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Considerations for Treating Impurities in Oxy-Combustion Flue Gas Prior to Sequestration

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Abstract

Various design, engineering, and economic analyses are being investigated to better understand the cost and performance of retrofitting oxy-combustion technologies for existing power plants. Currently, we are in the process of evaluating all downstream operations in which flue gas impurities may impact the design and performance of an oxy-combustion capture system. It is our plan to identify two geological storage reservoirs that are different in their characteristics and require different degrees of gas purifications to illustrate the economic impact on reservoir selection.

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Oxycombustion; impurities; thermodynamic property; CO₂ capture; CO₂ storage

1. Introduction

Although the concept of carbon capture and storage has so far dealt with nearly pure carbon dioxide (CO₂), flue gas from oxycoal combustion contains a host of compounds which may dramatically alter this concept. In an ideal situation the flue gas could be injected into deep geologic formations with little to no prior conditioning. At the other extreme the flue gas could require such extensive purification that presumed benefits of an oxygen blown system are soon negated. To determine whether the true scenario is more optimistic than pessimistic, a top down assessment must be employed to understand the effects of non-CO₂ flue gas constituents on the entire sequestration process. We have begun studying such an approach by investigating the physical and chemical differences between pure CO₂ and oxycombustion flue gas. This provides a starting point from which to examine the sensitivities of individual operations throughout the sequestration process. Another aspect of this research has been to investigate reactive transport of CO₂ and SO₂ injection into deep saline formations and their effect on the hydraulic properties of host rocks, which is described by Bacon et al. [1].

Optimization of the boiler and flue gas purification train enable cost savings. The key is to view the whole process of oxygen separation, coal combustion, steam generation, flue gas purification (if required), transportation and sequestration together. Cost savings can be realized by optimizing the flue gas handling through two fundamental options: one is to compress the flue gas with minimal conditioning and inject it directly into a suitable geologic formation; another is to selectively separate gas components that may not be advantageous to long-term injection. The former case could require less environmental control equipment that is commonly used in air blown pulverized coal (PC) combustion units to remove sulfur oxides (SO_x) and nitrogen oxides (NO_x). However, the feasibility of this option will require a thorough understanding of reservoir mechanics and geochemistry. For example, non-condensable gases, such as nitrogen, oxygen and argon, may affect the transport processes of the flue gas in the subsurface by creating multi-phase flow, which could reduce the injectivity and/or the capacity of the aquifer for CO₂ storage over the lifetime of the power plant. If, in certain situations, additional purification is determined to be needed

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for removing non-condensable gases or some impurities, due to their effects on compression, handling, or regulatory compliance, then equipment for scrubbing these non-condensable gases or impurities would need to be brought on line, thus adding to the cost of storing CO₂ produced by oxycoal combustion. Considerations for flue gas purity as it leaves the boiler and is processed in downstream unit operations are illustrated in Figure 1.

