Plains CO_2 Reduction (PCOR) Partnership
Energy & Environmental Research Center (EERC)

MATCHING CAPTURE TECHNOLOGIES WITH POINT SOURCES IN THE PCOR PARTNERSHIP REGION

White Paper

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EXECUTIVE SUMMARY

The Plains CO_2 Reduction (PCOR) Partnership Initiative region is expansive, covering ten U.S. states and four Canadian provinces. The geographic and socioeconomic diversity of the region is reflected in the variable nature of the carbon dioxide (CO_2) sources found there. While the CO_2 emissions from the individual PCOR Partnership point sources are similar to those from sources located around the United States, the wide range of source types within the PCOR Partnership region offers the opportunity to evaluate the capture, separation, and transport of CO_2 in many different scenarios.

Most of the region's carbon capture and storage (CCS) can potentially reduce 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. 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 associated with the large-scale CO_2 capture technologies and the commercial sources of CO_2 in the PCOR Partnership region.

Much of the CO_2 produced by large point sources is due to combustion of fossil fuels to provide heat or energy to an industrial process or to generate electricity at a utility. Three opportunities, or platforms, are available for capturing CO_2 from fossil fuel combustion systems: before (pre-), during (through combustion modification), and after (post-) combustion. Several processes have been and are continuing to be developed to separate and remove CO_2 from mixed gas streams, with selection of a technology based primarily on the pressure and concentration of CO_2 in the gas stream. The specific categories 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.

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.

The potential variety of CO_2 sources, capture processes, and end uses makes formulation of a single, optimal-cost CO_2 quality specification difficult. The technologies most likely to be employed for capture at the electrical power-generating stations and other industrial applications are analyzed. The PCOR Partnership region's earliest application of carbon capture has started from the ethanol, gas-processing, and electricity-generating facilities. Minimal processing is required to prepare the CO_2 produced during the fermentation step at ethanol plants for pipeline transportation, making them attractive for initial CO_2 capture implementation efforts. Capture of the CO_2 from the region's coal-fired power plants could significantly reduce the overall regional point-source emission of CO_2, making them targets for impactful capture.

Plains CO_2 Reduction (PCOR) Partnership
Energy & Environmental Research Center (EERC)

MATCHING CAPTURE TECHNOLOGIES WITH POINT SOURCES IN THE PCOR PARTNERSHIP REGION

BACKGROUND

The PCOR Partnership Initiative region is expansive, covering the states of Wisconsin, Minnesota, Iowa, Missouri, Nebraska, North Dakota, South Dakota, Montana, Wyoming, and Alaska as well as the Canadian provinces of Alberta, Saskatchewan, Manitoba, and British Columbia. The geographic and socioeconomic diversity of the region is reflected in the variable nature of the carbon dioxide (CO_2) sources found there. The CO_2 is emitted during electricity generation; energy exploration and production activities; agriculture; fuel, chemical, and ethanol production; and various manufacturing and industrial activities. Most of the region's emissions come from just a few source types: electricity generation, ethanol production, petroleum refining, manufacture of paper and wood products, petroleum and natural gas processing, cement/clinker production, and chemical and fuel production.

While the CO_2 emissions from the individual PCOR Partnership point sources are similar to those from sources located around the United States, the wide range of source types within the PCOR Partnership region offers the opportunity to evaluate the capture, separation, and transport of CO_2 in many different scenarios. The earliest deployment is likely to feature the capture, dehydration, compression, and pipeline transport of CO_2 from the "easiest" sources: primarily gas-processing plants and the fermentation step of ethanol plants. This will likely be followed by capture, dehydration, compression, and pipeline transport of the CO_2 produced during coal combustion at the region's electricity generation facilities, as these are the largest sources of CO_2 in the region.

Several processes have been and are continuing to be developed to separate and remove CO_2 from mixed-gas streams, with selection of a technology based primarily on the pressure and concentration of CO_2 in the gas stream.

CAPTURE TECHNOLOGIES

Much of the CO_2 produced by large point sources is due to combustion of fossil fuels to provide heat or energy to an industrial process or to generate electricity at a utility. There are three opportunities, or platforms, for capturing CO_2 from fossil fuel combustion systems: before (pre-), during (through combustion modification), and after (post-) combustion. The specific categories 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. These are shown in Figure 1.

