

**Carbon Dioxide Capture for Storage  
in Deep Geologic Formations –  
Results from the CO<sub>2</sub>  
Capture Project**

**Geologic Storage of Carbon Dioxide  
with Monitoring and Verification**

*Volume 2*

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# **Carbon Dioxide Capture for Storage in Deep Geologic Formations – Results from the CO<sub>2</sub> Capture Project**

**Geologic Storage of Carbon Dioxide  
with Monitoring and Verification**

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## Chapter 17

# IMPACT OF SO<sub>x</sub> AND NO<sub>x</sub> IN FLUE GAS ON CO<sub>2</sub> SEPARATION, COMPRESSION, AND PIPELINE TRANSMISSION

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### ABSTRACT

This study is an assessment of the effects of impurities in CO<sub>2</sub> streams on aboveground processing equipment. It is primarily a literature review that focuses on SO<sub>x</sub> and NO<sub>x</sub> impurities in flue gas. The three main components of the data analysis include:

1. Impact of impurities on the performance of amine separation systems.
2. Evaluation of the phase behavior of multi-component gas mixtures on multi-stage compressors.
3. Literature review of compressed gases to determine the corrosivity of pipeline materials in contact with CO<sub>2</sub>, SO<sub>x</sub>, and NO<sub>x</sub> species with moisture present.

Flue gas impurities, such as SO<sub>x</sub>, NO<sub>x</sub>, other trace gases, and volatile metals have the potential of interacting unfavorably with capture, compression, and pipeline transmission of CO<sub>2</sub>. Absorption and regeneration characteristics of amines and other solvents used to separate CO<sub>2</sub> are affected adversely by acid gas impurities, as their amine salts form essentially irreversibly. Compression of gas mixtures is subject to condensation of the higher boiling constituents, which may limit the ability to achieve adequate interstage cooling and may damage the compressor and other related processing equipment. Materials used in separation, compression, and transmission are subject to corrosion by acids formed from hydrolysis of SO<sub>x</sub> and NO<sub>x</sub> species in the presence of water. Finally, metals such as arsenic and mercury are accumulated from the coal and oil, and may hinder downstream processes.

### INTRODUCTION

Flue gas produced by combustion of carbon-rich fuels consists mainly of carbon dioxide (CO<sub>2</sub>), inert nitrogen (N<sub>2</sub>), and excess oxygen (O<sub>2</sub>) from the combustion air. Nitrogen oxides NO, NO<sub>2</sub>, and NO<sub>3</sub> (collectively NO<sub>x</sub>) form due to reactions between available nitrogen and oxygen. Compounds such as sulfur oxides SO<sub>2</sub> and SO<sub>3</sub> (collectively SO<sub>x</sub>), hydrogen sulfide (H<sub>2</sub>S), arsenic, and mercury occur from the coal combustion process, as well as, to a smaller extent, from oil and natural gas combustion processes. Ash and other particulate also are present in combustion gases.

These various acid gas impurities have the potential to interact unfavorably with capture, compression, and pipeline transmission of CO<sub>2</sub>. The impurities have an adverse impact on absorption and regeneration characteristics of amines and other solvents used to separate CO<sub>2</sub> from flue gas. Compression of gas mixtures is subject to condensation of the higher boiling constituents, which may limit the ability to achieve adequate interstage cooling and may damage the compressor and other related processing equipment. Finally, materials used in separation, compression, and transmission are subject to corrosion by acids formed from hydrolysis of SO<sub>x</sub> and NO<sub>x</sub> species in the presence of water.

This article reviews the current status of existing technologies used for CO<sub>2</sub> gas separations. It addresses major issues affecting the industry and suggests potential research areas where further advancement is required. Most of the discussion in this chapter is limited to information obtained from published literature.

However, some thought has been given to devising an alternative scrubbing system, which to the authors' knowledge, has not been discussed elsewhere.

Chemical absorption by aqueous solutions of amine solvents or alkaline salt solutions is regarded as the most efficient CO<sub>2</sub> scrubbing process for low pressure, dilute gas streams. At higher pressure, or when the feed is more highly concentrated, physical absorption or a mixture of chemical and physical solvents (hybrid systems) may be cost effective. Other methods such as pressure swing adsorption, membrane separation, and cryogenic separation also are possible options for capturing CO<sub>2</sub> from flue gas but at higher cost [1]. The characteristics of CO<sub>2</sub> capture methods are summarized in Table 1. Prior cleanup to remove SO<sub>2</sub>, NO<sub>x</sub>, or H<sub>2</sub>S also may be needed for many of these methods.

CO<sub>2</sub> can be produced as a by-product of many natural and chemical processes, which makes it somewhat unique in relation to the industrial gas market. However, CO<sub>2</sub> derived from combustion gases may contain sulfur oxides, nitrogen oxides, several different low molecular weight hydrocarbons, carbon monoxide, and mercury. The concentrations of these impurities may vary greatly in individual processes; also, the variety of possible CO<sub>2</sub> sources is responsible for a large number of potential impurities in the produced CO<sub>2</sub>. Examples of possible impurities in several typical sources of CO<sub>2</sub> are listed in Table 2.

Successful implementation of a CO<sub>2</sub> storage system requires capture, compression, pipeline transmission, and injection steps that provide reliable and cost-effective operation. Impurities in the flue gas are potentially able to move through each step of the process and may interact adversely with equipment used in unit operations, as well as with the geologic media. A preliminary survey of some potential effects is shown in Table 3.

#### ***Chemistry of Amine Absorption Systems***

Amine absorption is a chemical absorption process that involves capturing CO<sub>2</sub> using a reversible reaction between CO<sub>2</sub> and an aqueous solution of an amine giving either the carbonate ion salt or the carbonate as illustrated by the following reactions [3]:



The reaction proceeds to the right at low temperature [25–65 °C (77–149 °F)] allowing absorption from the gas stream. The solvent can be regenerated, and the CO<sub>2</sub> recovered as a concentrated stream, by heating the solvent solution into the temperature range of 100–150 °C (212–302 °F) to reverse the absorption chemistry. Examples of solvents used for CO<sub>2</sub> recovery are summarized in Table 4.

CO<sub>2</sub> capture with solvent absorption is conducted using a pair of contacting columns typically referred to as the absorber and the reactivator (see Figure 1). Flue gas containing CO<sub>2</sub> enters the bottom of the absorber where it contacts amine solution flowing down through the column. High temperature in the absorber increases the rate of reaction between the CO<sub>2</sub> and the solvent, but also decreases the affinity of the solvent for CO<sub>2</sub>. The competing effects of reaction rate and absorption affinity limit the optimum operating temperature in the absorber to about 50–60 °C (122–140 °F) [5]. The absorber typically operates at a pressure in the range from 30 to 45 kPa (207–310 psi). The amine solution, laden with CO<sub>2</sub>, needs to retain fluidity so it can exit the bottom of the absorber, where it passes through a heat exchanger to recover some of the heat from, and cool, the reactivated amine, and then enters the top of the reactivator. The reactivator is equipped with a reboiler circulating and heating solution at the bottom of the tower such that steam rises up through the column, stripping CO<sub>2</sub> out of the amine solution thereby shifting Reactions (1)–(3) to the left. The reactivator typically operates at about 100 °C (212 °F) and 150–175 kPa (22–25 psi). The stripped CO<sub>2</sub> and steam exit the top of the reactivator and pass through a condenser to remove water vapor and produce a concentrated CO<sub>2</sub> stream containing about 6–8 v/o % water and traces of N<sub>2</sub>, O<sub>2</sub>, and NO as impurities. The reactivated amine solution exits the bottom of the reactivator and passes through the recovery heat exchanger, where it gives up some of its heat to the CO<sub>2</sub>-loaded solution, thereby recovering its CO<sub>2</sub> sorptive property, and then it passes on to the top of the absorber.

TABLE 1  
SUMMARY OF CO<sub>2</sub> CAPTURE METHODS

Capture process type	Description	Example separation materials	Comments
Amine solution absorption	Process involves capturing CO <sub>2</sub> using a reversible reaction between CO <sub>2</sub> and an aqueous solution of an amine. The amine is regenerated (by pressure reduction and heating) and recirculated	Monoethanolamine (MEA), diethanolamine (DEA), diglycolamine (DGA), methyldiethanolamine (MDEA), sterically hindered amines	Used at the commercial scale to remove low concentrations of acid gases (e.g. CO <sub>2</sub> ) from natural gas or breathing air Solution tends to saturate with high CO <sub>2</sub> loading, so the process is more efficient for lower CO <sub>2</sub> concentrations
Alkaline salt solution absorption	CO <sub>2</sub> captured using a reversible reaction between CO <sub>2</sub> and an aqueous solution of an alkaline salt. The salt solution is regenerated (by pressure reduction and heating) and recirculated	Potassium carbonate with additives such as boric acid or glycine to increase the solution capacity for CO <sub>2</sub>	Used at the commercial scale to remove low concentrations of acid gases (e.g. CO <sub>2</sub> ) from natural gas Solution tends to saturate with high CO <sub>2</sub> loading so the process is more efficient for lower CO <sub>2</sub> concentrations CO <sub>2</sub> capacity of salt solution (even with additives) is lower than that of amine solutions
Physical absorption	CO <sub>2</sub> captured using physical dissolution in an absorption fluid. The fluid is regenerated (by pressure reduction and moderate heating) and recirculated	Propylene carbonate, <i>N</i> -methyl-2-pyrrolidone, methanol, dimethyl ether of polyethylene glycol, methyl isopropyl ether of polyethylene glycol	Used at the commercial scale to remove high concentrations of acid gases (e.g. CO <sub>2</sub> ) from natural gas More efficient for high CO <sub>2</sub> partial pressure (i.e. concentration and/or pressure) Does not typically remove acid gases as completely as chemical or hybrid absorption

(continued)

