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Experimental investigations of the effects of acid gas (H_2S/CO_2) exposure under geological sequestration conditions

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Abstract

Acid gas (mixed CO_2 and H_2S) injection into geological formations is increasingly used as a disposal option. For example, more than 40 acid gas injection projects are currently operating in Alberta, Canada [1]. In contrast to pure CO_2 injection, there is little understanding of the possible effects of acid gases under geological sequestration conditions on exposed materials ranging from reactions with reservoir minerals to the stability of proppants injected to improve oil recovery to the possible failure of wellbore cements. The number of laboratory studies investigating effects of acid gas has been limited by safety concerns and the difficulty in preparing and maintaining single-phase H_2S/CO_2 mixtures under the experimental pressures and temperatures required.

In an effort to address the lack of experimental data addressing the potential effects of acid gas injection, the Plains CO_2 Reduction Partnership (PCOR) in the United States has developed approaches using conventional syringe pumps (ISCO 260D pumps) and reactor vessels (Parr Instruments) to prepare and maintain H_2S/CO_2 mixtures under relevant sequestration conditions of temperature, pressure, and exposure to water and dissolved salts. Exposures up to several months can be conducted at temperatures and pressures up to 350°C and 414 bar (6000 psi) using any desired H_2S/CO_2 mole ratio. Up to 16 individual samples racked in separate glass vials can be exposed at one time, and the use of separate glass vessels allows different salt brine concentrations to be evaluated.

In addition to performing static exposure experiments, the pumps and vessels are sufficiently leak-free that reaction rates can be determined by monitoring mass flow at the pumps. Interestingly, this is much easier to perform for reactions with H_2S than with CO_2, because H_2S is much less compressible and has lower Joule–Thompson heating/cooling effects than CO_2. Thus, obtaining accurate values for the mass of CO_2 used during an experiment based on pump volume is much more difficult than for H_2S, although controlling the pump cylinder temperature with a water jacket allows reasonable measurements to be made. These systems have been used to determine reaction rates of model systems, such as the formation of magnesium carbonate from magnesium silicate and the formation of pyrite from iron oxide (Fe_3O_4). For example, the use of H_2S (as measured at the pump) was steady at ca. 0.5 grams per day (for 18.6 grams of Fe_3O_4) until the reaction was complete. The half-life of the reaction was 20 days, and the mass balance (0.54 moles H_2S actual compared to 0.48 moles theoretical) was reasonable.

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Introduction

The experimental difficulties and safety issues associated with performing acid gas exposures at conditions relevant to carbon sequestration/storage have greatly limited the understanding of potential effects of injecting acid gas ranging from mineralogical reactions in the reservoir to wellbore integrity. Few studies of acid gas effects have been reported [2, 3]. Experimental systems that are described in the literature to perform pure CO_2 and/or acid gas exposures under geologically relevant conditions can be unnecessarily complex (and expensive), often because of a lack of understanding of the characteristics of CO_2 and H_2S which dictate how to best handle these fluids. It is the purpose of this report to provide a background in the issues involved in assembling and operating an experimental laboratory system to perform acid gas exposures. Several of the comments about how the characteristics of CO_2 affect experimental design also relate to performing pure CO_2 exposures as well as acid gas exposures. This report describes the construction and operation of a relatively simple and reliable apparatus to perform pure CO_2 and acid gas exposures. Examples of how the system can be used to gain experimental data on topics ranging from effects on wellbore cement and reservoir minerals to measuring fundamental reaction rates are then described.