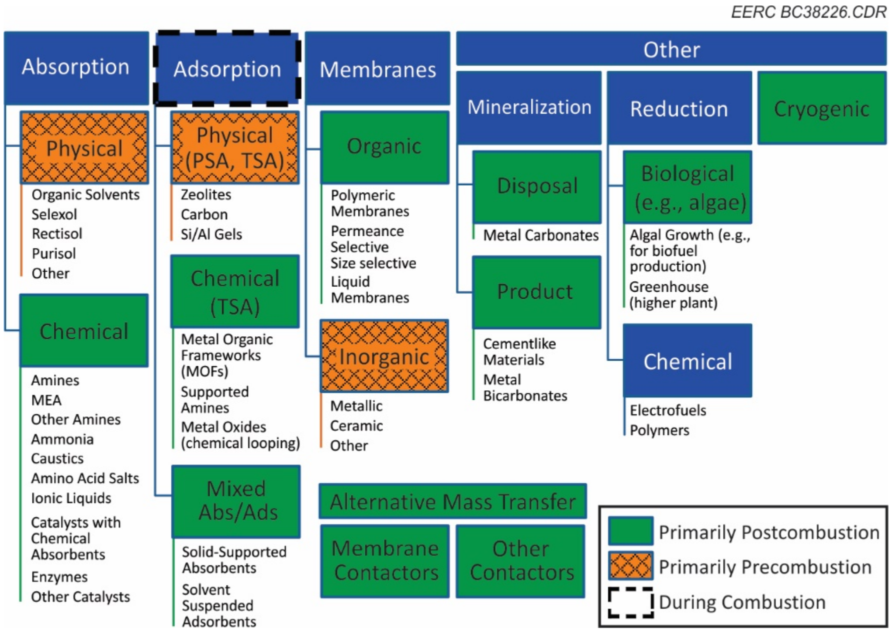

Figure 1. Carbon capture technology categories.

Precombustion

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 via 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 volume percent at pressures ranging from 360 to 725 psia. This high partial pressure of CO_2, relative to that of combustion flue gas, enables separation using physical solvents. A physical solvent utilizes 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. These processes include commercial technologies such as Selexol™, Rectisol®, and Purisol®. Physical adsorbents (e.g., zeolites, activated carbon), chemical adsorbents (e.g., metal oxides and metal hydroxides), and membrane systems are under development, including those that are selectively permeable to oxygen, hydrogen, or carbon and are commercially applied in the gas-processing industries, and some are at small pilot demonstration scale for use in CO_2 capture.

The majority of the commercial precombustion capture technologies, e.g., Selexol, Rectisol, and Purisol, were developed in the mid-1900s and were utilized for acid gas (H_2S [hydrogen sulfide] and CO_2) removal by the early developers of commercial synthetic fuel (synfuel)-manufacturing plants (such as coal gasification).

During Combustion

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 minimum processing before use or permanent storage. Typically, 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 contaminants that may be present such as nitrogen (N_2), nitrogen oxides, oxygen (O_2), and argon can be removed by flashing in a gas–liquid separator.

The oxycombustion processes that are being developed include technologies represented by modified or retrofitted combustion units, new combustion units, and other processes that incorporate membranes into the combustion chamber, combine high-pressure combustion and exhaust gas condensation, or utilize oxygen provided by metal oxide oxygen carriers to combust the fuel (chemical looping).

In addition to improved oxycombustion technologies, there is also a need to optimize the separation of oxygen from air, minimizing the parasitic power load associated with this unit operation of oxycombustion. Relative to coal gasification, combustion requires up to three times the amount of pure oxygen. The air separation unit capacity and its associated parasitic power load are commensurately larger. Separation of oxygen from air is expensive and is usually performed at very large scale by cryogenic distillation. Other methods of separating oxygen for use during oxycombustion are being developed, most notably oxygen or ion transport membranes. These membranes operate at temperatures of roughly 500°C, meaning that oxygen separation can be integrated with the combustion process, providing a theoretically significant reduction in parasitic power loss and O_2 production cost.

Postcombustion

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. Several types of postcombustion processes have been and are being developed to separate and remove the CO_2 from a flue gas stream, such as absorption, adsorption, membrane, and cryogenic processes and other methods that include mineralization for either disposal or to produce a mineral product and reduction to produce beneficial products such as fuels and/or plastics.