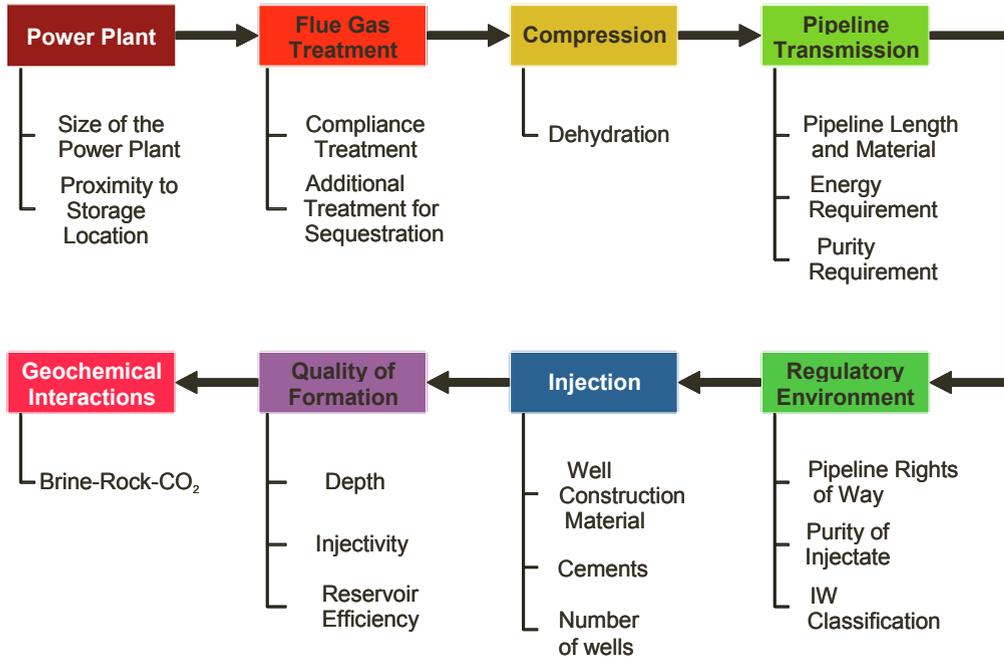


Figure 1. Process description for flue gas interactions

Our approach to evaluating whether physical or chemical treatment is needed prior to sequestering oxycoal flue gas is summarized in the following four bullets:

- Determine the flue gas composition from an oxy-fired boiler
- Review the pipeline gas requirement
- Determine the steps that are required for the flue gas purification
- Perform reservoir and geochemical modelling to ensure feasibility of sequestering the flue gas.

2. Estimation of Flue Gas Properties

Pure CO₂ has been thoroughly characterized for a wide range of conditions, as compiled by NIST [2]. A general behavior of all gases is that a slight change in pressure or temperature near the critical point has a large effect on the density. It is not essential that the fluid be in the supercritical state once it is either in the pipeline undergoing transport, or in the injection well being carrier to a storage reservoir, but it is desirable that the phase state be constant. For safety to equipment and human operators, abrupt changes in fluid properties near the critical point phase should be avoided throughout the transportation and injection processes.

Aspen-Plus simulations were performed on models of retrofitted oxycombustion boilers for three coal types: North Dakota Lignite, Decker (Montana), and Illinois #6. Expected compositions for flue gas streams cooled to 160°F are shown in Table 1, where it can be seen that the CO₂ content is between 58 and 60% by volume. When dehydration and oxygen scrubbing are performed on these same flue gas streams the CO₂ content increases to between 74 and 76% by volume (Table 2).

Table 3 shows the critical pressure and temperature for the components of the flue gas. After SO₂, CO₂ has the next highest critical pressure and temperature of the gases listed.

Table 1. Estimated flue gas composition after cooling to 160°F

Coal Type	O ₂	H ₂ O	CO ₂	N ₂	Ar	SO ₂
	(%)	(%)	(%)	(%)	(%)	(ppmv)
North Dakota Lignite	4.1	17.4	59.6	16	2.4	3825
Decker	4.0	17.4	59.5	16.3	2.5	1348
Illinois #6	4.1	17.4	58.1	17.6	2.5	1003

Table 2. Estimated flue gas composition following dehydration and oxygen scrubbing

Coal Type	O ₂	H ₂ O	CO ₂	N ₂	Ar	SO ₂
	(ppmv)	(ppmv)	(%)	(%)	(%)	(ppmv)
North Dakota Lignite	100	650	76.0	20.4	3.1	4877
Decker	100	650	75.8	20.8	3.2	1718
Illinois #6	100	650	74.2	22.5	3.2	1280

Critical properties of gas mixtures are important in understanding their behavior in transportation and injection. However, these properties are not well known for multi-component systems near the critical point of CO₂, and they are not easily estimated because such systems do not obey simple mixing rules. In fact, the behaviors of certain gas mixtures can be counterintuitive. The thermophysical properties of fluid mixtures can be estimated using a combination of theoretical and empirical techniques which are based on evaluated data. These techniques have been tested and incorporated into interactive computer programs that generate a large variety of properties based upon the specified composition and the appropriate state variables. One such program is REFPROP [3], which was developed by NIST.

