Capture and storage of CO_2 with other air pollutants

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Abstract

This report focuses on the combined capture and storage of multiple gases (CO_2 and at least one other gas) from processes that use or treat fossil fuels. It concentrates on coal-based power systems, although many of the issues associated with co-capture and storage from power systems would apply to other fossil fuel-related processes. The potential benefits of co-capture are associated with lower costs for capture of the combined stream of gases, and desirable changes in geochemistry which may improve injectivity and even 'self-seal' small underground fissures. However, there are a number of concerns about co-capture and storage. Some relate to the handling and transport of liquid or supercritical mixed fluids that pose greater health and safety risks than relatively pure CO_2 streams, and the potential for the more acidic co-capture mixtures to lead to undesirable chemical reactions near the injection point, including reactions with the steel well pipe and well completion cements.

Acronyms and abbreviations

CCS	carbon capture and storage
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
DOE	Department of Energy (US)
EOR	enhanced oil recovery
EPA	Environmental Protection Agency (US)
FBC	fluidised bed combustion
H_2S	hydrogen sulphide
IDLH	immediately dangerous to life or health
IGCC	Integrated Gasification Combined Cycle
IPCC	Intergovernmental Panel on Climate Change
MPa	mega-pascals (equals 145 pounds per square inch, or 9.9 atmospheres)
NIOSH	National Institute for Occupational Safety and Health (US)
PC	pulverised coal
ppm	parts per million
SCPC	supercritical pulverised coal
SCR	selective catalytic reduction
SNG	substitute natural gas
USDW	underground source of drinking water
WRI	World Resources Institute

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Executive summary

This report focuses on the combined capture and storage of multiple gases (CO_2 and at least one other gas) from processes that use or treat fossil fuels. It concentrates on coal-based power systems, although many of the issues associated with co-capture and storage from power systems would apply to other fossil fuel-related processes. In general the potential benefits of co-capture are associated with lower costs for capture of the combined stream of gases, and desirable changes in geochemistry which may improve injectivity and even 'self-seal' small underground fissures. There are a number of concerns about co-capture and storage. Some relate to the handling and transport of liquid or supercritical mixed fluids that pose greater health and safety risks than relatively pure CO_2 streams, and the potential for the more acidic co-capture mixtures to lead to undesirable chemical reactions near the injection point, including reactions with the steel well pipe and well completion cements. Although much work has been done, particularly in the area of handling and injecting mixtures of CO_2 and H_2S, many uncertainties remain, particularly for mixtures of CO_2 and SO_2.

Potential benefits of the capture system relate primarily to the reduced cost of capture at a power plant, for a system that co-captures multiple pollutants with the CO_2. Co-capture of sulphur and perhaps nitrogen species (with CO_2) at a new coal-fired power plant could eliminate conventional capture systems that cost approximately 8% (for subbituminous coal) or 13% (for bituminous coal) of the total levelised cost of electricity at carbon capture and storage (CCS)-equipped supercritical pulverised coal (SCPC) systems, and approximately 5% (bituminous) for H_2S capture systems with IGCC systems. Actual savings would be somewhat less than these amounts because even a combined capture system would incur some costs for the capture of these contaminants. The formation of heat stable salts with conventional amine systems applied to SCPC power plants constitutes a barrier to co-capture at traditional power plants. The relatively large savings projected for SCPC co-capture systems presume that economical sulphur and nitrogen tolerant CO_2 capture systems will be developed. Additionally, as discussed in Chapters 3 and 4, savings in the capture area may be partially or fully offset by additional costs related to transport and/or storage of mixed gases. Co-capture and storage may provide additional benefits where CO_2 capture is retrofit to an existing power plant, but these benefits are likely to be site-specific (*see* Chapter 2).

CO_2 pipelines currently transport very high (50%) concentrations of H_2S mixed with CO_2 for limited distances (for example 20 km) as a supercritical fluid. A 325 km pipeline conveys CO_2 with up to 0.9% H2S from the Dakota Gasification Facility in North Dakota, USA, to enhanced oil recovery (EOR) fields in Saskatchewan, Canada. Hence, transport of mixed fluids, at least with H_2S, is clearly feasible. Potential transport problems include dual phase flow, which can damage compressor equipment, and health and safety issues associated with the possible release of the low-concentration gases. For example, US workplace recommended exposure limits for short-term exposures allow CO_2 concentrations as high as 30,000 ppm (15 minute average), but limit SO_2 to 5 ppm (15 minute average) and H_2S to 10 ppm (10 minute average). There is no commercial-scale experience with pipelines conveying mixtures of CO_2 and significant concentrations of SO_2; this is an area where additional research is warranted.