Experimental

Apparatus

The apparatus for exposing samples to known mixtures of CO_2 and H_2S was assembled using commercially available components including two 260-mL syringe pumps (Model 260D, Teledyne-ISCO, Lincoln, NE) (Figure 1). The pump for CO_2 used a conventional stainless steel barrel, while a Hastelloy® pump barrel for the H_2S was purchased on the advice of the manufacturer. Both pumps were equipped with water jackets for reasons described below. Connections among the various components were made with 1/16-inch stainless steel tubing, including 1/16th-inch shutoff valves (High Pressure Equipment, Erie, PA) between each pump and its supply gas cylinder and (for the mixed CO_2/H_2S experiments) between each pump and a “tee” fitting that leads to the reactor vessel. The system shown in Figure 1 uses a 1000-mL stainless steel vessel (Model 4653, Parr Instruments, Moline, IL) with an inner diameter of 6.35 cm (2.5 inches) and an interior length of 33 cm (13 inches). These vessels are rated up to 414 bar (6000 psi) and 600°C. The vessel temperature was controlled with a Model 4926 heater assembly controlled by a Model 4843 temperature controller (Parr Instruments). An alternate (and less expensive) system was also constructed using 600-mL stainless steel vessels with an inside diameter of 6.35 cm and interior length of 20 cm (Parr Model 4764). These vessels are rated to 207 bar (3000 psi) and 350°C. Temperature control with this system is achieved by placing the vessel in a general-use lab oven (e.g., an old gas chromatographic oven).

It should be noted that the style of seal used in the vessels can be very important for constructing a leak-free system. While slow leaks are not of major concern for exposures to pure CO_2, experiments with known mixtures of CO_2 and H_2S require that no leaks exist so that the composition of the mixed gases in the reactor vessel can be known (not to mention the safety issues if a vessel leaks significant amounts of H_2S). In our experience with multiple manufacturers of high-pressure equipment, we have found that vessels using a dynamic spring-loaded seal (commonly known as “Bal Seal®Seals”) leak significantly at the relatively low pressures that are of interest for CO_2 and acid gas exposures. For example, our original system had a vessel rated to 690 bar (10,000 psi) and, although it sealed well at pressures above ca. 300 bar, there was an unacceptably high leakage rate at lower pressures. In contrast, vessels which use static flat surface seals (such as the vessels listed above) are capable of completely leak-free operation.

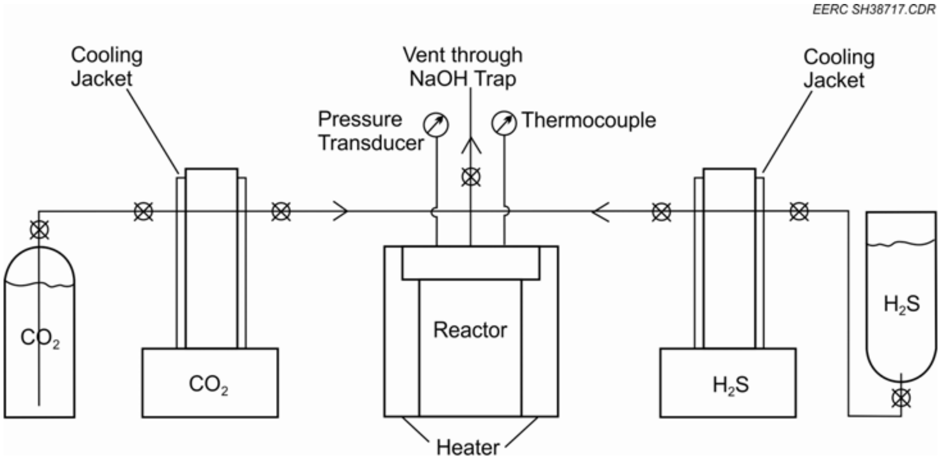

Figure 1 Schematic diagram of the system used for acid gas exposures. System components and operation are described in the text.

It should also be noted that, since H_2S sorbs into stainless steel, a vessel for H_2S/CO_2 mixtures should not be used for pure CO_2 exposures. Before its use for acid gas experiments, the reactor vessel should be passivated by previous exposure to H_2S. Similarly, any pump used for CO_2 should never be exposed to H_2S.