TABLE 1  
CONTINUED

Capture process type	Description	Example separation materials	Comments
Hybrid absorption	CO <sub>2</sub> captured using a combination of chemical absorption and physical dissolution. The fluid is regenerated (by pressure reduction and moderate heating) and recirculated	Sulfolane (tetrahydrothiophene 1,1-dioxide) (physical solvent) and diisopropanolamine (DIPA) or MDEA (chemical solvent), sterically hindered amines, MDEA plus proprietary solvents	Used at the commercial scale to remove intermediate concentrations of acid gases (e.g. CO <sub>2</sub> ) from natural gas
Pressure swing adsorption (PSA)	Process involves using the intermolecular forces between gases and the surfaces of solid sorbent materials to capture CO <sub>2</sub> . The sorbent is loaded at high pressure and regenerated by pressure reduction and, in some cases, heating	Molecular sieves, activated alumina, zeolites, activated carbon	Used at the commercial scale to remove CO <sub>2</sub> and other impurities from H <sub>2</sub> . Some hydrogen gas cleanup processes also produce high purity CO <sub>2</sub>
Gas separation membrane	Process involves pressurizing the flue gas and separating CO <sub>2</sub> from other gases by preferential permeation through a membrane. CO <sub>2</sub> is collected near atmospheric pressure as a permeate	Semipermeable membranes made of polyphenylene oxide, cellulose acetate, polysulfone, or polyamide	Used at the commercial scale to recover CO <sub>2</sub> used for enhanced oil recovery (EOR) (i.e. high CO <sub>2</sub> concentration) Requires two or more separation stages to reach a CO <sub>2</sub> removal of 90% and purity of 99%. Each stage requires compression, which increases cost, so the process typically is used for gas with high CO <sub>2</sub> content (e.g. pulverized coal/O <sub>2</sub> plants) Membranes are very sensitive to particulate fouling



Gas absorption membrane	The process involves using a semipermeable membrane as a barrier between the flue gas and an absorption fluid. Preferential removal of CO <sub>2</sub> from the gas stream occurs because the fluid (e.g. MEA) selectively absorbs CO <sub>2</sub>	Microporous membranes made of Teflon <sup>®</sup> , polyphenyleneoxide, or polydimethylsiloxane	<p>Innovative process</p> <p>The membrane allows a high surface area for transfer between the gas and liquid phases without requiring the two streams to mix. As a result the gas separation unit is more compact than the tall towers needed for chemical or physical absorption</p> <p>Membranes are very sensitive to particulate fouling</p> <p>Used at the commercial scale to recover CO<sub>2</sub> used for EOR (i.e. high CO<sub>2</sub> concentration)</p> <p>Gas fed to the cryogenic separation unit must be dehydrated to prevent formation of solids (e.g. ice and CO<sub>2</sub> clathrates)</p> <p>Due to energy needed to reach cryogenic conditions, cryogenic separation typically is used for gas with high CO<sub>2</sub> content (e.g. pulverized coal/O<sub>2</sub> plants)</p>
Cryogenic separation	Flue gas is cooled and compressed to condense CO <sub>2</sub> which can then be captured and purified by distillation	Not applicable	

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TABLE 2  
POSSIBLE TRACE LEVEL IMPURITIES BY SOURCE TYPE (EXCLUDING AIR GASES AND WATER)

Component	Combustion	Wells/ Geothermal	Fermentation	Hydrogen or ammonia	Phosphate rock	Coal gasification	Ethylene oxide	Acid neutralization
Aldehydes	X	X	X	X		X	X	
Amines	X			X				
Benzene	X	X	X	X		X	X	X
Carbon monoxide	X	X	X	X	X	X	X	X
Carbonyl sulfide		X	X	X	X	X		X
Cycloaliphatic hydrocarbons	X	X		X		X	X	
Dimethyl sulfide		X	X		X	X		X
Ethanol	X	X	X	X		X	X	
Ether		X	X	X		X	X	
Ethyl acetate		X	X			X	X	
Ethyl benzene		X		X		X	X	
Ethylene oxide						X	X	
Halocarbons	X					X	X	
Hydrogen cyanide	X					X		
Hydrogen sulfide	X	X	X	X	X	X	X	X
Ketones	X	X	X	X		X	X	
Mercaptans	X	X	X	X	X	X	X	
Mercury	X					X		
Nitrogen oxide	X		X	X		X	X	X
Phosphine					X			
Radon		X			X			X
Sulfur dioxide	X	X	X	X	X	X		X
Toluene		X	X	X		X	X	
Vinyl chloride	X					X	X	
Volatile hydrocarbons	X	X	X	X		X	X	
Xylene		X	X	X		X	X	

Source: Ref. [2].

Note: The source types are generic sources, and there are variations in individual processes.

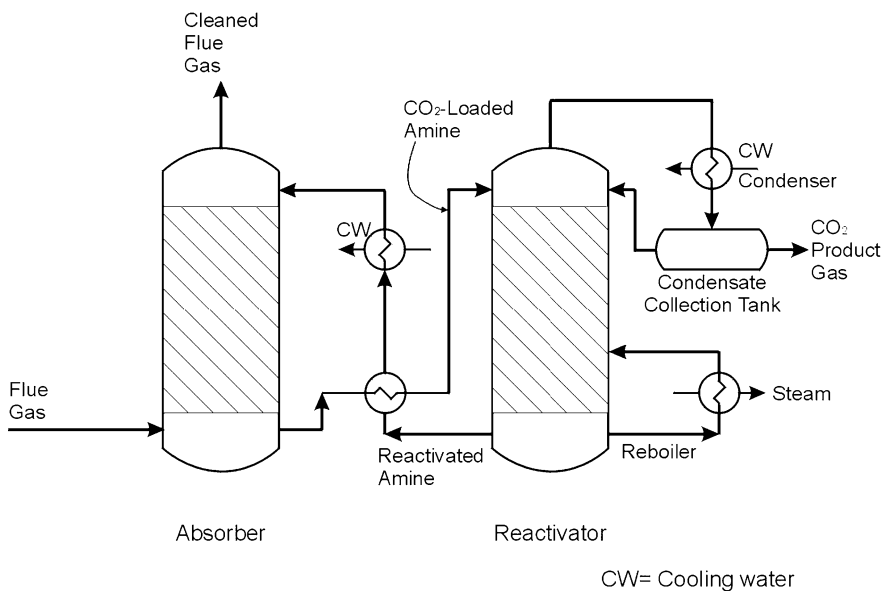
TABLE 3  
SUMMARY OF IMPURITIES AND POTENTIAL EFFECTS ON SEQUESTRATION OPERATIONS

<b>Impurity</b>	<b>Potential effects on capture by amines</b>	<b>Potential effects on compression</b>	<b>Potential effects on pipeline transmission</b>	<b>Potential effects on injection</b>
N <sub>2</sub>	None identified	Will increase compression energy consumption	Will increase transmission energy consumption	Will occupy space in the reservoir
O <sub>2</sub>	None identified	Will increase compression energy consumption	Will increase transmission energy consumption	Will occupy space in the reservoir
Ar	None identified	Will increase compression energy consumption	Will increase transmission energy consumption	Will occupy space in the reservoir
H <sub>2</sub> O	None identified	Condenses creating corrosive environment in presence of acid gases (e.g. CO <sub>2</sub> and SO <sub>2</sub> )	Condenses creating corrosive environment in presence of acid gases (e.g. CO <sub>2</sub> and SO <sub>2</sub> )	None
SO <sub>2</sub>	Reacts irreversibly with some amine absorbents	Dissolves in water to form corrosive acid	Dissolves in water to form corrosive acid	May help form stable compounds to provide a long-term benefit to sequestration
SO <sub>3</sub>	Reacts irreversibly with some amine absorbents	Dissolves in water to form corrosive acid	Dissolves in water to form corrosive acid	None identified
N <sub>2</sub> O	Not strongly absorbed and tends to remain in flue gas	Not applicable	Not applicable	Not applicable
NO	Not strongly absorbed and tends to remain in flue gas. Readily converts to NO <sub>2</sub> with O <sub>2</sub>	Not applicable	Not applicable	Not applicable
NO <sub>2</sub>	Reacts irreversibly with some amine absorbents	Dissolves in water to form corrosive acid	Dissolves in water to form corrosive acid	None identified
Hydrocarbons	Increased toxicity (e.g. dioxins and furans)	Some hydrocarbons may increase compression energy consumption Increased toxicity (e.g. dioxins and furans)	Some hydrocarbons may increase compression energy consumption Increased toxicity (e.g. dioxins and furans)	Potential for unfavorable interaction with aquifer rock or fluid Increased toxicity (e.g. dioxins and furans)
Metals	Increased toxicity	Increased toxicity	Increased toxicity	Increased toxicity

TABLE 4  
MAJOR CHEMICAL ABSORPTION SOLVENTS [4]

Chemical absorbent solvent	Solution strength (% amine)	Acid gas loading (mole gas/mole amine)	Amine heat of reaction with CO <sub>2</sub> (kJ/kg)
Monoethanolamine (MEA)	15–20	0.3–0.35 <sup>a</sup>	1917
Diethanolamine (DEA)	25–35	0.3–0.35 <sup>a</sup>	1517
Diglycolamine (DGA)	50–70	0.3–0.35 <sup>a</sup>	1975
Methyldiethanolamine (MDEA)	20–50	>0.3	1394

<sup>a</sup> Limited by corrosion of carbon steel unless a corrosion inhibitor is used.



**Figure 1:** Recovery of CO<sub>2</sub> using solvent absorption.

As suggested by Reactions (1)–(3), the solubility of CO<sub>2</sub> in ethanolamines is influenced by temperature, amine solution strength, and pressure. Increasing the pressure of the flue-gas stream increases the potential concentration of CO<sub>2</sub> in the amine solution, which reduces the volume of solution circulating through the absorber and reactivator. The reduced volume decreases the required size and thus the capital cost and energy consumption of the process. However, a higher CO<sub>2</sub> concentration also increases the corrosiveness of the CO<sub>2</sub>-rich amine solution. The CO<sub>2</sub> concentration typically is limited to 20% unless a solvent with corrosion inhibitors is used [3].

