PCO$_2$R Partnership

Plains CO$_2$ Reduction (PCOR) Partnership
Energy & Environmental Research Center (EERC)

OPPORTUNITIES AND CHALLENGES ASSOCIATED WITH CO$_2$ COMPRESSION AND TRANSPORT DURING CCS ACTIVITIES

Plains CO$_2$ Reduction Partnership Phase III
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ABSTRACT

Carbon capture and storage (CCS) can potentially reduce carbon dioxide (CO_2) emissions from large stationary sources, thereby helping to achieve national and international CO_2 reduction goals. This report examines the concept that pipeline transport can play a part in identifying the types of CO_2 capture technologies that could be deployed as well as the end uses based on the quality of the CO_2 that is specified for transport in a pipeline. This study researched whether a universal CO_2 pipeline specification can be produced that is applicable to the majority of capture technologies.

The study found that the gas streams that are captured from various industries or utilities are remarkably similar in composition and generally can meet Kinder Morgan pipeline specifications, which were developed with enhanced oil recovery (EOR) in mind. EOR is the largest profitable use of CO_2 that is currently practiced in the United States, although other beneficial uses include the production of fuels and chemicals and the food and beverage industries. The consumption of CO_2 in these uses is estimated to be small, approximately only 10% of the energy-related CO_2 emissions. Depending on the end use, additional purification may be needed for the CO_2 to meet the end user's purity requirements. The locations at which the additional purification could be performed—centralized or distributed, located near the sources or near the end users—were studied. The economics of the specific situation would guide the location of the purification.

CO_2 stream composition standards have been developed to ensure safe transport and the structural integrity of a pipeline that carries CO_2. Limits for many impurities are based on health, safety, use, and other considerations. Pipelines transport CO_2 that contains various impurities, requiring that they be structurally robust enough to transport even corrosive mixtures of CO_2. Three approaches to address issues created by impurities are to upgrade the pipe metal and/or thickness, adopt lined pipe, or switch to organic polymer composite pipe. Composite pipelines offer an opportunity to transport lower-purity CO_2 that might otherwise damage steel pipelines. It was found that steel would be the most economical choice for larger main transmission pipelines, with spoolable composite pipe a less expensive alternative for gathering and distribution pipelines.

The goal of CO_2 stream optimization to maximize its usability is to identify acceptable concentrations of impurities that can still produce an acceptable product at a minimum cost. The variability of the needs of each end use make it difficult to predict a single desired range of component concentrations. Although a universal CO_2 specification could not be identified, the concepts studied in this project offer a different approach to thoughtful integration of a more cost-effective, complete CCS system, especially if a larger-scale pipeline network is considered.

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NOMENCLATURE

Ar	argon
As	arsenic
atm	atmosphere
bpd	barrels per day
°C	degrees Celsius
CC	combined cycle
CCS	carbon capture and storage
CCUS	carbon capture, utilization, and storage
Cd	cadmium
CGMP	current good manufacturing practices (FDA)
CH_4	methane
C_2H_6	ethane
Cl	chlorine
Co	cobalt
CO	carbon monoxide
CO_2	carbon dioxide
COS	carbonyl sulfide
Cr	chromium
CS_2	carbon disulfide
Cu	copper
DOE	U.S. Department of Energy
ECRA	European Cement Research Academy
ENCAP	ENhanced CAPture of CO_2 (project)
EOR	enhanced oil recovery
EP	European Pharmacopeia
EPA	U.S. Environmental Protection Agency
°F	degrees Fahrenheit
FAO	Food and Agriculture Organization (of the United Nations)
FCCU	fluidized catalytic cracking unit
FDA	U.S. Food and Drug Administration
FRP	fiber-reinforced polymer
ft	foot
H_2	hydrogen
HCl	hydrogen chloride (hydrochloric acid)
HF	hydrogen fluoride (hydrofluoric acid)
HFCP	Hydrogen and Fuel Cells Program
Hg	mercury
Hg^{2+}	oxidized mercury
H_2O	water
H_2S	hydrogen sulfide
IGCC	integrated gas combined-cycle
lb	pound mass

Continued…

NOMENCLATURE (continued)

i.d.	inside diameter
in.	inch
kg	kilogram
IEAGHG	IEA Greenhouse Gas R&D Programme
JECFA	Joint FAO/WHO Expert Committee on Food Additives
MAOP	maximum allowable operating pressure
MEA	monoethanolamine
mg	milligram
mg/m^3	milligrams per cubic meter
mi	mile
mm	millimeter
MMcf	million cubic feet
MMP	minimum miscibility pressure
MMscf	million standard cubic feet
Mn	manganese
mol%	mole percent
MPa	megapascal
MPaA	megapascal, absolute
N_2	nitrogen
NETL	National Energy Technology Laboratory
NH_3	ammonia
Ni	nickel
N_2O	nitrous oxide
NO_2	nitrogen dioxide
NO_x	nitrogen oxides
O_2	oxygen
OCAP	Organic Carbon Dioxide for Assimilation of Plants
o.d.	outside diameter
Pb	lead
pc	pulverized coal
PCC	precipitated calcium carbonate
ppm	parts per million
ppmv	parts per million by volume
ppmw	parts per million by weight
PSA	pressure swing adsorption
psi	pounds per square inch
psig	pounds per square inch gauge
Sb	antimony
Se	selenium
Sn	tin
SO_2	sulfur dioxide
SO_3	sulfur trioxide

Continued…

NOMENCLATURE (continued)

SO_x	sulfur oxides
SS	stainless steel
Te	tellurium
TEG	triethylene glycol
TEQ	toxicity equivalence
Tl	thallium
TOC	total organic carbon
µm	micrometer
UNS	Unified Numbering System (for Metals and Alloys)
USP–NF	United States Pharmacopeia–National Formulary
V	vanadium
v/v	volume/volume; on a volume basis
VOC	volatile organic carbon
vol%	volume percent
WAG	water alternating gas
WHO	World Health Organization
w/w	weight/weight; on a weight basis
yr	year
Zn	zinc

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EXECUTIVE SUMMARY

Carbon capture and storage (CCS) can potentially reduce carbon dioxide (CO_2) emissions from large stationary sources, such as power plants and industrial facilities, thereby helping to achieve national and international CO_2 reduction goals. Large scale (>1 Mt per year CO_2), integrated CCS projects have been deployed over the last two decades using established and nascent technologies for each element of the CCS chain – capture, transport, and storage. The majority of the research to date has focused on either capture processes, representing the most expensive element of typical CCS projects, or storage, as the most uncertain element. This report assesses factors affecting pipelines, the predominant means of transporting CO_2 at large scale, and considers the potential for a universal CO_2 pipeline specification that is applicable to the majority of capture technologies. Topics studied included the quality of CO_2 streams produced by selected industries and capture processes, the purity requirements for various utilization options for CO_2, the processes required to meet purity requirements, and the effects of impurities on transport infrastructure.

Solvent-based methods currently are the most common means to capture CO_2 from industrial processes and are especially well-suited to retrofit situations. Despite the range of processes amenable to solvent-based methods and their greater range of impurities, once separated and dehydrated the product CO_2 streams of these solvent-based methods are remarkably similar. Such product streams are composed of at least 98% CO_2, with only low levels of residual N_2, O_2, water, and other impurities. Some commercial processes, such as ethanol production, produce very pure streams of CO_2 without purification other than dehydration. The quality of CO_2 stream that is produced by an ethanol plant or would be captured using amine scrubbing is sufficient for most end uses unless very low O_2 levels are required. If that is the case, additional processing to remove the O_2 would be needed.

The largest current beneficial use of CO_2 is enhanced oil recovery (EOR). Captured CO_2 from most commercial processes is sufficiently pure for use in EOR, as long as moisture levels are reduced to levels of less than 630 ppm and N_2 and O_2 levels are reduced appropriate to the needs of the oil reservoir. Other theoretical utilization options include the production of fuels or chemicals, although CO_2 specifications for the associated processes are typically not yet defined.

Depending on the end use, additional purification may be needed for the CO_2 to meet specific quality requirements. Purification could occur at distributed locations (e.g. points of capture or use) or in advantageous centralized locations. Centralized sites that receive CO_2 from multiple capture sites have the advantage of economy of scale because of the larger process quantities. Distributed locations possess major advantages related to the ability to customize and handle limited ranges of impurities and volumes of CO_2.

Composition standards have been developed to ensure transport safety of CO_2 and structural integrity of pipelines. CO_2 quality specifications are not based strictly upon physical and chemical considerations relative to the pipeline, but also health, safety, use, cost, and other considerations. These considerations can be competitive and complicate the development of quality specifications.

Pipeline design and construction must account for any potential corrosion that could result from impurities in the CO_2 stream. Three obvious approaches to address any issues created by impurities are to upgrade the pipe metal and/or thickness, adopt lined pipe, or switch to organic polymer composite pipe. Composite pipelines are flexible and offer an opportunity to transport lower-purity CO_2 that might otherwise damage steel pipelines and, by so doing, potentially reduce capture and purification costs. Because of limitations with larger-diameter composite pipelines, steel would be the most economical choice for the larger main transmission pipelines, with spoolable composite pipe a less expensive alternative for gathering and distribution pipelines.

The potential variety of CO_2 sources, capture processes, and end uses makes formulation of a single, optimal-cost CO_2 quality specification difficult. This study presents an integrative, total-systems perspective from which to consider CO_2 quality and its implications on pipeline design and operation.

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INTRODUCTION

Carbon capture and storage (CCS) hold the potential to reduce carbon dioxide (CO_2) emissions from large stationary sources, such as power plants and industrial facilities, thereby helping to achieve national and international CO_2 reduction goals. CCS is essentially a four-step process: capture of CO_2 from a large stationary facility, compression, pipeline transport, and injection of the CO_2 into a secure geologic formation for permanent storage. Alternatively, the CO_2 could be put to some type of beneficial use. Technologies exist for all of the CCS steps, but the steps have only recently been integrated into large-scale CCS projects. Two primary drivers for CCS research have been to demonstrate the integration of the steps and to decrease the overall cost. The majority of the research to date has focused on the capture and end use of the CO_2 (e.g., for enhanced oil recovery [EOR]). This report examines the concept that pipeline transport could help to identify the types of CO_2 capture technologies that might be deployed as well as the end uses of the CO_2. This concept could offer a different approach to thoughtful integration of a more cost-effective, complete CCS system, especially if a larger-scale pipeline network is under consideration.

BACKGROUND

Most conceptual CCS projects begin with a known point source and a desired end use for the CO_2. The most appropriate capture technology for that source is identified, and CO_2 purification is expected to be performed during or just after capture so that the CO_2 that arrives at the end use location meets the purity requirements of that end use. Generally, it is assumed that the CO_2 will be transported via pipeline and that if CO_2 from other sources is carried at the same time in the pipeline, the CO_2 from the other sources will be of the same purity. Likewise, if multiple end users offtake CO_2, it is assumed that all of them will have the same CO_2 quality requirements. This approach, while understandable this early in the deployment of CCS, may not be the most cost-effective for all parties.

When planning for possible future CO_2 pipeline networks carrying anthropogenic CO_2, other options could be investigated, such as:

- Can CO_2 streams from multiple sources and/or industries be carried in the same large pipeline or should there be smaller, one-to-one pipelines between specific types of sources and specific end users?

- If there is a mismatch between CO_2 quality generated at a source and that desired by an end user, which one should remove the unwanted impurities?

- Should impurities that are harmful to the environment or health be allowed in a pipeline, even if they are acceptable to the end user?

- Can purity requirements be identified that will ensure that a pipeline maintains its structural integrity? Is it possible that CO_2 that meets the pipeline requirements may also meet (or come close to meeting) the needs of all end users?

Variations in CO_2 sources may make it difficult to identify a single CO_2 specification from the perspective of the capture processes. It is also difficult to identify components that could be present in a captured stream that could be utilized by any end user. In this report, the authors survey the quality of CO_2 streams that could be produced by a few industries, the purity requirements of different end uses for CO_2, the purification processes required to meet the end users' purity requirements, and the effects of impurities on the transport infrastructure. Using a systems analysis approach, integrated CCS was assessed to determine if placing a focus on the CO_2 composition and impurities that are transported via pipeline might be able to improve the efficiency and/or cost-effectiveness of the integrated CCS process.

COMMERCIAL SOURCES OF CO_2 AND THEIR MOST COMMON IMPURITIES

There are three opportunities (called platforms) for capturing CO_2 from fossil fuel combustion systems, whether for power generation or at an industrial facility: before (pre), during (through combustion modification), and after (post) combustion. The specific types of CO_2 capture technologies that are available for use in one or more of these platforms include absorption, adsorption, membranes, and other techniques such as mineralization, reduction, and cryogenic methods (Cowan and others, 2011).

Precombustion removal refers to near-complete capture of the CO_2 prior to fuel combustion and is usually implemented in conjunction with gasification (of coal, coke, waste biomass, or residual oil) or steam reforming/partial oxidation of natural gas to produce syngas, which contains carbon monoxide (CO) and hydrogen (H_2). Subsequent conversion by the water–gas shift reaction produces CO_2 from the CO, resulting in H_2-rich syngas. This syngas (often with nitrogen added for temperature control) can be combusted in gas turbines, boilers, or furnaces. Purified H_2 can be used in fuel cells. Typical CO_2 stream concentrations before capture are 25 to 40 vol% at pressures ranging from 2.48 to 5.0 MPaA. This high partial pressure of CO_2, relative to that of combustion flue gas, enables separation to be performed using physical solvents. A physical solvent uses the pressure-dependent solubility of CO_2 in the solvent (as opposed to a chemical reaction with the solvent) to separate the CO_2 from the mixed-gas stream (Cowan and others, 2011). Water present in the CO_2 stream would be removed prior to pipeline transport.

With process modification, a concentrated stream of CO_2 can be generated during combustion in a process called oxygen combustion, or oxycombustion. Substitution of pure oxygen for the combustion air produces a CO_2-rich flue gas that requires minimal processing before use or permanent storage. Theoretically, the CO_2 can be recovered by compressing, cooling, and dehydrating the gas stream to remove traces of water that are generated during combustion. When the end use requires it, any noncondensable impurities that may be present such as nitrogen (N_2), nitrogen oxides (NO_x), oxygen (O_2), and argon (Ar) can be removed by flashing in a gas–liquid separator (Cowan and others, 2011).

The most common CO_2 separation platform is postcombustion, where the CO_2 is removed from low-pressure, low-CO_2-concentration flue gas following other pollution control devices so that the postcombustion sorbent (either an amine solvent or a dry adsorbent) or membrane is not deleteriously impacted by the non-CO_2 flue gas components. Several types of postcombustion processes have been and are being developed to separate and remove the CO_2 from a flue gas stream. These include absorption, adsorption, membrane, and cryogenic processes. Other methods include mineralization for either disposal or production of a mineral product and reduction to beneficial products such as fuels and/or plastics (Cowan and others, 2011). Postcombustion is the CO_2 capture technology platform that would most likely be applied at existing conventional coal-fired power plants in the near term because it has been applied commercially at other industrial facilities.

In a presentation given at the EC FP7 Projects: Leading the Way in CCS Implementation Conference, Porter (2014) presented a summary comparison of the impurities expected to be present in captured CO_2 streams from the three platforms as estimated by the CO_2QUEST project. These data are shown in Table 1.

Different industrial processes and different capture technologies can produce captured CO_2 streams that have somewhat different compositions. In general, postcombustion amine-scrubbing processes will produce very similar streams, irrespective of flue gas source. The same is true for precombustion capture and oxycombustion processes. Examples of captured CO_2 stream compositions for electric power generation (both pulverized coal [pc] and integrated gas combined-cycle [IGCC]) are shown in Table 1 in the precombustion (IGCC) and postcombustion columns. The captured CO_2 stream compositions from cement manufacture, petroleum refining, coke production, and lime manufacture were reported by Porter (2014) and Last and Schmick (2011) and are shown in Table 2. While reported typical impurities for postcombustion processes are relatively low (except perhaps for water), precombustion technologies could contain up to a few percent hydrogen or H_2S/COS and oxycombustion could carry a couple of percent of oxygen and nitrogen as well as water (Porter, 2014). De Visser and others (2008) prepared a CO_2 quality recommendation that was based upon the ENCAP project as well as health, safety, and operational considerations. The recommendations developed by de Visser and others are based on precombustion processes and take into account multicomponent cross-effects (such as between water and H_2S and water and methane) on CO_2 transport. Irrespective of its composition, once the CO_2 has been captured, it is dehydrated to remove water and compressed for transport via pipeline to the geologic storage site.

