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The effect of Na–Ca–Cl brines on the dissolution of arsenic from arsenopyrite under geologic carbon dioxide storage conditions

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ABSTRACT

Arsenopyrite (FeAsS) is one of the most common mineral sources of arsenic in rocks, sediments, and ores. The dissolution of arsenopyrite releases arsenic, which has potential implications for human and environmental health. With carbon dioxide storage in saline, sedimentary geologic formations being an important component of mitigation strategies for global warming, the effect of injected CO_2 mixed with anoxic brines on dissolution of arsenic from arsenopyrite merits examination. Arsenopyrite dissolution was studied using anoxic Na–Ca–Cl brines in the presence and absence of CO_2, at both ambient and high temperature and pressure conditions. Results revealed that the dissolution rate of arsenic ranged from 10^{-10} to 10^{-12} mol/m^2 s, with an average dissolution rate of $10^{-10.7 \pm 0.2}$ mol/m^2 s in the absence of CO_2. Understanding effects of particular brine constituents on arsenopyrite dissolution requires further investigation, however. The observed arsenopyrite dissolution rates under anoxic conditions are about two orders of magnitude lower than those observed under oxidizing conditions. The presence of dissolved CO_2 in brines resulted in dissolution rates marginally lower than those observed in the absence of CO_2, with an average dissolution rate of $10^{-11.2 \pm 0.5}$ mol/m^2 s, even though a reduction in pH to approximately 3.5 was observed. Increase in temperature and pressure from 25 °C to 60 °C, and 1 bar to 100 bars respectively, increased As dissolution rate from arsenopyrite by 1 log unit.

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1. Introduction

Geologic carbon dioxide storage (GCS) involves the capture of CO_2 from large point sources, such as coal-fired power plants, and transporting it to deep geologic formations for safe and permanent storage (North American Carbon Atlas Partnership (NACAP), 2012). Among the many types of reservoirs considered for CO_2 storage in the United States, deep saline sedimentary formations are estimated to have the largest storage capacity (National Energy Technology Laboratory (NETL), 2010).

Saline sedimentary formations are layers of porous sedimentary rock containing pore waters with total dissolved solids exceeding 10,000 mg/L (NACAP, 2012). Typical conditions reported for CO_2 storage reservoirs span 74–500 bars for pressure, salinity up to 7 m in NaCl equivalents, and temperatures of 304–433 K (Wang et al., 2013). Multiple ionic species such as Na$^+$, Ca^{2+}, K$^+$, Mg^{2+}, Cl$^-$, and SO$_4^{2-}$ are often present in high concentrations in the brines of deep sedimentary formations, with substantial variability among different storage formations (Wang et al., 2013). An analysis of data from the U.S. brine well database (NETL, 2003), which provides water chemistry parameters for nearly 65,000 wells, assimilated from different sources, confirms this large variability. The three most abundant ions in these brines are Na$^+$, Ca^{2+} and Cl$^-$, with a wide range of relative sodium and calcium concentrations.

CO_2 injection in saline formations can induce upward movement of brines (Oldenburg and Rinaldi, 2011), compression of injected and resident fluids, and pore space expansion (Bachu, 2008). Although injected CO_2 is expected to be trapped by a number of physical and chemical mechanisms, it is also anticipated that there will be slow leakage of CO_2, brines, or CO_2-saturated brines and these fluids may enhance dissolution of minerals in the overlying formations leading to mobilization of naturally occurring heavy metals such as arsenic, lead, and cadmium (Karamalidis et al., 2012). Elevated concentrations of As and Pb have been observed upon CO_2 injection in preliminary dissolution experiments with rock samples from GCS sites (Karamalidis et al., 2012). This release of As into the environment may impact human and environmental health (Corkhill and Vaughan, 2009).

The common mineral sources of arsenic in rocks, sediments, ores, and coals are primary sulfide minerals like pyrite, arsenopyrite, and realgar (McKibben et al., 2008). Of these, the most common arsenic bearing sulfide mineral is arsenopyrite, which is found in a range of ore deposits (Corkhill and Vaughan, 2009).