Issues associated with the co-injection of CO_2 with either H_2S or SO_2 have been reported from both empirical studies and mathematical modelling analyses. In general, mixtures of CO_2 with small amounts of SO_2 lead to the formation of more acidic species when they mix with formation waters, causing a lower pH near the injection well, and promoting additional chemical reactions with the formation rock material. Increased porosity can occur near the injection well through rock dissolution, and creation of sulphate precipitates can occur along the frontier of the more acidic region. The significance of these changes is as yet undetermined, and different studies have reached different conclusions. For example, one study simulating CO_2-SO_2 mixtures (96.5% CO_2 and 3.5% SO_2) predicted a much lower pH and changes in porosity within 200 m of the injection well for up to 100 y, compared with pure CO_2. Another study simulating a 1% mixture of SO_2 with 99% CO_2 found no significant change in porosity or permeability near the injection well, compared with CO_2 only. The basis for such differences are unclear, but could include alternative assumptions regarding whether a disproportionation reaction (simultaneous oxidation and reduction) of SO_2 to SO_3 and H_2S occurs. Studies involving injection of mixtures of CO_2 and low concentrations of H_2S have generally found a smaller impact on geochemistry near the injection well, but changes do occur. In one case involving EOR, CO_2 breakthrough at the oil production well preceded breakthrough of the co-injected H_2S, indicating that the H_2S reacted more rapidly with the formation rocks than the CO_2 did. Another study found that the impacts of relatively high concentrations of H_2S with CO_2 were highly dependent on the nature of the formation chemistry (for example, sandstone versus carbonate rock). Studies also cited the extremely slow movement of formation waters and concluded that the additional acidity would be neutralised before the injected fluids could migrate to a point where they could have an impact on reservoirs with non-saline groundwater. If co-injected fluids include significant amounts of nitrogen, as could happen with oxyfuel systems if air infiltration occurs, then the density of the fluids could change significantly. They would then require additional compression and injection at deeper depths to assure storage in a dense state. Moreover, because nitrogen is inert and would not react with formation rocks, over time the nitrogen concentration in the stored mixture would probably increase. This would lead to increased formation pressure (*see* Chapter 4). Little research has been conducted on the chemistry associated with CO_2 or mixed fluids while they remain in their supercritical state, versus after their dissolution into formation water. The physics and chemistry of these water/supercritical acid gas mixtures differ from gases dissolved in saline water. There is the potential that these mixtures could form precipitates that could ‘self-seal’ small fissures in a formation.

Regulatory authorities may impose more stringent requirements on the transport or injection of mixtures of gases than for relatively pure CO_2. The US Environmental Protection Agency (EPA) has indicated that stricter storage requirements would be imposed if significant quantities of mercury, SO_2, or H_2S were mixed with CO_2 injectate, although final regulations have not yet been adopted.

The knowledge base on underground reactions of mixed fluids is limited by the difficulty of obtaining data on activities more than a kilometre below the surface, and by the long time scales needed for reactions (decades or longer). These factors suggest that greater insights into potential benefits and problems associated with the co-storage of mixed fluids are likely to come from computer modelling supported by controlled experiments.

Both the potential benefits and concerns associated with co-capture and storage are significant and warrant additional research to determine the full impacts of such systems.

1 Introduction

This report addresses issues associated with co-capture, which is defined here as the capture and permanent geological storage of carbon dioxide (CO_2) with small amounts, typically 0.5–2.0%, of other gases, such as hydrogen sulphide (H_2S) or sulphur dioxide (SO_2). Technically, almost any CO_2 capture system is likely to capture some additional acid gases, and perhaps other air pollutants, which persist after upstream collection systems. The focus of this report is on those systems which do not apply 'best technology' intentionally for these other gases upstream of the CO_2 capture system. Interest in co-capture and storage has been based primarily upon the assumption that it would be less costly to capture and secure multiple acid gases together than to capture and secure them in separate processes. The most often cited argument against co-capture and storage is that the additional acid gases introduce significant environmental concerns that are not present with pure CO_2 capture and storage.