MEA used to separate CO<sub>2</sub> from flue gas also removes nearly all of the SO<sub>2</sub> and some of the NO<sub>2</sub> but very little NO and N<sub>2</sub>O [6]. The SO<sub>2</sub> and NO<sub>2</sub> react with the amine to form stable salts that cannot be regenerated by heating in the reactivator and so represents a loss of solvent from the system, while increasing viscosity undesirably. The limits on SO<sub>2</sub> and NO<sub>2</sub> concentration in the flue gas being treated for CO<sub>2</sub> removal by MEA absorption are recommended to be in the range from 10 [6] to 50 ppmv [7].

### ***Compression of CO<sub>2</sub> with Impurities Present***

The importance of fluid properties, notably the phase behavior, and the associated impact on pipelines and compressors is well established. Applicable equations of state are known and numerical methods for predicting fluid properties, phase behavior, and sizing of equipment are available. However, very little specific information concerning the properties and phase behavior of CO<sub>2</sub>/SO<sub>x</sub>/NO<sub>x</sub> mixtures was found in published literature. The bulk of the information available discusses either pure CO<sub>2</sub> or mixtures of hydrocarbons and CO<sub>2</sub>. This section discusses what is known about the impact of impurities on the compression of CO<sub>2</sub> and recommends a path forward for research and development.

Injection of CO<sub>2</sub> for enhanced oil recovery (EOR) or disposal requires processing, compression, and transmission of very large fluid volumes. CO<sub>2</sub> can be transmitted as a gas, liquid, or supercritical dense phase depending on the characteristics of the source, ambient temperature along the route, and other process and economic considerations. Transmission in the gas phase is not cost effective because of the volume requirement. Liquid transmission requires high purity and refrigeration, and may require heating for vaporization upon use. It is now accepted that high-pressure supercritical pipelines are the most cost-effective mode of CO<sub>2</sub> transmission. In this mode, the gas must be compressed to pressures well above the critical pressure, usually in the range of 8.3–15.9 MPa (1200–2300 psia).

### ***Corrosive Effect of Impurities in CO<sub>2</sub> Stream***

A literature search was carried out to identify available information related to the effect of impurities on corrosion properties of CO<sub>2</sub> pipeline. The impurities of interest to corrosion are SO<sub>x</sub> and NO<sub>x</sub>. Various resources covered for the search included technical publications, journals, conference proceedings, Internet searches, and industry reports. The scope of the search was limited to information related to the pipeline industry and to a lesser extent atmospheric pollution control of SO<sub>x</sub> and NO<sub>x</sub>.

Based on the analysis of the information from various resources, the following observations can be highlighted:

- CO<sub>2</sub> corrosion is a well-defined phenomenon in the literature. The mechanism, factors affecting, and prevention of corrosion related to CO<sub>2</sub> pipelines are covered extensively.
- The presence of H<sub>2</sub>S in CO<sub>2</sub> and its effect on CO<sub>2</sub> corrosion is also well documented in the literature.
- Very little information is available on the effect of SO<sub>x</sub> and NO<sub>x</sub> on the corrosion properties of CO<sub>2</sub>-carrying pipelines.
- No guidelines are available on maximum allowed concentrations of SO<sub>x</sub> and NO<sub>x</sub> to protect pipeline steel against corrosion.

## **RESULTS AND DISCUSSION**

### ***Chemistry of Amine Unit Operations***

A substantial amount of worldwide activities, both recently completed and still under way, have targeted the development of CO<sub>2</sub> recovery technologies from power plant flue gas. In support of these efforts to achieve operability and cost-effectiveness, information is needed that will lead to an understanding of the complex physicochemical mechanisms within the proposed CO<sub>2</sub> capture concepts. To date, all such capture concepts appear very costly from capital and operating cost perspectives.

Nearly all proposed CO<sub>2</sub> sorption process schemes indicate a need to remove certain contaminants (notably dust, NO<sub>x</sub>, and SO<sub>x</sub>) prior to CO<sub>2</sub> scrubbing. The following unit operations are involved:

- A caustic wash of the flue is recommended to remove particulate and water by cooling/condensation because they can cause excessive foaming when alkyl amine solutions are used for capturing CO<sub>2</sub>.
- The gas is dried may be sent through a catalytic converter to remove remaining O<sub>2</sub> because O<sub>2</sub> can oxidize the amine, most likely to N-oxides, olefinic compounds, aldehydes, carboxylic acids, etc.; the latter form stable emulsifying salts with the amine or metal ions (from corrosion), i.e. RCOO<sup>-</sup>M<sup>+</sup> or (RCOO<sup>-</sup>)<sub>2</sub>M<sup>+2</sup> (where M represents a monovalent or divalent metal ion).

- The stream is sent through a desulfurization plant for sulfur removal to <100 ppm, and preferably <20 ppm(v/v), to minimize ammonium-SO<sub>x</sub><sup>2-</sup> salt formation in the CO<sub>2</sub> scrubber, which does not thermally regenerate easily and in high yield.
- The gas is compressed prior to CO<sub>2</sub> capture by MEA or other amine technology to reduce needed equipment size and to increase sorption yield.

These unit operations each handle the full flue-gas stream and, therefore, are very capital intensive. These operations are required for performing CO<sub>2</sub> capture with minimal degradation of the amine. With respect to the specific CO<sub>2</sub> sorption unit operation, vendors have and are optimizing amine structures and formulations to minimize this degradation, to maximize CO<sub>2</sub> loading capacity, and to reduce the energy requirements for amine regeneration. What is lacking is a sufficient understanding of the mechanisms for amine degradation, and loss of CO<sub>2</sub> throughput capacity, in the face of natural contaminants contained in the flue gas, at flue gas scrubber conditions, and the conditions needed to minimize them. This section offers a preliminary examination of the impact of impurities on CO<sub>2</sub> capture by amines to illustrate where useful areas for mechanistic research exist.

#### *Flue gas compositions for CO<sub>2</sub> scrubber feeds*

Flue gas compositions are determined by several factors, including

- Fossil fuel composition (reservoir-specific).
- Fuel beneficiation process.
- Combustion process conditions, including O<sub>2</sub>/fuel ratio, operating temperatures, and other process parameters.
- Pretreatment of the gas prior to CO<sub>2</sub> scrubbing (for example, manner and operational details of dust removal, N<sub>2</sub> conversion to NO<sub>x</sub>, SO<sub>x</sub> scrubbing and other components of the feed).

Specific compositions of flue gas are provided in the references cited throughout this chapter, with theoretical values for coal, oil, and natural gas provided in Table 5.

TABLE 5  
MAJOR COMPONENTS OF FLUE GASES (MOLE %) FROM THREE HYDRO-CARBON FUEL TYPES BURNED WITH 110% THEORETICAL AIR [8]

Fuel	CO <sub>2</sub>	H <sub>2</sub> O	O <sub>2</sub>	N <sub>2</sub>
Coal	15.4	6.2	1.8	76.6
Oil	12.9	10.3	1.8	74.9
Natural gas	8.7	17.4	1.7	72.1

The level of NO<sub>x</sub> in flue gas is determined by the fuel-bound nitrogen content, where increasing nitrogen concentration (normally 0.1–2% for certain coals) results in lower conversion efficiencies to NO<sub>x</sub> [1]. Fuel nitrogen oxidation is controlled kinetically by the physical make-up of the feed and the chemical form of the nitrogen. In contrast to nitrogen, where only about half the fuel-bound N is converted to NO<sub>x</sub>, essentially all the sulfur present in the fuel is converted to SO<sub>x</sub>. Because CO<sub>2</sub> is a product of air/O<sub>2</sub> combustion of fossil fuels, and because carbon represents substantial portions of fossil fuels, especially coals, enormous amounts of CO<sub>2</sub> are present in the flue gas. Much more CO<sub>2</sub> is present in the flue gas than NO<sub>x</sub> and SO<sub>x</sub>. For example, flue gases from pulverized coal combustion are listed in Table 6, and compared to the postcapture product.

#### *Pertinent amine chemistry relative to CO<sub>2</sub> scrubbing*

Amines have a demonstrated ability to capture CO<sub>2</sub> from many types of gas streams, ranging from such extremes in application as removal from breathing air and flue gas from large power plants [9].

TABLE 6  
TYPICAL COMPOSITION OF FLUE GAS AND CAPTURED CO<sub>2</sub> FROM  
A PULVERIZED COAL COMBUSTION POWER PLANT

Component	Flue gas composition (vol%)	Captured gas composition <sup>a</sup> (vol%)
CO <sub>2</sub>	13.5	93.2
N <sub>2</sub>	74.7	0.17
O <sub>2</sub>	4.0	0.01
Ar	Trace	Trace
H <sub>2</sub> O	7.7	6.5
SO <sub>2</sub>	0.016 <sup>b</sup>	Trace
SO <sub>3</sub>	Trace	Trace
NO <sub>x</sub>	0.06	Trace
Hydrocarbons	Trace	Trace
Metals	Trace	Trace <sup>c</sup>

<sup>a</sup> Assuming amine absorption.

<sup>b</sup> Assumes 2.2 wt% sulfur coal with flue gas desulfurization at 90% efficiency.

<sup>c</sup> Depends on fuel source and number of process factors; there is potential for volatile metals to be present in trace quantities.

The following list summarizes the key information regarding flue gas composition and the effectiveness of primary, secondary, and tertiary amines to scrub CO<sub>2</sub> from this environment [9–11].