Postcombustion technologies range in scale. Some commercial processes have been in use for acid gas management for many years. Research and development involve testing of new chemicals, catalysts, membranes, and/or process configurations. Postcombustion capture technologies are critically important to meeting CO_2 emission reduction goals because they are the technologies that can be applied to the existing power generation fleet. Implementation of this emission control strategy can begin immediately through the application of available commercial technologies, but it is critical that parallel efforts continue to further optimize these technologies to improve both CO_2 capture efficiency and cost. Also of critical importance is the continued development of innovative techniques that are less capital- and energy-intensive, are amenable to in-plant retrofits, and can produce usable by-products from the captured CO_2.

Some of the postcombustion technology types that could be applied to CO_2 capture from combustion systems are briefly discussed in the following paragraphs. It is important to note that some of the technologies listed here could also be applied to precombustion applications.

Absorption

Absorption systems that are used to capture CO_2 include physical solvent-based absorption systems that would be applicable for precombustion applications and chemical solvent-based absorption systems for both precombustion and postcombustion applications. The most typical system design for both physical and chemical solvent use involves contacting the lean solvent and the CO_2-containing gas stream in an absorption tower. The loaded, or rich, solvent is then regenerated in a stripping tower. A schematic of a generic solvent system is shown in Figure 2.

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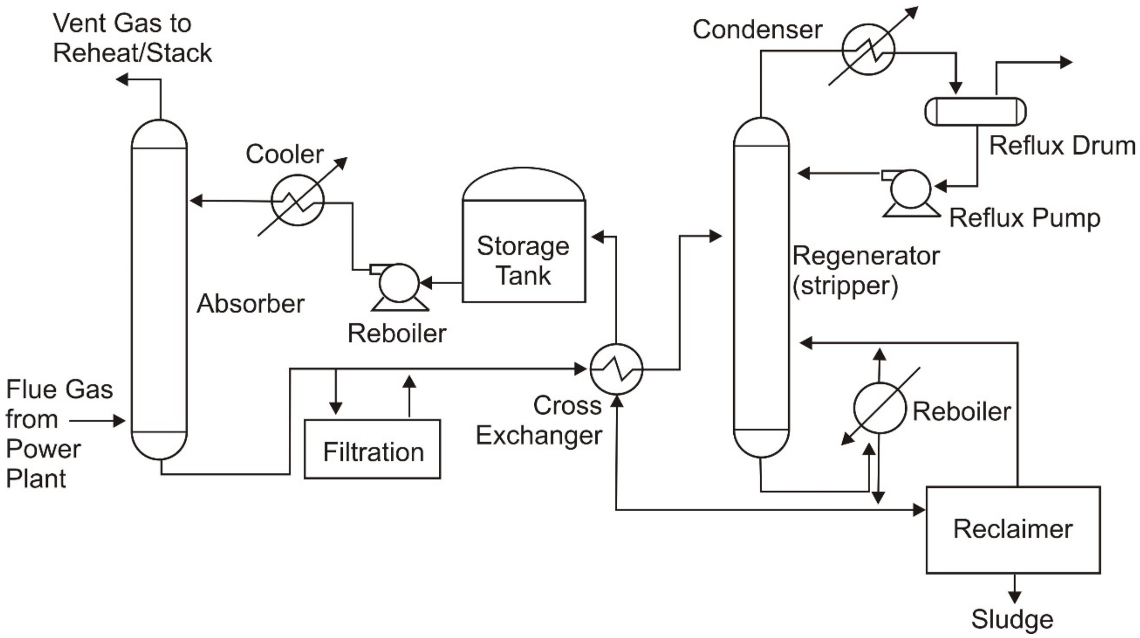

Figure 2. Generic liquid solvent system for CO_2 capture.

Physical solvents can be regenerated through pressure reduction and/or heating. Chemical solvents are generally regenerated by heating, which reverses the reaction and releases the CO_2. The CO_2-lean solvent is then recirculated for reuse. Amines are the most commonly used chemical absorbent for CO_2 separation from mixed-gas streams. Development of improved chemical absorption systems includes increasing the cost-effectiveness of CO_2 capture through higher CO_2 absorption capacities, faster CO_2 absorption rates, reduced solvent degradation, reduced solvent corrosiveness, and lower regeneration energy requirements. Other developments in the area of chemical absorption include the use of additional solvents in absorber–stripper systems, the use of enzyme-based and enzyme-inspired catalysts, the development of new absorbents for CO_2 capture, and the development of mass-transfer devices other than absorption towers.