Table 1. Summary of Impurities in Captured CO_2 Streams from the Three Capture Platforms

	Oxycombustion				
Component	**Raw/ Dehumidified**	**Double Flashing**	**Distillation**	**Precombustion**	**Postcombustion**
CO_2, vol%	74.8–85.0	95.84–96.7	99.3–99.4	95–99	99.6–99.8
O_2, vol%	3.21–6.0	1.05–1.2	0.01–0.4	0	0.015–0.0035
N_2, vol%	5.80–16.6	1.6–2.03	0.01–0.2	0.0195–1	0.045–0.29
Ar, vol%	2.3–4.47	0.4–0.61	0.01–0.1	0.0001–0.15	0.0011–0.021
NO_x, ppm	100–709	0–150	33–100	400	20–38.8
SO_2,[a] ppm	50–800	0–4500	37–50	25	0–67.1
SO_3,[b] ppm	20	–	20	–	N.I.[1]
H_2O,[c] ppm	100–1000	0	0–100	0.1–600	100–640
CO, ppm	50	–	50	0–2000	1.2–10
H_2S[d]/COS,[e] ppm				0.2–34,000	
H_2, ppm				20–30,000	
CH_4,[f] ppm				0–112	

[a] Sulfur dioxide; [b] sulfur trioxide; [c] water; [d] hydrogen sulfide; [e] carbonyl sulfide; [f] methane.

Table 2. Captured CO_2 Stream Compositions from Non-Electric Power Emitters

	MEA[a] Refinery[b]	**MEA Cement Plant[b]**	**Cement Kiln[e]**	**Coke Production[c]**	**Lime Production[c]**
CO_2, vol%	99.6	99.8	99.00	99.4	99.52
N_2, vol%	0.29	0.0893			
CO, ppmv	1.2	1.2	1620	701	2000
Ar, ppmv	11	11			
H_2O, ppmv	640	640			
NO_x, ppmv	2.5	0.86	3330	1690	1100
SO_x, ppmv	1.3	<0.1	4410	3030	1800
O_2, ppmv	35	35			
CH_4, ppmv				206	
Cl,[d] ppmv	0.41	0.41	65.7	26.89	
Ash, ppmv		5.7			
Hg,[e] ppmv		0.00073	0.1		
As,[f] ppmv	0.29	0.0029			
Se,[g] ppmv	1.2	0.0088			
VOC,[h] ppmv				96.9	
TOC,[i] ppmv			81		

[a] Monoethanolamine.
[b] Porter (2014).
[c] Last and Schmick (2011).
[d] Chlorine.
[e] Mercury.
[f] Arsenic.
[g] Selenium.
[h] Volatile organic compound.
[I] Total organic carbon.

Coal-Fired Power Plants

In 2015, roughly 37% of the energy-related CO_2 emissions from fossil fuel combustion in the United States were attributed to power plants (U.S. Energy Information Administration, 2016). Power plants built in the 1990s and early 2000s typically have been designed for baseload operation with a main objective of producing electricity at minimum cost (Domenichini and others, 2013). Variable electricity demand, coupled with increased use of renewable energy sources such as solar and wind (which are themselves variable sources) and the relatively poor flexibility of low-CO_2 generation technologies such as nuclear, means that future power plants will need to be capable of flexible operation (Ferrari and others, 2012).

In general, a conventional coal-fired power plant produces a flue gas having the relative proportions of components shown in Table 3. A postcombustion process that makes use of amines to separate the CO_2 from the rest of the flue gas is the technology that is most likely to be applied to an existing coal-fired power plant because that technology already has been demonstrated at commercial scale. Coal composition does not substantially affect the composition of the CO_2 stream produced because the requirements of existing amine processes (and other solvents as well) dictate that the flue gas be scrubbed to very low levels of SO_x, NO_x, particulate, and Hg. Removal of these constituents limits the production of heat-stable salts that take a portion of the amine out of service. This processing scheme renders most flue gases very similar at the entrance to the capture technology after which the amine scrubber itself removes virtually all of any remaining SO_x, NO_x, and particulate. Once the CO_2 stream is dehydrated and compressed in preparation for pipeline transport, it is likely that it will be very pure, containing only small amounts of nitrogen, oxygen, and water. This purity will not likely change substantially even if other capture technologies are used, because they virtually all require the same flue gas pretreatment and produce very similar CO_2 streams.

Cement Plants

The cement industry accounts for about 4% of all of the CO_2 emissions produced globally (Global Greenhouse Warming, 2017). Approximately 1 tonne of CO_2 is produced for every tonne of cement (Rubenstein, 2012). CO_2 is produced directly through the calcination process; this accounts for about 50% of the CO_2 emissions from a cement plant (Rubenstein, 2012). CO_2 is also produced indirectly by burning fossil fuels to heat the kiln (equaling roughly 40% of the emissions) as well as by producing the electricity needed for the remaining cement plant machinery and during transport of the cement product (totaling about 5% to 10% of the CO_2 emissions). A simplified process flow diagram showing the steps in the cement-manufacturing process and gaseous emission locations is shown in Figure 1.

Life cycle assessments carried out for the industry point to the parts of the process where emissions are expected: in the raw meal preparation and pyroprocess steps. There are four main pyroprocessing routes for the production of cement: wet process, semi wet process, semidry process, and dry process (IEA Greenhouse Gas R&D Programme, 2008). In the United States, the processes are described as wet, long dry, preheater, and precalciner (Greer, 2003; Marceau and others, 2010). Each process type can have multiple gas vents that can remain independent or

Table 3. Relative Concentrations of Components in Raw Flue Gas from a Conventional pc Power Plant and a CO_2 Stream Separated Using Amine Absorption

Component	Relative Proportions in Flue Gas,[a] vol%	Estimated Composition of CO_2 Stream from Amine Absorption,[a] vol%	Estimated Composition of CO_2 Stream After Dehydration,[b] vol%	Estimated Composition of CO_2 Stream from MEA Absorption,[c] vol%
CO_2	13.5	93.2	99.75	99.7
SO_2	0.016	Trace		<0.0001
SO_3	0.00325	Trace		
N_2	74.7	0.17	0.18	0.18
NO_2[d]	0.0025			0.00015
NO_x	0.06	Trace		
HCl[e]	0.00525			
O_2	4	0.01	0.01	0.006
H_2O	7.7	6.5	0.06	0.064
Hydrocarbons	Trace	Trace		
Metals	Trace	Trace		
Hg^{2+}[f]	Trace			

[a] From Last and Schmick (2011).

[b] Estimated by removing water to ~640 ppmw and normalizing the remaining components that are present in larger than trace amounts. This level of water can be thought of as a maximum concentration for consideration for transport in a pipeline. In fact, it is quite likely that the amount of water present would be lower. This calculation provides the "least pure" stream composition.

[c] From Porter (2014).

[d] Nitrogen dioxide.

[e] Hydrochloric acid.

[f] Oxidized mercury.

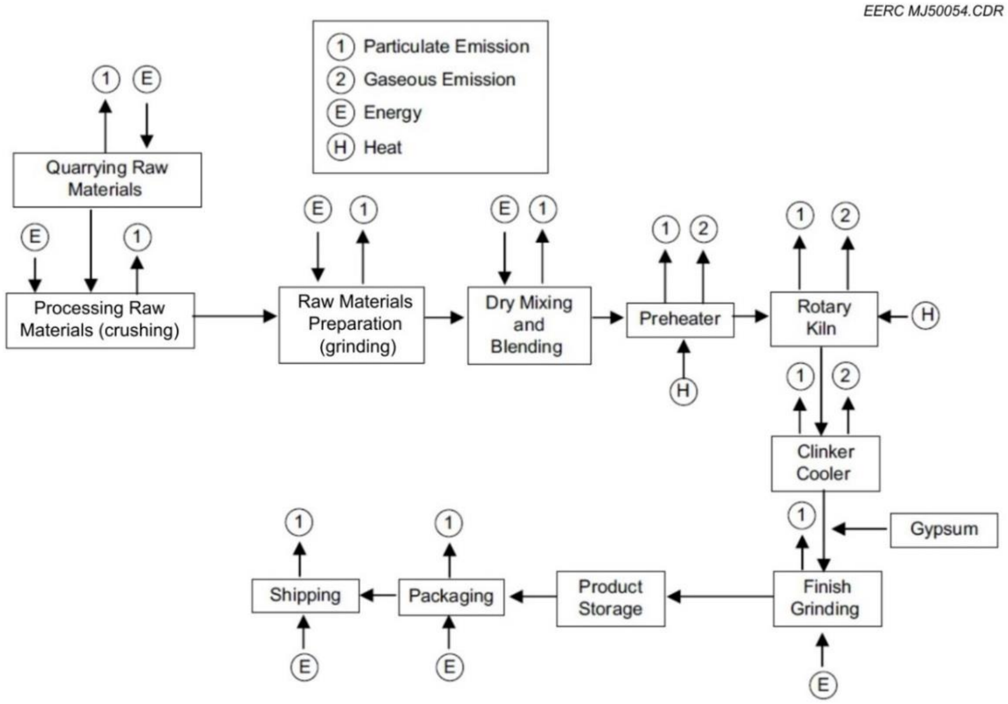

Figure 1. Flow diagram of the cement-manufacturing process (taken from Huntzinger and Eatmon, 2009).

combined to exit via a main stack. Therefore, the composition of the gas stream available for CO_2 capture can be highly variable and, at each facility, depends upon the fuels used, the configuration of the process, the ratio of clinker to cement, and the venting configuration.

The IEA Greenhouse Gas R&D Programme's (IEAGHG's) 2008 report on CO_2 capture in the cement industry reported emission information primarily from European sources looking at various clinker/cement ratios and fuels used. Table 4 summarizes the findings. Marceau and others (2010) reported emission data for cement production in the United States. These data are presented in Table 5. Ali and others (2011) reported a wide range of concentrations of exhaust gas components, believed to be a generalized worldwide average. These average concentrations are given in Table 6. Finally, a report issued in 2009 by the European Cement Research Academy (ECRA) examined the feasibility of CO_2 capture from clinker production. Emission data from German cement kilns were collected. Concentrations of SO_x were below 100 mg/m^3 for the majority of kilns, while the average NO_x concentration was about 410 mg/m^3.

Table 4. Process Emissions from Cement Production, Primarily in Europe (summarized from IEA Greenhouse Gas R&D Programme, 2008)

Component	Wet Process	Dry Process
CO_2 (calcination), kg/kg of clinker produced	0.5 (estimated)	0.5 (estimated)
CO_2 (kiln fuel), kg/kg of cement produced [a,b]	0.36–1.09	0.28–0.89

	kg/tonne clinker
No Distinction of Process Type for Components Given Below	
O_2, %	10% (typically)
NO_x (as NO_2), kg/tonne clinker	<0.4–6
SO_2, kg/tonne clinker	<0.02–7
Dust, kg/tonne clinker	0.01–0.4
Hydrofluoric Acid (HF), kg/tonne clinker	<0.0008–0.01
HCl, kg/tonne clinker	<0.002–0.05
Dioxins/Furans, mg/tonne clinker	<0.002–0.001
Metals, mg/tonne clinker	
Total Hg, cadmium (Cd), thallium (Tl)	200–600
Total As, cobalt (Co), nickel (Ni), Se, tellurium (Te)	2–200
Total antimony (Sb), lead (Pb), chromium (Cr), copper (Cu), manganese (Mn), vanadium (V), tin (Sn), zinc (Zn)	10–600

[a] Emissions from electricity consumption are included.

[b] Clinker content (clinker/cement ratio) varies from 0.5 to 0.95.

It would be possible to apply CO_2 capture to a cement plant. The most appropriate approaches would be either oxycombustion or postcombustion processes (IEA Greenhouse Gas R&D Programme, 2008). At a cement plant, oxycombustion is the process in which the fuel used to heat the kiln is burned in a pure oxygen environment and CO_2-rich flue gas is recycled to the burner to control the combustion temperature. Theoretically, oxycombustion would produce a flue gas with a very high concentration of CO_2 requiring little postseparation processing. However, it is likely that some type of stream purification would still be required (IEA Greenhouse Gas R&D

Table 5. U.S. Pyroprocess Emissions from Fuel Combustion[a] and Calcination (Marceau and others, 2010)

	Wet	Long Dry	Preheater	Precalciner	Average
Emission	**kg/tonne of Cement**				
Particulate Matter, total	0.280	0.347	0.148	0.152	0.201
CO_2	1090	1000	846	863	918
SO_2	3.87	4.79	0.262	0.524	1.65
NO_x	3.49	2.88	2.28	2.00	2042
VOC	0.0548	0.00991	0.00304	0.0507	0.0380
CO	0.0624	0.103	0.469	1.77	1.04
CH_4	0.0544	0.0096	0.00269	0.0501	0.0375
Ammonia (NH_3)	0.00472	0.00479	0.00475	0.00476	0.00476
HCl	0.043	0.055	0.0013	0.065	0.0446
Hg	5.51E-05	8.43E-05	2.69E-05	6.94E-05	6.24E-05
Dioxins and Furans, TEQ[b]	6.53E-11	3.69E-10	2.38E-12	9.97E-11	9.97E-11

[a] Includes mobile equipment allocated to the pyroprocess step. According to the source, mobile equipment makes up 15% of the reported emissions.

[b] Toxicity equivalence.

Table 6. Average Exhaust Gas Concentration from the Cement Process (Ali and others, 2011)

Component	Concentration
CO_2	14%–33% (w/w)
NO_2	5% vol%–10 vol% of NO_x
NO_x	<200–3000 mg/Nm^3
SO_2	<10–3500 mg/Nm^3
O_2	8%–14% (v/v)

Programme, 2008). According to the IEAGHG (2008), application of oxycombustion to a cement plant may require the following:

- A process redesign in order to prevent excessive equipment wear.
- A second combustion point using recycled CO_2 if a precalciner is used.
- An assessment of effects on process chemistry, particularly the calcination process.
- A better understanding regarding whether or not the plant can be made sufficiently free of air in-leakage to prevent dilution of the concentrated CO_2 stream.
- On-site CO_2 storage may be required to maintain appropriate burner temperature during periods when there may not be enough CO_2 from the exhaust gases to recycle, such as at start-up.

Efficient, cost-effective application of almost any postcombustion CO_2 capture process to a cement plant would require the same unit operations that a coal-fired power plant would require, i.e., processes that can dramatically reduce SO_x, NO_x, particulate, and mercury levels (IEA Greenhouse Gas R&D Programme, 2008). In addition, there would be space, power, and heat integration requirements (IEA Greenhouse Gas R&D Programme, 2008). The IEAGHG (2008) concludes that postcombustion capture could be readily retrofitted to existing cement plants, assuming that there is enough space at the cement plant for the capture facility, but that further research and development are needed to address technical issues with applying oxycombustion to a cement plant. If an amine-scrubbing technology were applied to a Portland cement plant, the expected composition of the concentrated CO_2 stream that would be produced is given in Table 7.

Table 7. Summary of Component Relative Proportions for Portland Cement Kilns (Last and Schmick, 2011)

Component	Relative %[a]
TOC	0.008
CO	0.162
CO_2	99.048
NO_x	0.333
SO_2	0.441
HCl	0.007
Acetone	0.000
Benzene	0.001
Toluene	0.000
Chloromethane	0.000
Benzoic Acid	0.000
Bis(2-ethylhexyl)phthalate	0.000
Phenol	0.000
Hg	0.000

[a] Values rounded to thousandths place.

Petroleum Refineries

Even though the cumulative amount of CO_2 emissions from petroleum refineries is a small fraction of the emissions from electric power plants, the volume of CO_2 that refineries produce is substantial. Reports by large emitters to the U.S. Environmental Protection Agency (EPA) in 2015 indicate that U.S. petroleum refineries emitted approximately 9% as much CO_2 as power plants and represented about 176 million tonnes of the annual CO_2-equivalent emissions (U.S. Environmental Protection Agency, 2015). Emissions from a typical refinery are also more heterogeneous than those from a typical power plant because there are multiple disparate emission sources, such as the oxygen-fired fluidized catalytic cracking unit (FCCU) catalyst regenerator, various furnaces, and natural gas-based hydrogen production.

A refinery is a collection of different processing units optimized to accept a range of crude oil feedstocks for the economical production of a range of products. The specific ranges of feedstocks and products are determined by the particular design of the refinery. While it may be said that there are generic configurations, such as hydrocracking for enhanced diesel production or fluidized catalytic cracking for gasoline production, in fact, there are no standard refineries; each is different. Refineries differ in the amount of CO_2 produced per barrel of oil that is processed by the plant overall as well as in the relative amounts produced by similar processing units across plants. This can be seen in Table 8, which shows where CO_2 is produced in a typical refinery, and Table 9, which shows how CO_2 emissions can be assigned to processes across a notional refinery.

Table 8. Typical CO_2 Refinery Emission Sources (Taraphdar, 2011)

Source	Fraction of Refinery CO_2 Emissions, vol%
Process Heaters	50
Utilities	30
Hydrogen Plant	16
FCCU Regenerator	4

Table 9. Emissions from a Notional 235,000-bpd Refinery (Ferguson and others, 2011)

Source	Fraction of Refinery CO_2 Emissions, vol%
FCCU	21
Crude and Vacuum Distillation Units	17
Natural Gas Boilers	16
Hydrogen Unit	13
Continuous Catalytic Reforming Unit	12
Visbreaking Unit	7
Fuel Oil Boilers	4
Gas Turbine Generator	4
Other	5

The relative contributions of these processes can also vary within a single refinery because crude oil feeds vary and the relative performances of the processes vary over time. The process units differ with respect to choice of capture technologies that could appropriately be applied to each and the compositions (under normal and upset conditions) of the captured streams. In other words, the composition and rate of CO_2 produced from a given refinery vary as the relative processing rates of different units vary. Composition variation across units can be reduced if the same capture technology is applied across the refinery, but this might not be the least cost approach.