- O<sub>2</sub>, SO<sub>x</sub>, and NO<sub>x</sub> in flue gases can reduce the operational capacity of amines to scrub (absorb) CO<sub>2</sub> emissions by several chemical mechanisms.
- Amines can be lost by degradation mechanisms involving oxidation elimination, free radical C–N bond cleavage, catalyzed by trace emission species.
- Too much CO<sub>2</sub> also can diminish the operational capacity of amines by changing the chemical form of the sorbed species; more is not always better. Problems of this nature can occur due to buffer effects and solubility equilibria. Amine chemical structure has major impacts on these effects.
- Trace constituents also can create operational problems, such as accelerated corrosion.
- To avoid these problems, contaminant levels must be reduced by means of appropriate pretreatment methods.
- Amine tolerance levels are reported to be 90 ppm O<sub>2</sub>, 10 ppm SO<sub>2</sub>, and 20 ppm NO<sub>x</sub>. These parameter values do not prevent the above degradation effects, but simply reduces them to economically and operationally acceptable rates.

Not much is known or understood about these amine decomposition reaction mechanisms, let alone the conditions that enhance or discourage them. Therefore, controlled and systematic laboratory and on-site testing are needed that uses actual flue gas slipstreams and commercial-scale supplied chemicals to elucidate these chemical reactions and the impact of trace contaminants on them. General amine reactive mechanisms have been extensively studied in other areas of technology which might offer some fundamental science from which candidate mechanisms and amine stabilizer chemistries could be drawn.

#### *Flue-gas cleanup technologies*

Future CO<sub>2</sub> removal technology research is being performed in several areas, including

- Improving amine scrubbing technology, where absorption is performed using “formulated amines”, which include corrosion inhibitors, amine stabilizers, and other additives.
- Dry scrubbing technologies (adsorption media, membranes).
- Electrochemical capture of CO<sub>2</sub>.

The impact of contaminants on these new and novel technologies remains to be determined and presents an important area of needed research. Potential problems may exist for membranes, for which adsorption sites are notoriously sensitive to fouling by low-level contaminants that bind surface reaction sites and small pores, causing accumulation, scale buildup, or direct chemical reactions in unfavorable directions. For example, poisoning of hydrogenation catalysts by low levels of sulfur is well known to occur. Reduction of cathodic over-potential in electrochemistry is another example.

More examples of flue-gas cleanup technologies, both commercially available and undergoing laboratory development, have been reported [12–63]. One such development is Ammogen™, a product that generates ammonia from hydrolyzing aqueous urea under pressure, but also produces CO<sub>2</sub>. Ammogen™ is used to reduce flue gas levels of NO<sub>x</sub>, SO<sub>x</sub>, and other impurities.

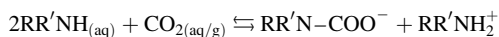
Formulated amines (FA) are expected to offer substantial advantages over MEA alone. For example, improvements can include oxidation resistance, reduction in regeneration energy requirements, faster kinetics, higher selectivity, and less degradation. However, it is important to realize that impurities/contaminants may not react uniformly with each ingredient in the formulation. Therefore, proper amine sorbent make-up procedures are essential for these formulated products, as well as an understanding of how the various components of the FA react with the expected contaminants, concentration levels, and physical conditions of the CO<sub>2</sub> scrubber. Formulations also allow continuous improvements to be made to incrementally improve operability and reduce cost of overtime. Making such improvements is a typical challenge faced by formulations chemists.

#### *Flue-gas cleanup chemistries and the impact of impurities on CO<sub>2</sub> removal*

This section describes CO<sub>2</sub> scrubber chemistry in more detail. The following section describes the impact of other flue gas components, especially the NO<sub>x</sub> and SO<sub>x</sub> impurities, on the CO<sub>2</sub> removal process in terms of physical behavior, process operability, and economics.

Two major chemical products of CO<sub>2</sub> are formed during sorption: carbamate and bicarbonate ion. Although carbamate formation has advantages over bicarbonate in terms of selectivity for CO<sub>2</sub>, the reverse reaction (regeneration) involves breaking covalent bonds that require large amounts of energy and can be slow. In contrast, bicarbonate ions form more slowly than carbamate since the carbamate is formed as an intermediate first, but requires significantly lower energy for regeneration. (Reaction kinetics are attributed to lower free OH<sup>−</sup> ion activity than the free amine activity requires the carbamate to form first rather than forming HCO<sub>3</sub><sup>−</sup> directly; therefore, the regeneration of CO<sub>2</sub> from the ionic species (e.g. MDEA<sup>+</sup>, HCO<sub>3</sub><sup>−</sup>) is a slower reaction.) Interaction of contaminants can take place at many points along the chemical pathway, including impacting the solubilization rate of CO<sub>2</sub> in the aqueous phase, the formation of OH<sup>−</sup> from amine/H<sub>2</sub>O reaction, and the breakup of bicarbonate ions into water, CO<sub>2</sub>, and amine.

The degree to which carbamate forms depends primarily on the amine used in the sorber. Carbamate formation is decreasingly favored in the series primary > secondary ≫ tertiary (with tertiary amines, carbamate is not observed as the intermediate because it is unstable with respect to bicarbonate salt formation). Bicarbonate salts represent “ionic” capture of CO<sub>2</sub> as HCO<sub>3</sub><sup>−</sup>, which is efficient but slow for all aliphatic amines. In scrubbing operations, carbamate formation is preferred due to its fast CO<sub>2</sub> sorption chemistry:



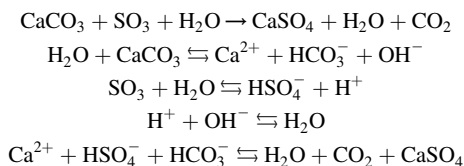
For carbonate formation, no water is required for CO<sub>2</sub> sorption, so the reaction also can occur in the gas phase. However, specific amine groups (identified by R and R') generally are chosen to be very water soluble and having low volatility so that the amine is not lost to the large volume of flue gas passing through the contactor or vaporized with the CO<sub>2</sub> during regeneration. When impurities are present, their impact on water-soluble amines needs to be considered, for both cost and performance reasons.

Because a number of proprietary amine formulations exist, it is important for fundamental chemical mechanism studies to focus on understanding the interactions between other components of the flue gas,



particularly  $\text{SO}_x$  and  $\text{NO}_x$ , dust, trace metal catalysts, and mercury. (Note that thiols and amines both tend to be strong sorbers for Hg.)

Typically it is necessary to accommodate the effects of flue gas contamination, resulting from upstream processing (dust,  $\text{SO}_x$ , and  $\text{NO}_x$ ). For example,  $\text{SO}_x$  scrubbers using limestone or dolomite slurries will contribute additional  $\text{CO}_2$ , where water is both consumed and released in the reaction:



Whether sulfate (as shown) or sulfite is the main product depends upon scrubber pH, amount of excess  $\text{O}_2$  present, combustion process temperatures, and presence of catalysts.

MEA is both low cost per pound, and nonvolatile, however it is expected to be particularly sensitive to contaminants because it readily degrades, especially by catalytic oxidation to compounds such as  $^- \text{OOCCH}_2\text{NH}_3^+$ . Inhibitors are sacrificial in nature and require replacement, and free radical inhibitors are also particularly sensitive to catalyzed oxidation of the inhibitors (as part of their beneficial action in protecting the amines from degradation). Hence consumption rates of the amine and stabilizers depend strongly upon contaminant effects, as does process complexity needed to deal with maintaining these reagents at operable levels.

#### *Contaminant effects on $\text{CO}_2$ sorption chemistry*

A number of process configurations exist for purification of flue gases. Detailed impacts of each possible process scenario are possible but outside of the scope of this chapter. An overview of the contaminant impact on  $\text{CO}_2$  recovery processing is appropriate and illustrates the challenges, difficulties, and opportunities. Given the large size of the flue gas flow stream and, therefore, the high capital cost for handling such a large stream inherent in any such process, there will always be a strong incentive to minimize the number of gas treatment unit operations. Since gas decontamination is the objective, it is not necessary that the captured contaminants also be separated from each other as such operations would be more cost effective on small condensed product streams. However, separation of contaminants may be required at the large scale in order to accommodate different contaminant chemistries. For example, amines will effectively capture acid gases in one unit operation at the appropriate scrubber conditions ( $\text{NO}_x$ ,  $\text{SO}_x$ ,  $\text{CO}_2$ , and any HCl) but not low reactivity, volatile gases and vapors, e.g.  $\text{NO}$  or  $\text{N}_2\text{O}$ . Storage of toxic metals (Hg, etc.), if suitable sorbent chemistry and temperature are applied and  $\text{NO}$  oxidation to  $\text{NO}_x$  might be accomplished during dust and ash recovery in an initial treatment step, leaving  $\text{N}_2\text{O}$  in  $\text{N}_2$ , with some  $\text{O}_2$  (added for  $\text{NO}$  oxidation) to be dealt with at the end of the process. Some of the water also would be captured, but could be minimized by operating the  $\text{NO}_x/\text{SO}_x/\text{CO}_2$  scrubber at elevated temperature.

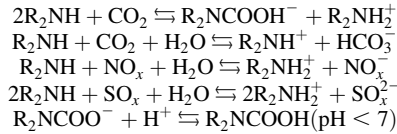
A key contaminant effect control consideration during  $\text{CO}_2$  absorption is the prevention of premature hydrolysis of the carbamate driven by the strong acid ( $\text{H}^+$ ) effect of the  $\text{HNO}_x$  (nitric and nitrous) and  $\text{H}_2\text{SO}_x$  (sulfuric and sulfurous) acids, i.e.



