

**FLOW-THROUGH DISSOLUTION RATES OF K-JAROSITE IN WATER AND BRINES.** E. M. Dixon<sup>1</sup>, B. N. Pritchett<sup>2</sup>, A. S. Elwood Madden<sup>1</sup>, M. E. Elwood Madden<sup>1</sup>; <sup>1</sup>School of Geology and Geophysics, University of Oklahoma, 100 E. Boyd, Norman, OK 73019, Emily.Dixon@ou.edu; <sup>2</sup>Oklahoma Geological Survey, Norman, OK.

**Introduction:** Jarosite is a ferric sulfate mineral that is found on Earth and on Mars [1, 2]. Dissolution rates of jarosite are used to constrain the duration of aqueous diagenesis on Mars [3]. Late-forming diagenetic sulfate and chloride minerals observed at Meridiani Planum indicate that brines may have interacted with jarosite [4, 5]. Previous dissolution batch experiments using brines found a slower initial dissolution rate, but accelerating dissolution higher rates over time, likely due to chloride complexation with iron [6].

This study examines hydrologic influences on jarosite dissolution rates and mechanisms through comparison of flow-through dissolution rates with previous batch dissolution experiments. The flow-through reactor represents an open system with fresh solution constantly flowing in one direction, such as a regional groundwater environment where fluids flow through sediment and carry away by-products of any reactions. Previous batch experiments represent a more constrained fluid system, where liquid water enters, reacts with the mineral, but is not transported away, similar to an evaporative pond.

**Methods:** K-Jarosite was synthesized using the method described by Driscoll et al. [7]. The mineralogy was confirmed with X-Ray Diffraction and microprobe analysis. The surface area ( $1.5 \text{ m}^2 \text{ g}^{-1}$ ) was measured using the BET method. Dissolution rates were measured in a flow-through reactor with ultra pure water (UPW), NaCl brine, and  $\text{CaCl}_2$  brine. In each experiment, synthetic jarosite ( $\sim 0.1 \text{ g}$ ) was placed on a  $0.2 \mu\text{m}$  filter paper and secured in a 13 mm polycarbonate filter holder. The experimental solution was pulled through the filter holder at  $0.005$  or  $0.048 \text{ L hr}^{-1}$  using a Haake Buchler duostaltic pump, which allows for the experiment to be run in duplicate. Samples were collected from the outflow solution at predetermined intervals and filtered again using a  $0.2 \mu\text{m}$  syringe filter. The pH was recorded in separate aliquots of solution, but was not measured in the brine experiments.

The samples were diluted 1:1 using a matrix modifier ( $\text{HNO}_3 + \text{NaCl}$ ) for potassium analysis using matrix-matched flame Atomic Absorption Spectrophotometry. The dissolution rates were determined using the equation:

$$r = \frac{(m_{out} - m_{in})v}{AM_S}$$

where  $r$  is the rate of appearance of product ( $\text{mol m}^{-2} \text{ s}^{-1}$ ),  $m_{out}$  is the concentration output ( $\text{mol L}^{-1}$ ),  $m_{in}$  is the concentration of the input solution ( $\text{mol L}^{-1}$ ),  $v$  is the flow rate ( $\text{L s}^{-1}$ ),  $A$  is the surface area per g of solid in the reactor ( $\text{m}^2 \text{ g}^{-1}$ ),  $M_S$  is the mass of the solid in the reactor (g) [8]. The  $m_{out}$  was determined by plotting the concentration data over time and averaging the concentrations of 19 samples that represented a “steady state” time period in the flow-through reaction.

**Results:** The dissolution rates of the NaCl brine flow-through experiment were slower than the rates in the UPW flow-through experiment, consistent with previous batch dissolution experiments (Figure 1). In addition, all the flow-through experiments showed significantly slower dissolution rates compared to batch experiments under similar conditions (averaging  $\log r = -13.69 \text{ mol m}^{-2} \text{ s}^{-1}$  compared to  $\log r = -9.57 \text{ mol m}^{-2} \text{ s}^{-1}$  in the batch reactor).

A 3-day UPW flow-through experiment was also analyzed at an increased flow rate ( $0.048 \text{ L hr}^{-1}$  compared to  $0.005 \text{ L hr}^{-1}$ ) to examine the effects of flow rate on the dissolution rate. The dissolution rates observed in the faster flow rate experiments were similar to those observed in the slower flow rate experiment.

In all of the UPW experiments, the pH increases sharply at the beginning of the experiments (Figure 2), but then lowers and levels off around  $\text{pH} = 5$  for the higher flow rate experiment and around 4.6 for the lower flow rate experiment. Previous UPW batch experiments had a pH of 4.4.