Emissions from boilers, heaters, and utilities are amenable to capture by a wide range of CO_2 capture technologies from all three capture platforms. Such is not the case for hydrogen units and FCCUs, which, by their nature, are not compatible with precombustion technologies. This is unfortunate because the locations of refinery emission sources tend to be widely distributed around the refineries, meaning that collecting CO_2 emissions for capture involves large amounts of awkward ductwork. This situation is avoided by precombustion because capture can be centralized and limited to hydrogen units. The effects of simultaneously employing a variety of capture technologies at a refinery mean that the various CO_2 streams leaving different processes could have different compositions or even compositions that change with time.

Even though there are about 140 operating refineries in the United States (U.S. Environmental Protection Agency, 2015), and hundreds of other refineries elsewhere in the world, reports in the open literature of CO_2 capture facilities processing refinery emissions are rare, and with the exception of the data shown in Table 2, specific CO_2 stream compositions could not be found.

Gas-Processing Plants

Gas-processing facilities separate the various hydrocarbons and fluids from the raw natural gas (NaturalGas.org, 2013). Oil and condensate are often removed in equipment located at or near the wellhead. Free water can be removed by simple separation at or near the wellhead, but water vapor is removed through dehydration using glycol or solid desiccant. Natural gas liquids can be removed using absorption or cryogenic expansion, while acid gases (H_2S and CO_2) are removed from the natural gas stream using amines or iron sponges (NaturalGas.org, 2013). Acid gas removal can be performed by other processes as well, including chemical solvents (generally amines), physical solvents, and membrane systems (Kohl and Nielsen, 1997). Choosing a process depends on the process economics and effectiveness. Solvent cost, equipment cost, and the energy required for regeneration are the most important factors when selecting a process (El Ela, 2014).

Once dried and compressed, the CO_2-rich stream from a gas-processing plant can be fairly pure. As an example, the average CO_2 vent stack compositions for the ConocoPhillips Lost Cabin Gas Plant in Wyoming are presented in Table 10. Table 11 shows the composition and metered volume of vent stack gas supplied to the CRC pipeline in Texas as measured by five separate metering systems at the McCamey Hub. As the tables both show, CO_2 makes up a significant percentage of the gas stream with a concentration exceeding 94 vol%.

Table 10. Average CO_2 Vent Stack Composition for Lost Cabin Gas Plant (Lohnes, 2007)

Component	Train I	Train II	Train III
CO_2, mol%	98.318	98.447	98.273
CH_4, mol%	1.472	1.389	1.550
C_2H_6, mol%	0.016	0.015	0.027
N_2, mol%	0.103	0.057	0.052
COS, mol%	0.091	0.092	0.098
H_2S, ppmv	5	4	8

Ethanol Production

Ethanol plants are considered to be among the easiest facilities from which to capture CO_2. The ethanol process involves a fermentation step that produces a wet and nearly pure CO_2 stream. Typically, the off gas from ethanol fermentation is rinsed to remove any ethanol, dehydrated, and compressed for pipeline transport. A typical water-saturated CO_2 stream composition from an ethanol plant is given in Table 12. As the table indicates, once dried the stream would consist of CO_2, with small percentages of N_2 and O_2 from air as well as parts-per-million levels of other compounds such as acetaldehydes.

Table 11. Metered Sales Gas Volume and Composition by Month (Blue Source, LLC, 2006)

		Gas Composition, mol%	
Month–Year	**Metered Volume, kscm^3[a]**	**CO_2**	**CH_4**
July 2004	44,721	96.437	2.196
August 2004	45,911	95.921	2.707
September 2004	40,338	95.711	2.943
October 2004	50,141	96.588	2.34
November 2004	47,069	96.588	2.34
December 2004	50,247	97.409	1.347
January 2005	55,598	95.122	3.699
February 2005	54,125	95.141	3.919
March 2005	69,008	95.141	3.919
April 2005	56,820	95.455	3.4
May 2005	56,603	97.106	1.721
June 2005	52,281	96.145	2.605
July 2005	59,073	96.662	2.148
August 2005	62,852	96.705	1.97
September 2005	61,171	94.564	4.255
October 2005	59,659	94.564	4.255
November 2005	54,915	94.453	4.46
December 2005	56,984	95.422	3.615
January 2006	53,815	95.681	3.202
February 2006	47,951	96.849	1.23
March 2006	59,661	97.348	1.863
April 2006	60,160	95.595	3.364
May 2006	66,145	96.398	2.698
June 2006	61,639	94.91	4.107
July 2006	62,346	94.824	4.188

[a] At U.S. oil and gas standard conditions of 15.56°C and 0.101 MPa.

Table 12. CO_2 Stream Composition from an Ethanol Plant (Chen and others, 2004)

Component	Wet Concentration[a]	Dry Concentration[b]
CO_2, vol%	87.2	98.4
H_2O, vol%	11.1	0
Air, vol%	1.2	1.35
N_2[c], vol%		1.053
O_2[c], vol%		0.2835
Ar[c], vol%		0.0135
Ethanol, ppmv	1350	1519
Methanol, ppmv	180	202
Acetaldehyde, ppmv	270	303
Sulfur Compounds (H_2S, CS_2[d]), ppmv	35	39
Acetic Acid, ppmv	10	11
Amyl Alcohol, ppmv	50	56
Isopropanol, ppmv	25	28
Butanol, ppmv	25	28
Methane, ppmv	20	22
Ethyl Acetate, ppmv	80	90

[a] At 120°F, 1 atm, and saturated with water.

[b] Calculated by backing out water from the wet composition given in the source.

[c] Assuming dry air is composed of roughly 78% N_2, 21% O_2, 1% Ar.

[d] Carbon disulfide.

END USES OF CO_2 AND THEIR PURITY REQUIREMENTS

CO_2 is produced by an array of processes that include combustion of transportation fuel and industrial or biological processes. In theory, many of these processes could be reversed to convert the CO_2 back to its starting materials, such as fuels. Many other products, such as organic polymer materials, could be produced from a CO_2 feedstock. However, with the exception of food and beverage production and greenhouse agriculture, CO_2 rarely serves as a feedstock because of two impediments to large-scale adoption: unfavorable energetics (and related economics) and the relatively small volume of CO_2 that many products would require.

Energetically, CO_2 is very stable. This means that reversing a process to produce the original starting material requires at least as much energy as was released in the original process. The energy source must be low carbon in order to avoid inducing the release of additional amounts of CO_2 during this activity. While hydroelectric and nuclear power sources can be less costly than combined cycle (CC) gas turbine-based power, many sources of low-carbon energy are more expensive, which makes many carbon conversion techniques economically unattractive. Additionally, in the case of producing fuels from CO_2, the question arises as to whether the energy used to convert the CO_2 could be used more efficiently by avoiding combustion of the original fuel and substituting the low-carbon energy for the original fossil fuel.

The second impediment to large reductions in CO_2 emissions through CO_2 conversion is that the markets for conversion products require only small amounts of CO_2 when compared to the quantity of CO_2 emitted annually. Recent U.S. energy-related CO_2 emissions have ranged from 6 billion tonnes in 2005 to 5.3 billion tonnes in 2015 (U.S. Energy Information Administration, 2015). The theoretical quantities of CO_2 that could be consumed to produce organic chemicals is orders of magnitude smaller. For example, using chemical consumption values for the United States in 2008, the quantity of CO_2 needed to produce various organic chemicals (based solely on the amount of carbon contained in the volumes of products manufactured) ranged from 0.81 million tonnes for phthalic anhydride to 69.77 million tonnes for ethylene (Chemical Data, 2008a). Similarly, the calculated values of the amount of CO_2 that would be needed to produce the quantities of jet fuel and gasoline consumed in the United States in 2008 (if they were to be produced from CO_2) are 215.7 and 1156.7 million tonnes, respectively (Chemical Data, 2008b).

Based on the relative amounts of the materials consumed, the greatest opportunity for CO_2 emission reduction through conversion will come from converting CO_2 into fuels rather than chemicals. However, it might be more efficient to direct the energy required for conversion directly to energy production rather than conversion to fuels, if possible. In this concept, none of the CO_2 emissions that might be produced while the conversion to products is occurring are considered and it is assumed that the economics would justify total substitution of hydrocarbon-derived products with CO_2-derived products.

Even though conversion to products is not likely to reduce the majority of CO_2 emissions, it still provides opportunities to reduce CO_2 emissions when considered on a product-by-product basis. There are many existing uses for CO_2. Several major routes to various chemicals have been identified around which new and better processes can be created. Figure 2 depicts the estimated relative consumption of CO_2 by various categories of end uses.

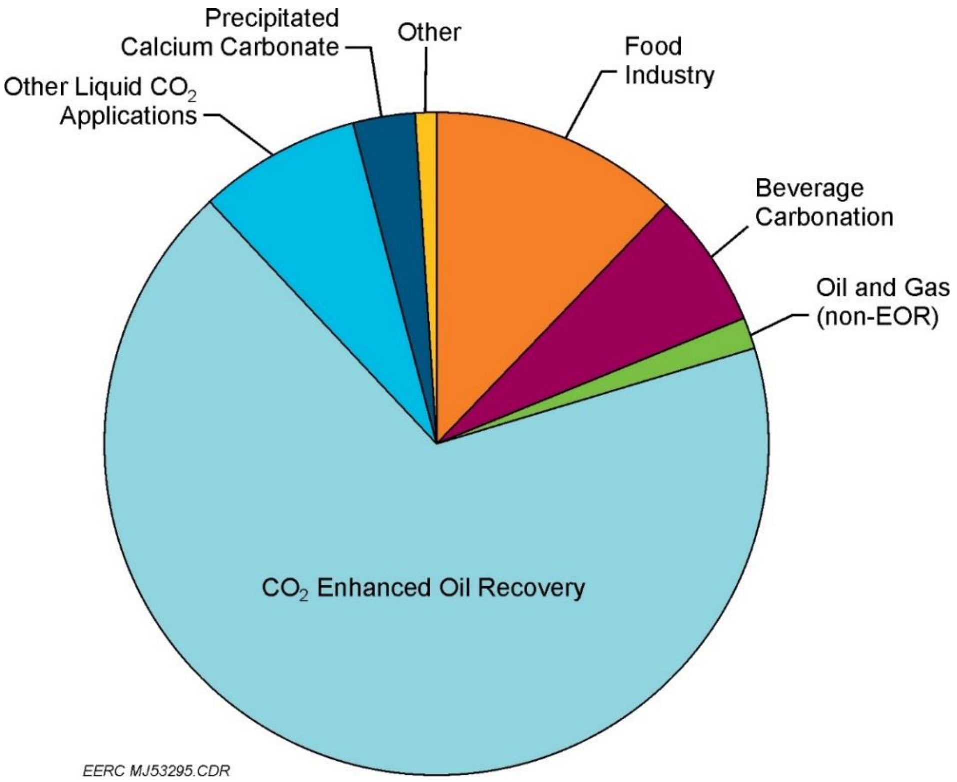

Figure 2. Approximate consumption of CO_2 by end use (from Global CCS Institute, 2011).

Injection of CO_2 for EOR is the largest potentially profitable use of CO_2 that is currently being practiced in the United States. The desired quality of CO_2 for such applications typically matches the Kinder Morgan pipeline specification, which is given in Table 13. The Kinder Morgan specification requires a CO_2 content of at least 95 vol%. Other constituents are limited based on their effect on the reservoir. N_2 and hydrocarbons affect the MMP of the oil in the reservoir (Haynes and Alston, 1990; Holm, 1986). Water is limited to avoid pipeline corrosion issues. Noncondensable gases (N_2, Ar, O_2, H_2, and CH_4) are limited because they increase the compression energy required for the gas stream and reduce the volume available to store CO_2. In addition, O_2 can encourage microbial growth in the injection well and formation. H_2S is limited because it presents a toxicity safety risk, even though its presence decreases MMP.

Another potentially profitable, albeit more modestly sized, use of CO_2 is in food and beverage manufacture. According to the Global CCS Institute (2011), an estimated 16.5 million tonnes was consumed globally by the food and beverage industries in 2010. In these industries, CO_2 can be used as a leavening agent; a processing aid; a propellant; an aerating agent; in chilling, freezing, and introducing an inert atmosphere in packaging; and in temperature control. Other applications include grain fumigation, pH control, sparging, and blanketing. In beverages, CO_2 generally is employed to carbonate water, beer, and wine. Table 14 shows the composition requirements for CO_2 used in the food and beverage industries and compares the food- and beverage-grade requirements to those of carbon steel pipeline, EOR, or injection into a saline formation. Foods and beverages manufactured in the United States generally fall under the U.S. Food and Drug Administration (FDA) current good manufacturing practices (CGMP) regulations.

Table 13. Kinder Morgan Specifications for Pipeline Transport of CO_2 (Havens, 2008)

Species	Specification		Reason
CO_2	95 mol%	Minimum	MMP[a]
N_2	4 mol%	Maximum	MMP
Hydrocarbons[b]	5 mol%	Maximum	MMP
Water[c]	30 lb/MMcf (~600 ppm by weight)	Maximum	Corrosion
O_2	10 ppm by weight	Maximum	Corrosion
H_2S	10–200 ppm by weight	Maximum	Safety
Total Sulfur	35 ppm by weight	Maximum	Health and Safety
Glycol[d]	0.3 gal/MMcf	Maximum	Operations
Temperature	120°F	Maximum	Pipeline coating

[a] In an oil field.

[b] In addition, the dew point of the CO_2 stream (with respect to hydrocarbons) must be less than –29°C (–20°F).

[c] No free water; these values are for water in the vapor phase.

[d] At no time may the glycol be present in a liquid state at the pressure and temperature conditions of the pipeline.

Medical uses of CO_2 represent another set of applications that are regulated by FDA's CGMP. Medical use regulations are more rigorous than those for food and beverages. Medical-grade CO_2 is used for various purposes, including an inflation gas for minimally invasive surgery to enlarge and stabilize body cavities, to stimulate or increase the depth of respiration, to increase cerebral blood flow during some surgeries, and for research investigations. It should be noted that these applications of CO_2 do not sequester CO_2. At best, they remove it from the atmosphere until use. The CO_2 composition requirements for medical use are shown in Table 15.

Figure 2 indicates that another major use of CO_2 is for precipitated calcium carbonate (PCC). Calcium carbonate is primarily used as a whitener in paper (its major market), paints and coatings, pharmaceuticals and plastics industries (IHS, 2014). Calcium carbonate manufacture for medical purposes falls under CGMP. In 1999, about 1.2 million tonnes of PCC was produced in the United States, which represented 6.1% of 19.6 million tonnes of lime produced (Research Triangle Institute, 1999). Assuming PCC has maintained its portion of the market and that CO_2 comprises about 44% of PCC by weight, PCC absorbs about 0.53 million tonnes of CO annually. Rates of PCC formation are directly related to CO_2 concentration. At the elevated levels established in typical CO_2 pipeline specifications, rates should be near the maximum. No CO_2 quality specification for PCC could be found in the open literature.

Another major use of CO_2 is in the production of urea, or urea yield boosting. Urea production in the United States makes up about 35% of ammonia production by weight (C&E News, 2008). Ammonia production in 2015 totaled 9.59 million tonnes (Apodaca, 2017), making urea production in 2015 approximately 3.36 million tonnes. This would have required the input of about 0.9 million tonnes of CO_2. Urea is a product of the reaction of CO_2 and ammonia. The urea reactor is sensitive to sulfur and oxygen, and the reaction is somewhat impeded by the presence of inert gases and water vapor (Kirk-Othmer Encyclopedia of Chemical Technology, 1955). No specific guidelines regarding the quality of the CO_2 feed stream were uncovered in preparation of this report. As in the case of medical uses of CO_2, sequestering of CO_2 by production of urea is only a temporary condition as CO_2 is released to the atmosphere a little more than a week after application as a fertilizer (Tierling, 2016).