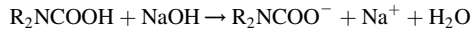
This reaction, facilitated by moisture, would lower  $\text{CO}_2$  absorption capacity. To prevent this sorption reversal reaction requires maintaining a high pH of the scrubber fluids ( $\text{pH} > 7$ ). Although pH control would normally be accomplished with slaked or unslaked lime, the presence of  $\text{SO}_x$  would give rise to solids formation ( $\text{CaSO}_x \cdot y\text{H}_2\text{O}$  and  $\text{CaCO}_3$ ), if the pH is sufficiently high ( $> 7$ ), thereby requiring the recovery of alkyl amine from a solid/aqueous slurry. This mixture normally leads to unacceptable losses of amine through adsorption onto solid particles and requiring make-up.

Instead, water-soluble sulfates and carbonates could be produced using low-cost, water-soluble alkaline raw materials, such as NaOH and KOH, which can be used to prevent the solids from forming. These water-soluble alkalis are commodity priced, but still more costly than lime—and especially limestone. Hence, to improve the economics, NaOH would have to be regenerated from lime on site.

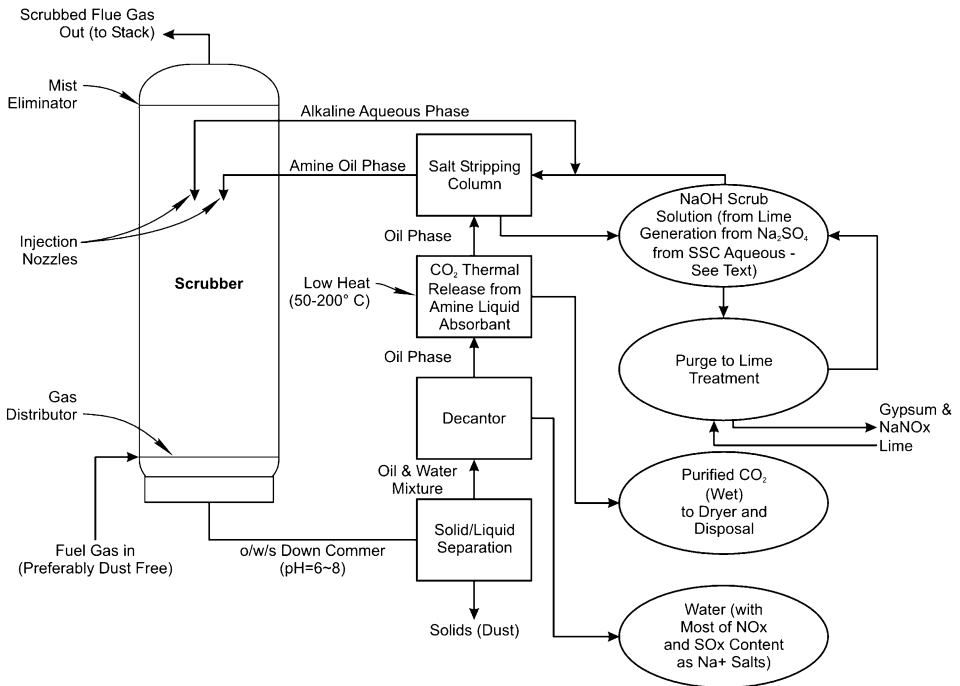
Using a water insoluble amine concept absorption occurs by the following set of reactions:



If caustic soda is provided to maintain the pH at approximately 6–8:



The use of water in insoluble amine leads to advantages in lower CO<sub>2</sub> regeneration temperatures, better water balance control, higher solubility of CO<sub>2</sub> in the organic phase, and ease of separations. The involvement and role of the major contaminants in flue gases (dust, NO<sub>x</sub>, and SO<sub>x</sub>) on the CO<sub>2</sub> recovery process using amines can be appreciated from the hypothetical process illustrated in Figure 2.



**Figure 2:** One-step flue gas cleanup concept using a water-insoluble amine.

Some scenarios can be envisaged where the organic amine losses are minimized by avoiding excessive heating, using mild pH, decreasing the maximum temperature for CO<sub>2</sub> release, and recovering amine from

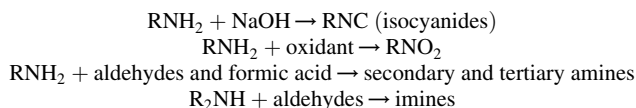
$\text{NO}_x$  and  $\text{SO}_x$  amine salts. Costs are further minimized by reducing the equipment size and complexity by a small inventory requirement for the flue gas by designing fast mixing conditions and short reaction times. Process reliability is enhanced by maximizing the use of proven, large-scale unit operations. All of these opportunities represent needed areas of research, development, and/or demonstration.

Another significant impact of these contaminants on the  $\text{CO}_2$  capture process is that the high heat of neutralization of the  $\text{NO}_x$  and  $\text{SO}_x$  acid compounds by the amine causes high local heating at the absorption sites in the scrubber. This heat reverses the  $\text{CO}_2$  sorption reactions, which occur in the 100–200 °C region, depending on the amine used. Due to the enormous amount of  $\text{CO}_2$  present, such losses in capacity tend to be very adverse to process economics.

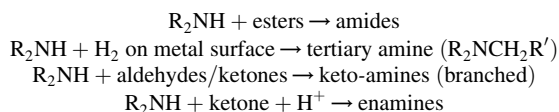
#### *Chemistry of amine sorbent degradation chemistry related to contaminants*

Because amines are reactive organic compounds, they can degrade into other compounds as process feed compositions and conditions change. Since such reactions represent losses of throughput capacity and increase raw material costs, such degradation reactions and conditions are minimized. Therefore, although MEA is readily available and of low cost relative to current  $\text{CO}_2$  separation processes serving the specialty chemical market, substantial improvements in amine chemical structures with respect to stability and regenerability are needed to cost-effectively concentrate  $\text{CO}_2$  waste from power plant flue gas. Some new structures and supporting formulations development are in progress. Amine decomposition reactions to be avoided are given in the three reaction sequences:

#### *Decomposition reactions of primary amines*

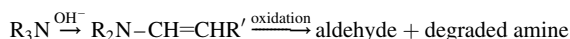


#### *Decomposition reactions of secondary amines*



#### *Decomposition reactions of tertiary amines*

Far fewer degradation reactions exist for tertiary amines than for secondary and primary amines. One such process involves alpha elimination to form an enamine, followed by oxidation and bond cleavage of the olefinic bond:



Oxidation to the amine N-oxide ( $\text{R}_3\text{N} + \text{O}_2 + \text{catalyst} \rightarrow \text{R}_3\text{N} \rightarrow \text{O}$ ).

Many of these reactions involve other components, which can be contaminants formed in the process or which enter with the feed. Nitrous acid ( $\text{HNO}_2$ ) readily reacts with amines to form compounds with N–N bonds, which often readily decompose by hydrolysis to  $\text{N}_2$  and  $\text{N}_2\text{O}$ , organic acids, ketones, aldehydes, and alcohols. Nonvolatile, water-insoluble amines may allow better control and purging of such degradation products. Therefore, amine structure is key to its performance and manufacturing cost, so further research is needed to optimize the amine structure best suited for  $\text{CO}_2$  storage from power plant flue gas.

#### *$\text{CO}_2$ product exit stream purity projections*

As previously noted,  $\text{CO}_2$  is released from the amine thermally during the regeneration step. Because the  $\text{CO}_2$ -loaded amine is in liquid form, it can be sharply separated from the inlet flue gas phase. Hence, the feed

gas “as is” can be cleanly prevented from carrying over into the CO<sub>2</sub> product gas. On the other hand, the sorbent amine solution is a concentrated aqueous solution of amine organic, so this stream is capable of scrubbing many other contaminants from the feed gas. Due to the alkalinity of the amine solution, SO<sub>x</sub> (as H<sub>2</sub>SO<sub>3/4</sub> and NO<sub>x</sub> (as HNO<sub>2/3</sub>) will be absorbed quantitatively (i.e. theoretically to ≪ 1 ppm) provided adequate spray tower contact mixing in the scrubber and mist elimination is provided, and the amine is maintained in excess. In fact, the levels of passage of HNO<sub>x</sub> or especially H<sub>2</sub>SO<sub>x</sub> is a direct measure of contactor stage efficiency. Therefore, unless these gases are removed in earlier separate steps, they will be completely absorbed into the amine solution during CO<sub>2</sub> sorption. However, because the CO<sub>2</sub> is desorbed from the amine at such mild conditions, and the nitrate and sulfate salts are not, these acids are not to be expected in the CO<sub>2</sub> product stream provided mist elimination is provided for in the CO<sub>2</sub> product gas as it exits the amine regeneration tower. However, for H<sub>2</sub>SO<sub>3</sub> and HNO<sub>2</sub>, the indications are much different. These acids break down at low temperatures back into SO<sub>2</sub> and NO<sub>x</sub>, respectively. Hence, if sulfur and nitrogen oxidation was not complete, then some sulfur (S) and nitrogen (N) are expected to report to the CO<sub>2</sub> stream. These S and N products are expected to be quite corrosive, especially because moisture also is present (see below).

Water vapor is expected to be both absorbed by the amine scrubbing solution, as it occurs at < 100 °C, and evaporated with the CO<sub>2</sub> during amine sorbent regeneration as this occurs at > 100 °C. Hence, the CO<sub>2</sub> will be saturated with a high level of water vapor. Since water vapor will condense if compressed, leading to corrosion conditions and other problems, it is advisable to chill out most of the water vapor prior to CO<sub>2</sub> compression and/or use corrosive resistant compressor materials of construction.

With respect to toxic metal ions, mercury, lead, cadmium, and many other volatile metals (e.g. Zn, Ag, etc.), these ions form strong water-soluble complexes with amines



and so would absorb along with the CO<sub>2</sub> if not already removed at an earlier stage (e.g. as dust or with gypsum during SO<sub>2</sub> scrubbing). It is not expected that these nonvolatile metal ion complexes will follow the CO<sub>2</sub> concentrate stream during regeneration, other than by physical entrainment as aerosols, which can be eliminated by an in-line mist eliminator stage.

