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. 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.

We have developed approaches using conventional syringe pumps and reactor vessels to prepare and maintain H_2S/CO_2 mixtures under relevant sequestration conditions of temperature, pressure, and exposure to water and dissolved salts. These methods have been used to investigate and compare the effects of acid gas with those of pure CO_2 on several materials including reservoir cores, oil recovery proppants, and wellbore cements, as well as to investigate the rates of model reactions such as the conversion of Fe_3O_4 to pyrite. The apparatus and methods used to perform acid gas exposures and representative results from the various exposed materials will be presented.

Introduction

More than 50 acid gas injection wells are in the Plains CO_2 Reduction (PCOR) Partnership region, mostly in Alberta, but there are very few studies on long-term effects of acid gas.

The Energy & Environmental Research Center (EERC) is developing equipment to perform CO_2/H_2S studies relevant to sequestration and EOR such as:

- Wellbore integrity (erosion rates, relative H_2S vs. CO_2 penetration, fracture healing/ erosion, related materials
- Geological reactions (coal, minerals, brine, reservoir plugging)
- Enhanced oil recovery (EOR) proppants
- Model mineral and geological reaction rates

Relevant Experimental Conditions

800 to 3000 psi
40° to 150°C
0 to 40 mole %
Wet and headspace moisture
0 to 10 wt% salt
Flow-through vs. immersion
Weeks to years of exposure

Acknowledgments

The Plains CO_2 Reduction (PCOR) Partnership is a collaborative program assessing regional CO_2 storage opportunities. Its primary sponsor is the U.S. Department of Energy National Energy Technology Laboratory, with additional support from its more than 80 partners.

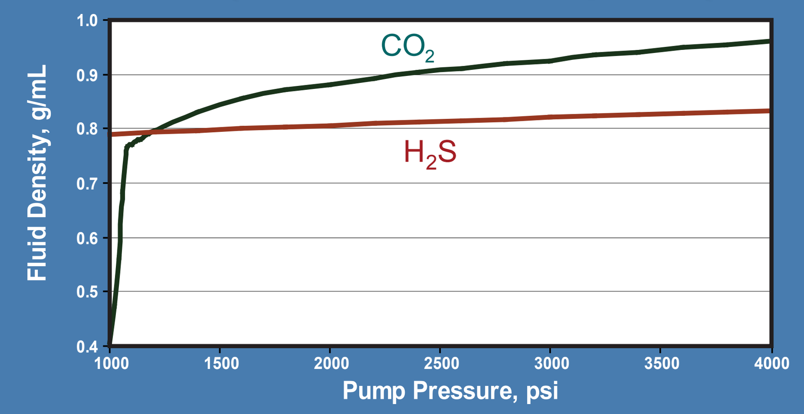
PCOR Partnership 2003 – Present

Experimental Challenges for Acid Gas Experiments

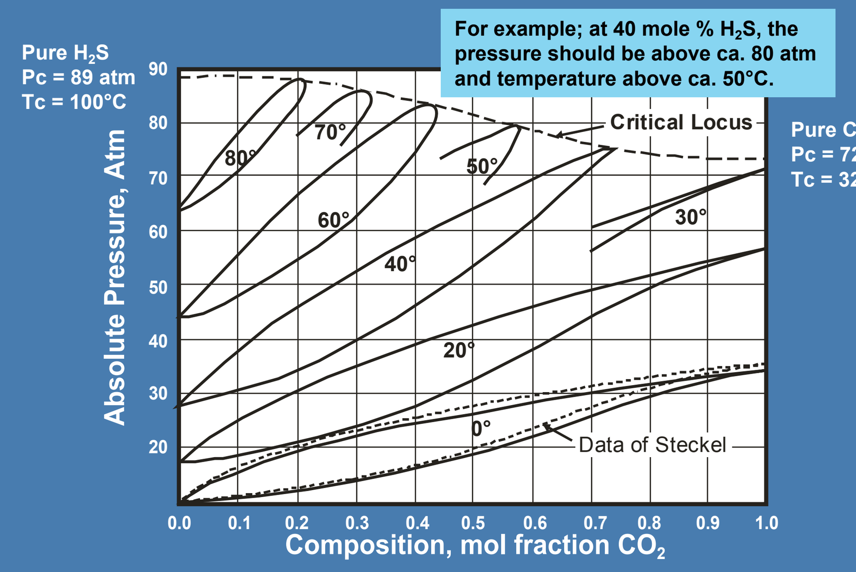
Challenges in performing mixed H_2S/CO_2 experiments are based on fluid "naughty and nice" characteristics.