Table 14. CO_2 Stream Compositional Requirements for Various End Uses

	Unit (max. unless otherwise noted)	Carbon Steel Pipeline[a]		Enhanced Oil Recovery[a]		Saline Reservoir Sequestration[a]			
Component		**Conceptual Design**	**Range in Literature**	**Conceptual Design**	**Range in Literature**	**Conceptual Design**	**Range in Literature**	**Food Grade[b]**	**Beverage Grade[c]**
CO_2	vol% (min.)	95	90–99.8	95	90–99.8	95	90–99.8	≥99.9	≥99.9
H_2O	ppmv	500	20–650	500	20–650	500	20–650	≤20 ppmv	≤20 ppmv
N_2	vol%	4	0.01–7	1	0.01–2	4	0.01–7	NRL[d]	NRL
O_2	vol%	0.001	0.001–4	0.001	0.001–1.3	0.001	0.001–4	≤30 ppmv total	≤30 ppmv
Ar	vol%	4	0.01–4	1	0.01–1	4	0.01–4	O_2 and Ar	NRL
CH_4	vol%	4	0.01–4	1	0.01–2	4	0.01–4	≤50 ppmv (part of "Total Volatile Hydrocarbons")	≤50 ppmv (part of "Total Volatile Hydrocarbons")
H_2	vol%	4	0.01–4	1	0.01–1	4	0.01–4	NRL	NRL
CO	ppmv	35	10–5000	35	10–5000	35	10–5000	≤10	≤10
H_2S	vol%	0.01	0.002–1.3	0.01	0.002–1.3	0.01	0.002–1.3	≤0.1 ppmv	≤0.1 ppmv*
SO_2	ppmv	100	10–50,000	100	10–50,000	100	10–50,000	≤1 ppmv	≤1 ppmv
NO_x	ppmv	100	20–2500	100	20–2500	100	20–2500	≤2.5 each for NO and NO_2	≤2.5 each for NO and NO_2
Dissolved O_2	ppmv	NRL		NRL		NRL		<5	NRL
≤Total Hydrocarbons Excluding CH_4 (C1 + C2)	ppmv	NRL		NRL		NRL		≤20	≤20

[a] Values taken from Quality Guidelines for Energy System Studies CO_2 Impurity Design Parameters, Report DOE/NETL-341/011212, January 2012.

[b] Values taken from Logichem Process Engineering CO_2 Food Grade Specifications, 2011.

[c] Values taken from Technical Committee of the Brewers Association Draught Beer Quality Manual 2nd Edition, Appendix A, 2011.

[d] No requirement listed.

[e] Entry given in the source table; presumably means none is allowed.

[f] Joint FAO/WHO Expert Committee on Food Additives (FAO is the Food and Agriculture Organization of the United Nations, WHO is the World Health Organization).

Continued. . .

Table 14. CO_2 Stream Compositional Requirements for Various End Uses (continued)

Component	Unit (max. unless otherwise noted)	Carbon Steel Pipeline[a]		Enhanced Oil Recovery[a]		Saline Reservoir Sequestration[a]		Food Grade[b]	Beverage Grade[c]
		Conceptual Design	Range in Literature	Conceptual Design	Range in Literature	Conceptual Design	Range in Literature		
Nonvolatile Residue		NRL		NRL		NRL		≤10 ppmv	≤0 ppmw
Nonvolatile Organics		NRL		NRL		NRL		≤5 ppmv	≤5 ppmw
Volatile Mercaptans, Sulfides, Disulfides		NRL		NRL		NRL		Nothing[e]	NRL
Volatile Mercaptans, Sulfides, Disulfides		NRL		NRL		NRL		Nothing[e]	NRL
Ammonia	ppmv	NRL		NRL		NRL		2.5	2.5
Ethylene Glycol		NRL		NRL		NRL		Nothing	NRL
Aromatic Hydrocarbon (benzene)	ppmv	NRL		NRL		NRL		0.02	0.02
Unsaturated Hydrocarbons		NRL		NRL		NRL		Nothing	NRL
Oil and Grease Nonvolatile Organic Compounds	ppmw	NRL		NRL		NRL		1.6	NRL
Vinyl Chloride		NRL		NRL		NRL		Nothing	NRL

[a] Values taken from Quality Guidelines for Energy System Studies CO_2 Impurity Design Parameters, Report DOE/NETL-341/011212, January 2012.

[b] Values taken from Logichem Process Engineering CO_2 Food Grade Specifications, 2011.

[c] Values taken from Technical Committee of the Brewers Association Draught Beer Quality Manual 2nd Edition, Appendix A, 2011.

[d] No requirement listed.

[e] Entry given in the source table; presumably means none is allowed.

[f] Joint FAO/WHO Expert Committee on Food Additives (FAO is the Food and Agriculture Organization of the United Nations, WHO is the World Health Organization).

Continued. . .

Table 14. CO_2 Stream Compositional Requirements for Various End Uses (continued)

Component	Unit (max. unless otherwise noted)	Carbon Steel Pipeline[a]		Enhanced Oil Recovery[a]		Saline Reservoir Sequestration[a]		Food Grade[b]	Beverage Grade[c]
		Conceptual Design	Range in Literature	Conceptual Design	Range in Literature	Conceptual Design	Range in Literature		
Ethylene Oxide		NRL		NRL		NRL		Nothing	NRL
Other Volatile Oxygenates		NRL		NRL		NRL		Nothing	NRL
Acidity Test (JECFA)[f]		NRL		NRL		NRL		To pass the test	NRL
Hydrogen Sulfides, Other Organic Reductive Substances (JECFA)		NRL		NRL		NRL		To pass the test	NRL
COS	ppmv	NRL		NRL		NRL		≤0.1	NRL
Total Sulfur	ppmv	NRL		NRL		NRL		≤0.1	≤0.1
Acetaldehyde	ppmv	NRL		NRL		NRL		≤0.2	≤0.2
Ethanol		NRL		NRL		NRL		Nothing	NRL
Phenols		NRL		NRL		NRL		Nothing	NRL
Appearance in water		NRL		NRL		NRL		No color or turbidity	No color or turbidity
Odor of Solid CO_2 (snow)		NRL		NRL		NRL		No foreign odor	No foreign odor
Odor and Taste in Water		NRL		NRL		NRL		No foreign taste or odor	No foreign taste or odor

[a] Values taken from Quality Guidelines for Energy System Studies CO_2 Impurity Design Parameters, Report DOE/NETL-341/011212, January 2012.
[b] Values taken from Logichem Process Engineering CO_2 Food Grade Specifications, 2011.
[c] Values taken from Technical Committee of the Brewers Association Draught Beer Quality Manual 2nd Edition, Appendix A, 2011.
[d] No requirement listed.
[e] Entry given in the source table; presumably means none is allowed.
[f] Joint FAO/WHO Expert Committee on Food Additives (FAO is the Food and Agriculture Organization of the United Nations, WHO is the World Health Organization).

Table 15. Medical-Grade CO_2 Requirements (Linde, 2009)[a]

	EP[b]	USP-NF[c]
Carbon Dioxide, minimum % v/v	99.5	99.0
Water	67	0.150 g/m^3
Ammonia		25
Carbon Monoxide	5	10
Nitric Oxide	2	2.5
Hydrogen Sulfide	1	1
Sulfur Dioxide	2	5
Total Sulfur	1	
Air		

[a] All values are maximum values in units of parts per million volume to volume unless otherwise indicated.
[b] European Pharmacopeia.
[c] United States Pharmacopeia–National Formulary.

There are many uses of CO_2 that are highly specialized and are not capable of eliminating emissions. These include such uses as inert gas blanketing in welding or the chemical process industry and fire suppression (Bernard, 2017).

With the exception of horticulture and coffee decaffeination, this study was unable to identify CO_2 specifications for other applications. The Netherlands is home to an existing horticultural application called Organic Carbon Dioxide for Assimilation of Plants, or OCAP. In OCAP, 99%-pure CO_2 from a refinery hydrogen unit and an ethanol plant are directed to more than 500 greenhouses at a pressure of approximately 300 psi (Limbeek, 2013; Mikunda and others, 2015). Horticulture applications recommend introducing CO_2 to a maximum of 1300 ppmv to the greenhouse atmosphere, which is less than 0.1% by volume over atmospheric CO_2. Therefore, a dilute source of CO_2 can support this application. Additional limits on constituents in the CO_2 stream include limiting SO_2 in the greenhouse atmosphere to less than 0.2 ppmv, ethylene and propylene to less than 0.05 ppmv, and N_2O to less than an undisclosed amount (Blom and others, 2002). This study could not locate an industrial supercritical CO_2 coffee decaffeination specification. However, gas company specifications for supercritical fluid and supercritical fluid extraction are assumed to be applicable (Airgas, 2017)

Numerous review articles (e.g., Song, 2006), books (e.g., Song and others, 2002; Hu, 2011; Centi and Perathoner, 2014; Styring and others, 2014; and Morgado and Esteves, 2014), and journals (e.g., Journal of CO_2 Utilization edited by Park, 2013) discuss CO_2 conversion and utilization. They described a myriad of technologies that are in development to produce a variety of products from CO_2. These products include fuels, chemicals, and plastics, among others. Few techniques have been commercialized. At this early point of development for many of these technologies, the goal is to demonstrate technical feasibility. Consequently, it is common for the current approaches to incorporate sophisticated and expensive catalysts that require very pure CO_2 feed streams. However, once reaction mechanisms are elucidated, optimization can occur to reduce costs, such as accepting cheaper, lower-quality CO_2 feed streams that contain lesser CO_2 concentrations and more impurities. Ultimately lower concentrations and more impurities have effects that will place a limit on the minimum acceptable quality. In addition, the sensitivities of different catalysts vary toward different impurities.

The goal of CO_2 feedstock optimization for any product is to identify acceptable concentrations of CO_2 and impurities in the feed stream that will produce an acceptable product at a minimum cost. It is difficult to predict a range of components and concentrations that would be desired so that a single specification could be established.

REMOVAL OF IMPURITIES AND THE RELATIVE COSTS OF THE CARBON CAPTURE, UTILIZATION, AND STORAGE (CCUS) SUPPLY CHAIN

CCUS Supply Chain

The primary use of CO_2 in the United States to date has been for EOR. In 2011, EOR use accounted for more than 60% of global CO_2 consumption (Global CCS Institute, 2011). Much of the CO_2 that has been consumed by this application has come from underground reservoirs of CO_2. These reservoirs, e.g., McElmo Dome, Bravo Dome, Doe Canyon, and Sheep Mountain, produce CO_2 purities in excess of 95% (Eppink and others, 2014). As a result, treatment to produce an acceptable CO_2 stream has been relatively straightforward, in some instances only requiring water removal. The CO_2 supply chain for EOR from geologic sources has been relatively simple and homogeneous, as represented in Figure 3. Ownership (as indicated by the dashed lines) also has been quite simple, with much of the supply chain for individual fields owned and/or operated by a single or only a few entities.

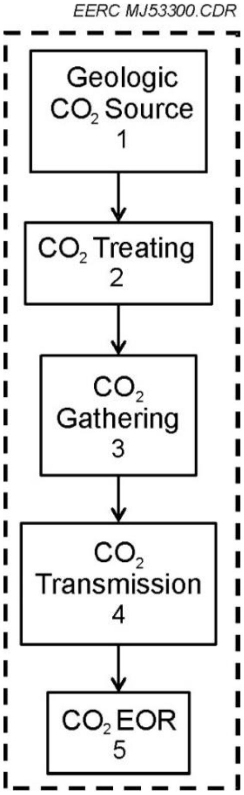

Figure 3. Integrated CO_2 supply chain for EOR.

Application of CCUS to impact rising atmospheric CO_2 levels, however, will require sourcing CO_2 from many different anthropogenic sources and disposing of it in more than just oil reservoirs. Not only will the physical supply chain become more heterogeneous and complex, but as commercialization of CCUS progresses, the number and variety of owners and operators, especially CO_2 sources, will increase. Figure 4 depicts a future, more mature supply chain.

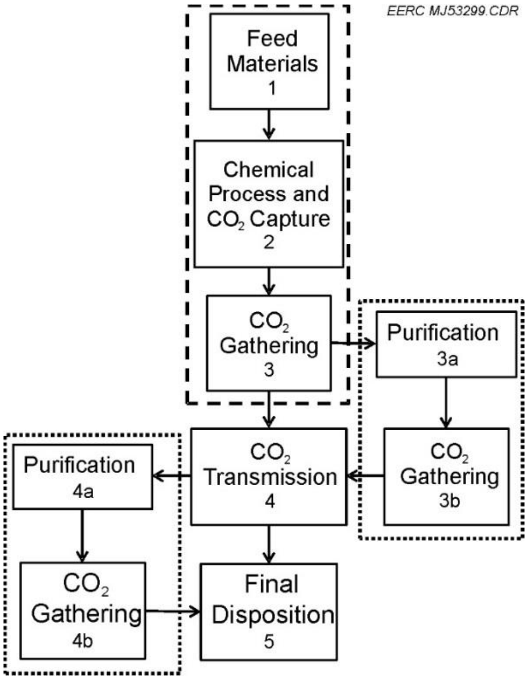

Figure 4. CO_2 capture, transport, and utilization or storage pathway.

The dashed-line box in Figure 4 denotes source ownership of raw materials, the processing that generates and captures CO_2, and gathering lines that carry the CO_2 toward larger transmission pipelines. If situations dictate, purification steps might be added to bring CO_2 streams into compliance with transmission line specifications or the specifications of the end use sites. The dotted-line box around purification indicates the independence of such processing from the traditional, linear supply chain. Purification could be accomplished in a distributed fashion near CO_2 capture locations or end use sites, in which case the capture or disposition process owner might own the process. Alternatively, purification might be centralized, in which multiple captured streams are merged and purified remotely from capture and disposition locations, such as near CO_2 transmission pipelines, in which case another entity might own the purification step. The centralized situation presents an opportunity for cost reduction due to economy of scale as long as the streams to be purified are sufficiently similar that the purification process does not require unusual (i.e., expensive) flexibility necessary to handle the dissimilarities of the streams. The distributed situation has advantages in circumstances in which a site’s impurities are quite different from impurities in other streams and impurity removal requires minimal resources.

A future, mature, commercialized CCUS system will change technologically over time. As owners and operators seek lower-cost means of performing CCUS functions, they will be incentivized to acquire and adopt newer and cheaper technologies and operational concepts. It is possible that a disruptive technology might appear that could make existing infrastructure and technologies economically less competitive or even obsolete. A change in one component of the supply chain could affect other components. Thus, while it is possible to optimize costs along a homogeneous supply chain that is owned and operated by a one or a few entities, such optimization will be much more difficult in a dynamic heterogeneous environment in which new captured streams, pipelines, disposition sites, and technologies change the composition of the system while many owners and operators attempt to minimize their costs, and while equipment and service providers seek competitive advantages by differentiating their products.

The components that incur the greatest costs offer the greatest potential for change to the CCUS system. Rubin and others (2015) reported cost ranges of several capture technologies in power generation applications, pipeline transport costs at different CO_2 flow rates, and onshore geologic storage cost. Figure 5 depicts these cost ranges on a CO_2-avoided basis. The chart indicates that the cost of even the least expensive capture technology is nearly 5 times the transportation cost by the most expensive pipeline. Conversely, the reported cost of the most expensive capture technology is more than 93 times the transportation cost by the least expensive pipeline. The impact on transport cost could be reduced by introducing a purification step to bring the captured stream into compliance with pipeline requirements, although the additional purification cost would need to be less than the capture cost savings for the change to be economically attractive.

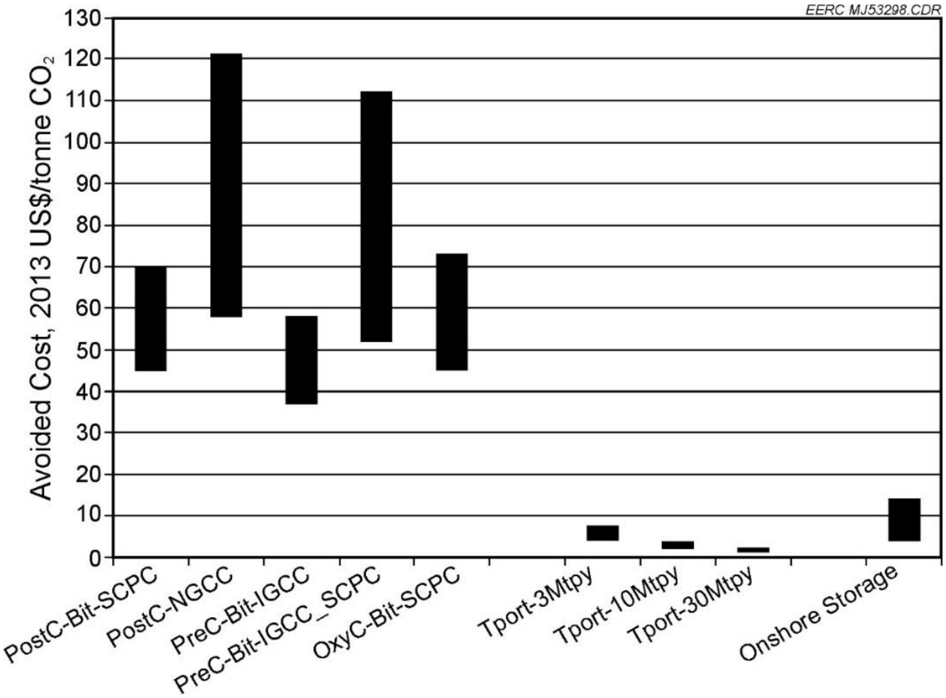

Figure 5. Comparison of unit costs of several power generation CO_2 capture technologies, transport scales, and onshore geologic storage (Rubin and others, 2015).

The major linkage with the biggest cost implications for different components of the supply chain are the CO_2 product stream's characteristics, that is, its composition and properties. In the first two steps of the supply chain, the nature of the CO_2 that is captured depends on the composition of the feed to the process, the process that converts the feedstock to CO_2 and the capture technology.