Because the CO<sub>2</sub> will be released from the amine under low to moderate pressure conditions, care will be necessary to avoid even small air leaks that will allow noncondensable gases from the air to enter the CO<sub>2</sub> product stream (N<sub>2</sub>, O<sub>2</sub>, or Ar). Noncondensable gases will not liquefy or dissolve in downhole storage of CO<sub>2</sub> and therefore will result in undesirable back pressure and downhole gas pockets.

As the CO<sub>2</sub> sorbent is a reactive organic phase, which degrades at a very slow rate if selected and used properly, some low levels of organics, mostly derivatives and fragments of the amine used to sorb the CO<sub>2</sub>, will be sufficiently volatile to follow the CO<sub>2</sub> stream. Some of these organics will report to the dry condenser condensate, and the balance would proceed to accompany the CO<sub>2</sub> through to deep well disposal. Very low levels of these organics are expected so it should not create a disposal problem. Higher levels of organics are to be avoided for economic reasons, and also to avoid supplying nutrients for microbial growth once the CO<sub>2</sub> has been disposed of downhole.

### ***Effect of Impurities on Compression***

A literature search to determine thermodynamic properties of gas mixtures resulted in a compilation of sources, which are listed in the references section [64–76].

### ***Impact of impurities on compression of CO<sub>2</sub>***

Pressurizing the CO<sub>2</sub> to the dense phase can be accomplished using a number of thermodynamic paths. A low-compressibility path involves both pumps and compressors because the fluid is taken thermodynamically through a two-phase region during the cooling cycle. In this path, the fluid is compressed, cooled to a liquid, and then pumped to its final pressure. The advantages of such a system are that refrigeration is not required and pressurization of a liquid requires less work. A high-compressibility

thermodynamic path involves compression only and requires that the pressure and temperature of the fluid be maintained above the critical point to prevent two-phase conditions. Both centrifugal and reciprocating compressors are used for pressurization. Centrifugal machines are best suited for the initial stages, where large volumes are compressed from low pressure to a certain intermediate pressure. Multi-stage reciprocating compressors then are used to bring the fluid to its final pressure [69].

In the supercritical state, CO<sub>2</sub> behaves partly as a liquid and partly as a gas. In the normal pressure and temperature ranges of an operating pipeline, the presence of even small amounts of impurities can have a significant and nonlinear effect on density and compressibility and, therefore, flow behavior [64]. Table 7 shows the effect on flow capacity from the addition of small amounts of methane and nitrogen. Loss of flow capacity and increased flowing pressure drop increase the power requirements of the compression system. Figure 3 shows a pressure–enthalpy phase diagram for pure CO<sub>2</sub> and Figure 4 shows a similar plot for CO<sub>2</sub>

TABLE 7  
EFFECT OF IMPURITIES ON CO<sub>2</sub> PIPELINE CAPACITY [64]

Composition of flowing fluid	Flow velocity at design pressure drop (m <sup>3</sup> /s)	Flow relative to pure CO <sub>2</sub>
Carbon dioxide	98.3	1.00
Methane	90.8	0.92
Nitrogen	63.9	0.65
Carbon dioxide plus 5% methane	89.5	0.91
Carbon dioxide plus 10% methane	82.3	0.84
Carbon dioxide plus 5% nitrogen	85.9	0.87
Carbon dioxide plus 10% nitrogen	77.0	0.78

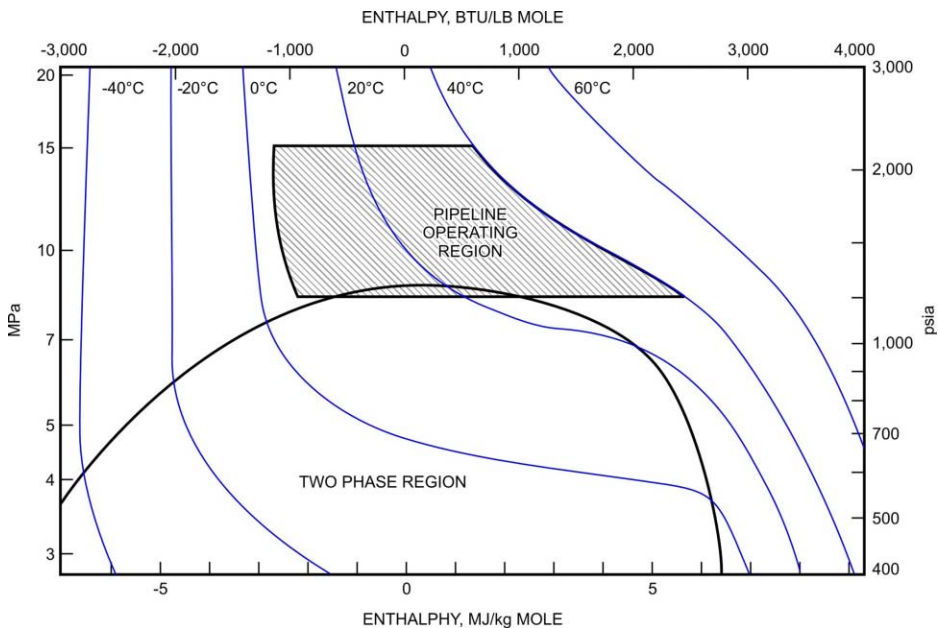
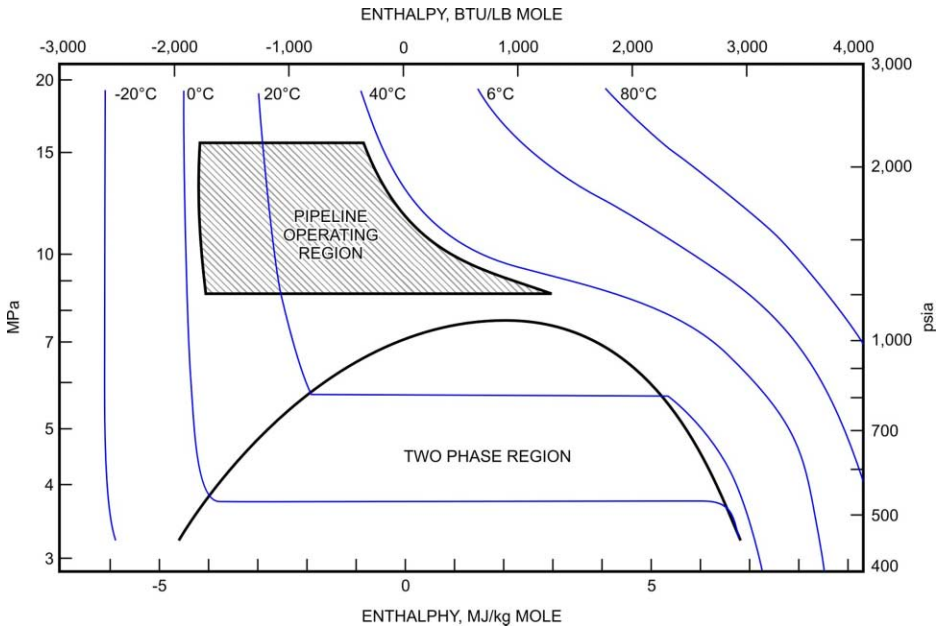


Figure 3: Pressure–enthalpy phase diagram for pure CO<sub>2</sub> [64].



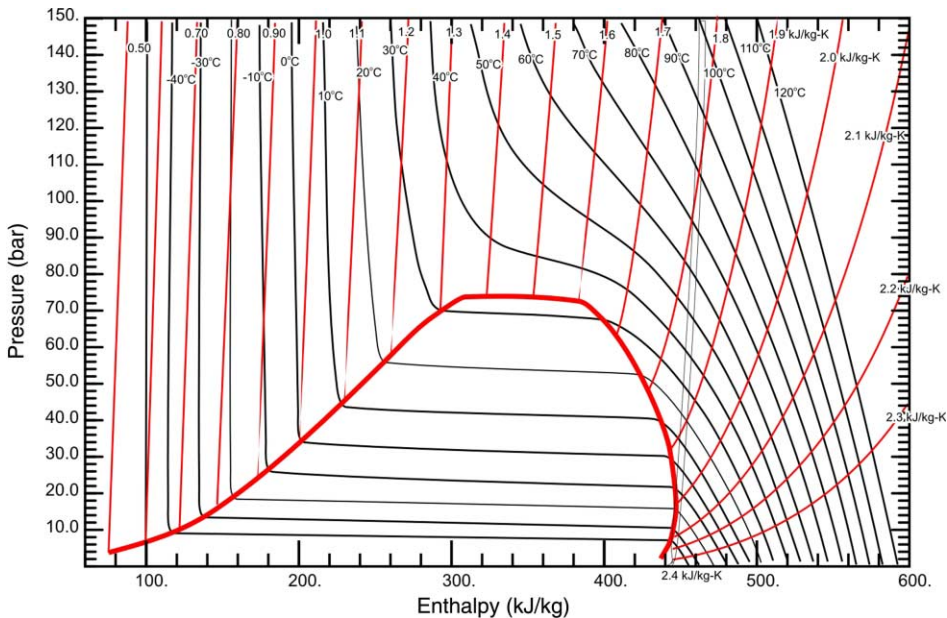
**Figure 4:** Pressure–enthalpy phase diagram for CO<sub>2</sub> with 5% methane and 5% nitrogen [64].

with 5% methane and 5% nitrogen. The operating range of a pipeline is shown on the plots. Comparison of the two diagrams shows that the operating range of a pipeline extends into the two-phase region when methane and nitrogen are present.

