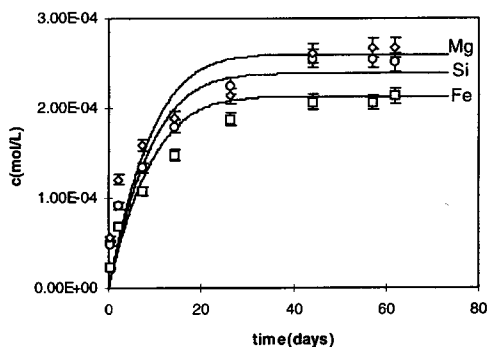


FIG. 1. Time evolution of solute concentration in the output: Mg (diamonds); SiO₂(aq) (circles); Fe (squares). The calculated concentrations are also plotted.

After 40 days, the magnesium, iron and silicon concentrations reached a steady value as the ion activity product equates the equilibrium constant. These concentrations confirmed that the dissolution of olivine is congruent. For the calculated values to match the experimental ones a reactive surface area of 0.0085 m² g⁻¹ was required. This area value is 20 times lower than that measured by BET, and is attributed to the fact that the solution was not efficiently in contact with the solid, which was not stirred at any time.

The same column geometry described for the thin-layer was used for column experiments. In this case, however, the column was filled with 7.5 g of rock (5 cm of column, with a porosity of 0.29). The dissolution experiment was carried out at pH = 3.6 under anoxic conditions and a flow rate of 7 · 10⁻⁶ L s⁻¹.

Steady state concentration for iron, magnesium and silicon (5.22 · 10⁻⁵, 4.84 · 10⁻⁵ and 2.74 · 10⁻⁵ mol L⁻¹) were achieved in 20 hours. The solution was far from olivine equilibrium through the experiment. In order to predict experimental concentrations a reactive surface area of 0.035 m² g⁻¹ had to be used in the simulations. This value is 4 times lower than that obtained from BET.

Therefore, a good estimation of the reactive surface area is required to predict more accurately the behaviour of the engineering barrier. Once the dissolution rate is known, column experiments and numerical simulations may be useful to constraint the reactive surface area as a fitting parameter.

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