Consider, for example, a mixture containing 80 mole% CO₂ and 20 mole % N₂. Using REFPROP the critical point properties were estimated to be of 10.2 MPa, 53.6 F, and 480.3 kg/m³. Surprisingly, the critical pressure of the mixture is much higher than either of the pure endpoints. This dramatic increase in critical pressure is a common behavior for mixtures of fluids and is well established for binary mixtures. Within the limitations of REFPROP a mixture can be defined that is an approximation of the flue gas mixture: 0.7259 CO₂, 0.1948 N₂, 0.0292 Ar, 0.0002 CO, 0.0499 O₂ (mole fraction). This mixture has estimated critical conditions of 9.09 MPa, 31.1°F, and 478 kg/m³. Compared to pure CO₂ this has a higher critical pressure and lower critical temperature.

Table 3. Critical point conditions for the constituents of the flue gas.

Component	Critical Pressure (MPa)	Critical Temperature (°C)	Critical Density (kg/m ³)
CO ₂	7.39	31.0	467.6
N ₂	3.39	-147.0	313.3
O ₂	5.04	-118.6	436.1
Ar	4.87	-122.4	535.6
SO ₂	7.87	157.8	525.0
CO	3.49	-140.3	303.9

3. Transporting CO₂ with Impurities

Most of the experience in CO₂ pipelines is with a nearly pure product. These pipelines have a good operating history with a safety record that is on par with natural gas piping systems. For pipelines with significant amounts of constituents other than CO₂, the composition has a significant impact on pipeline design, compressor power, pressure drop, and pipeline capacity. These factors influence both the technical and economic feasibility of developing a carbon dioxide transport infrastructure. While pipelines can be designed to meet the safety and handling needs of almost any situation, the cost of the pipeline can vary significantly depending on the way specific situations are handled.

Methods for analysis of CO₂ pipelines with significant levels of inert constituents, such as nitrogen and argon, are only recently becoming available in the literature. Selecting an appropriate equation of state (EoS) is an important part of understanding the transport properties of CO₂ with significant amounts of other constituents. Unfortunately, there is no consensus in the literature regarding the level of applicability of various approaches to pipeline modeling. Additional work, particularly in model development and experimental verification, is required to understand the implications of impurities and to ensure that

pipelines transporting CO₂ are designed and operated safely and economically. If these issues are not considered in the pipeline design, transportation issues for CO₂ with impurities could present significant problems

The composition of the product flow in the pipe has a significant impact on integrity and selection of materials. Water is the important factor. Most current CO₂ pipelines operate with very low level of water, which is undersaturated with respect to the liquid state, so that it exists only as a vapor. The presence of liquid water in a mixture of carbon dioxide (CO₂), sulfur dioxide (SO₂), and oxygen (O₂) can cause severe internal corrosion in steel pipelines, which of course is detrimental to the safety and operability of such pipelines. Corrosion in pipelines that contain CO₂ in solution (i.e., dissolved phase) is influenced by temperature, CO₂ partial pressure, water chemistry, flow velocity, water wetting and composition and surface condition of the steel. The flow conditions are often extremely turbulent, which has the effect of increasing corrosion rates above that which would occur under static level. However, attaining dry product can add significant cost to the capture process. Another complicating factor is that some capture systems may introduce small amounts of solvent vapor due to break-through, which that could accelerate corrosion or initiate stress corrosion cracking in the pipeline steel. Detailed corrosion analysis is needed to assess the viability of simple carbon steel materials as well as the array of corrosion resistant materials.

3.1. The need for optimization

The plant design and operation define the amount of CO₂ that needs to be stored and the rate at which it is delivered to the storage reservoir. Reservoir geology and depth determine the temperature and constrain the injection pressure to a lower limit needed to induce flow of CO₂ into the formation and to an upper limit of approximately two-thirds the fracture pressure of the formation (this is a practical “rule of thumb”). Design variables also need to be considered. For example:

Smaller diameter pipelines are less expensive but can experience higher pressure drops. The increased cost of a larger diameter pipeline must be traded against the cost of compression.

The diameter of the well is significant variable since this is a principal source of pressure drop. The increased cost of a larger diameter well, or multiple wells, also needs to be factored against the cost of compression.

That oxycombustion flue gas contains nitrogen, oxygen, argon and several minor constituents in addition to CO₂, has significant bearing on many of the fundamental parameters that affect fluid flow. For example, N₂ mixed with CO₂ reduces the density of the gas mixture compared with pure CO₂, which of course decreases the hydrostatic pressure inside the well column. Consequently, wellhead pressure must be increased to compensate for the reduced bottom hole pressure (which determines the rate of fluid ingress), thus demanding higher compression pressures. Frictional factors also increase with mixing of CO₂ with nitrogen and other incondensable gases. This causes a greater pressure drop, which of course increases with pipeline distance, and again must be compensated with higher compression or more frequent recompression (booster) stations.