Capturing CO_2 Streams and Associated Cost

The relationship between the feedstock and CO_2 emission composition is fairly straightforward. If the feeds to the process are sulfur-free, the CO_2 stream will be free of sulfur and downstream transport and storage will not be required to be sulfur-tolerant or resistant. If inputs contain sulfur, then sulfur compounds might appear in the captured CO_2 stream and downstream transport and storage must be designed to tolerate those compounds. Other inputs are less straightforward. For example, while a hydrocarbon feed might not contain nitrogen, NO_x might be formed during high-temperature combustion from the N_2 in the air.

Capture processes are, to varying extents, purification processes. Most capture processes do not produce perfectly pure streams of CO_2, although cryogenic processes can produce very high quality CO_2 product streams. The composition of the concentrated CO_2 product stream depends upon the feedstock and processing as well as the nature of the capture process. Even economics can affect composition. For example, some of the raw emission stream could bypass the capture system if the capture process produces a CO_2 stream that exceeds product specifications and there is no financial incentive to provide excess purity. Situations in which capture processes do not produce CO_2 product streams of acceptable quality require a purification step (Steps 3a and 3b in Figure 4 in situations in which the CO_2 stream fails to comply with pipeline specifications or Steps 4a and 4b in Figure 4 in situations in which the CO_2 stream fails to comply with end use specifications).

Table 16 presents a matrix of industries and capture technologies that provides an idea of the suitability of specific categories of capture technologies that could be applied to specific categories of industrial processes. Although not identified as such, the five left-most capture technology columns are related to postcombustion capture. Because there are multiple industrial and capture processes within each category, suitability refers to the appropriateness of applying the most representative capture technology within a category to the most representative industrial process within its category. For example, MEA would be representative of chemical solvents applied to typical refinery heaters and boilers.

Table 17 shows the expected CO_2 product quality for some capture technologies. Capture technologies produce CO_2 streams having characteristic patterns of impurities. For example, it can be seen in the table that oxyfuel combustion product tends to contain elevated O_2 levels when compared to the CO_2 streams produced by other capture technologies.

Table 16. Notional Applicability of Various Capture Technology Categories to Various Industrial Processes (Schlasner, 2012)

	Solvent Absorption					Oxy-Fired			
	Physical	Chemical	Adsorption	Membrane	Cryogenic	Cryo	Mem	CL	Precombustion
Electric Power Generation									
Circulating fluidized bed	–[a]	++[a]	−	−	−	++	++	+N[b]	
pc	−	++	−	−	−	++	++	+N	
Supercritical pc	++		++	++C[c]	+	++	++	−	
Natural gas CC	−	++	−	−	−	++	++		++N
IGCC	++		++	++H[d]	++	++	++	+N	
Petroleum Refining									
Fluidized catalytic cracker	−	++	−	−	−	++	++	−	
Hydrogen unit PSA[e] tail gas	−	++	−	−	−				
Steam methane reformer flue gas	−	++	−	−	−	++	++	+N	
Natural gas fired heaters/boilers	−	++	−	−	−	++	++	++N	++
Iron and Steel Production									
Blast furnace	+N	++	++V[f]N	+CN	+N	++	++		
Coke plant	−	++	−	−	−	++	++		++
Cement Manufacture	−	++	+[a]	+C	+	+	+	—[a]	—
Petrochemical Production	−	++	−	−	−	++	++	−	++
Pulp and Paper Manufacture	−	++	−	−	−	++	++	−	++
Food Processing	−	++	−	−	−	+	+	+	+
Hydrogen Production									
PSA inlet	++		++	++C	++				
PSA tail gas	−	++	−	−	−				
Steam methane reformer flue gas	−	++	−	−	−	++	++	+N	
Lime Manufacture	−	++	−	+C	−	−	−	—	—
Ammonia Production									
CO_2 separation	+	++	++	+C	+				
Steam methane reformer flue gas	−	++	−	−	−	++	++	+N	
Glass manufacture	−	++	−	−	−	++	++		++

[a] – –, –, +, ++ denote increasing suitability from unsuitable to very high suitability.
[b] New build.
[c] CO_2 separation membrane.
[d] Hydrogen separation membrane.
[e] Pressure swing adsorption,
[f] Vacuum.

Table 17. Expected CO_2 Quality for Capture as Applied to Various Processes (van der Ham and Nelle, 2015)[a]

	Coal with Amine	Coal with Ammonia	Coal with SELEXOL™	Oxyfuel Coal	Natural Gas with Amine	Syngas with RECTISOL®
CO_2	99.8%	99.8%	98.2%	95.3%	95.0%	96.7%
N_2		2000	6000	2.5%	5000	30
O_2		200	1	1.6%		5
Ar		100	500	6000		
NO_x		50		100		
SO_x		10		100		
CO		10	400	50		
H_2S			100		200	
H_2			1.0%			1000
CH_4			1000		4.0%	9000
C_2+					5000	500
NH_3	1	100				7000
Amine	1					1.5%

[a] Units are in ppm or vol%.

The types of impurities that could be present in CO_2 streams emanating from different sources were discussed in the first section of this report. Table 18 shows the types and sources of impurities that can be present in CO_2 generated by various processes. As discussed earlier in the report, different end uses typically require the removal of specific CO_2 stream impurities. The Kinder Morgan pipeline specification is essentially the specification for EOR. The food and beverage industries require a much deeper removal of impurities, while use of CO_2 in horticulture requires a very dilute CO_2 stream containing ultralow levels of SO_2, ethylene, and propylene. The conversion of CO_2 to fuels and organic products is not commercial and, as such, the typical development-scale systems utilize ultrapure CO_2. A search of the open literature did not identify many specifications or guidelines for the CO_2 streams used in other processes.

Tables 19 and 20 show assessments by Abbas and others (2013a) that evaluated oxygen removal and dehydration technologies, respectively, for their application to postcombustion CO_2 capture streams. Based upon a qualitative analysis of the various techniques, they concluded that the least costly approach to O_2 and water removal was catalytic oxidation of H_2, followed by Joule–Thomson cooling and condensation. When applied to captured CO_2 streams whose O_2 and water content were 10–300 ppmv and 2.8 to 7.3 mol%, respectively, the approach added only \$2.97/tonne CO_2 (or about 4%) to the cost of capture and compression of CO_2 from a typical coal-fired steam turbine power plant. For a typical natural gas CC power plant, approximately \$5.25/tonne CO_2 (or about 6%) was added to the cost of capture and compression of CO_2. For comparison, typical costs of capture from coal-fired power plants at an initial demonstration stage of development were reported by Folger (2009) to be \$73–\$94/tonne CO_2. Relaxing the water specification from 50 to 400 ppmv reduced purification cost by about 50%. Postpurification compression of the product CO_2 stream was estimated to cost \$10.12/tonne CO_2 and \$11.98/tonne CO_2 for the coal- and natural gas-fired cases, respectively (Abbas and others, 2013b).

Table 18. Potential Impurities Other than Air Gases and Water from Different Sources (Ringo, 2000/2001)[a]

	Acid Neutralization	Ethylene Oxide	Coal Gasification	Phosphate Rock	Hydrogen or Ammonia	Fermentation	Well/ Geothermal	Combustion
Aldehydes		X	X		X	X	X	X
Amines					X			X
Benzene		X	X		X	X	X	
Carbon Monoxide	X	X	X	X	X	X	X	X
Carbonyl Sulfide	X		X	X	X	X	X	X
Cyclic Aliphatic		X	X		X		X	
Dimethyl Sulfide	X		X	X	X		X	
Ethanol		X	X		X	X	X	
Ethers		X	X		X	X	X	
Ethyl Acetate		X	X			X	X	
Ethyl Benzene		X	X		X		X	
Ethylene Oxide		X	X				X	
Halocarbons		X	X					X
Hydrogen Cyanide			X					X
Hydrogen Sulfide	X	X	X	X	X	X	X	
Mercaptans		X	X	X	X	X	X	X
Methanol		X	X		X	X	X	
Nitrogen Oxides	X	X	X		X	X		X
Phosphine				X				
Radon				X			X	
Sulfur Dioxide	X		X	X	X	X	X	X
Toluene		X			X	X	X	
Vinyl Chloride		X	X					X
Xylene		X	X		X	X	X	

[a] X indicates the potential of the chemical noted to appear in the process listed at the top of the table.

Table 19. Assessments of Oxygen Removal Technologies to Purify Postcombustion CO_2 Capture Streams (Abbas and others, 2013a)

Purification Technology	Assessment
Catalytic Oxidation of H_2	Moderate operating conditions (80°C). Produces only water, which dehydration removes.
Cryogenic Distillation	Removes CO_2 from impurities other than water. Large energy requirement. Relatively costly equipment. Detailed evaluation required.
Catalytic Oxidation of Methanol	Complete oxidation occurs Excessive operating conditions (320°C)
Chemisorption of O_2 on Cu	Hydrogen addition does not exceed specifications. Energy-intensive process. Somewhat excessive operating conditions (200°C).
Oxidation of Coal	Combustion forms toxic CO.
Catalytic Oxidation of Propane	Relatively high cost. Excessive operating conditions (350°C). Purity of CO_2 stream is unaffected.
Catalytic Oxidation of CO	Somewhat excessive operating conditions (200°C). Purity of CO_2 stream is unaffected. Presence of toxic CO.

Table 20. Assessments of Water Removal Technologies to Purify Postcombustion CO_2 Capture Streams (Abbas and others, 2013a)

Water Removal Technology	Assessment	Approximate Water Content in Product, lb/MMscf
Joule–Thomson Cooling	Relatively low costs. Heat integration with compression. Only some decompression occurs. Compressor redesign required.	30
Adsorption Using Silica Gel	Higher costs than activated alumina. Regeneration is easy.	10–100
Adsorption Using Activated Alumina	Relatively high costs. Large heat required for regeneration.	5–100
Molecular Sieves	Higher costs than silica gel. Large heat required for regeneration.	1–30
Absorption Using Ethylene Glycol	Relatively high costs. Solvent loss.	6–260
Compression and Cooling	Unable to comply with specification.	100–1000
Absorption Using Methanol	Larger solvent losses than glycol.	5–260

Alternate Purification Locations

Conceptually, there are four general locations at which purification can be performed: 1) decentralized, near the CO_2 capture site; 2) remote from capture sites, but centralized upstream of the transmission pipeline; 3) remote from end use sites, but centralized downstream of the transmission pipeline; and 4) decentralized near the end use site. This concept is shown in Figure 6. Admittedly, combinations of these could be included, such as centralized processing near a generation or disposition site, to simplify; however, these four locations will serve as the basis for the following discussion. Table 21 provides an overview of the advantages of different purification locations.

Distributed locations show major advantages relating their ability to customize and handle limited ranges and volumes of CO_2 streams. Smaller volumes mean less resource (equipment, chemicals, and energy) requirements which, in turn, equals less capital and operating expenses. Impurities from single sources can be better characterized and targeted, requiring that only limited effort be expended. Purification can be sized with less regard for future expansion if frequent changes are not expected. Because distributed locations are near existing sites, purification processes can integrate with resources existing at those sites. End use sites have an additional opportunity to control or make local changes to adapt to the needs of their associated disposition site.

Centralized locations can access economies of scale because of the larger volumes that they process. Because they are not associated with generation or end use sites, centralized locations can

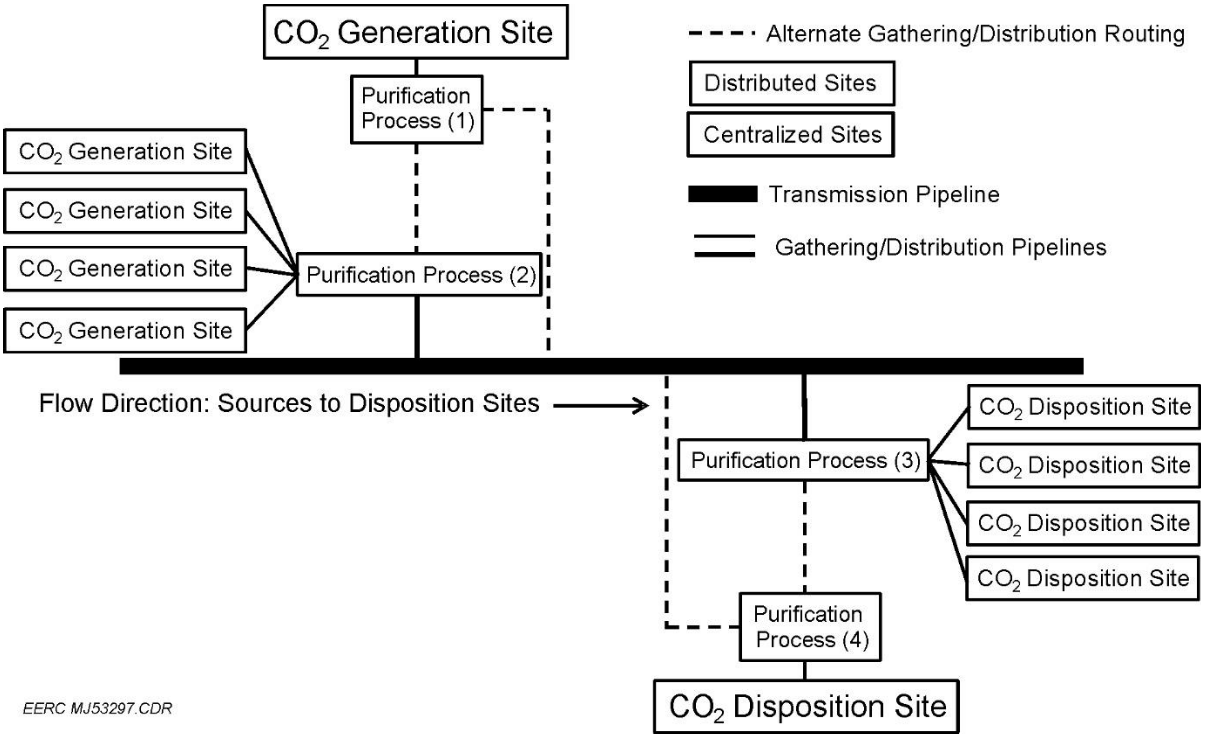

Figure 6. Conceptual captured CO_2 purification locations.

Table 21. Conceptual Advantages of Different Purification Locations

Distributed, Near Generation Site	Distributed, Near Disposition Site
•Purification can be limited and targeted. •Limited range of impurities. •Integration opportunities. •Limited volumes to purify.	•Purification can be limited and targeted. •Integration opportunities. •Limited volumes to purify. •Local ability to control and modify.
Centralized Upstream of Transmission Pipeline	**Centralized Downstream of Transmission Pipeline**
•Able to take advantage of economy of scale. •Opportunity to access special resources. •Similar-feed-stream advantages. – Variations attenuated – Less need for flexibility	•Able to take advantage of economy of scale. •Opportunity to access special resources. •Similar-feed-stream advantages. – Less need for flexibility

be more flexible when locations are selected, potentially near resources that offer opportunities such as lower-cost resources or integration with other processes. In situations in which its feed streams are similar, variations within individual streams can be counteracted by variations in other streams, resulting in a more stable overall product.

Advantages of one type of location tend to be disadvantages for the other type. Centralized facilities can be challenged if their feed streams and processes that generate those streams are dissimilar, resulting in the need to install expensive flexibility to address the cumulative issues of the bulk stream. Centralized facilities can be underutilized if they are overdesigned to accommodate future additional streams or if existing streams go off-line. If the volumes that must be processed exceed the maximum scale of processing equipment, an aspect of economy of scale can be lost and its benefit reduced. Because of pipeline location, centralized facilities also might suffer from a lack of available infrastructure, requiring expensive facilities such as roads to be constructed and access to utilities acquired to provide for processing needs.

Distributed locations can potentially suffer from issues related to either economy of scale or exceeding maximum equipment size as volumes from some point sources can be larger than the current largest scale of some processes. Additionally, generation or end use sites can lack resources required by purification. One such resource could be the land on which to build as generation sites in large cities might be surrounded and existing real estate occupied by equipment.

Opportunities and challenges for purification are strongly related to the circumstances of particular situations, which can change with advancements in technologies and equipment, relative costs of materials, chemicals and energy, construction costs, and other factors over time. It is possible that environments in which gathering, transmission, and distribution lines are highly regulated based on composition would limit opportunities for purification other than, perhaps, at generation sites. Conversely, less regulation and the use of nontraditional pipe materials could increase the opportunity for purification.

Competition, technological advances, regulatory flexibility, and a systemwide cognizance can identify situations in which purification in association with CO_2 capture could provide minimum-cost solutions.