Sample Loading

Ultimately, the sample size is limited only by the interior dimensions of the reactor vessel. However, we generally use smaller samples that are placed in individual glass vials for four reasons: 1) to minimize the chances of catalytic effects from the stainless steel, 2) to protect the reactor vessel from chemical attack (e.g., brine solutions), 3) to allow multiple samples per procedure, and 4) to allow experimental variations (e.g., different brine concentrations or different reactants) in a single procedure. To this end, several different racks have been constructed which accommodate anywhere from two 250-mL glass bottles up to 16 individual samples in 15-mL glass vials (Figure 2). The vial racks include a top deflector plate to prevent the CO_2 and H_2S from blowing directly onto the sample vials during filling. Vials are capped with a polypropylene septum cap with the septum replaced with a disc of polyoxymethylene (POM, 76 µm) that has a 3-mm hole to allow pressurization of the sample, (note that some cap materials such as bakelite react with acid gas). Water (or brine) and other reactants can be added to the individual vials as desired. For example, exposures of wellbore cement were conducted with enough brine added to cover one-half of the cement rods being tested. This allowed the cement samples to simultaneously be exposed to water saturated by acid gas in the bottom of the vial and acid gas saturated with water in the top of the vial [3]. For exposures involving water, additional water is added directly into the bottom of the reactor vessel to ensure that individual vials are not dehydrated during the exposures.

Filling Pumps from CO_2 and H_2S Gas Cylinders

CO_2 pumps should be filled from a supply cylinder equipped with a dip tube so that liquid rather than gaseous CO_2 is transferred to the pump (Scott Specialty Gases, Plumsteadville, PA). In contrast to the difficulties in using a conventional CO_2 cylinder to fill pumps, using a dip tube-equipped cylinder eliminates the need for any prepumping or precooling apparatus to fill the CO_2 pump. If cylinders with dip tubes are not available, a similar advantage can be gained by inverting a conventional cylinder (with proper procedures and racks to ensure safety) as was done with the H_2S cylinder (Figure 1). No commercial supplier of H_2S cylinders equipped with a dip tube could be found, so a smaller (26 kg H_2S) cylinder was purchased that could be inverted into a rack and placed in a laboratory hood to supply liquid H_2S to the H_2S pump. However, during filling, it was

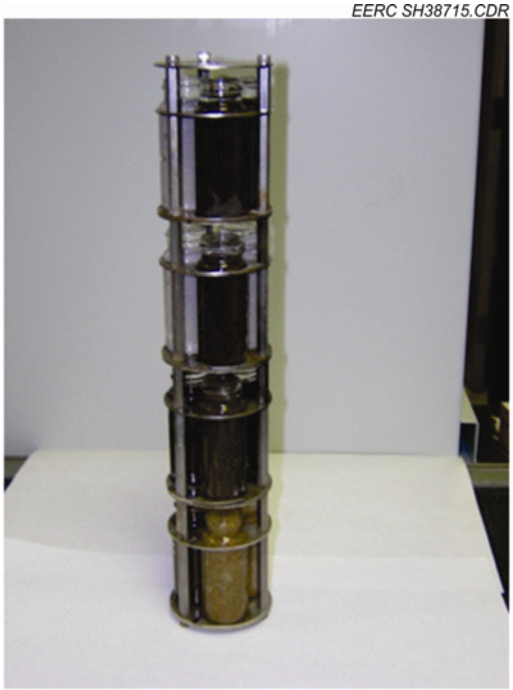

Figure 2 Sample rack with 12 sample vials.

also advantageous to cool the H_2S pump cylinder by circulating ice water through the pump's water jacket to aid in transferring and condensing liquid H_2S in the pump. After the H_2S pump was filled, no further water circulation was needed to stabilize the pump flow since (as discussed below) H_2S is much less compressible than CO_2 and shows much less heating and cooling upon pressurization and decompression than CO_2.

After ca. 30 minutes of filling time, the valve between the supply cylinder and pump is shut and the pump is pressurized to the working pressure in the constant pressure mode. Because of the heating which occurs with CO_2 upon pressurization, the pump is typically allowed to stabilize (as noted by a near-zero flow rate) for at least an hour before use. Room temperature water is continually circulated through the CO_2 pump to aid in stabilizing the cylinder temperature (and therefore the CO_2 density in the pump). Note that this long temperature equilibration step is not needed for H_2S since it shows very little heating upon compression.

