Experimental Investigations of the Effects of Acid Gas (H_2S/CO_2) Exposure under Geological Sequestration Conditions

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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. 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 well-bore 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 ^{o}C and 6000 psi (414 bar) using any desired H_2S/CO_2 mole ratio. Up to 24 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 Joules-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.

Several static exposure experiments have been performed to compare the relative effects of acid gas and pure CO_2 exposure, as well as the effects of brine concentration, on mineral samples from geological reservoirs, oil reservoir proppant stability, and well-bore cement stability. Typical reaction times are for one month, with pressures and temperatures selected to match the "down-hole" conditions (typically 1500 to 3000 psi, 50 to 150 ^{o}C, zero to 40 mole % H_2S in CO_2). Individual samples are exposed to water, brine, or water-saturated headspace fluid. Oil reservoir proppants have shown degradation in strength under both pure CO_2 and H_2S/CO_2, with some proppants showing markedly more degradation in acid gas. Investigations into mineral reactions under pure CO_2 and acid gas are currently being conducted, but differences in reactions are readily apparent. For example, pure CO_2 appears to solvate iron from several minerals (e.g., ankerite, pyrite, and illite) and form hematite while acid gas does not, possibly because of reaction of the iron to form pyrite in acid gas.

A major experimental focus to date has been the effect of acid gas on well-bore cement stability, including class H cements with and without Pozzolan additives. Obvious differences were observed between 20 mole % H_2S/CO_2 and CO_2-only exposed cement, with acid gas-exposed cement showing more reactivity than cements exposed to CO_2 only. Cements with additives showed generally better resistance to acid gas than pure cement. Differences were also observed between the submerged and headspace exposed portions of the samples, with the submerged portions showing more reactivity. The acid gas exposed cement underwent a combination of carbonation and redox reactions that ultimately degraded the cement's physical strength. The outer rim of the cylindrical cement samples were characterized by a zone of carbonation and the sulfidation of tetracalcium aluminoferrites to pyrite. Beyond the carbonation rim is evidence of significant impact from the H_2S in the form of ettringite and very small grains of pyrite. Ettringite is formed due to oxidation of H_2S which produces sulfides which in turn reacts with Ca-compounds. The carbonation reaction lowers the pH in the cement matrix to allow dissolution of ettringite and the tetracalcium aluminoferrite for pyrite formation. Because the implications of the observed acid gas reactions regarding geologic co-sequestration and wellbore integrity are significant, additional experiments to determine the rate and ultimate extent of sulfidation reactions with cement are currently being conducted.

This paper will present the methods and apparatus used to perform acid-gas experiments under conditions relevant to geological reservoirs. Example results from acid gas and pure CO_2 exposures on oil field proppants, various mineral types, reaction rate determinations, and well-bore cement chemistry and stability will be discussed.