Because many facilities produce flue gas containing SO_x and NO_x that can react with the liquid absorbent to form heat-stable salts, application of liquid scrubbing technology to a power plant or other industrial facility that emits CO_2 through combustion may require the installation of additional pollution control equipment to reduce the concentrations of these contaminants prior to CO_2 capture.

Adsorption

Adsorption CO_2 capture technologies move CO_2 from mixed-gas streams onto the surface of solid sorbents. These sorbents generally have very high porosity; therefore, high surface areas are available per unit mass and per unit volume. As is the case with absorption, adsorption can be a simple phase-partitioning physical adsorption, or it can involve a chemical reaction between the sorbent and CO_2. Regeneration of the sorbent beds is typically performed by temperature- or pressure-swing techniques.

Mixed Absorption–Adsorption

Mixed absorption–adsorption processes are those that employ a liquid absorbent (typically a chemical absorbent) trapped in or on the solid support. These are often classified with adsorption processes because they employ similar gas–solid contact arrangements (fixed-bed, fluid-bed, or moving-bed reactors), but the actual capture process occurs in a liquid layer or liquid droplet contained on or in the support. Most commonly, the chemical sorbent is an amine, although ionic liquids are being investigated for this use.

Membrane Processes

Membranes employ a permeable barrier between two fluid-phase zones. This permeable barrier provides selective transport of CO_2 or other gas component. Desirable membranes are highly selective and have a high permeability for the molecule to be transported. Development of successful membrane processes involves not only selection of membrane materials with favorable properties but also the development of the physical devices or membrane modules that allow the membranes to be used and the processing system in which the membrane module is employed.

Cryogenic

In cryogenic CO_2 capture, a mixed-gas stream is compressed, and the heats of compression and condensation are removed. The stream can be 1) compressed to about 1100 psia, with water used to cool the stream; 2) compressed to 250–350 psia at 10° to 70°F, dehydrated using activated alumina or silica gel, and the condensate distilled in a stripping column; or 3) dehydrated and cooled to even lower temperatures (−78.5° to −109°F or lower) to condense the CO_2.

Mineralization

CO_2 capture by mineralization occurs when the CO_2 forms a stable mineral carbonate or bicarbonate. Typically, these materials are formed using calcium and magnesium cations. The end products of the mineralization processes can either be disposed of, sold as a product, or used to generate another useful product such as aggregate or a type of cement.

Reduction

Reduction is the chemical transformation of the CO_2 to a reduced state through the input of energy. This concept incorporates the conversion of CO_2 into an organic compound such as a polycarbonate plastic, a fuel, or some other desired product. The process makes sense from an energy balance perspective only when the product is of high value, the fuel is effectively an energy storage product made from an intermittent energy supply source (e.g., wind, solar), and/or the fuel produced is useful in ways that the original source fuel was not (e.g., production of a transportation fuel from coal-derived CO_2). While many projects dealing with the beneficial reuse of CO_2 will use precaptured and prepurified CO_2, some projects will be focused on the direct capture of the CO_2 from flue gas (after removal of common contaminants).

CO_2 capture also can be coordinated with reduction of CO_2 to a beneficial use product. This approach is being performed and/or investigated in closed-environment agriculture for growth of flowers and food crops and in coordination with the growth of algae, microalgae, and cyanobacteria used in the production of biofuels. The reducing equivalents for these processes are provided through the photosynthetic capture of solar energy.

Capture Technology Summary

Several processes have been or are being developed to separate and remove CO_2 from flue gas streams. Selection of a particular technology is based primarily upon the pressure and concentration of CO_2 in the gas stream, as summarized in Table 1. Absorption is commercially available for high-volume, mixed-gas streams. Physical sorbents are ideal for gasification flue gas streams, whereas chemical sorbents are used to remove CO_2 from fossil fuel combustion systems. Adsorption can also be implemented for mixed-gas streams; however, commercial systems are not yet available. Membrane and cryogenic systems are ideal for smaller flow rates. Membranes may be applied to gasification or reforming flue gas streams, and cryogenic conditions benefit carbon capture from high CO_2 concentration streams.