**Discussion:** Significantly slower rates observed in the flow-through experiments compared with previous batch reaction experiments are likely due to differences in the method for determining dissolution rates between the two different experimental regimes. The rates determined from the batch reaction experiments are initial rates, extrapolated to time = 0s using the initial rate method described in Rimstidt and Newcomb [9]. In flow-through experiments, the rate is determined once the solution achieves steady state (little to no change in solute concentration), often after several hours or days of reaction, excluding the initial solute data from the calculation. Therefore, absolute values of initial dissolution rates determined from batch reactors cannot be directly compared to steady state dissolution rates determined from flow-through experiments.

However, rates of dissolution in the NaCl brine were approximately one order of magnitude slower than those observed in UPW, similar to the difference

in rates observed in the batch reaction experiments. This suggests that differences in rate trends may hold, despite differences in how the rates were determined.

The similar dissolution rates found in the slower and faster flow rate experiments with UPW suggest that the mineral dissolution rate is the rate-determining step in both experiments and the system is not transport-limited under the range of flow-rates determined here.

Differences in pH observed between the varying flow-rate experiments with UPW (Figure 2) may be due to differences in reaction products. The higher pH in the short-term experiments may be due to a lack of formation of reaction products due to limited time for nucleation in higher velocity fluids. XRD analysis of the reaction products and Fe concentration measurements of the solutes are ongoing and results will be applied to test this hypothesis. Flow-through dissolution experiments using a  $\text{CaCl}_2$  brine are ongoing and will be compared to both UPW and NaCl results to further test the effects of brines and reaction products on jarosite dissolution rates.

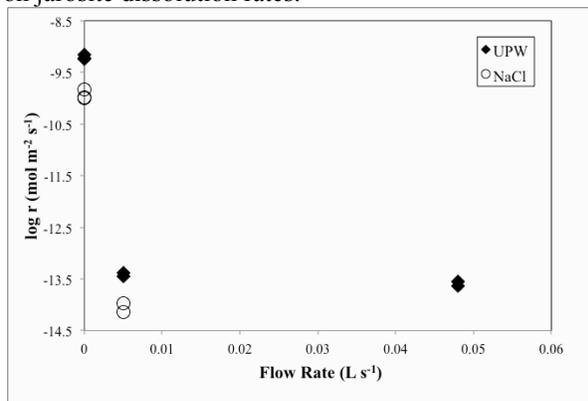


Figure 1. UPW (solid diamonds) and NaCl brine (open circles) flow-through dissolution rates are significantly slower than initial rates determined from reactor batch experiments (flow velocity = 0). However, within the flow-through experiments, increased flow rate had little effect on the dissolution rates. The NaCl dissolution rate is consistently slower than the UPW dissolution rate, in both experimental systems.

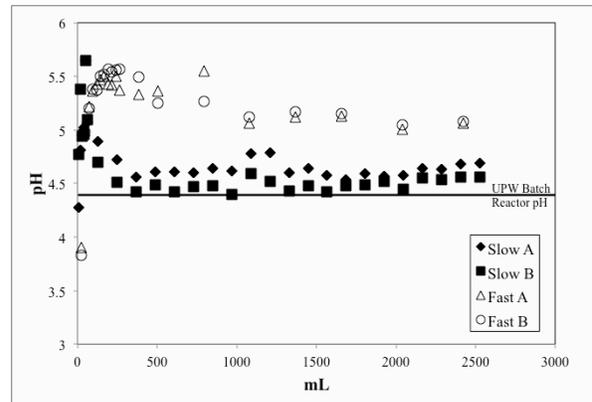


Figure 2. The pH of the faster flow rate UPW experiment (open triangles and circles) is higher than the slower flow rate UPW experiments (solid diamonds and squares). A and B are replicates of the same experimental conditions. The line at 4.4 represents the pH for previous UPW batch reactor experiments, where hematite was commonly observed as a reaction product.

**References:** [1] Christensen P. R. et al. (2004) *Science*, 306, 1733-1739. [2] Glotch T. D. and Christensen P. R. (2005) *J. Geophys. Res.-Planet.*, 110 [3] Elwood Madden et al. (2009) *Geology*, 37, 635-638. [4] Barron V. et al. (2006) *EPSL*, 251, 380-385. [5] Reider R. et al. (2004) *Science*, 306, 1746-1749. [6] Pritchett B. N. et al. (2012) *EPSL*, 357-358, 327-336. [7] Driscoll R. and Leinz R. (2005) *U.S. Geol. Surv. Tech. Methods* 05-D1. [8] Icenhower J. P. and Dove P. M. (2000) *Geochim. et Cosmochim. Acta*, 64, 4194-4203. [9] Rimstidt J. D. and Newcomb W. D. (1993) *Geochim. et Cosmochim. Acta*, 57, 1919-1934.