Pressurizing the Reactor Vessel with CO_2 and CO_2/H_2S

To accurately mix acid gas, good control and measurement of the mass of fluid delivered by each pump must be achieved. Since the syringe pumps used are filled with the liquid phase of CO_2 and H_2S (respectively) at room temperature, pumping known amounts of each fluid initially sounds simple. Unfortunately, the physical characteristics of CO_2 make this surprisingly difficult. Ironically, H_2S is a much easier fluid to control during high-pressure experiments than CO_2 for two important reasons. First, CO_2 is very compressible compared to H_2S. For example, the density of liquid CO_2 in the pump (water jacket controlled at 25°C) changes from ca. 0.80 to 0.97 g/mL over a common experimental range of 100 to 300 bar, while the density of the H_2S under the same conditions only changes from 0.79 to 0.82 g/mL. Therefore, determining the exact mass of CO_2 delivered by a pump is much more difficult than for H_2S.

However, the most difficult challenge in accurately measuring CO_2 mass results from the very large heating and cooling that occurs upon pressurization and depressurization of CO_2 (while very little occurs with H_2S). When the pump is first pressurized with CO_2, the pump cylinder warms dramatically (even with the water jacket), causing the density of the liquid CO_2 in the pump to decrease significantly until the pump cylinder returns to the water jacket temperature. Thus, after reaching the desired pressure in the CO_2 pump with the pump in the constant pressure mode, the pump will continue to run at a significant rate until the liquid CO_2 and pump cylinder all return to the water jacket temperature. This is often wrongly ascribed to a leak since the pump keeps showing a significant flow rate, even when the system is entirely leak-free.

The opposite effect occurs when the reactor vessel is pressurized with CO_2, i.e., the expansion of the CO_2 into the reactor causes significant cooling of the vessel. If the valve between the vessel and CO_2 pump is then shut, and the vessel and its contents are heated back to the operating temperature, the pressure can rise significantly, thus raising the CO_2 pressure significantly above the desired conditions. Alternatively, if the valve is left open (and the pump is in constant pressure mode), the expansion of the CO_2 in the reactor as it warms will cause the pump to run backward to maintain its set point pressure. These problems in accurately delivering a known mass of CO_2 obviously make preparing accurate mixtures of CO_2/H_2S complicated. Fortunately, there are procedural solutions to these challenges as described below.

To accurately fill and pressurize the reactor with pure CO_2, a sequence of additions followed by temperature equilibration steps is followed. For example, for the 152 bar operating pressure used for the cement exposure discussed below, the vessel was first pressurized to ca. 83 bar, the valve between the pump and vessel was closed, and then the vessel and pump temperatures were allowed to stabilize to 50°C for about an hour, which resulted in a vessel pressure of ca. 120 bar. Two or three smaller fill steps (followed by allowing the pump and vessel temperatures to stabilize) were then used to slowly approach the 152 bar reactor pressure. With the procedure of allowing both the pump and reactor temperatures to reequilibrate between each addition, an accurate mass of CO_2 delivered by the pump can be determined.

While it is not necessary to know the mass of CO_2 introduced into the reactor for pure CO_2 exposures, it is necessary to be able to accurately measure the mass of the CO_2 (and H_2S) for the CO_2/H_2S exposures so that the mole ratio of the fluids can be determined. By following the step wise fill/equilibrate procedure listed above for the CO_2, the pump volume could then be accurately read and the mass of CO_2 delivered to the vessel calculated based on the liquid CO_2 density of 0.89 g/mL in the pump (at the pump pressure of 152 bar and 25°C temperature). For the mixed CO_2/H_2S experiments, known mixtures were produced by alternating CO_2 and H_2S additions to the reactor. The ratio of H_2S and CO_2 pump volumes to be added at each pressurization step were calculated from the fluid densities in the pump (0.89 g/mL and 0.79 g/mL for CO_2 and H_2S, respectively, under the conditions used for the cement study). This procedure requires three or more rounds of $CO_{2,}$ then H_2S addition, but can result in accurate mixes of the desired acid gas composition. Depending on the vessel temperature and volume, this sequence can be completed in ca. 1–3 hours.