Table 1. Common Applications for CO_2 Capture Technologies

Technology	Application
Absorption	Commercial plants, mixed-gas streams
Chemical	Fossil fuel-fired systems, e.g., boilers, gas turbines
Physical	Gasification systems
Adsorption	Mixed-gas streams
Membranes	Gasification and reforming, flue gas
Cryogenics	High-concentration, mixed-gas streams

COMMERCIAL SOURCES OF CO_2 AND THEIR MOST COMMON IMPURITIES

Typical CO_2 Stream Compositions

Different industrial processes and different capture technologies can produce captured CO_2 streams that have somewhat different compositions. More or less stringent control of impurities may be required for different end uses of a CO_2 stream or to maintain pipeline integrity. For example, according to the Kinder-Morgan pipeline specification (Havens, 2008), CO_2 that will be transported for enhanced oil recovery (EOR) via pipeline requires that oxygen be removed to levels as low as 10 ppmw. In a presentation given at the EC FP7 (European Commission, 7th Framework Programme) 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 (precombustion, oxycombustion, and postcombustion). The stream compositions were estimated by the CO_2QUEST project. The results of the comparison are shown in Table 2.

Table 2. Summary of Impurities in Captured CO_2 Streams from the Three Capture Platforms As Estimated by the CO_2QUEST Project (Porter, 2014)

	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.
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/COS,[d] ppm				0.2–34,000	
H_2, ppm				20–30,000	
CH_4,[e] ppm				0–112	

[a] Sulfur dioxide.

[b] Sulfur trioxide.

[c] Water.

[d] Carbonyl sulfide.

[e] Methane.

In general, postcombustion amine scrubbing processes 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 gasification combined-cycle [IGCC]) are shown in Table 2 in the precombustion (IGCC) and postcombustion (pc) 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 3. 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 consider 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 3. Captured CO_2 Stream Compositions from Nonelectric Power Emitters

	MEA[a] Refinery[b]	MEA Cement Plant[b]	Cement Kiln[c]	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 general, a conventional coal-fired power plant produces a flue gas having the relative proportions of components that are shown in Table 4. A postcombustion process that makes use of amines to separate the CO_2 from the rest of the flue gas 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 because

Table 4. 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.

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 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 3.

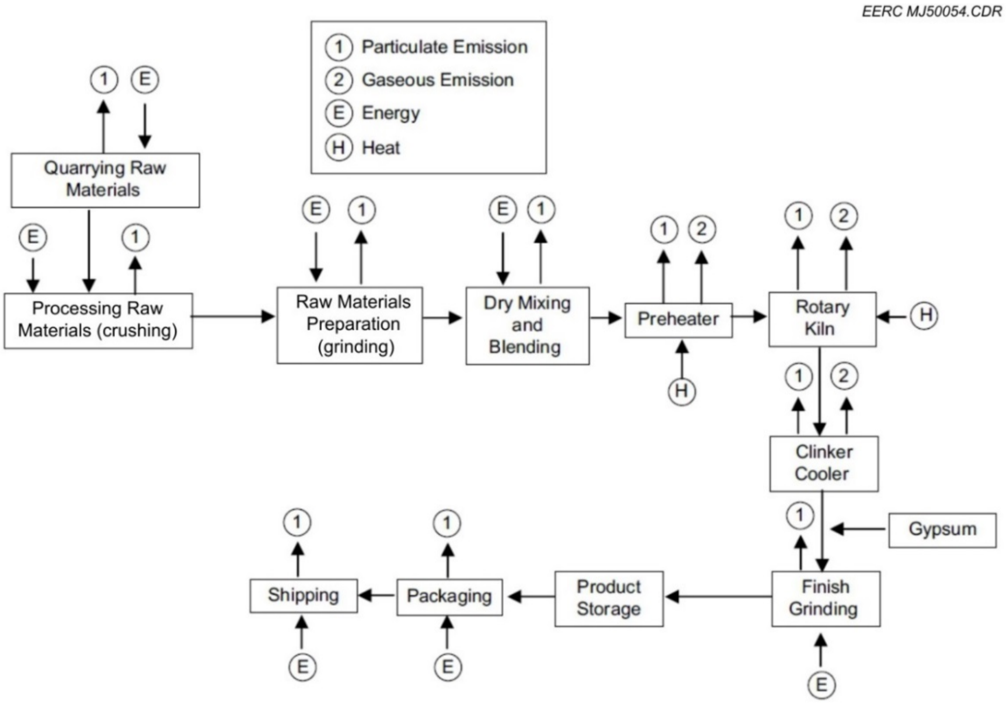

Figure 3. Flow diagram of the cement-manufacturing process (taken from Huntzinger and Eatmon, 2009).