A number of studies have determined the effect of oxidants, such as dissolved oxygen and Fe^{3+}, on the rate of arsenic release from arsenopyrite (Rimstidt et al., 1994; Walker et al., 2006; Yu et al., 2007;

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McKibben et al., 2008; Asta et al., 2010). These studies have also included study of the effects of pH and temperature.

The dissolution of arsenopyrite under anoxic, high salinity conditions, representative of brine, or CO_2-saturated brine leakage from a GCS reservoir, remains unexplored. Parthasarathy et al. (2015) observed arsenopyrite dissolution under anoxic conditions in simple alkali metal electrolyte solutions at ambient temperature and pressure. With increasing interest in CO_2 storage in the subsurface, the effect of brines under anoxic conditions on the release of arsenic from arsenopyrite merits examination. Aside from GCS, understanding the effects of concentrated salt solutions on arsenic release from arsenopyrite is applicable to other systems where high salinity anoxic solutions may be encountered such as shale gas exploration.

In this work, arsenopyrite dissolution experiments with synthetic Na–Ca–Cl brines, at a fixed ionic strength of 1.54 ± 0.01 M, were conducted under anoxic conditions to investigate the effect of brines on the rate of release of arsenic from arsenopyrite. The effect of CO_2 presence in brines on arsenic release rates was also studied at ambient, high pressure, and high temperature conditions. The specific objectives were (1) to investigate the effect of Na–Ca–Cl brines on arsenic release from arsenopyrite under anoxic conditions, (2) to investigate the effect of CO_2 dissolution in deoxygenated brines (and the subsequent decrease in pH) on the rate of arsenic release, and (3) to determine the effect of high temperature and pressure on the dissolution of arsenopyrite by brines.

2. Materials and methods

2.1. Mineral preparation and characterization

Arsenopyrite was obtained from Wards Sci. Inc. (Rochester, NY), crushed in a porcelain mortar and pestle, and size separated using nylon sieves to a range of 150–250 μm. The mortar, pestle, and sieves were soaked overnight in 10% (w/w) HNO_3 prior to use. Crushed samples required for each dissolution experiment were pre-treated to remove fines and surface oxides according to the method described in Parthasarathy et al. (2014). The method involves sonication of ground particles in 50% ethanol, followed by rinsing with 12 N HCl and 50% ethanol, and drying in N_2 atmosphere.

X-ray diffraction (XRD) analysis of the prepared mineral confirmed arsenopyrite as the primary crystalline phase, with no major secondary phases detected. Scanning electron microscopy–energy dispersive X-ray spectroscopy (SEM–EDS) analysis revealed the stoichiometry of the prepared mineral to be $Fe_{1.03 \pm 0.05}As_{1.01 \pm 0.05}S_{0.87 \pm 0.05}$. The specific surface area was measured in triplicate using BET analysis (Brunauer et al., 1938) with a Kr adsorption isotherm and was found to be 0.125 ± 0.005 m²/g.

2.2. Experimental system

All dissolution experiments in this study were conducted using a small-scale plug flow column system developed by Parthasarathy et al. (2013). In this system, a 5 cm PEEK column is connected to a HPLC pump, a backpressure regulator and a sample auto-collector. The system used in this study utilized a column with a 20-micron frit at the effluent end, which prevented the 150–250 micron sized arsenopyrite particles from washing out of the column. The system has been shown to be capable of determining dissolution rates of minerals without mass transfer limitations (Parthasarathy et al., 2013). At moderate and slow rates of dissolution, as in the case of this study, the dissolution in the column is reaction-rate controlled (Parthasarathy et al., 2013). The column was filled with prepared arsenopyrite and connected to a backpressure regulator to maintain constant the desired pressure. Dissolved oxygen (D.O.) in the influent solutions was removed by purging with laboratory grade N_2 for 15 h prior to each experiment. N_2 sparging was continued through the entire duration of each experiment. The D.O.