It should be noted that, since H_2S is not highly compressible and does not show large temperature changes up on pressurization and depressurization, it is not necessary to wait more than a couple of minutes after pressurization in order to get an accurate reading of the H_2S used—in contrast to the much longer time required for the CO_2 pump to stabilize sufficiently to obtain accurate pump volume readings.

Ensuring Single-Phase Behavior in the Reactor Vessel

It is obviously important that the phase behavior of the fluid in the reactor be understood and controlled. For a pure fluid, this is simple since the single-phase supercritical state exists as long as the temperature and pressure are above the critical values. Without these conditions being met, the samples in the reactor vessel can have only gas, only liquid, or both gas and liquid. Mixed fluids are somewhat more complicated since, depending on their composition, H_2S/CO_2 mixtures have different critical temperatures and pressures somewhere between those of pure CO_2 (74 bar, 31°C) and H_2S (89 bar, 100°C). The critical temperatures and pressures of different H_2S mixtures can be described by the critical locus on a pressure composition diagram [4], and the reader is referred to that reference for more details. However, for most H_2S/CO_2 mixtures of interest, the temperature and pressures typical for studies related to acid gas injection should suffice. For example, single-phase behavior is assured at temperatures above 50°C and pressures above ca. 85 bar for any

H_2S/CO_2 mixture up to 40 mole % H_2S and at temperatures above 40°C and pressures above 80 bar for mixtures up to 20 mole % H_2S [4].

Safety

Because H_2S is toxic, all experiments and related apparatus including the H_2S pump and the 1/2-sized (26-kg) H_2S supply cylinder are located in a ventilated lab hood. Hood sashes are kept nearly closed unless the operator is working with the apparatus. Redundant H_2S monitor/alarms are placed on the inside surface and outside of the hood. The outlet tubing of the reactor vessel is submerged in ca. 500 mL of a 1.0 molar NaOH trapping solution during the exposures, and at the end of the exposure period, the CO_2/H_2S from the reactor is slowly vented (several hours) through the trapping solution to remove H_2S from the gas stream. In addition, maintenance personnel are personally informed each time the vessel is to be vented and are trained to not perform any repair or maintenance operations on the hood ventilation system that could result in exposure at any time without real-time authorization from the laboratory personnel responsible for the CO_2/H_2S experiments.

Results and Discussion

The apparatus described above has proven reliable at typical injection/sequestration temperatures and pressures for exposures up to several months. With the procedures detailed earlier, accurate mixes of H_2S and CO_2 can be prepared. Duplicate vessels have been used to compare the effects of pure CO_2 and acid gas (typically 10 to 20 mole % H_2S) on a variety of materials related to sequestration, and the effects of acid gas compared to CO_2 are often dramatically different. For example, while wellbore cement exposed to CO_2 forms a carbonate “sheath” on the cement surface (Figure 3), cement exposed to acid gas reacts with H_2S throughout the depth of the sample, leading to significant alteration throughout [3]. Similarly, some oil reservoir proppants exposed to acid gas show a ca. 50% loss in structural integrity compared to those only exposed to pure CO_2. Obvious visual differences occur when exposing various minerals to acid gas and pure $CO_{2,}$ as shown in Figure 4 (for a discussion of the different reactions occurring in various minerals exposed to CO_2 and acid gas, see Paper 1117.00).

Since, with the proper selection of vessels and their seals, the systems can be leak-free and reaction rates can be observed in real time by monitoring fluid use at the pump. This is demonstrated in Figure 5 by the reaction of iron oxide with H_2S (207 bar, 70°C, 40 mole % H_2S/CO_2) to form iron sulfide. The plot of H_2S used (as determined at the H_2S pump) versus exposure days demonstrates a reaction half-life of ca. 20 days. In addition, the mass balance of H_2S used is good, with 0.54 moles of H_2S used compared to a theoretical 0.48 moles. Real-time monitoring of carbonation reactions (e.g., conversion of magnesium silicate to magnesium carbonate) has also been performed,

