



A small-scale flow-through column system to determine the rates of mineral dissolution at high temperature and pressure

Hari Prasad Parthasarathy^{a,b}, David A. Dzombak^b, Athanasios K. Karamalidis^{a,b,*}

^a National Energy Technology Laboratory-Regional University Alliance (NETL-RUA), Pittsburgh, PA-15236, USA

^b Department of Civil and Environmental Engineering, Carnegie Mellon University, Pittsburgh PA- 15213, USA

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ABSTRACT

Mineral dissolution is a critical phenomenon in many geochemical systems, including those of geologic CO₂ storage. It affects the mobilization, fate and transport of toxic metals in subsurface waters. A small-scale plug-flow system was designed and demonstrated for use in determining dissolution rates and simulating mineral–water interactions under a wide range of conditions, including high pressure (*P*, up to 300 bar) and temperature (*T*, up to 120 °C). The system enables rapid achievement of steady-state rates, and minimizes the experimental time to study such mineral–water systems. The performance of the system was evaluated through study of the oxidative dissolution of arsenopyrite (FeAsS (s)). Rates of arsenic release induced by dissolved Fe³⁺ (10^{−4} M) in anoxic systems at 25 °C and pressures of 1 bar and 100 bar were measured. The performance testing confirmed the ability to obtain reproducible results under the wide range of conditions tested, and to obtain similar results to certain benchmark cases, e.g., the FeAsS (s) dissolution rate of 10^{−8.09} mol As/m² s at 25 °C and 1 bar was comparable to previously reported values. Potential mass-transfer limitations associated with the system were studied and results indicate such limitations can be avoided at flow-rates higher than 0.8 mL/min.

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1. Introduction

Mineral dissolution contributes to processes controlling soil fertility, porosity in aquifers and oil reservoirs, transport and sequestration of chemical constituents, cycling of metals and formation of ore deposits, and many other geochemical characteristics and phenomena (Brantley et al., 2008). Understanding of mineral dissolution rates under a wide range of physical and chemical conditions is important, especially for effective and environmentally safe operation of geologic CO₂ storage in deep saline sedimentary formations.

Numerical models have shown that as CO₂ is injected into a saline reservoir, the pH of the reservoir water, close to the injection zone, could reduce to as low as pH 3 (Kharaka et al., 2007; Xu et al., 2007), which may initiate or increase mineral dissolution from formation and cap rocks. The implications for such dissolution are many, including release of toxic metals (Wang and Jaffe, 2004) like arsenic (As), and transport to overlying aquifers via potential reservoir leakage. Understanding the mechanism and kinetics of release of such metals is important to be able to predict and calculate the risks associated with metal dissolution associated with geologic CO₂ storage.

While aqueous dissolution rates of many minerals at moderate temperatures and pressures, including calcite, kaolinite, quartz, pyrite and arsenopyrite have been reported in the literature (e.g., Sjöberg and Rickard, 1984; Knauss and Wolery, 1988; Papangelakis and Dempoulos, 1991; Wieland and Stumm, 1992; McKibben et al., 2007), kinetics of dissolution under the unusual physical and chemical conditions associated with geologic storage of CO₂ remains unexplored. Mineral dissolution experiments spanning wide ranges of temperatures and solution conditions have been performed but measurements at pressures other than 1 atm are quite limited. Although the effect of pressure on activation volumes and hence the dissolution rates of minerals is limited (Drljaca et al., 1998), higher pressures as seen in geologic reservoirs could affect other phases in the system including the physical state of CO₂.

The majority of experiments measuring the dissolution rate of minerals use three basic types of reactor systems: batch reactors, mixed-flow reactors and flow-through reactor systems (Levenspiel, 1972; Hill, 1977; Rimstidt and Dove, 1986), with batch reactors employed most commonly owing to their simplicity (Rimstidt and Dove, 1986) and adaptability to high pressure and temperatures. The mineral is placed inside the reactor, which is then filled with the solution of interest. The temperature of the system is maintained through a water jacket or other means. The solution is mixed continuously, and samples of the solution are extracted at regular time intervals to determine the dissolved concentrations of elemental components of the mineral, which are used to determine dissolution rates. Since these systems rely on change in concentration of analytes

* Corresponding author at: Dept. of Civil and Environmental Engineering, Carnegie Mellon University, 119 L, Porter Hall, 5000 Forbes Avenue, Pittsburgh, PA 15213, USA. Tel.: +1 412 268 1175.

E-mail address: akaramal@andrew.cmu.edu (A.K. Karamalidis).

to determine rates, a challenge in interpreting the data is the buildup of reaction products in solution (Paschka and Dzombak, 2004). This is apparent with iron releasing reactions, which tend to be limited by iron oxy-hydroxide saturation, especially at high pH values (McKibben et al., 2007). Batch systems are not ideal for studying oxidative/reductive dissolution processes as product accumulation during experiments can change the redox conditions in the system.

Some of the drawbacks of batch systems can be overcome by using mixed flow and plug flow reactors. Mixed flow systems are configured like batch reactors but with continuous flow of solution. The mineral is held in a holder in the middle of the reactor, the reactor is filled with solution and mixed continuously, an influent solution is continuously added, and an effluent stream is withdrawn from the reactor at the same rate as the influent flow. Once steady-state concentration of the target dissolution product is attained in the effluent stream, the rate of dissolution is determined by multiplying the difference in concentration of the analyte (mol/L) in the influent and effluent by the flow-through rate (L/s) (Rimstidt and Dove, 1986). These systems have been widely used to study dissolution rates at ambient pressures and temperature (Yunmei et al., 2004; Walker et al., 2006; Yunmei et al., 2007). Past studies of kinetics at high temperatures and pressure, however, have been hindered by experimental difficulties and labor intensive processes required with producing reliable results (Dove and Crerar, 1990). This is overcome by using hydrothermal mixed flow reactors, constructed from industrial grade titanium which forms a non reactive oxide layer (passivated TiO₂) on its surface and can hence be used at temperatures up to 300 °C and pressures up to 124 bar (Dove and Crerar, 1990; Berger and Cadore, 1994; Carroll and Knauss, 2005). Hydrothermal mixed flow systems are expensive to construct, however, and tedious to assemble and operate.