The effect of small quantities of SO<sub>2</sub> and NO<sub>2</sub> on the properties and behavior of CO<sub>2</sub> in a pipeline and compression system is uncertain. Although CO<sub>2</sub> and SO<sub>2</sub> have similar critical pressures (7.3 MPa for CO<sub>2</sub> and 7.9 MPa for SO<sub>2</sub>), their compressibilities at 150 °C (300 °F) and 6 MPa (880 psia) are 0.91 [71] and 0.60 [74], respectively. Compressibility is the ratio of actual gas volume to ideal gas volume. The lower the compressibility, the easier the gas is to compress. Furthermore, SO<sub>2</sub> condenses at a higher temperature than CO<sub>2</sub>. Based on the comparison of compressibility, it appears possible to compress a mixture of CO<sub>2</sub> and SO<sub>2</sub> without substantially increasing pressure or compressor energy per unit of fluid volume. Figure 5 shows a pressure–enthalpy phase diagram for CO<sub>2</sub> containing 2.5% SO<sub>2</sub> by weight [65]. The plot was computed from simulation, but the equations used were not cited. Comparison of the bubble pressures on the 20 °C isotherm from Figures 3 and 5 reveals some important differences. At 20 °C, CO<sub>2</sub> vaporizes at a pressure of approximately 5.5 MPa (800 psi), whereas the CO<sub>2</sub>–SO<sub>2</sub> is shown to vaporize at 5.3 MPa (770 psi). Apparently, a distinct difference in the phase behavior exists, even with less than 5% SO<sub>2</sub>.

#### *Cost factors*

Compression usually is the highest cost component in a CO<sub>2</sub> transmission system. In some cases, compressor equipment costs are as high as 2/3 the capital costs for the transmission system [68]. Equipment selection, energy requirements, number of stages, and interstage process components all must be given careful consideration in the design. All these design decisions depend on the composition and properties of the fluid being processed. It is essential to either maintain operating conditions above the critical point to prevent phase separation or tailor process steps where generation of multiple phases is unavoidable. If phase separation is unavoidable, it may be more economical to choose a low-compressibility thermodynamic path for compression (where the fluid is pumped to its final pressure as a liquid). Phase behavior of mixtures can be estimated using a number of well-known correlations and equations of state



**Figure 5:** Pressure–enthalpy phase diagram for 97.5% CO<sub>2</sub> and 2.5% SO<sub>2</sub> [65].

such as the Benedict–Webb–Rubin–Starling and Wilson–Redlich–Kwong equations [64,75]. Numerical techniques and tools for computing bubble curves and other thermodynamic data for mixtures are also available [67,72].

#### *Characterization of CO<sub>2</sub> streams*

The composition of the flue-gas process stream depends on a number of factors, which include the source fuel for power generation, power plant operating conditions, and the nature and efficiency of flue-gas processing steps prior to compression. Gas composition from applications of interest needs to be identified as the first step of the development process.

Once characterized, various available techniques for property and thermodynamic state estimation should be applied to generate phase diagrams, thermodynamic properties, fluid and flow properties, and heat transfer characteristics for the mixtures of interest. It is expected that equations available in the literature for high-ratio CO<sub>2</sub> mixtures can be suitably modified for this development effort [75].

#### *Compression equipment selection and design*

The property and phase data will enable precise estimation of limits and specification of requirements for the compression system. The conditions required to avoid phase separation will be known. The final phase of development would involve a review of the state of the art in compression technology, along with the associated applications and costs. A design optimization effort can then be performed, taking into account the most appropriate thermodynamic paths, compression equipment and size, and interstage processing requirements.

#### *Effect of Impurities on Corrosion*

A significant amount of effort has been expended to control external corrosion of buried pipeline and, in fact, an entire industry has developed around its corrosion prevention and control. The most common practice is the use of coatings in conjunction with cathodic protection. Cathodic protection involves the use

of either sacrificial anodes or impressed current, with the latter technique being the most common. Unfortunately, the corrosion control techniques used to protect the outside of pipelines are ineffective for protecting the pipeline from internal corrosion. This situation is often exacerbated by the fact that detection of internal corrosion is sufficiently difficult that problems may not be identified until an actual failure occurs. Perhaps the most common detection method for internal corrosion is the use of “pigs”, which are mechanical devices used to clean and inspect the internal surfaces of pipelines.

Failure to adequately monitor and prevent internal corrosion can be disastrous. An example was the rupture of a natural gas transmission pipeline in Carlsbad, NM, in August 2000. The pipeline failure killed 12 people and property loss approached \$1 million. The National Transportation Safety Board (NTSB) concluded that the pipeline failure was due to “significant reduction in pipe wall thickness due to severe internal corrosion” [77]. This report also suggests that internal corrosion was likely caused by a combination of microbes and such contaminants as moisture, chlorides, oxygen, carbon dioxide, and hydrogen sulfide. Cleaning pigs were not used in the section of pipe that failed because that section could not accommodate pigs. Among the recommendations of the NTSB was the request by the National Association of Corrosion Engineers (NACE) to update or replace guidelines for internal corrosion inspection of pipelines [78].

#### *Role of contaminants and pH in corrosion of pipeline steel*

SO<sub>2</sub> and NO<sub>2</sub> have high solubility in water/moisture. Similar to CO<sub>2</sub>, SO<sub>2</sub> and NO<sub>2</sub> will not cause corrosion in the absence of moisture. It was mentioned in the literature that impurities in CO<sub>2</sub> tend to increase the rate of corrosion, but no specific details were cited [79]. The mechanism of CO<sub>2</sub> corrosion, in the presence of impurities, is also not understood properly. Van der Meer [80] has mentioned the increase of CO<sub>2</sub> corrosion due to the presence of SO<sub>2</sub>, but no data or explanation was provided.

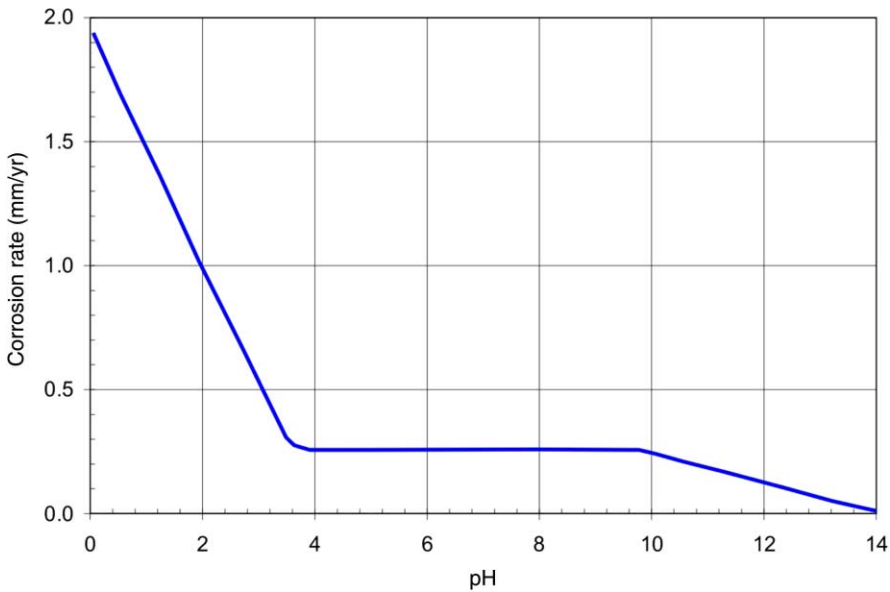
In the case of CO<sub>2</sub> transmission, the most important parameter determining possible corrosion damage will be the amount of water and dissolved O<sub>2</sub> present in the gas. The role of water in corrosion is its ability to act as an electrolyte and solvent for dissolved gases such as O<sub>2</sub> and other contaminants. O<sub>2</sub> is important in corrosion mechanisms because it provides several of the cathodic reaction paths for corrosion to proceed. Removing O<sub>2</sub> or de-aerating the solution will significantly reduce corrosion rates. According to Farthing [81] the internal corrosion rate of the pipe containing CO<sub>2</sub> is directly related to its concentration (when H<sub>2</sub>O is present) and the system’s temperature and pressure.

The maximum allowed moisture content in the pipeline should be evaluated and the tradeoffs for the dehydration systems examined. Experience with existing CO<sub>2</sub> compression and pipeline systems has established the requirement to reduce the moisture sufficiently to prevent condensation of liquid water. Dry CO<sub>2</sub> is generally considered noncorrosive. However, when combined with H<sub>2</sub>O, carbonic acid is produced, which will corrode carbon steel. As the partial pressure of the CO<sub>2</sub> increases, the corrosivity of carbonic acid increases. At a CO<sub>2</sub> partial pressure greater than 207 kPa (30 psi), the carbonic acid formed is sufficiently strong to rapidly corrode carbon steel [82]. Therefore, CO<sub>2</sub> entering the pipeline must be dehydrated to minimize the potential for the formation of liquid water. Water concentrations between 288 and 480 kg/10<sup>6</sup> m<sup>3</sup> (18–30 lb/10<sup>6</sup> scf) typically are adequate for CO<sub>2</sub> transmission in carbon steel pipe [83].

A preliminary analysis indicates that the compression, pipeline, and injection systems designed for CO<sub>2</sub> also should accommodate SO<sub>2</sub>. Prior to the introduction of chlorofluorocarbons, SO<sub>2</sub> was the working fluid of choice for large commercial refrigeration systems. This application provides background data about compressing and handling SO<sub>2</sub>. Performance in these systems indicates that corrosion is acceptable as long as the moisture content is < 0.005% [70]. This dehydration requirement is similar to that for CO<sub>2</sub>.