	Naughty	Nice
CO_2	Very compressible High J-T cooling/heating Difficult to control flow	Low toxicity Doesn't stink
H_2S	Stinks Highly toxic	Noncompressible Low J-T cooling/heating Easy to control flow

CO_2 is very compressible in the pump, even with temperature control (25°C). This makes flow/mass control difficult for CO_2, while H_2S is easy since it is not very compressible.



The T and P conditions required to be single phase (supercritical) vary with H_2S/CO_2 mole ratios.



J. Bierlien and W. Kay, Ind. and Eng. Chem. 1953.

Safety

- All storage, handling, and use of H_2S is done in a hood.
- Total quantities of H_2S are limited to <50 lb.
- Lab air is exchanged ca. every 4 minutes.
- Redundant H_2S alarms are located by each hood.
- H_2S is vented through a NaOH trap.

Apparatus

Accurately mixing H_2S and CO_2 requires temperature-controlled pumps and leak-free vessels.

Pumps: ISCO model 260D syringe pumps, capable of dual pump control for fluid mixing.
Water jacket for CO_2 to aid in flow control
Hastalloycylinder for H_2S.

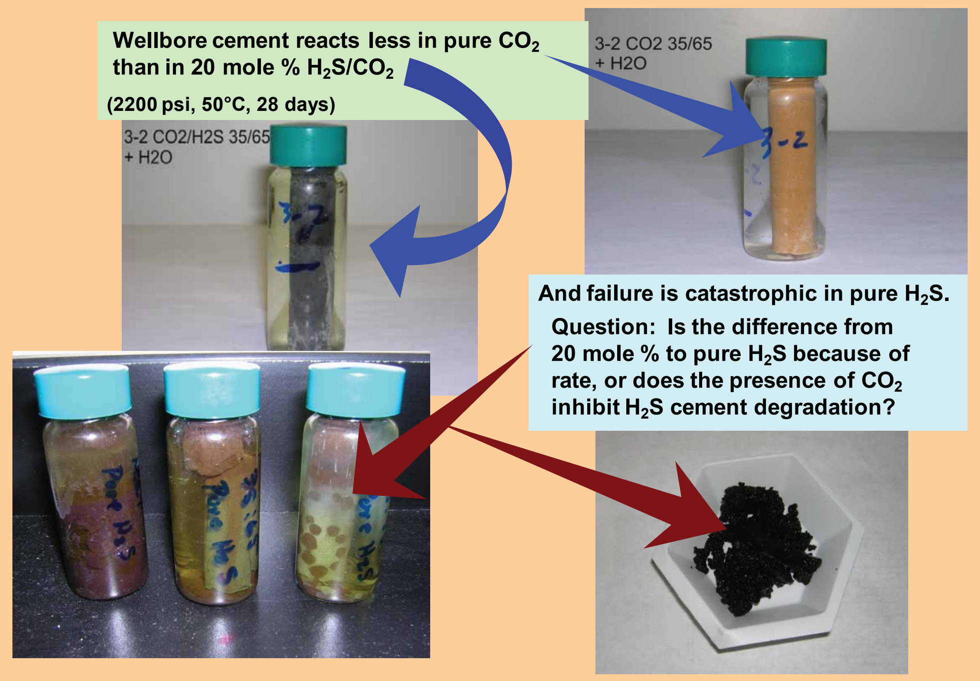
Vessels: Parr Instruments (others leaked).
600 mL and 1000 mL, 2.5 in i.d., up to 6000 psi
Separate systems for CO_2/H_2S and pure CO_2

1-L vessel and heater

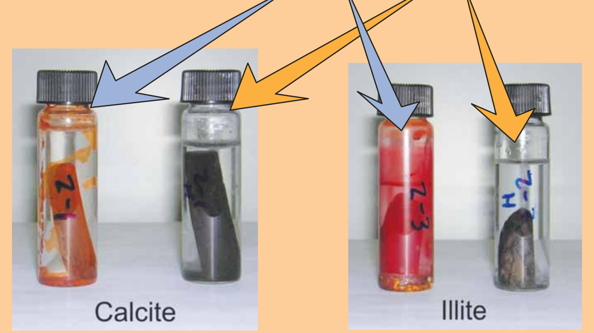
0.6-L vessel

Exposures are done in glass vials to allow multiple samples and varying salt concentrations in a single reactor.

Representative Results



Mineral reactions show dramatic visual differences occur with pure CO_2 and CO_2/H_2S.