EFFECTS OF IMPURITIES ON TRANSPORT INFRASTRUCTURE INTEGRITY

Current CO_2 Pipeline Specifications

Because many species can be present in a captured CO_2 stream, stream composition standards have been developed to ensure the safety of stream transport and the structural integrity of a pipeline that carries CO_2. A specification can ensure that streams from multiple sources that will be transported in a single pipeline meet at least minimum standards such that the bulk product that is delivered also will meet the minimum standards. One such standard that is used widely in the United States is the Kinder Morgan specification, which was provided in Table 13. The Kinder Morgan standard was developed for the transport of CO_2 for use in EOR and therefore reflects both the requirements of EOR as well as the effects of CO_2 and its impurities on the pipeline itself. The limits specified in the Kinder Morgan specification are the upper boundaries, with various species present in lower concentrations. It should be noted that the Kinder Morgan specification would not have to be applied to pipelines that are only intended to carry CO_2 from one source to a single end use. In such a case, the pipeline would be designed to tolerate the specific impurities in that stream, such as is the case with the pipeline that carries CO_2 from the Great Plains Synfuels Plant to the Weyburn oil field in Saskatchewan, Canada. The Great Plains Synfuels Plant product CO_2 has a typical composition shown in Table 22. Instead of Kinder Morgan, other specifications could be used, such as the Dynamis CO_2 quality recommendation that is based on the ENCAP Enhanced CAPture of CO_2) project or the Ecofys specifications. The Dynamis and Ecofys specifications are shown in Table 23.

CO_2 can be captured using different technologies, each of which produces a CO_2 stream containing different impurities in differing concentrations. Even the same capture technology does not produce a CO_2 stream of exactly the same composition when applied to emission sources of different processes. The cotransport of CO_2 via different technologies and/or different source types in a single pipeline imply that a universal specification be put in place that considers all impurities and their concentrations that might be present in the streams produced by any capture technology (Race and others, 2012). This makes it difficult to specify a single composition of a CO_2 stream produced during any capture activity. Alternatively, a bulk composition could be defined based on the requirements of the pipeline (Race and others, 2012). Such a specification would have to be developed using information on the types and quantities of impurities that could be found in a captured CO_2 stream and their effects on the pipeline.

Table 22. Composition of Product CO_2 from the Great Plains Synfuels Plant (Perry and Eliason, 2004)

Component	vol%
CO_2	96.8
H_2S	1.1
C_2H6	1.0
CH_4	0.3
Other	0.8
Total	100.00

Table 23. Pipeline Specifications Put Forth by the Dynamis and Ecofys Projects (Race and others, 2012)[a]

	Dynamis		
Component	**Storage**	**EOR**	**Ecofys**
CO_2	>95%	>95%	>95%
H_2O	500 ppm	500 ppm	500 ppm
SO_x	100 ppm	100 ppm	Not critical
NO_x	100 ppm	100 ppm	Not critical
H_2S	200 ppm	200 ppm	200 ppm
CO	2000 ppm	2000 ppm	2000 ppm
H_2	Total noncondensable gases	Total noncondensable gases	Total noncondensable gases
Ar			
N_2			
O_2		100 ppm	
CH_4		100 ppm	

[a] On a volume basis.

Effects of Impurities on a Pipeline

The impurities contained in captured CO_2 can technically and/or economically impact its transport in a pipeline. These impurities can include water, O_2, H_2S, N_2, hydrocarbons, noncondensable gases, and liquids such as glycol or compressor oil (McKaskle, 2014). Impurities change the phase behavior of CO_2, depending on their critical pressures and temperatures, which impact pipeline design and operation as well as integrity and health and safety aspects of pipeline transport (Race and others, 2012). The effects of specific impurities or types of impurities on the pipeline structure will be discussed first, followed by an overview of the effects on pipeline design.

Effects of Specific Impurities

Water

Pure, dry CO_2 does not corrode carbon steel (Race and others, 2012). However, the combination of water and CO_2 forms carbonic acid, which is highly corrosive. Internal pipeline corrosion is one of the risks when water is present in a CO_2 stream at concentrations that exceed the saturation limit of CO_2 at typical pipeline operating temperatures, in other words, when there is a free water phase in the CO_2. The Kinder Morgan specification limiting water content to 30 lb water/MMscf is well below the saturation limit of CO_2 at typical CO_2 pipeline operating temperatures (McKaskle, 2014). The corrosion rate generally increases with increases in the partial pressure and temperature of the CO_2 or with the presence of O_2 or H_2S in a saturated CO_2 stream (McKaskle, 2014).

While there is universal acceptance in the literature that free water increases corrosion rates, a consensus regarding a specific maximum amount of water that is acceptable in supercritical or dense-phase CO_2 does not exist. Kaufmann (2008) reviewed the literature and concluded that corrosion was not considered to be a major issue in the transport of CO_2 after dehydration of the stream to water concentrations of 0.039 to 0.48 g/m^3 (or approximately 50–630 ppmv). Mohitpour and others (2012) reported a lower standard of 20 ppmv for the Weyburn pipeline. Choi and Nešić (2011) claimed that corrosion even occurs in a water-saturated CO_2 phase without free water but at low rates of about 0.2 mm per year. Experimental results reported by Dugstad and others (2014) showed that elemental sulfur as well as sulfuric and nitric acids were formed under conditions that have been recommended by the Dynamis project and considered acceptable by a U.S. Department of Energy (DOE) National Energy Technology Laboratory (NETL) conceptual design. In the Dugstad and others (2014) study, a weight loss-based corrosion rate of less than 0.1 mm per year was observed. Sandana and others (2012) concluded that, depending upon the types and amounts of other impurities, 300–500 ppmw H_2O (730–1200 ppmv) could be excessively high and that 50 ppmw (120 ppmv, or 60% relative humidity) could be too stringent. The lack of consensus can largely be explained by the effect of other impurities upon water solubility. For example, it has been reported that increased CH_4 concentration tends to decrease water solubility in supercritical CO_2 (Austegard and others, 2006), while the reverse is true for increased H_2S concentrations (Race and others, 2012).

In addition to corrosion issues, the presence of water in a CO_2 stream can form hydrates when there is a temperature drop. Hydrates can block pipelines and damage equipment. Under CO_2 pipeline operating pressures, it may be possible for hydrates to form at temperatures of 10°–11°C (Hart and others, 2012). Race and others (2012) note that some studies consider that if water levels are low enough to prevent corrosion in a pipeline, any hydrate formation would not be sufficient to cause operational problems. They also note that dehydration requirements to prevent hydrate formation may be more stringent when H_2 is present (Race and others, 2012).

Three technologies that can be used to remove water from CO_2 include absorption by ethylene glycol or triethylene glycol (TEG); adsorption using silica gel, molecular sieves, or activated alumina; or refrigeration and condensation (Abbas and others, 2013c). The most commonly used technology is TEG-based dehydration (McKaskle, 2014). If the pressure at which dehydration occurs is higher than about 1000 psig, glycerol is often used instead of TEG because its solubility in CO_2 increases with pressure and the losses would be unacceptably high (McKaskle, 2014). If refrigeration-based processes such as CO_2 liquefaction for distillation or natural gas liquids recovery are involved, then an adsorption process (e.g., molecular sieve) may be needed (McKaskle, 2014).

Oxygen

When O_2 is present in a CO_2 stream undergoing dehydration using an absorption technique, the O_2 can oxidize the TEG or glycerol (depending on the pressure at which dehydration is taking place). The presence of O_2 in a stream containing CO_2 and water worsens the corrosiveness of the stream when compared to CO_2 and water (McKaskle, 2014). In addition, O_2 can react with H_2S under certain conditions to form sulfur compounds such as sulfuric acid or elemental sulfur (McKaskle, 2014). Oxygen is one of the impurities that requires removal to a minimal concentration because of the effects on CO_2 infrastructure (and the geologic subsurface, if the CO_2 is used for EOR) when it is present (Abbas and others, 2013c). It is difficult to remove O_2 from a CO_2 stream, typically requiring a liquefaction and distillation approach (McKaskle, 2014).

Hydrogen Sulfide

H_2S is toxic and its concentration in CO_2 in a pipeline is limited to 10 ppmv for health and safety reasons. It can react with O_2 or SO_2 under certain conditions to form sulfur compounds such as elemental sulfur or sulfuric acid (McKaskle, 2014). When H_2S is present in CO_2, the corrosion mechanism changes from general or pitting corrosion (as is the case with CO_2 and water) to cracking (Race and others, 2012). Resistant steel and appropriate welds must be used in the construction of pipelines that will transport CO_2 containing H_2S in order to prevent rapid failure. Failure times as short as days or hours have been observed under test conditions in oil and gas environments (Race and others, 2012). The corrosion cracking effects of H_2S can be minimized by ensuring that the CO_2 stream is completely dry (Race and others, 2012).

Nitrogen

N_2 decreases the saturation water content of CO_2, increasing the potential for free water formation (McKaskle, 2014). It also increases the potential for hydrate formation and can require increased transport pipe strength because of ductility issues (McKaskle, 2014).

Hydrogen

Like N_2, the presence of H_2 can require increased transport pipe strength because of ductility issues. However, since H_2 is a valuable gas, it would likely not be present in a CO_2 stream at concentrations approaching 4 vol% under normal operating conditions (McKaskle, 2014).

Methane

CH_4 tends to decrease the saturation water content of CO_2 and increases the potential for hydrate formation (McKaskle, 2014).

Other Hydrocarbons

Removal of hydrocarbons is typically accomplished using membranes or a liquefaction and distillation approach (McKaskle, 2014).

CO, NO_x, SO_2, and COS

Limits on the levels of CO, NO_x, and SO_2 are driven primarily by health- and safety-related exposure limits (McKaskle, 2014). The pipeline transport of more anthropogenic CO_2 sources will enable a better understanding of their impacts, which may alter their current pipeline limits (McKaskle, 2014).

Glycol and Compressor Oil

Excess glycol carryover from the dehydration process can damage seals and other components and should probably not be present in a liquid state at the pressure and temperature conditions of the pipeline (McKaskle, 2014). Mineral oil used for compressor cylinder lubricant can cause asphaltene plugging issues in injection wells. Synthetic oil avoids the problem but must be kept separate for mineral oil as the mixture can form a gel (McKaskle, 2014).

Effects of Impurities on Pipeline Design

Hydraulic Efficiency

The most efficient and economical way to transport CO_2 through a pipeline is as either a supercritical (above both the critical pressure and temperature of CO_2) or dense-phase fluid. This is because, at these conditions, the fluid has the density of a liquid but the viscosity of a gas. The difference between supercritical CO_2 and dense-phase CO_2 is the temperature: both phases exist above the critical pressure of CO_2, which is 1180 psi. Supercritical CO_2 exists above the critical temperature of 31°C, while dense-phase CO_2 exists at a temperature that is less than 31°C (Race and others, 2012).

Operating Pressure

When impurities are present, the phase behavior of the CO_2 changes. The amount and type of change directly relates to the type, amount, and combination of impurities present (Race and others, 2012). When the impurities have a critical temperature and pressure higher than the CO_2 (such as SO_x and NO_x), a dense-phase pipeline should be operated at a higher pressure to reduce the risk of two-phase flow during upset conditions. In this case, the pipe will have to be thicker-walled, the diameter will have to be reduced, or higher-strength steel will be needed to accommodate operation at a higher pressure. If the pipeline is operated at gaseous conditions, the presence of SO_x and NO_x reduce the maximum allowable operating pressure (MAOP) so that two-phase flow can be avoided and should therefore be limited in gas-phase transport of CO_2. Reducing the pipeline pressure restricts the throughput of the pipeline (Race and others, 2012). Impurities with lower critical conditions, such as H_2 and N_2, should be limited when transporting CO_2 in the dense phase (Race and others, 2012).

Pipeline Inside Diameter

A pipeline's capacity depends on the pressure, temperature, and the fluid's physical properties, especially compressibility and density. CO_2 density changes with temperature and pressure and exhibits a sharp discontinuity close to the vapor–liquid equilibrium curve on a pressure–temperature diagram. When impurities having lower critical temperatures and pressures than CO_2, such as H_2 and N_2, are present, the density discontinuity shifts to higher pressures. Conversely, the presence of impurities that have higher critical temperatures and pressures than CO_2, such as SO_x and NO_x, shift the discontinuity to lower pressures (Race and others, 2012).

The effects of this type of behavior can be explained as follows. As one would expect, as temperature increases and pressure decreases, the pipeline diameter must increase for a given fluid at a given flow rate. The presence of H_2 increases the required diameter over that required for pure CO_2, and the increase is greater at higher flow rates and lower pressures. It should be stressed that this result is not true for all impurities. It depends on the density of the CO_2 mixture at the inlet temperature and pressure relative to that of pure CO_2. For example, the presence of NO_2 is more dense than CO_2 at some conditions, while at others it is less dense and the pipe diameter required to transport NO_2-containing CO_2 may be larger or smaller than that required for pure CO_2 based on the pipeline operating conditions (Race and others, 2012).

In the case of dense-phase pipeline transport, CO_2 throughput can be maximized if the inlet temperature is lower, the inlet pressure is higher, and low-density impurities such as H_2 are minimized. Smaller-diameter pipelines can therefore be used for the same flow rate (Race and others, 2012).

Pressure and Temperature Drop

Avoiding two-phase flow in a pipeline during transport of CO_2 in the dense phase requires that the pipeline pressure remain above the critical pressure for the length of the pipeline. Pressure can be lost because of friction or gravity and, in many pipelines, this is addressed one of three ways: by installing booster stations to raise the pressure back to the dense-phase region, increasing the pipeline diameter, or increasing the initial pipeline pressure so that the CO_2 remains in the dense phase for the entire length of the pipeline. The presence of impurities in the CO_2 has an impact on the pressure drop along a pipeline. All impurities with lower critical temperatures and pressures increase the pressure and temperature drop when compared with pure CO_2. The largest effect is exhibited by H_2. Therefore, in a pipeline transporting CO_2 in a dense-phase, the concentration of H_2 should be minimized. However, the presence of NO_2, SO_2, and H_2S, which have higher critical temperatures and pressures than CO_2, have the opposite effect, resulting in lower pressure drops than are observed for pure CO_2. Their presence could be beneficial to pipeline hydraulics when operating in dense-phase mode (Race and others, 2012).

Compression and Pumping

The concentration of noncondensable impurities in a CO_2 stream affects the energy required to compress or pump the CO_2. As the level of impurities increases, the energy required to operate the compressors and pumps increases. If a higher inlet pressure is required in order to maintain single-phase flow in the pipeline (as discussed in the preceding subsection), this requires additional pump or compression stages (Race and others, 2012).

Summary

Three types of CO_2 stream composition guidelines and specifications that are based strictly on pipeline considerations could be characterized as:

- Specifications established for existing operating pipelines, such as those described in Dugstad and others (2014) and Herron and Myles (2013).

- Guidelines derived from experimental or conceptual pipeline research studies, such as those reported by Bilio and others (2009), Dugstad and others (2014), and de Visser and others (2008).

- Guidelines based upon surveys of research studies, such as Herron and Myles (2013).

CO_2 quality specifications for existing pipelines with associated recommended impurity maxima are not based strictly upon physical and chemical considerations relative to the pipeline. Maximum concentrations for many components could be much higher than those stated in specifications, if the specifications are based exclusively upon the physical and chemical effects of the impurities on pipelines. Instead, limits for many impurities are based on health, safety, use (such as phase considerations related to compression and reservoir MMP in the case of EOR), and other considerations.

Some commonalities were noted when the literature that addresses the effects of CO_2 impurities on pipelines was surveyed. A summary of the findings is shown in Tables 24 and 25, which present the transport-related and materials change-related design factors, respectively. Several aspects of CO_2 pipeline transport specifications were consistent among the various studies, such as:

- It was assumed that CO_2 pipelines would be composed of carbon steel.
- The majority of literature collected by this survey presented broad, somewhat qualitative guidelines rather than narrow specifications, presumably because of:
  - The wide range of potential impurities and concentrations that are produced from different sources and capture technologies.

Table 24. Transport-Related Pipeline Design Factors Affected by CO_2 Impurities as Discussed in the Open Literature

Study	Transport Capacity	Pipe Internal Diameter	Pipe Wall Thickness	Pipe Material of Construction
De Visser and others, 2008 (Dynamis)				
Noncondensables, vol%	4			
Bilio and others, 2009				
General Discussion[a]		×	×	×
Race and others, 2012				
Noncondensables, vol%	Dynamis[b]			
General Discussion	×	×	×	×
Wetenhall and others, 2014				
Noncondensables, vol%	Dynamis			
General Discussion	×	×	×	
Kaufmann, 2008				
General Discussion		×	×	×
Cosham, 2012				
Noncondensables, vol%	Dynamis			
General Discussion	×	×	×	×
Det Norske Veritas, 2010				
General Discussion	×			×

[a] No specific values given.

[b] Agreeing with the Dynamis specification in De Visser and others, 2008.