When H<sub>2</sub>O is present, the main factor affecting the corrosion rate can be related to pH. In the absence of CO<sub>2</sub>, the corrosion rate of iron and steel is fairly independent of pH between 4 and 10 (see Figure 6), but increases significantly below 3.5. The presence of CO<sub>2</sub> can complicate the dependency of corrosion rate on pH. De Waard et al. [89] indicated that the pH will largely be controlled by the concentration of dissolved iron carbonate (FeCO<sub>3</sub>). Figure 7 is a graph showing the calculated corrosion rate, based on De Waard’s

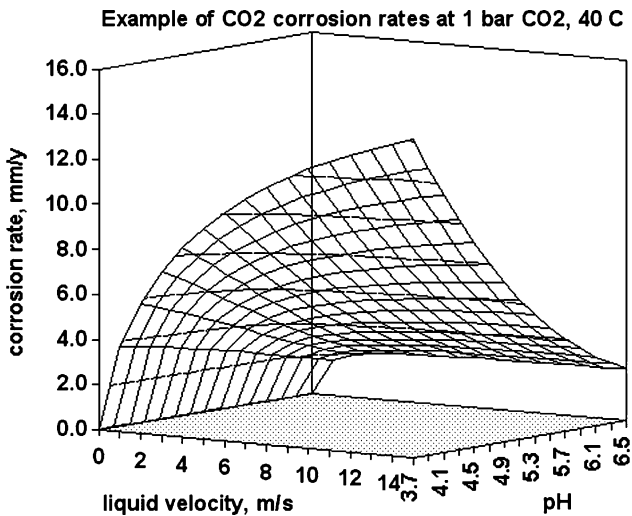




**Figure 6:** Corrosion of steel as a function of water pH [85].

semi-empirical model, as a function of both pH and liquid flow rate at a temperature of 40 °C and partial pressure of CO<sub>2</sub> of 1 bar (14.5 psi).

Studies on flue-gas condensate corrosion for residential high-efficiency furnaces [84] have shown that low concentrations of dissolved chlorides, nitrates, and sulfates can lead to dilute mixed acid solutions



**Figure 7:** Corrosion of steel as a function of flow velocity and pH [89].

having a pH less than 2.5. It is not entirely clear to what degree  $\text{NO}_x$  and  $\text{SO}_x$  will lower the pH of any aqueous phase in pipeline condensate, but this is an area that should be studied to further understand its effect on internal corrosion rates.

Water is typically removed from a system using various devices such as separation equipment, dryers, and dehydrators. Water present in the system might be removed using drip pots, pig launders, valves, and separators. Addition or injection of compatible corrosion inhibitors to the pipeline stream should be considered when  $\text{H}_2\text{O}$  cannot be reduced below an acceptable concentration. Amines are often used as corrosion inhibitors, but other commercially available compounds exist that may improve on their effectiveness.

#### *Pipeline alloy selection*

Pipeline steels are typically made from high-strength American Petroleum Institute (API) grade material. Common grades are X52, X60, and X80 where the number following the “X” refers to the minimum yield strength in ksi or thousands of pounds per square inch. These alloys do not have an inherently good corrosion resistance, particularly to aqueous solutions with low pH. It is imperative, therefore, that an internal corrosion control program be implemented for pipelines carrying  $\text{CO}_2$ . Alloys that have greater corrosion resistances are not likely to be a cost-effective alternative. Chemical process industries, which often use stainless steel (300 series) alloys to minimize corrosion, would be at least three times more expensive than the carbon steels used in gas transmission pipelines.

#### *Corrosion by acid gases*

$\text{CO}_2$  corrosion or “sweet corrosion” is a common phenomenon for carbon and low-alloy steels. Pure, dry  $\text{CO}_2$  is essentially noncorrosive except at temperatures exceeding  $400^\circ\text{C}$  [85]. However,  $\text{CO}_2$  in the presence of  $\text{H}_2\text{O}$  will form carbonic acid, which will corrode the pipeline steel. The corrosiveness of the carbonic acid increases with an increase in  $\text{CO}_2$  partial pressure.  $\text{CO}_2$  corrosion occurs primarily in the form of general corrosion but also as localized corrosion (e.g. pitting, mesa attack).  $\text{CO}_2$  corrosion is affected by a number of parameters [86], including environmental, physical and metallurgical variables. All parameters are independent and can influence the  $\text{CO}_2$  corrosion in many different ways.

#### *Options for corrosion control*

In the absence of data related to the effect of  $\text{SO}_x$  and  $\text{NO}_x$  on  $\text{CO}_2$  corrosion, the effect of the presence of  $\text{SO}_x$  and  $\text{NO}_x$  on variables affecting  $\text{CO}_2$  corrosion (as mentioned in “Introduction” section) should be considered. One of the factors affected by the presence of  $\text{SO}_x$  and  $\text{NO}_x$  will be the pH of the corroding fluids. Based on the concentration of  $\text{SO}_x$ ,  $\text{NO}_x$ , and moisture in  $\text{CO}_2$ , the pH of the corroding fluid will change. The effect of pH on  $\text{CO}_2$  corrosion is defined in the literature and, therefore, can be used to define the change in corrosion properties. However, a number of mechanisms were cited in the literature [87] to correlate the effect of pH on  $\text{CO}_2$  corrosion depending on variables such as type of steel, composition of gasses, temperature, and pressure of gases. Sridhar [88] mentions that the increase in pH in  $\text{CO}_2/\text{H}_2\text{S}/\text{O}_2$  systems results in the decrease of the corrosion rate.

## **CONCLUSION**

Flue-gas impurities such as  $\text{SO}_x$  and  $\text{NO}_x$ , as well as arsenic and mercury present in solid fuels, have the potential of interacting unfavorably with the capture, compression, and pipeline transmission of  $\text{CO}_2$ . Absorption and regeneration characteristics of amines and other solvents used to separate  $\text{CO}_2$  are affected adversely by acid gas impurities. Compression of gas mixtures is subject to condensation of the higher boiling constituents, which may limit the ability to achieve adequate interstage cooling and may damage the compressor and other related processing equipment. Finally, materials used in separation, compression, and transmission are subject to corrosion by acids, which include carbonic, sulfuric, sulfurous, nitric, and nitrous acids.

#### ***CO<sub>2</sub> Capture Chemistry***

With respect to the specific  $\text{CO}_2$  sorption unit operations, amines and amine formulations have been developed commercially to minimize degradation, maximize  $\text{CO}_2$  capacity, and reduce the energy requirements for amine regeneration. What is lacking is a sufficient understanding of the mechanisms for

amine degradation and energy balance control factors in the face of natural contaminants contained in the flue gas, at flue gas scrubber conditions, and the conditions needed to minimize them. The important research and development needs in the capture area are as follows:

- Identification of degradation-resistant amines and associated stabilizers with low volatilities. Generally, these amines will have branched structures of deactivated “R” groups and be essentially nonvolatile.
- Identification of synergistic formulations for CO<sub>2</sub> absorbents that will enable low-energy regeneration and release and that are stabilized against degradation by O<sub>2</sub> oxidation. Note that, as the regeneration temperature is lowered, substantial reduction in degradation is to be expected.
- Identification, and validation at continuous, flow, and sorbent recycle conditions, of a “one stage of contact” technology for scrubbing all of the needed contaminants (especially CO<sub>2</sub>, NO<sub>x</sub>, SO<sub>x</sub>, dust, and toxic metals) from flue gas, with the objective of achieving substantial decreases in the capital cost of flue-gas cleanup.
- Characterization of the mechanisms for the reactions between NO<sub>x</sub> and amine, with the objective of limiting interactions that lead to loss of the amine.
- Evaluation of the oil/water concept for “one step” flue-gas cleanup (including CO<sub>2</sub>) and removal proposed in the “Results and Discussion” section of this chapter (Figure 2).

### **Compression**

The effect of small quantities of SO<sub>2</sub> and NO<sub>2</sub> on the behavior of CO<sub>2</sub> in a pipeline and compression system has not been well established due to lack of data about specific systems of interest. It is known that CO<sub>2</sub> and SO<sub>2</sub> have similar critical pressures (7.3 and 7.9 MPa, respectively), but their compressibilities at 150 °C and 6 MPa are substantially different (0.91 and 0.60, respectively).

There is a clear need for more detailed information regarding CO<sub>2</sub> streams and the influence of NO<sub>x</sub> and SO<sub>x</sub> impurities on fluid properties and compressor performance. It is not possible to conclude from this study whether multi-phase conditions should be expected during compression stages or whether the impurities would cause substantial increases in energy consumption, other operating costs, or capital costs. It is recommended that research and development be undertaken in this area to clarify these issues. An experimental program may be needed to measure all important properties as a function of temperature and pressure, including

- thermodynamic properties, including enthalpy, compressibility, and boiling points (bubble curve);
- fluid flow properties, especially viscosity and density data; and
- heat transfer properties, including thermal conductivity and convective heat transfer coefficients.

### **Corrosion**

Corrosion due to hydrolysis of acid gases is a common phenomenon for carbon and low alloy steels. Pure, dry CO<sub>2</sub> is essentially noncorrosive at ambient to moderate temperatures. However, CO<sub>2</sub> in the presence of water will form carbonic acid, which will corrode pipeline steel. When H<sub>2</sub>O is present, the main factor affecting corrosion rate can be related to pH. For iron or steel, the corrosion rate increases significantly below pH 3.5. SO<sub>2</sub> and NO<sub>2</sub> have high solubility in water/moisture. It is not clear to what degree they will lower the pH of any aqueous phase in pipeline condensate; however, this is an area that should be studied to further understand its effect on internal corrosion rates.

There is a need to understand the interaction of SO<sub>x</sub> and NO<sub>x</sub> with CO<sub>2</sub> under pressurized wet conditions. A fundamental approach is suggested to qualitatively evaluate the effect of small amounts of SO<sub>x</sub> and NO<sub>x</sub> in CO<sub>2</sub> on corrosion properties of pipeline material. Among the necessary data needed are

- The effect of pH on the rate of CO<sub>2</sub> corrosion.
- Dissolution behavior of SO<sub>2</sub> and NO<sub>2</sub> in moisture, which generates sulfurous and nitrous acids.
- The effect of O<sub>2</sub> on these acids, which can further oxidize them to H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> (strong acids).
- The combined effect of these additional acids with carbonic acid, which will change the pH of the corroding media.

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