3.2. Technical Assessment of Transport

The flow characteristics for CO₂ pipelines for enhanced oil recovery (EOR) are sufficiently well understood to enable safe and economic operation. However, transporting products comprised of multiple constituents can lead to significant problems. In the natural gas industry, additional engineering is needed for natural gas pipelines when even small amount of heavier hydrocarbons are present.

The composition of the product to be transported has a great impact on pipeline design, compressor power, recompression distance, pipeline capacity, and could also have implications on decompression behavior at potential points of pipeline failure. These effects have direct implications for both the technical and economic feasibility of developing a CO₂ transport infrastructure.

The flow of the mixture through the pipelines is relatively straightforward and predictive design equations are well established, however, if the fluid is a mixture and not pure CO₂ there are two challenges: First, it is important to determine the mixture transport parameters for a given fluid state. The major component of the fluid is CO₂, which is quite compressible and undergoes significant changes in properties, hence constant properties cannot be assumed for the mixture even if the lesser constituents' transport properties were constant in behavior (which they are not). Second, the phase behavior of the components must be compatible, also, since a phase change during pipeline transport is typically avoided for reasons of safety and pipeline integrity.

Additionally, the equilibrium composition needs to be studied to ascertain if any significant reactions are present as the fluid undergoes transport. For example reactions between the species may be negligible for the surface pipe pressures and timescales. A check needs to be done to ensure this is also true near the bottom of the well where the pressures are substantially higher.

The transport properties of fluid mixtures can be difficult to predict over a wide range of conditions. Many pure fluids have been tested experimentally and validated predictive equations of state exist, but arbitrary mixtures do not always have data. Binary mixtures can be predicted and ternary and multicomponent mixture models continue to be developed Wei and Sadus [4]. The behavior depends on the type of fluid, the composition, and the conditions. Predictions for mixtures depend heavily on the accuracy of the EoS and dependent empirical parameters.

Of interest here is a comparison of the bulk transport properties of the flue gas as compared to pure CO₂. If we ignore heat transfer effects in the pipe flow, then the main transport properties necessary are the fluid viscosity and the fluid density. The ratio of these properties (fluid viscosity / fluid density) is called the kinematic viscosity. A preliminary analysis shows that the kinematic viscosity of the dry flue gas mixture can range between 0.7 to 1.4 times that of pure CO₂ as shown in Figure 2. This is an important transport quantity, because it can affect the pipeline flow, and most certainly affects the injectability into the geologic formation. The fluid density is important because in the vertical well pipe it contributes to the downhole pressure due to body forces and it also affects the transport. Temperature and heat transfer effects also need to be considered since they can affect the bottom hole pressure.

3.3. Technical Assessment of Corrosion Issues

Carbon steel used for most energy pipeline applications is the most cost-effective material for transportation of carbon dioxide. The mechanical properties and the low cost are important considerations when long distances are planned. However, steels are susceptible to corrosion in the flue gas environment due to water, O₂, CO₂ and other constituents that can cause corrosive products. The corrosion shortens the service life; therefore the steel pipelines should have different physical and chemical properties to be compatible with the product.

While the oxygen and sulfur composites define the corrosion rates, the water content defines the potential corrosion sites with the corrosion rates calculated according to the operation conditions. Figure 3 shows the number of sites that the 0.2mm/yr corrosion rate that might appear according to the water content. The low free water content minimizes the general corrosion conditions, but does not eliminate the number of localized spots in the pipeline wall. The 2500 ppm of water in an area of 1m² might have 10 potential sites for localized corrosion at corrosion rates described in the previous two plots. A Kinder Morgan specification for water is 30 lb per MMscf in the vapor phase, which is equivalent to 650 ppm. Even under these relatively dry conditions, 1 or 2 corrosion sites could be expected to form per square meter of steel surface.

3.4. Injection Process

The injection process relies on moving the injection stream from the wellhead, through the injection tubing, and into the storage formation. Assuming a supply of CO₂ at the wellhead at supercritical conditions, no additional compression may be necessary at shallower depths. Deeper injection targets may require additional booster compression to reach injection pressures.