Table 25. Materials Change-Related Pipeline Design Factors Affected by CO_2 Impurities as Discussed in the Open Literature

Study	Hydrogen Embrittlement	Corrosion	Hydrate Formation	Ductile Fracture Propagation	Brittle Fracture Propagation	Sour Cracking	CO Cracking	Pipeline Flow Erosion	Supercritical CO_2 Attack on Nonmetallics	Fatigue
De Visser and others, 2008										
Maximum H_2O, ppmw		500	500							
Bilio and others, 2009										
General Discussion[a]	×	×	×	×	×					
Race and others, 2012										
Maximum H_2O, ppmv		Dynamis	Dynamis							
General Discussion		×	×			×	×			
Wetenhall and others, 2014										
Maximum H_2O, ppmv		Dynamis	Dynamis							
General Discussion								×		
Sandana and others, 2012										
H_2O, ppmw		300–500								
Kaufmann, 2008										
General Discussion		×	×	×	×			×	×	
Cosham, 2012										
General Discussion		×	×	×	×					
Det Norske Veritas, 2010										
General Discussion		×	×	×					×	×
Godec, 2011										
H_2O, mg/m^3		400								
O_2, ppmw		10								
Dugstad and others, 2014										
Max. H_2O, ppmv		300								

[a] No specific values given.

- The lack of multicomponent chemical (e.g., corrosion) and physical property data covering the range of impurities and concentrations. Data from systematic studies of complicated mixtures of CO_2 with multiple impurities under pipeline conditions have been mentioned in the literature as being valuable but essentially nonexistent.

Race and others (2012) note that developing any new specifications for pipeline transport of CO_2 must take into account that any changes in impurity level that could improve one facet of pipeline design or operation will impact another facet. For example, increasing NO_x levels to improve the operability of dense-phase pipelines will also increase corrosion if water is also present. New specifications will also have to acknowledge that the temperature and pressure of the pipeline alter the effects of impurities.

CHANGES TO TRANSPORT INFRASTRUCTURE THAT COULD ENABLE THE USE OF LOWER-PURITY CO_2 STREAMS AND RELATIVE COSTS OF THIS APPROACH

The open literature reflects a foregone conclusion that captured CO_2 will be transported in steel pipelines. This is easy to understand given that pipeline systems are widely accepted globally as a means to transport large quantities of oil, gas, and specialty products over long distances (Kaufmann, 2008). Steel CO_2 pipelines have been in use for roughly 40 years. Much study and thought have been devoted to issues that have been or might be encountered during the transport of impure CO_2 in steel pipelines (Mohitpour and others, 2012). As a result, several quality constraints have been developed to protect steel pipelines from possible damage due to CO_2 and its potential impurities under pipeline conditions. Limits on water, O_2, H_2, and other components are frequently recommended to avoid corrosion, embrittlement, or other effects that would be deleterious to steel pipelines.

Pipeline design is complicated by several factors, including the range of impurities and concentrations that captured CO_2 could contain in the future; the limited amount of physical and chemical data, especially that related to corrosion, over this range; and the subjective opinion as to what constitutes acceptable corrosion rates. Some data exist that make selection of a water limit more straightforward. When relative humidity exceeds 60%, carbon steel corrosion rates increase substantially. In fact, the rate of change in corrosion rate from 60% to 100% humidity is more than 30 times the rate of change over the 9% to 50% humidity range (Xiang and others, 2012). Based upon this, the authors expressed the opinion that 50% relative humidity, or about 2800 ppm mol under weight loss test conditions of 50°C and 100 bar, would be an appropriate maximum water concentration.

The relatively small amount of corrosion that has been observed in operational CO_2 pipelines that have transported naturally sourced CO_2 to oil fields for EOR also serves to simplify the specification of water content in the CO_2. Practical experience in EOR has exhibited very few problems with transport of high-pressure, dry CO_2 in carbon steel pipelines. Over a 12-year period, the corrosion rate in an operating pipeline was found to be 0.25–2.5 μm/yr (Doctor and others, 2005).

Significant safety margins have been established and other limits set to avoid reducing pipeline useful life caused by corrosion due to water. Relatively high inert gas concentrations should also be limited to avoid the increased costs related to larger pipe diameter and thicker walls because the inert gases reduce the amount of CO_2 that can be carried in the pipeline. Wetenhall and others (2014) estimate a 16% increase in the cost of transport based on hydraulics when the concentration of inert gases increases from 4% to 15%.

Alternatives to carbon steel must be identified for situations in which the source CO_2 cannot comply with tight specifications without significant additional purification expense. For example, alternatives to typical carbon steel pipelines must be identified for situations when the cost of removing impurities from a CO_2 stream in order to attain acceptable hydraulic properties exceeds the 16% cost increase. A second example is the case in which the expense of purifying a very corrosive CO_2 stream increases capture cost substantially. In the first instance, the additional cost comes from installing larger carbon steel pipe. In the latter instance, a comparison of increased capture cost with increased pipe (and potentially compression and storage) cost would be required.

Three obvious approaches to addressing issues created by impurities are to 1) upgrade the pipe metal, 2) adopt lined pipe, and 3) switch to (organic polymer) composite pipe. While changing to another material might resolve impurity-related issues, other issues can arise, not the least of which is additional cost, as indicated in Figure 7.

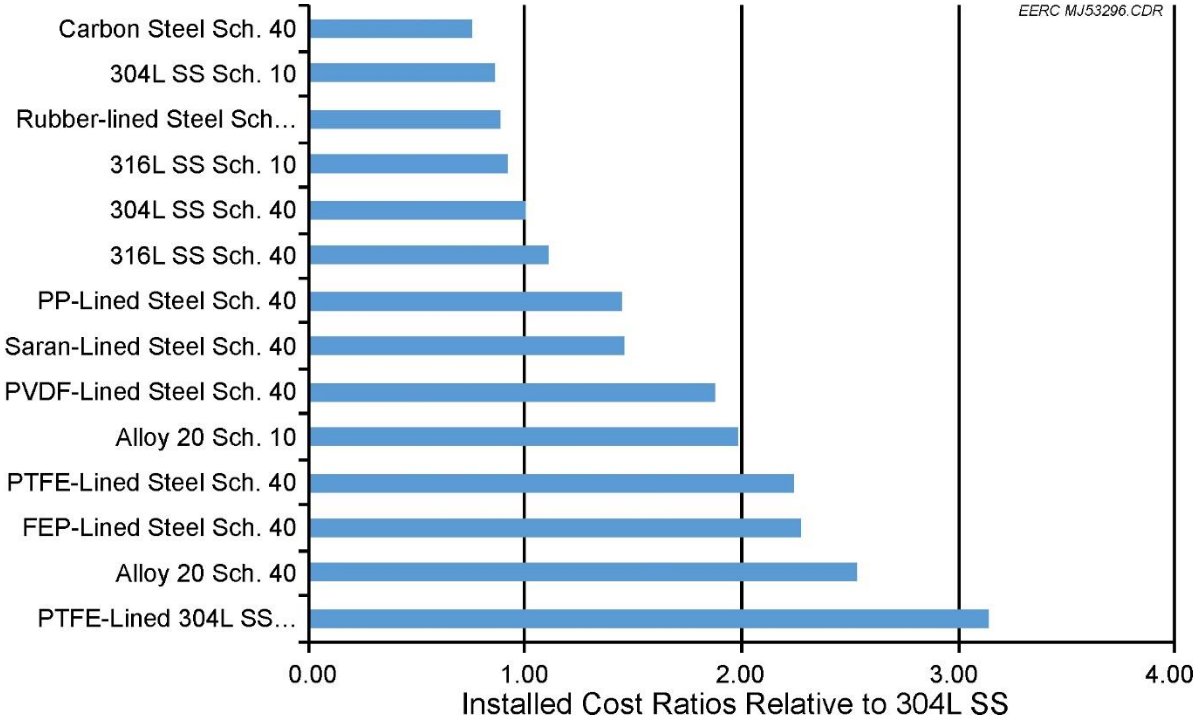

Figure 7. Installed cost ratios of different pipe relative to Schedule 40 304L stainless steel (SS) (based on 328 ft of 2-in. pipe) (data from the Engineering Toolbox, 2017).

Table 26 displays a list of metals that could substitute for carbon steel in pipelines to address issues of free water and the effects of H_2S. The table also lists ranges of reported metal price indices relative to SS Type 304 alloy (Unified Numbering System for Metals and Alloys, UNS S30400). It is immediately apparent that the more corrosion-resistant alloys are more expensive than carbon steel. Interestingly, the relative differences in the prices of carbon steel and 304 SS shown in Figure 7 are not as large as indicated in Table 26. This can be explained, to some extent, by the fact that costs depicted in Figure 7 are related to installed pipe, whereas Table 26 only includes the cost of the metal.

In addition to installed metal pipe costs, Figure 7 displays installed lined-metal pipe costs. Costs for lined metals are greater than the costs of carbon steel. In fact, the installed cost of most lined metals is greater than installed Type 316L alloy pipe. Polymer-lined pipe improves corrosion resistance. However, when placed in dense-phase CO_2 service, the CO_2 tends to penetrate the lining to promote delamination, especially under conditions of rapid depressurization. The loss of the lining means loss of corrosion protection.

Table 26. Suitability of Various Metal Alloys to Various Conditions and Their Relative Costs[a]

Metal Alloy	No Free Water		Free Water		Cost Range Relative to 304 SS	
	CO_2	CO_2, H_2S	CO_2	CO_2, H_2S	Low	High
Carbon Steel	X	X	N/R	N/R	0.19	0.31
304	X	X	X	X	1.00	
316	X	X	X	X	1.28	1.67
13Cr/410	X	X	X	X	1.58	1.58
22Cr/2205	X	X	X	X	1.20	1.96
25Cr/255/2507	X	X	X	X	1.97	5.83
Alloy 20	X	X	X	X	3.83	4.33
600	X	X	X	X	6.28	6.73
825	X	X	X	X	4.01	
825 Clad/5L X65 (4-in. Schedule 80)	X	X	X	X	2.12	
825 Clad/5L X65 (12-in. Schedule 80)	X	X	X	X	1.60	

[a] Sources: Det Norske Veritas (2010); SteelTank (2012); The Hendrix Group (2001) and Energy Pipe Supply, LLC (2001); Roylance (1999); AK Steel (2012); Global Technology & Engineering (2017).

Another lined-pipe approach is to clad, line, or otherwise protect the interior of a less expensive but corrosion-sensitive pipe with a more expensive but corrosion-resistant metal. A metallurgical bond is established by cladding the interior of a corrosion-sensitive pipe with a corrosion-resistant metal. In lining, a mechanical bond attaches a corrosion-resistant pipe to the interior of a corrosion-sensitive pipe. The cost of a bimetallic pipe can be significantly less than that of a solid pipe constructed of a corrosion-resistant metal (Swales and Todd, 1991). Despite this, bimetallic 825-clad X65 pipe cost remains many times greater than that of carbon steel, as indicated by the bottom two rows of Table 26.

The third approach to addressing impurity issues is through adoption of corrosion-resistant composite pipe. Composite pipe is available in two forms, stick and spoolable. As was true for corrosion-resistant metal pipe, both types tend to be more expensive than carbon steel pipe. The stick form is delivered in segments that are typically 30 ft in length (Makselon and others, 2008) and incur installation costs that are comparable to steel pipe. Spoolable composite pipe is delivered in spools of continuous pipe that can be thousands of feet long, presenting the opportunity to significantly reduce installation cost because fewer connections have to be joined than is the case with metal pipes. Stick composite pipe, such as glass fiber-reinforced epoxy, has been available for more than 30 years and has been installed by oil and gas companies since the early 1980s in petroleum production fields. Although the stick fiberglass pipe exhibits greater corrosion resistance when compared to carbon steel pipe, it has been reported that stick fiberglass pipe of that period had a tendency to develop leaks at joints, a condition that was exacerbated under higher-pressure conditions in the presence of CO_2 (Makselon and others, 2008).

Patents for high-pressure hose of designs similar to spoolable composite pipe appeared in the early-to-mid 1980s (Keister, 1982; Abdullaev and others, 1984). However, production of such pipe in commercial volumes did not appear until the late 1990s. Since that time, adoption of spoolable composite pipe has increased substantially. For example, use of spoolable composite for disposal of corrosive produced water is common in the oil fields of western North Dakota. Noncomposite pipe (plastic pipe that lacks stronger reinforcing materials such as fiberglass, aramid fiber, or steel) typically has maximum pressure ratings of hundreds of pounds per square inch. Composite pipe, which is made of multiple layers of plastic and reinforcing materials, can possess maximum pressure ratings in multiple thousands of pounds per square inch (Energy & Environmental Research Center, 2015). Spoolable composite pipe has been considered for use in various applications, including in H_2 pipeline service. DOE’s HFCP of the Fuel Cell Technologies Office stated in 2016 that steel transmission and fiber-reinforced plastic distribution pipelines appear to provide a technically acceptable and the most economic approach to H_2 delivery from central H_2 plants in the United States (Rustagi and others, 2016).

Table 27 lists product characteristics of several manufacturers of spoolable composite pipe that are available in the United States. Figure 8 depicts the operating envelopes of the product lines of manufacturers whose products are included in Table 27. The manufacturers of all products included in the table (except the manufacturer of SoluForce®) claim the products listed are suitable for high-pressure CO_2 transport. This is not true for products included in Figure 8. Figure 8 is more inclusive than Table 27 and incorporates properties of pipe that are not appropriate for high-pressure CO_2.

Improved corrosion resistance, decreased installation cost, and reduced surface roughness that can reduce pressure drop along the line (AdrialPetro, 2016; Fiber Glass Systems, 2016a; Polyflow, 2008) make spoolable composite pipe attractive when compared with carbon steel pipe. However, there are limitations to the appropriateness and competitiveness of spoolable pipe. The length of continuous pipe that can be carried on a spool decreases with increasing pipe diameter

Table 27. Reinforcement Composition and Physical Characteristics of Several Types of Commercial Spoolable Composite Pipe[a]

Product		**Fiberspar™**	**FlexPipe™** **FlexCord™**	**FlexSteel**	**Thermo-Flex®**	**Solu-Force®**
Production Start Year		2003	ca 2001	2005	After 1996	ca 2000
Reinforcing Material		Glass fiber-reinforced epoxy	Dry fiberglass or Steel	Steel	Aramid fiber	Aramid fiber
Temperature Range	Min. °F	–29	–50 32	–40		–40
	Max.°F	140–203	140	140	90–150	150
Largest Diameter Pipe, maximum pressure	Pressure, psi	1500	1500 2250	2250	750	754
	i.d., in.	5.60	3.90 3.90	7.625	5.01	5
	o.d., in.	6.83	5.11 5.07	9.525	6.00	6
	Length, ft	600	1870 1722	459	900	1312
Highest Maximum Pressured Pipe, largest diameter	Pressure, psi	3300	1500 2250	3000	1500	943
	i.d., in.	2.82	3.90 3.90	5.604	3.37	4
	o.d., in.	3.91	5.11 5.07	7.355	4.00	5
	Length, ft	4500	1870 1722	673	2900	1312
Longest Reel Length, highest maximum pressure	Pressure, psi	1500	1500 2250	1500	1500	943
	i.d., in.	2.37	2.12 3.02	1.939	0.61	4
	o.d., in.	3.04	2.86 3.95	2.689	1.00	5
	Length, ft	9000	3610 2018	6578	13900	1312

[a] Sources of data: Fiber Glass Systems (2010, 2016b) Bloomberg (2017); Shawcor (2015); AdrialPetro (2016); FlexSteel Pipeline Technologies (2014); Polyflow (2017); LinkedIn (2017), PipeLife Nederland (2009, 2014).