Plug flow reactors are an alternative to batch and mixed-flow systems for studying dissolution rates (Knauss and Wolery, 1988; Rimstidt and Newcomb, 1993; Tester et al., 1994). These reactors typically consist of a column maintained at a constant temperature and pressure through which, the solution moves as slugs without mixing in the forward or reverse direction and without the addition or loss of fluid along the flow path (Rimstidt and Newcomb, 1993). Influent solution at a constant rate is supplied to the column and the effluent is analyzed for concentration of dissolved mineral components to determine rates. Plug flow reactors are usually operated under steady state conditions and can be used to measure long-term dissolution rates. Non-steady state phenomena, such as preferential dissolution or rapid surface dissolution, may occur during the start-up period (Rimstidt and Dove, 1986) and such data are usually not considered representative. Since the dissolution within the column is not constant, data generated from plug flow systems are difficult to analyze. Hence, these systems are not ideal for initial rate determination. Plug flow systems can be used under a wide range of pressures, temperatures, solution compositions, and with different minerals without significant design changes.

In this work, we designed, constructed and operated a small-scale flow-through column system for use in rapid determination of long-term dissolution rates of minerals under a range of pressure, temperature and solution conditions, which are representative of deep geologic formations. The specific design objectives were to (i) be able to operate at high temperatures and pressure, (ii) eliminate mass transfer limitations within the system and (iii) maintain a constant rate of dissolution within the reactor to eliminate mathematical difficulties. The performance of the system was analyzed for the oxidative dissolution of arsenopyrite induced by a 10⁻⁴ M Fe³⁺ as the oxidizing agent.

2. Materials and methods

A small-scale flow-through system for studying mineral dissolution under a range of temperature and pressure conditions was

assembled and evaluated by study of the oxidative dissolution of arsenopyrite (FeAsS (s)). Evaluation of the system involved the following experiments: 1) A blank experiment, with deionized water adjusted to a pH of 2 with HCl to ensure that the system hardware did not release any arsenic or iron; 2) measurement of the rate of arsenic release from arsenopyrite at pH 2, temperatures of 25 °C and pressures of 1.0 bar and 100 bar, with an influent solution containing 10⁻⁴ M Fe³⁺, in the absence of oxygen; and 3) measurement of rate of arsenic release from arsenopyrite at temperatures of 25 °C and pressures of 1.0 bar, with an influent solution containing 10⁻⁴ M Fe³⁺ (pH = 2) and at different influent flow rates to determine the effects of fluid velocity on the dissolution rate. The system was also checked for its ability to maintain constant temperature and pressure within the column for extended periods of time.

2.1. Mineral preparation

Arsenopyrite samples were obtained from Wards Natural Science Inc. (Rochester, NY) in 10 g batches. They were crushed in ethanol and wet sieved to obtain a uniform size fraction of 150–250 μm (Wolfe et al., 2007), which was reported as the optimal particle size range for dissolution (McKibben et al., 2007). The particles were dried at 105 °C and stored in crimp-top vials under nitrogen gas. Samples required for each run were pre-treated to remove fines and surface oxide layers using the method developed by McKibben et al. (2007). The method entails cleaning the mineral with ultrasonication in methanol for 2 min, then rinsing it with 1.8 M HNO₃ for 1 min, followed by rinse with deionized water, rinse with ethanol and drying at 105 °C. The BET surface area of the cleaned arsenopyrite particles were measured in triplicate using a 5-point Kr adsorption isotherm and was found to be 0.04 ± 2% m²/g.

2.2. Experimental apparatus

The flow-through reactor consisted of six main parts (Karamalidis et al., 2012), as shown in Fig. 1: a thermally controlled influent tank, a pump (Isocratic piston pump: model P-1010; Chromtech, USA), a column, a pressure controller, a sampling port, and an effluent tank (waste). For the purpose of the arsenopyrite dissolution study, a Pyrex glass bottle (2 L) with screw cap having three ports was used as an influent tank. The tank was chosen based on the ability to withstand heat and maintain constant temperature, be chemically resistant, have low potential for cross contamination with the mineral sample, and allow for gas sparging. The temperature of the influent solution was maintained by heating the influent bottle using a Corning heat plate. The P-1010 piston pump was capable of supplying the system with influent solution at a constant rate (0.01–10 mL/min) for a range of pressures up to 6000 Psi (Fig. 1).

A PEEK (Poly Ether Ether Ketone) column from BioChrom Labs, Inc. (Indiana, USA) usually employed for high-performance liquid chromatography, was chosen for studying the dissolution of minerals under various conditions. PEEK is a high-performance thermoplastic with a high degree of mechanical and chemical resistance. PEEK is capable of withstanding pressures up to 300 bar and has a glass transition temperature of 140 °C. The low thermal conductivity of the material ensures that very little heat is lost to the surroundings, thereby maintaining the constant temperature conditions required for the experiments. PEEK is chemically inert and can be used in saline environments as well as under a wide range of pH values.

Downstream of the column (Fig. 1), a pressure regulation system consisting of an adjustable backpressure regulator (Swagelok KHB series high pressure backpressure regulator) and a pressure reducer (Swagelok KHP series) was used to maintain the pressure inside the column. The backpressure regulator allows flow only if a particular pressure is reached upstream of the regulator and the pressure

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