Despite the added complexity, impurities in the injection stream are unlikely to be detrimental to the concept of CO₂ storage by deep well injection. As long as the gas stream has low level of impurities, CO₂ production wells, as in Christopher [5] and sour gas (H₂S) injection wells, as in Bachu [6], generally encounter few problems with operations. The gas components would be in either supercritical or liquid phase at the wellhead. In pure phase, the compounds CO₂, SO₂, and NO₂ are not reactive until they react with water to form acids. Ar and N₂ are inert gases while O₂ can promote corrosion of well materials. The main issues with the injection process are less direct:

3.4.1. Volumetric Increase

The overall injection volume with impurities will be greater than a pure CO₂ stream. Additional injection wells, larger casing, larger diameter tubing, and associated equipment may be necessary to inject CO₂ on a mass basis. The added costs associated with this additional volume are likely to be a fraction (10-25%) of the capital and operation costs associated with an injection system. However, this increase may be substantial for larger sources (e.g. 10 million tonnes per year for CO₂ with impurities versus 12 million tonnes per year for CO₂ only stream).

3.4.2. Injection pressures

The impurities will lower the density of the injection stream to some extent, mainly due to N₂ and Ar. The injection process relies on the weight of the fluid column in the injection well to complement injection pressures. Thus, a lighter injection stream will require additional injection pressure and associated compression proportional to the density of the fluid.

3.4.3. Enhanced Oil Recovery Limitations

Impurities may limit potential to utilize the gas stream for enhanced oil recovery projects. NO_x can decrease oil recovery, and SO_x may improve oil recovery, but at the specified concentrations the compounds are not likely to affect recovery rates. Oxygen

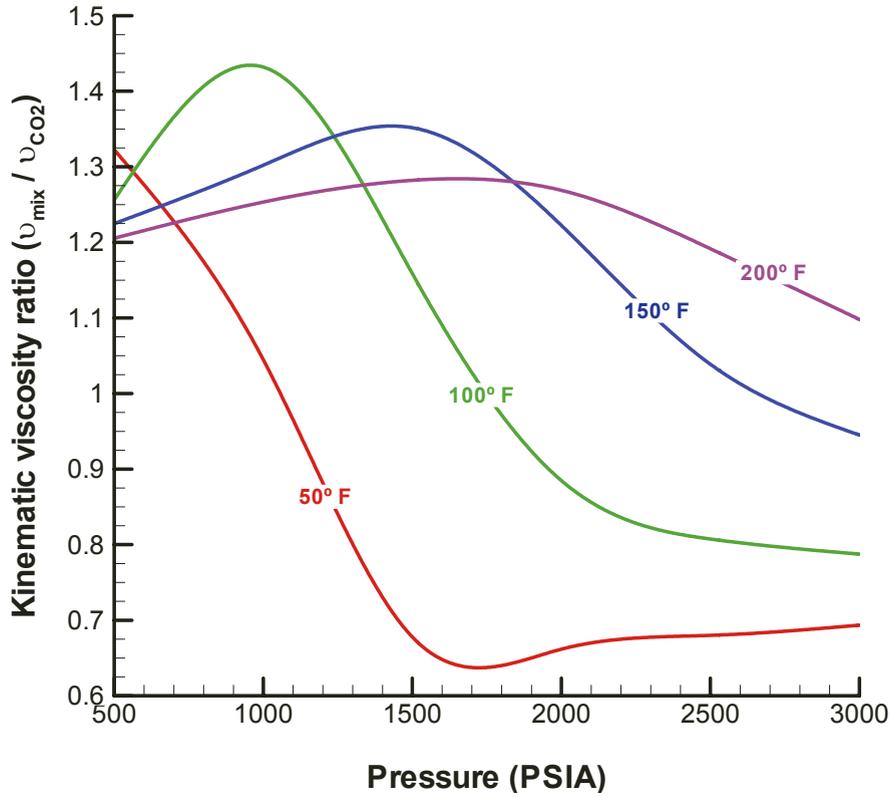


Figure 2. Kinematic viscosity of approximate flue gas mixture divided by the kinematic viscosity of pure CO₂.