The parts of the process where emissions are expected are in the raw meal preparation and pyroprocess steps. There are four main pyroprocessing routes for the production of cement: wet process, semiwet 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 be combined to allow the gas 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 5 summarizes the findings. Marceau and others (2010) reported emission data for cement production in the United States. These data are presented in Table 6. 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 7. 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 5. 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.

Table 6. 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 7. 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)

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 Programme, 2008).

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

- A process redesign 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 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 8.

Table 8. Summary of Relative Component 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.

Petroleum Refineries

Even though the cumulative amount of CO_2 emissions from petroleum refineries is a small fraction of power plant emissions, 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 9, which shows where CO_2 is produced in a typical refinery, and Table 10, which shows how CO_2 emissions can be assigned to processes across a notional refinery.

Table 9. 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 10. 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 of variance in both crude oil feeds and the relative performances of the processes over time. The process units differ with respect to the 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 FCCU, 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 125 operating refineries in the United States (U.S. Environmental Protection Agency, 2021), 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 3, 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 11. Table 12 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 11. 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 13. 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 12. 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.

APPLICATION OF CO_2 CAPTURE TO POINT SOURCES IN THE PCOR PARTNERSHIP

With respect to specific commercial point sources, the technology most likely to be employed for capture at the electrical power-generating stations and many other industrial applications is chemical absorption. Amine scrubbing will probably be used as it is a commercial (and, therefore, better defined) technology in other processes. Amine scrubbing is typically used to separate CO_2 from raw natural gas at gas-processing plants, but it also could apply to capture of the CO_2 produced during combustion of either natural gas or coal at ethanol plants (if enough CO_2 could be captured to make its sequestration economical). In contrast, the CO_2 produced during the fermentation step at ethanol plants would require only dehydration and compression, depending on the end use of the CO_2.

Table 13. 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 comprises roughly 78% N_2, 21% O_2, 1% Ar.

[d] Carbon disulfide.

The PCOR Partnership region's earliest application of carbon capture has started from the ethanol, gas-processing, and electricity-generating facilities. The CO_2 produced during the fermentation step at ethanol plants requires minimal processing to prepare it for pipeline transportation, making them attractive for initial CO_2 capture implementation efforts. Because the region's coal-fired power plants emit roughly two-thirds of the CO_2 produced by industrial stationary sources, capture of their CO_2 could significantly reduce the overall regional point-source emission of CO_2, making them targets for impactful capture.

During ethanol manufacture, the CO_2 vented from the fermenters is scrubbed with water to remove alcohol, acetaldehydes, and other volatile organic compounds (VOCs). The water used in the CO_2-scrubbing process is reclaimed into the process via the cook water tank and is considered to be a step within the ethanol production process rather than a separate CO_2 capture process. Historically, when collected, the CO_2 is marketed to the food-processing industry for use in carbonated beverages and flash-freezing applications.

Amine scrubbing is commonly used throughout the petroleum- and natural gas-processing industry for CO_2 capture because of the technology's high capture efficiencies and ability to provide the purity needed for EOR efforts. Therefore, amines are recommended for coal combustion in the electricity-generating industry. Amine scrubbing can also be used for carbon capture from other emission sources within the ethanol production process. For example, gas combustion in boilers used for drying by-products derived from corn solids during ethanol production generates a CO_2 flue gas typically emitted.

REFERENCES

Ali, M.B., Saidur, R., and Hossain, M.S., 2011, A review on emission analysis in cement industries: Renewable and Sustainable Energy Reviews, v. 15, p. 2252–2261.

Blue Source, LLC, 2006, Blue Sources' greenhouse gas emission reduction protocol for Petro Source's capture of vent-stack CO_2 in combination with enhanced oil recovery operations: Salt Lake City, Utah, 37 p.