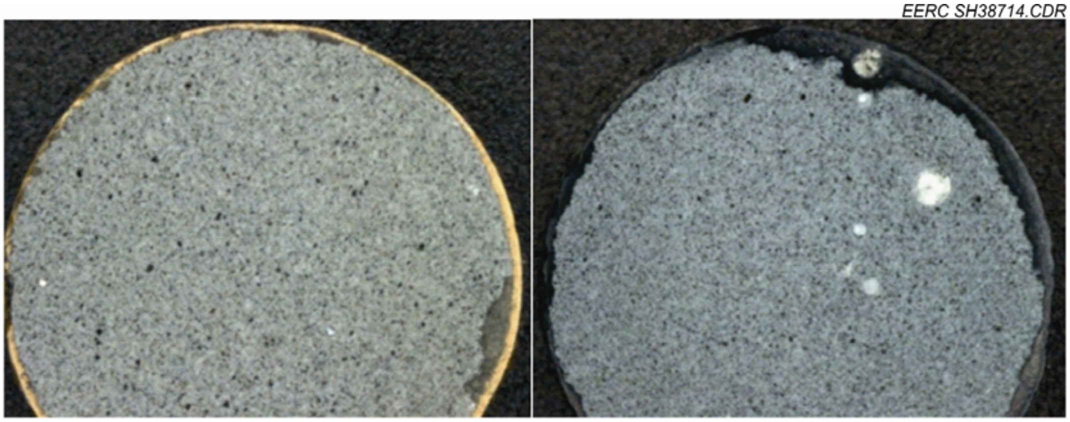

Figure 3 Wellbore cement exposed to pure CO_2 (left) and to acid gas (right) for 28 days.

Figure 4 Changes in calcite and illite minerals when exposed to pure CO_2 (left vial in each photo) and acid gas (right vial in each photo). Discussions of the mineralogical reactions that occur under pure CO_2 and with acid gas are in Paper 1117.00.

but it is more difficult to achieve accurate readings of CO_2 mass used (compared to H_2S) because of the high compressibility of CO_2 discussed earlier.

Conclusions

Careful consideration of the fluid properties of CO_2 and H_2S, especially phase behavior, compressibility, and compression/decompression heating and cooling, allows relatively simple systems to be assembled that can accurately prepare acid gas mixtures and expose a wide variety of materials related to the injection of CO_2 and acid gas. The systems described are capable of leak-free operation required for obtaining mass balance in monitoring reactions, and real-time measurements can be made to monitor and determine reaction rates of samples exposed to acid gas. Dramatic differences in the effects of CO_2 and acid gas have been demonstrated on a variety of samples related to sequestration ranging from wellbore cement to oil reservoir proppants and minerals, indicating the need for much more extensive studies on the potential effects of acid gas injection.

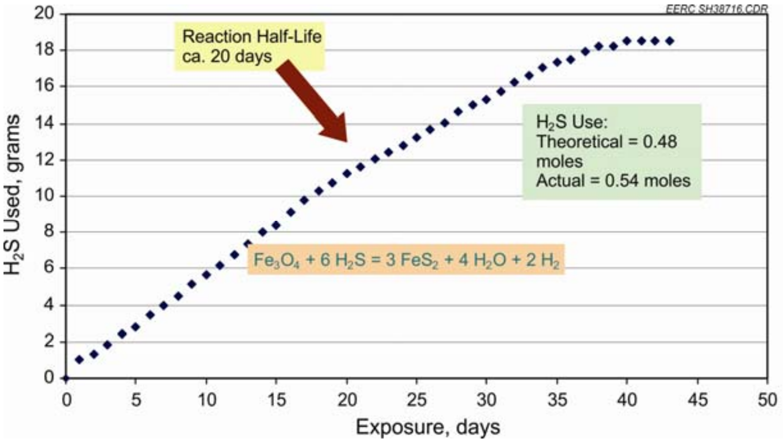

Figure 5 Determining the reaction rate of iron oxide with H_2S (207 bar, 70°C, 40 mole % H_2S/CO_2) to form iron sulfide by monitoring H_2S use at the pump.

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Disclaimer

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