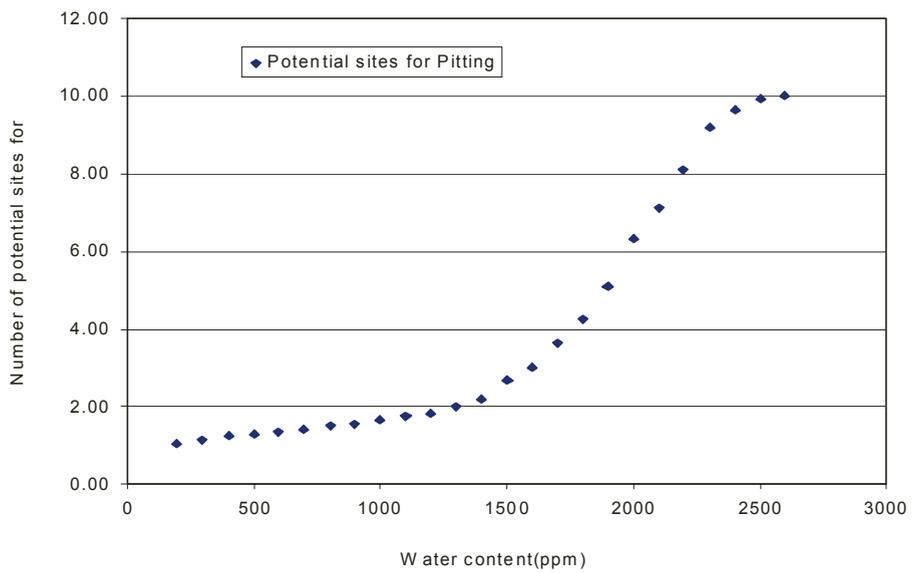


Figure 3. Water content vs. number of potential corrosion local sites

can react exothermally with oil in the reservoir and limit recovery. It can also promote bacterial growth and corrosion of metallic tools or instruments. For these reasons, oxygen is always removed from water for water flooding EOR operations. Nitrogen is often used for EOR floods, but it may reduce the effectiveness of CO₂ oriented EOR because the two gases facilitate oil displacement by slightly different processes.

3.5. Depth Requirements

The estimated phase behavior of the flue gas indicates that for the gas to trend towards a phase with supercritical properties, the pressures would need to be marginally greater (10-20%) than that of pure CO₂. The only way to increase the storage pressure is to inject into a deeper formation. Initial calculations show the minimum formation depth for the flue gas may have to be several hundred meters deeper than the minimum depth needed for pure CO₂. For example, in the Midwestern United States, CO₂ will be supercritical at an approximate depth of 800 meters. To create supercritical type conditions for the oxycombustion flue gas in the Midwest, that depth would need to be extended to between 1200 and 1500 meters.

3.6. Density and Volume Changes

Density is an important factor in effective storage. A less dense fluid will take up more volume per given mass and will reduce the storage capacity of a formation. This, in turn, will lead to more wells as each well will have to be abandoned with less mass stored. Due to lower compressibility of some flue gas components, the density of the flue gas is much lower than the density of pure CO₂. In addition, the flue gas cannot be compressed to a point where the density will approach that of CO₂, even if deeper (hence warmer) storage formations are used. Preliminary calculations show that the density of the flue gas will be between ¼ and ½ that of compressed CO₂. Consequently the injected flue gas will take 2 to 4 times more pore space to sequester than the pure CO₂. A volume increase of 2 to 4 times will have significant effects on aspects of storage such as monitoring and permitting. The predicted plume size will be much larger, causing the area of review for permitting to be extended. If the goal of the monitoring plan is to track the areal extent of the plume, more monitoring points will be needed to image the larger area.

An injection well will have a finite lifetime over which injection can occur. Eventually, the near borehole formation will be saturated with injectate and the injection pressures required to continue to push injectate into the formation will exceed the fracture pressure. In this scenario, the well would need to be abandoned. For the lower density flue gas, the need for new wells would occur much sooner than with pure CO₂. If specialized well materials are needed, building new wells could be a very large cost driver.