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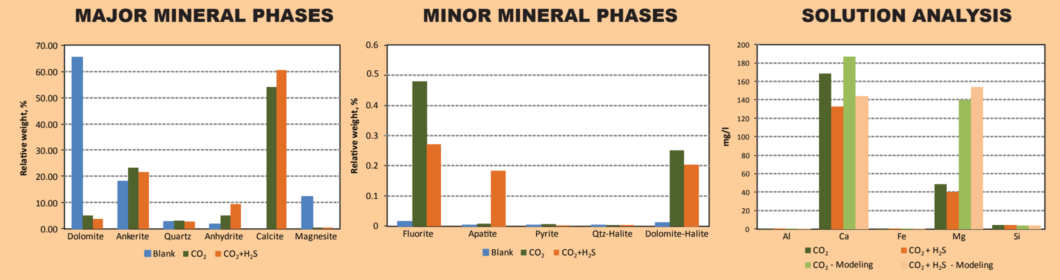
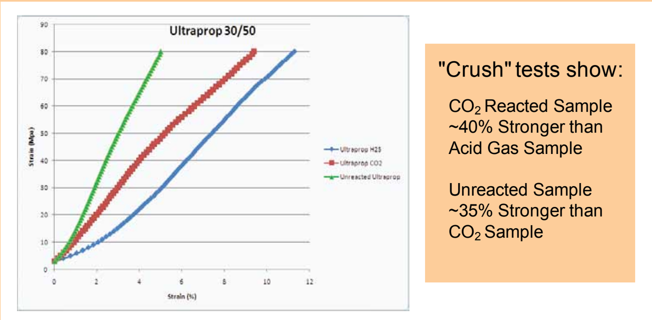
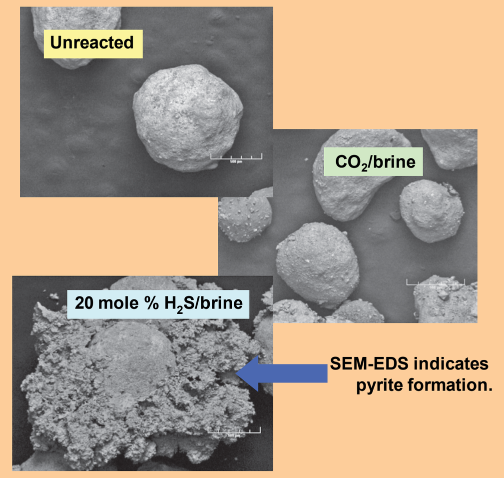
Original Sample | After Exposure (CO_2) | After Exposure (CO_2+H_2S) | After Exposure (CO_2) | After Exposure (CO_2+H_2S)



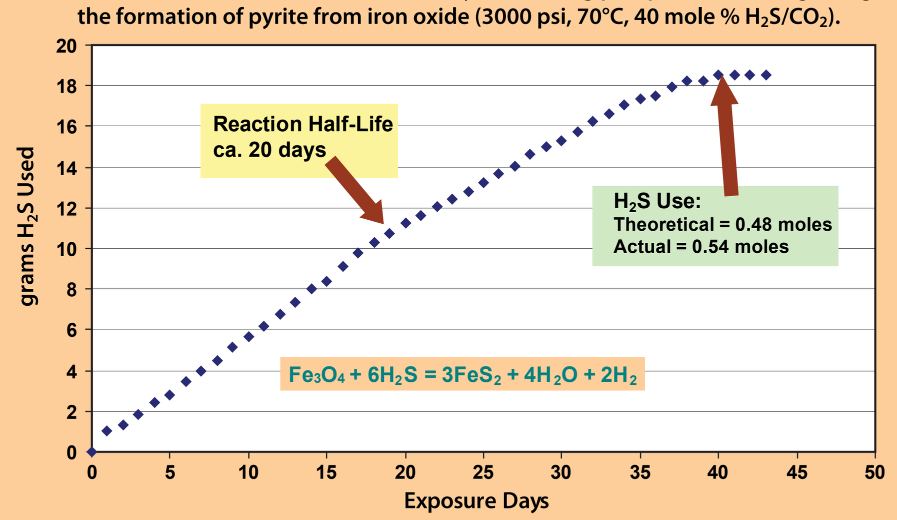
Exposure weakens most proppants, with acid gas causing more degradation than pure CO_2.





Some oil reservoir proppants show little reactivity in CO_2, but substantial reactions in H_2S/CO_2 (SG "Ultraprop" 50°C, 2200 psi, 28 days).

Reaction kinetics can be determined by monitoring pump volume changes, e.g., the formation of pyrite from iron oxide (3000 psi, 70°C, 40 mole % H_2S/CO_2).



Summary and Conclusions

Lab systems have been built for mixed H_2S/CO_2 exposures under geologically-relevant conditions. The systems can be used for:
- Exposures from ambient to 6000 psi and 350°C, zero to 100% H_2S
- Multiple samples (up to 21 or more) exposed simultaneously.
- Reaction rate studies by monitoring H_2S (or CO_2) consumption.

Initial results comparing acid gas to pure CO_2 show:
- Increased degradation of wellbore cements.
- Pyrite formation from iron-containing samples.
- Decreased strength of oil reservoir proppants.