in the system was continuously measured using an Accumet XL 60 dissolved oxygen meter (Fisher Scientific), and maintained at 0.00 mg/L dissolved oxygen. Deoxygenated influent solution was delivered at a constant flow-rate of 1.0 mL/min. The average pore volume of the column was 0.45 ± 0.05 mL. Prior to packing the column with arsenopyrite, the entire system was cleaned before every experiment by passing 10% HNO_3 (w/w) solution through the apparatus for 30 min followed by a rinse of deionized water for 30 min, to remove residual As and Fe from previous experiments. The absence of residual Fe and As in the system was confirmed by conducting blank experiments using D.I. water at pH 2 (HCl), without any mineral in the column. Synthetic brine solutions were analyzed for As and Fe every time a new batch was prepared.

2.3. Data analysis

Most mineral dissolution experiments are conducted in batch or mixed flow reactor systems. While plug flow reactor systems generally are less desirable to determine rate laws and constants for dissolution reactions because of the complexity of data interpretation, they are useful in determining relative rates (Rimstidt and Newcomb, 1993), which was of interest for this study. Further, plug-flow reactors are ideal systems for minerals with very slow dissolution, as they have inherently high solid–liquid ratios (Rimstidt and Newcomb, 1993). As the purpose of this study was to investigate the effect of brines on the dissolution of arsenic from arsenopyrite under anoxic conditions by comparison with dissolution caused by D.I. water, a plug-flow system was utilized.

For very slow reactions, Parthasarathy et al. (2013) showed that a plug-flow column system behaves like a mixed-flow reactor. Importantly, for slow reactions, the reaction rate in the column can be simplified to a 0th order reaction (Parthasarathy et al., 2013) and the resulting rates can be calculated based on the following expression (Eq. (1))

$$k' = \frac{(C_{out} - C_{in})}{\tau} \tag{1}$$

where k' (mol/L·s) is the apparent rate of arsenic dissolution, C_{out} (mol/L) is the steady state effluent arsenic concentration, C_{in} (mol/L) is the influent arsenic concentration, and τ (s) is the residence time of the fluid in the column. In these experiments $C_{in} \sim 0$, since the influent solutions were free of As.

To enable direct comparison between experiments that may exhibit variations in experimental parameters such as mass of mineral packed in the column, residence time of the brine solution, and mass of liquid in pore spaces, the apparent rate of arsenic dissolution was normalized to the surface area of the mineral in the column (Eq. (2))

$$k \left(\frac{mol}{m^2 \text{ mineral} \cdot s} \right) = k' \left(\frac{mol}{L \cdot s} \right) \times \frac{1}{\rho_{solution}} \left(\frac{L}{g} \right) \times \frac{M}{A} \left(\frac{g \text{ solution}}{m^2 \text{ mineral}} \right) \tag{2}$$

where, k ($\frac{mol}{m^2 \text{ mineral} \cdot s}$) is the reaction rate; k' ($\frac{mol}{L \cdot s}$) is the measured apparent rate of reaction; M (g solution) is the mass of liquid in the pore volume; A (m² mineral) is the specific surface area of the mineral, and $\rho_{solution}$ ($\frac{g}{L}$) is the density of influent solution.

Steady state was determined to be reached if the effluent concentration was within $\pm 15\%$ of the average concentration over 10 h in the small-scale flow-through system. Steady state concentrations were calculated after 15 h of dissolution, to allow for slower dissolution from surface irregularities. The random variation of the points used to determine steady state was verified by generating residual plots in relation to the calculated mean steady state concentration. In the experiments with arsenopyrite, a large variation was observed in Fe effluent concentrations, which could indicate the presence of amorphous Fe phases in these natural samples of arsenopyrite. As the objective of this study was to determine arsenic release rates, Fe concentrations were averaged over the same time frame as As for each experiment.