Chen, S.G., Lu, Y., and Rostam-Abadi, M., 2004, Carbon dioxide capture and transportation options in the Illinois Basin, *in* Assessment of geological carbon sequestration options in the Illinois Basin–Task 2—assess carbon capture options for Illinois Basin carbon dioxide sources: Topical report (October 1, 2003 – September 30, 2004) for U.S. Department of Energy Contract DE-FC26-03NT41994, Champaign, Illinois, Midwest Geological Sequestration Consortium.

de Visser, E., Hendriks, C., Barrio, M., Mølnvik, M.J., de Koeijer, G., Liljemark, S., and Le Gallo, Y., 2008, DYNAMIS CO_2 quality recommendations: International Journal of Greenhouse Gas Control, v. 2, no. 4, p. 478–484.

El Ela, M., 2014, Desert project illustrates selecting acid-gas removal technology: Oil & Gas Journal, v. 112, no. 1.

European Cement Research Academy, 2009, ECRA CCS project – report about Phase II: TR-ECRA-106/2009, Duesseldorf, Germany, 83 p.

Ferguson, S., Stockle, M., and Stamateris, B., 2011, Reducing CO_2 carbon capture options applied to the refining industry: Presented at the ERTC Annual Meeting, Barcelona, Spain, November 29 – December 1.

Global Greenhouse Warming, 2017, Cement CO_2 emissions: www.global-greenhouse-warming.com/cement-CO_2-emissions.html (accessed May 2020).

Greer, W.L., 2003, Interactions among gaseous pollutants from cement manufacture and their control technologies: Skokie, Illinois, Portland Cement Association R&D Serial No. 2728, p. 59.

Havens, K., 2008, CO_2 transportation: Presented at the Indiana Center for Coal Technology Research, June 5. www.purdue.edu/discoverypark/energy/assets/pdfs/cctr/presentations/Havens-CCTR-June08.pdf (accessed May 2020).

Huntzinger, D.N., and Eatmon, T.D., 2009, A life-cycle assessment of Portland cement manufacturing—comparing the traditional process with alternative technologies: Journal of Cleaner Production, v. 17, no. 7, p. 668–675. https://doi.org/10.1016/j.jclepro.2008.04.007.

IEA Greenhouse Gas R&D Programme, 2008, CO_2 capture in the cement industry: 2008/3, July.

Kohl, A., and Nielsen, R., 1997, Gas purification (5th ed.): Houston, Gulf Publishing Co.

Last, G.V., and Schmick, M.T., 2011, Identification and selection of major carbon dioxide stream compositions: Report for U.S. Department of Energy, Richland, Washington, Pacific Northwest National Laboratory, PNNL-20493.

Lohnes, B., 2007, ConocoPhillips Lost Cabin gas plant CO_2: Presented at the 1st Annual CO_2 Conference, University of Wyoming Enhanced Oil Recovery Institute, Casper, Wyoming, www.uwyo.edu/eori/_files/co2conference07/brent_lohnes_conocophillips_eori.pdf (accessed May 2020).

Marceau, M.L., Nisbet, M.A., and VanGeem, M.G., 2010, Life cycle inventory of portland cement manufacture: Skokie, Illinois, Portland Cement Association, R&D Serial No. 2095b, revised April.

NaturalGas.org, 2013, Processing natural gas: http://naturalgas.org/naturalgas/processing-ng/ (accessed May 2020).

Porter, R.T.J., 2014, CO_2QUEST typical impurities in captured CO_2 streams: Presented at EC FP7 Projects—Leading the Way in CCS Implementation meeting, London, United Kingdom, April 14–15. www.slideshare.net/UKCCSRC/r-porter-co2questfp714april2014 (accessed May 2020).

Rubenstein, M., 2012, Emissions from the cement industry: State of the Planet Blog, The Earth Institute at Columbia University. http://blogs.ei.columbia.edu/2012/ 05/09/emissions-from-the-cement-industry/ (accessed May 2020).

Taraphdar, T., 2011, Reducing carbon footprint: DigitalRefining.com article 1000399, p. 2. www.digitalrefining.com/article/1000399#.XsyOizOSlPY (accessed May 2020).

U.S. Environmental Protection Agency, 2021, Petroleum and other liquids. www.eia.gov/dnav/pet/pet_pnp_cap1_dcu_nus_a.htm (accessed November 2021).