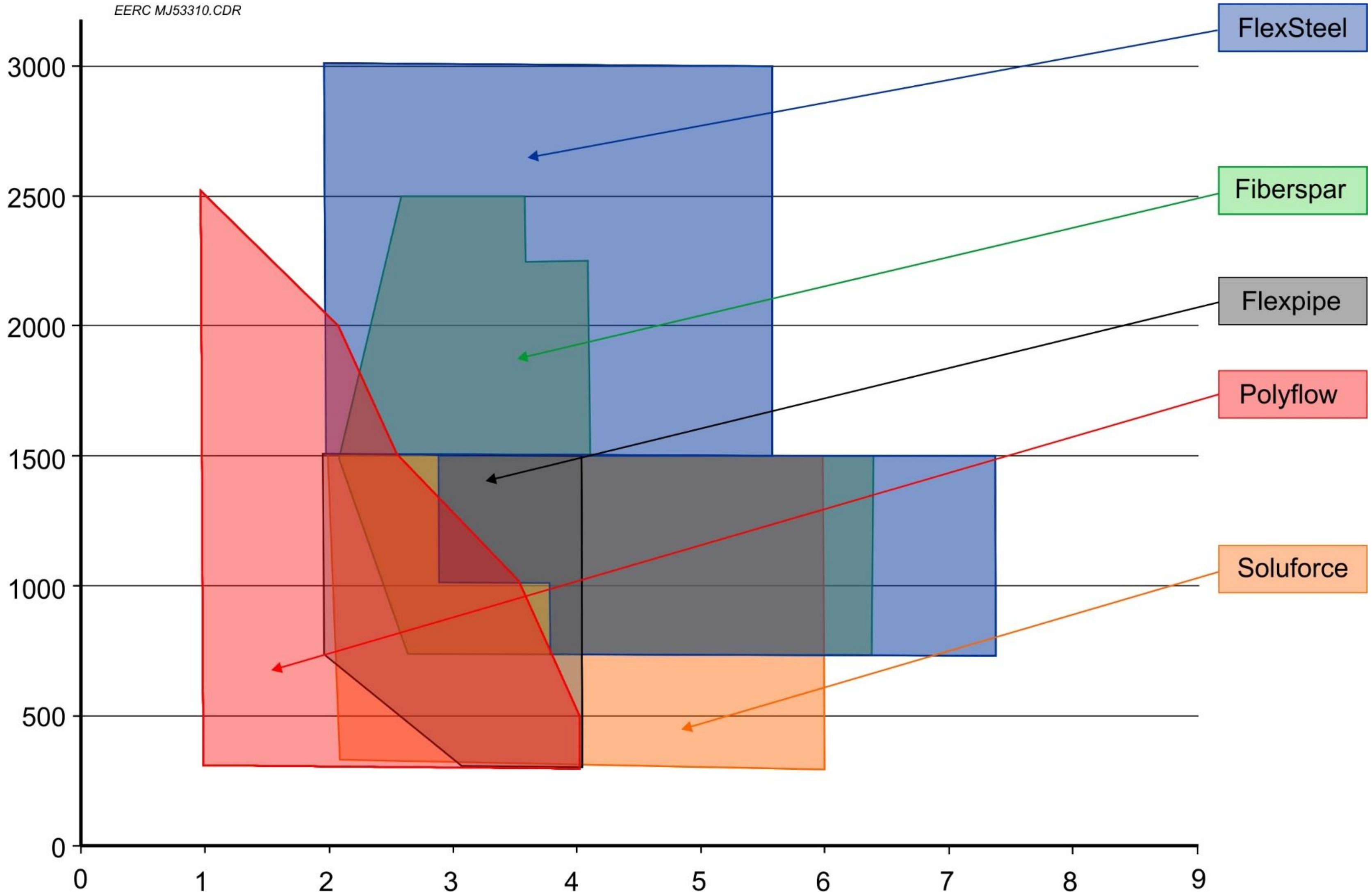

Figure 8. Operating envelopes of products of several spoolable composite pipe manufacturers in terms of pressure in pounds per square inch as a function of diameter in inches (taken from Burdeaux, 2015).

for the same pressure rating. CO_2 can permeate into plastic layers, collect at interfaces and, on rapid depressurization, induce microvoids or blistering (AdrialPetro, 2016). Other issues, such as promoting corrosion of metal reinforcement, have also been noted (FlexSteel Pipeline Technologies, 2012). The Alberta Energy Regulator has established maxima on allowable pressures and H_2S concentrations in specific service for specific Fiberspar™, FlexCord™ and FlexPipe™, and FlexSteel products (Alberta Energy Regulator, 2016).

The major advantage that steel possesses in comparison to spoolable composite pipe is that CO_2 pipeline operators have significant experience with steel pipeline and have optimized its use. This study was able to identify only one report of an application of spoolable composite pipe to CO_2 transport. The report described use of the pipe starting in 2004 in a challenging water alternating gas (WAG) CO_2 EOR application in the Weyburn oilfield (Makselon and others, 2008). Casual communication with a person familiar with the project revealed that the spoolable composite pipe was placed inside of a steel pipe for test purposes. Difficulties with creating a tight seal between the two pipes apparently terminated the test. It was also revealed that use of the pipe in water injection applications has been more successful than emulsion-gathering applications.

Based on this study's literature review, there is little to no experience with spoolable composite pipe in commercial high-pressure CO_2 transport applications. Estimating life cycle costs, such as installation and long-term operation and maintenance costs in large-scale deployment, with any accuracy is challenging. Developing a more comprehensive, systemwide optimization of costs could include employing transportation concepts similar to those under consideration by the DOE's HFCP, specifically the use of spoolable composite pipe instead of metal pipe for portions of the CO_2 transportation infrastructure. In 2011, analysts at Argonne National Laboratory and Pacific Northwest National Laboratories reported fiber-reinforced polymer (FRP) to be approximately 20% more expensive than steel but incurred 25% less installation expense (Elgowainy and others, 2011); thus FRP was estimated to be 15% less expensive than steel to install. In 2012, the Oak Ridge National Laboratory reported FRP pipe to be approximately 18% more expensive than steel, with the potential of a 10% reduction in future FRP material cost. FRP installation labor costs were said to be about 46% less than steel pipe installation labor costs (Smith and others, 2012). The ORNL report noted that current construction, inspection, and FRP pipe deployment costs were 25% less than metal pipe and that there was an opportunity that future costs could be 40% less. Field labor, project engineering, and construction management costs were said to be comparable for the two types of pipe, although the report stated that field learning could reduce field labor cost (Smith and others, 2012). It should be mentioned that the HFCP's pipe specification was different than an appropriate specification for dense-phase CO_2.

At this point in time, spoolable composite pipe cannot compete with metal pipe in large-flow, high-pressure applications. FRP installation cost advantages decrease with increasing pipe diameter since less length of pipe can be wound onto a reel as pipe diameter increases. This increases the number of connections that must be joined per mile. Pressure ratings for larger-diameter spoolable composite pipes tend to be less than for smaller-diameter spoolable pipes.

Of 47 pipelines included in a survey of U.S. CO_2 infrastructure (Wallace and others, 2015), 6% were 4-in.-diameter, 13% were 6-in.-diameter, 23% were 8-in.-diameter, 4% were 10-in.-diameter, and 15% were 12-in.-diameter steel pipelines. Pipelines of these diameters potentially could have been composed of single-pipe spoolable composite pipe instead of steel in 43% of existing U.S. CO_2 pipelines. Dual-pipe spoolable composite pipe potentially could have substituted for about 62% of existing U.S. CO_2 pipelines. While the number of pipelines that potentially could have been of spoolable composite pipe construction is impressive, it should be noted that their combined estimated capacity is only 23% of the estimated total capacity of all U.S. CO_2 pipelines.

This study acquired budgetary quotes for materials and installation labor of spoolable composite pipe from two manufacturers and installation contractors that were prepared in March 2016. (For the remainder of this report, the companies from which the quotes were obtained with be designated Company A and Company B.) Based upon these two budgetary quotes (each quoting two products) for materials and on manufacturer product specifications, a rudimentary analysis to model the material cost of spoolable composite pipe was performed. Regressions were developed that related linear weight to pipe inside diameter for each of the two types of pipe that each of the two manufacturers quoted.

To model pipeline material cost, a relationship between price, inside diameter, and length is required for each product line or manufacturer. Because the proposals submitted budgetary quotes for 4-in. spoolable composite pipe, no useful relationship could be ascertained between cost and inside diameter so a relationship between price per pound and linear weight was established for Companies A and B. This is shown in Figure 9.

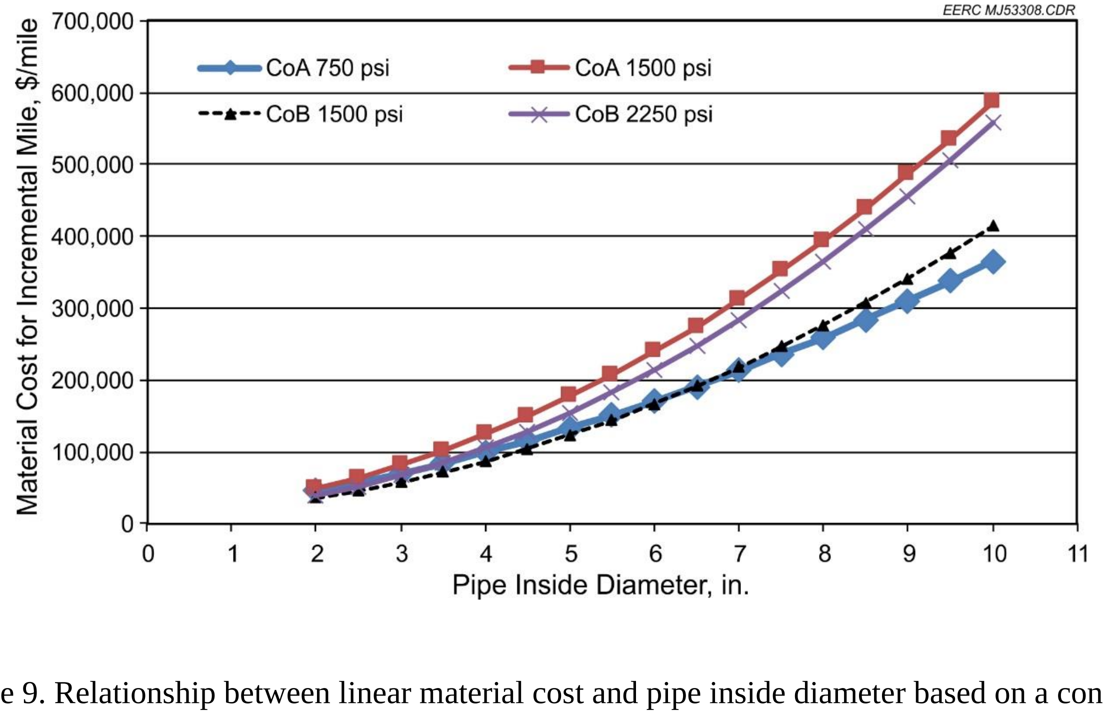

Figure 9. Relationship between linear material cost and pipe inside diameter based on a constant, average price as a function of linear weight.

Labor costs to install spoolable composite pipe have been reported in many ways, all of which show a substantially smaller labor cost than for steel pipe. Smith and others (2006, 2012) place labor costs for trenching and installation of FRP for high-pressure hydrogen transport to be $2/ft in soft soil to $12/ft in rocky terrain, with a mean cost of about $5/ft. In the 2012 presentation, Smith and others (2012) showed relative labor costs of FRP installation that are estimated to be 54% those of steel. Cost savings for FRP construction, deployment, and inspection relative to steel were (in 2011) approximately 25% less, with projected future costs potentially being 40% less. Elgowainy and others (2011) reported an Encana claim of FRP labor savings of 25%. Rawls and others (2011) quoted construction (trenching, joining, etc.) labor costs of $7/ft for steel and $2/ft for single-wrap FRP, representing more than a 70% installation labor savings for FRP.

As already mentioned briefly, this study acquired budgetary quotes from two spoolable composite pipe installation contractors. The quotes were for installation of 4-in. spoolable composite pipe rated at 750 to 2250 psi maximum allowable operating pressure (MAOP) in eastern Montana or western North Dakota in a produced water disposal application. One installation contractor provided a budgetary quote of $10/ft for installation plus $4/ft for sand bedding, while the other contractor's quote was $16.50/ft for installation that included sand bedding.

Figure 10 compares the incremental cost of steel pipe (as modeled using Parker's [2004] correlation developed for the HFCP) with the expected incremental cost of spoolable composite pipe. Despite limited analytical rigor, Figure 10 appears to support HFCP contention that steel would be the most economical choice for transmission pipelines, but spoolable composite pipe would be a less expensive alternative for the distribution pipelines. Elgowainy (2014) estimated steel transmission line capital costs to be $100,000 to $200,000/in.-mi and spoolable composite pipe to cost $50,000 to $200,000/in.-mi for hydrogen service.

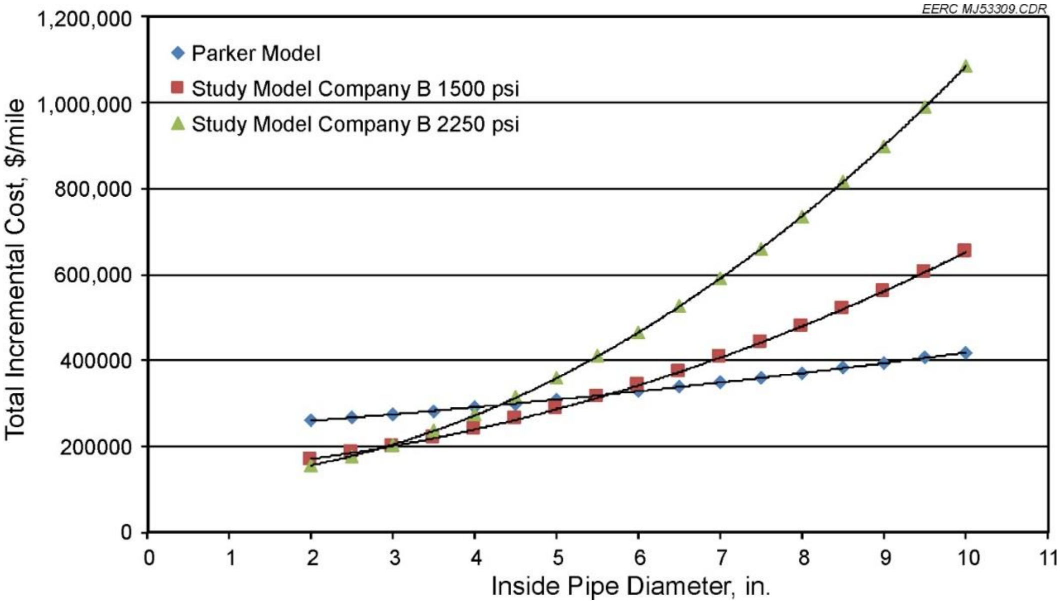

Figure 10. Estimated total incremental cost of steel pipe compared with total incremental cost of two spoolable composite pipelines based on inside pipe diameter.

Spoolable composite pipe might not appear to be economically competitive or available for CO_2 transmission pipelines unless multiple smaller-diameter pipelines are used in place of one large pipeline. However, it might offer a superior alternative for gathering and distribution pipelines in terms of both cost and corrosion resistance. Spoolable composite pipe construction in gathering line service could permit movement of unacceptably corrosive CO_2 to central purification facilities that could purify streams to comply with steel transmission pipeline quality specifications. A second use would be to transport the out-of-specification CO_2 to steel transmission pipelines in which the diluting effect of the main stream might render the bulk stream compliant. The first option provides the opportunity to take advantage of economy of scale by building fewer, large purification facilities rather than many distributed facilities. However, its effectiveness might decline the more that impurities vary between CO_2 gathering lines.

Important aspects of composite pipelines are the flexibility and potential for cost reduction they offer to capture and purification processes, that is, the opportunity to transport lower-purity CO_2 that might otherwise damage steel pipelines and, by so doing, potentially reduce capture and purification costs.

CONCLUSIONS AND RECOMMENDATIONS

Conclusions that were drawn from the research done for this study include the following:

- The volume of CO_2 that can be sequestered through production of chemicals and fuels is very limited. Production of fuels presents the largest theoretical CO_2 utilization opportunity, but it is less than half of overall emissions, even if no additional CO_2 were released during the production of the fuels. EOR is the most significant current and future utilization option for large quantities of CO_2.

- CO_2 purity requirements for conversion to chemicals and other materials will depend on the specific chemicals manufactured and conversion processes installed. At this time, the vast majority of conversion processes are too early in their development to predict economically acceptable CO_2 specifications.

- Purification of captured CO_2 streams can be performed in distributed situations near capture and disposition sites or in centralized situations; each type of situation has distinct advantages and disadvantages. Infrastructure availability and volumes to be processed as well as types, amounts, and variation of impurities over time can affect the attractiveness of any specific location or approach. As a result, the selection of a particular site or approach is better determined on a case-by-case basis.

  - Distributed purification sites located near CO_2 source sites have the ability to access and integrate with source site resources and to customize to the specific CO_2 streams captured. The smaller volumes and more limited range of impurities of individual sites reduce required flexibility and investment. Distributed purification sites near disposition sites share these advantages, except they might have to be more flexible, depending on the variety of streams that feed the transmission line. In so doing, they ensure disturbances and excursions in impurity levels do not reach disposition sites.

  - Centralized purification sites, which gather or distribute multiple CO_2 streams have the opportunity to be placed at advantaged locations that can access and integrate with resources or minimize pipeline costs. The major advantage of such sites is the economy of scale they achieve because of larger volumes of CO_2 that they process. This advantage is undermined by the need to install expensive flexibility if the streams they receive are dissimilar or by a failure to operate near capacity.

- Capture costs tend to outweigh transport and storage costs across a majority of CCS project scenarios. Therefore, potential savings from less expensive capture technologies with less pure CO_2 streams (for example, in oxyfuel capture processes) could outweigh additional costs from higher-specification transport requirements or reduction in utilization options. These factors would need careful consideration should disruptive low-cost capture technologies be developed.

- A universal specification seems unlikely to be identified or implemented.

Two recommendations can be made based on the results of this study:

- Spoolable composite pipe intriguingly offers advantages with respect to steel pipe. Although vendors of composite piping tout its corrosion resistance and ease of installation, it may not be robust enough for widespread service in CO_2 transport. This should be studied in real-world situations. If it proves to be able to tolerate CO_2 streams of varying qualities under the gamut of real-world conditions, the concept of using carbon steel pipe for the main transmission lines and composite pipe for the gathering and distribution lines could be more cost-effective than all-steel pipeline networks.

- The open literature has noted that, to date, CO_2 property studies have focused on CO_2 mixtures containing only one or two impurities. Further research on complex stream compositions may be needed to better define CO_2 specifications that would offer the most efficient, safe, and economical transport of CO_2 while ensuring the structural integrity of the pipeline.

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