

Measuring dissolution rates of illite in saline-acidic solutions using flow-through reactors

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The dissolution of phyllosilicates is one of the acid neutralizing processes that occurs in soils and is particularly important under extreme acidic soil conditions. Illite is a common clay mineral in many soils of Australia, including areas where inland acid sulfate soils exist. The determination of dissolution rates of minerals provides an estimate of their acid neutralizing capacity in soil. This study reports the first attempt to determine the dissolution rates of illite in saline-acid sulfate solutions under laboratory conditions.

Dissolution experiments were conducted using Silver Hill illite at a solution pH ranging from 1 to 3 and temperature of 25°C. The clay fraction (< 2 µm) was separated by sedimentation procedure and then saturated with sodium prior to conducting dissolution experiments. X-ray diffraction analyses of the clay fraction showed the presence of minor amounts of kaolinite and quartz. Transmission electron microscopic characterisation of the illite sample prior to dissolution showed particle aggregates, with individual particles in 200–500 nm size range; the BET surface area was 42 m²/g.

Dissolution experiments were conducted in stirred flow-through reactors. Input solutions at a specific pH were prepared by adding AR-grade H₂SO₄ to E-pure water, and ionic strength (M) of the solutions was maintained at 0.01 and 0.25 using solutions of AR-grade NaCl. Output solutions were collected every 24 hours, the pH measured and the solution analysed for a range of metals; Al and Si using colorimetric methods, potassium concentrations were determined by atomic absorption spectrometer (AAS, Varian Spectra 220 FS); Fe and Mg were determined using inductively coupled plasma atomic emission spectroscopy. Aqueous ion activities were calculated using Visual MINTEQ. The saturation state of the output solutions was determined in terms of Gibbs free energy of reaction, ΔG_r , from the ion activities of Si, Al, K, Fe and Mg at the steady state. The estimated log K_{eq} value for the illite dissolution reaction was 10.51 and this was used in the calculation of saturation state of the steady state solution with respect to dissolving illite sample. The dissolution rate of illite was calculated from steady state concentrations of Si and Al.

The experiments took between 1800 and 2300 hours to reach the steady state. The experiments conducted at the lowest pH took minimum time to reach the steady state (1800 h at pH 1) while the experiments conducted at the highest pH took maximum time to attain the steady state (2300 h at pH 3). However, no significant effect of ionic strength was observed on the time required to attain the

steady. The dissolution rate of mineral was very fast and non-stoichiometric at the onset of each experiment, which decreased afterwards until reaching the steady state. The release rate of elements was very fast during the initial 100 hours of the experiment with a favoured Al over Si release. At the steady state, the release rate of these elements became stoichiometric in low ionic strength input solutions, however, the experiments conducted at high ionic strength showed a preferential release of Al over Si.

Similar illite dissolution rates were observed at both ionic strengths showing no significant effect of the ionic strength on dissolution rate. The log dissolution rates at high ionic strength calculated from the steady state Si concentrations were -12.75, -13.21 and -13.42 mol m⁻² s⁻¹ at input solution pH of 1, 2 and 3, respectively. The log Si dissolution rates in the low ionic strength input solutions were -12.84, -13.17 and -13.40 mol m⁻² s⁻¹ at pH 1, 2 and 3, respectively. The dissolution rate of illite increased with an increasing acidity of the input solution, a trend typically observed for phyllosilicate dissolution in the acidic pH region.

Preferential release of K, Fe and Mg over Si was observed over the studied pH range and at both ionic strengths. The steady state output solutions were undersaturated with respect to illite in all experiments however, the system showed saturation with respect to secondary iron minerals especially akaganéite at pH 2 and 3 which is consistent with the presence of akaganéite in natural inland acid sulfate environments.

The results from this study suggest that illite dissolves at similar rates in saline and non-saline acidic environments, however, the stoichiometry of dissolution changes with higher Al release rates in the saline acid sulfate environments, and a stoichiometric release of Al and Si in the non-saline acidic environments. A rapid release of Al from the dissolution of illite under saline acidic sulfate conditions may have an adverse effect on the surrounding environment and should be considered in the management of saline acid sulfate soils.