3.7. Geochemical Interactions

The solubility of CO₂ in brine is less than that in pure water due to the “salting out” effect. Nevertheless, at pressures typical of deep saline formations, CO₂ is sufficiently soluble to lower the pH by forming carbonic acid. In addition to CO₂, any other acid gases in the injectate will tend to hydrolyze, making the brine acidic. It is of interest to consider the possibility of co-injecting sulfur dioxide (SO₂), for instance, for multi-pollutant reduction. In particular, SO₂ in the flue gas stream was identified as a suitable candidate for downhole disposal, with two provisions: (1) moisture content of the flue gas is sufficiently low that liquid water will not condense, thus dramatically raising the possibility of pipeline corrosion; (2) the SO₂ will not interact with the mineralogy of the reservoir formation to precipitate solids that could cause clogging within the pore spaces; and (3) immiscibility between CO₂ and SO₂ will not lead to two-phase conditions, which could be harmful to transportation equipment.

Geochemical modeling was used to understand the precipitation behavior of CaSO₄ when the chemistry of the formation fluid is altered by injection of the flue gas. In one scenario, calcium concentrations in the brine could be increased by dissolving carbonate cement with the carbonic acid that is produced by dissolved CO₂ in water.

4. Conclusions

Co-sequestration of CO₂ and SO₂ appears to be technically feasible in many deep saline reservoirs, but the injection lifetime of these reservoirs could be reduced if precipitation reactions take place. In carbonate-rich formations sulfate could be a problem. However, no such problem would likely exist in pure sandstone or feldspar-rich formations. Results of this preliminary modeling study indicate that screening must be done to identify potential problems with injection of flue gas.

Precipitation of a solid phase, such as calcium sulfate (anhydrite), is influenced to a much greater extent by dissolution of carbonate minerals in the storage formation, than by addition of sulfate in the form of SO₂ in the injection gas. Therefore, even if anhydrite precipitation is likely to occur in a formation where certain mitigating conditions exist that would minimize the impact on injectivity, it still may be unnecessary to scrub SO₂ from the flue gas because of the minor effect of SO₂ on precipitation. This is an important observation and needs to be explored in more detail.

In some reservoirs storage space may be so limited that it is necessary to remove N_2 and O_2 to maximize the storage capacity. Occupation of pore space and reduction in permeability were not investigated during this reporting period, but will be evaluated at a later time.

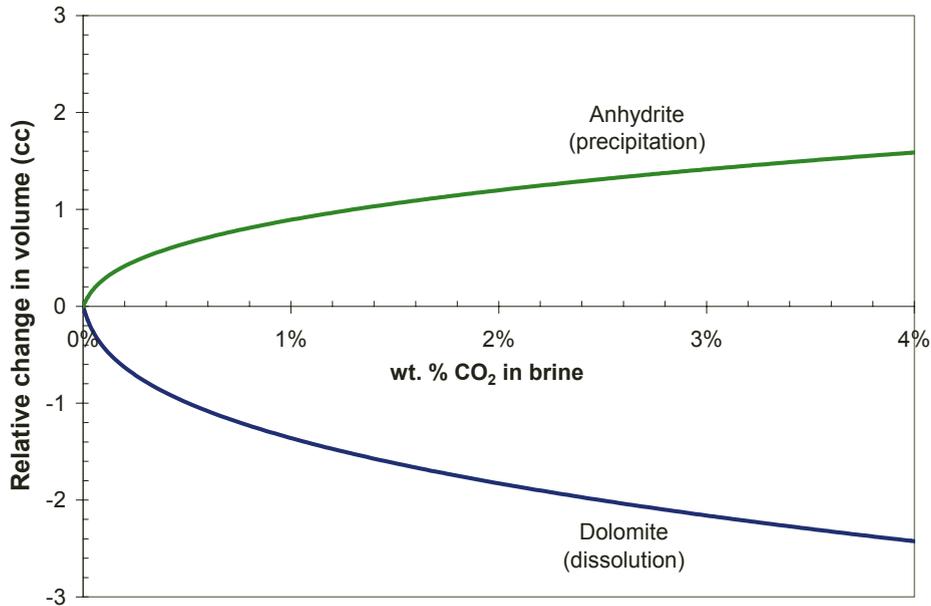


Figure 4. Relative volume change in dolomite and anhydrite after undergoing chemical reactions with CO₂

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