The report examines how co-capture might have an impact on the three primary elements of CCS: capture, transport, and storage. For each sector, an attempt is made to identify what is reported in the literature, what significant knowledge gaps remain, and what areas merit additional analysis or R&D. The main focus is on CCS associated with coal-based power generation, although many of the issues also apply to coal-to-liquids and coal-to-substitute natural gas (SNG) facilities. The report is not intended to apply to natural gas processing plants, where much higher fractions (for example more than 10%) of the captured gases could be H_2S.

Figure 1 shows the major components of CCS. In each of the three major areas, there are both potential benefits and problems associated with co-capture and storage. In general, the potential benefits extend beyond the presumed normally lower cost of replacing some air pollution control systems with broader gas capture and storage systems. The potential problems extend further than traditional environmental concerns regarding the release of SO_2 or H_2S beyond the power plant boundaries. The body of this report follows the general organisation of Figure 1. The report has been written by the US Carbon Sequestration Council, and so the examples given are from the USA.

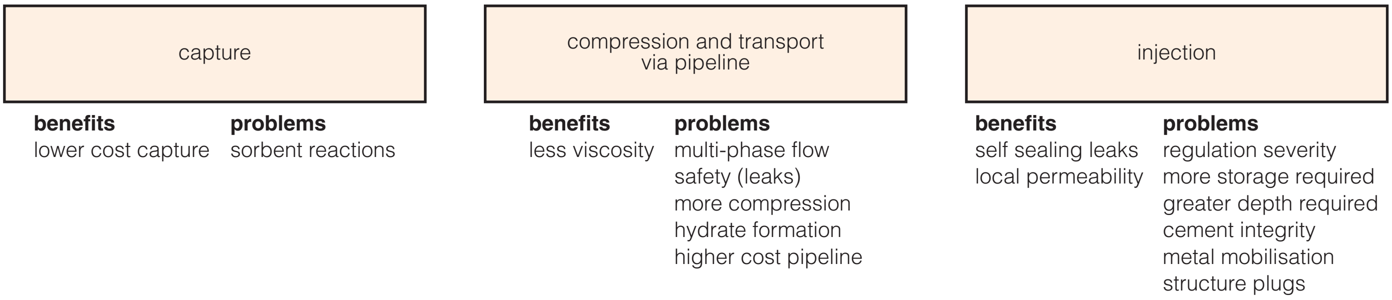

Figure 1 Benefits and problems associated with co-capture and storage, by activity type

2 Capture

The potential benefits of capturing CO_2 with other pollutants are assessed in this chapter. It covers emerging technologies, potential economic savings that may arise as well as potential problems.

2.1 Potential benefits

A potential benefit of co-capture is the ability to reduce the use of traditional air pollution control equipment by co-capture of some air pollutants with CO_2, followed by geological storage of the mixed gases. This concept has been employed extensively in Western Canada over the past several decades as a cost-effective approach to address acid gases (typically 50:50 mixtures of H_2S and CO_2) from oil and gas production (Alberta Geological Survey, 2009). Air pollution capture at a *new* coal-based power plant often differs depending on the type of generation technology employed. The basic types of generation which should be considered for co-capture analysis are gasification-based systems (IGCC), traditional combustion systems (fluidised bed combustion, FBC, and pulverised coal combustion, PC), and oxyfuel systems (both FBC and PC). Air pollutants from use of the same coal can vary significantly depending on which of these systems is used. The pollutants that vary the most depending on the method of generation are those involving trace amounts of sulphur in the coal. In an IGCC power plant, sulphur is converted primarily to H_2S, a compound which is toxic at relatively low concentrations. For both traditional and oxy-supplied PC and FBC systems, coal sulphur is converted primarily to SO_2, which is also damaging. As indicated in the box below, SO_2 and H_2S can be harmful at concentrations three orders of magnitude lower than harmful concentrations of CO_2. Additionally, when mixed with water, these sulphur compounds become corrosive, with SO_2 leading to greater acidity than H_2S (Singer and others, 2007). Consequently, operations involving even small concentrations of SO_2 or H_2S mixed with CO_2 are likely to receive greater regulatory scrutiny than operations with relatively pure CO_2. The pollution control systems employed, both to capture these traditional pollutants and to capture CO_2, also differ for the different power generation systems. Gasification-based systems generally operate at relatively high pressures and can use physical capture systems for acid gases (such as Selexol or Rectisol). Combustion-based systems on the other hand, tend to use chemical systems with thermal regeneration, such as amines or ammonia for CO_2 capture, or chemical systems without regeneration, such as calcium-based flue gas desulphurisation systems for SO_2 capture. Indeed, the co-capture and storage of CO_2 and SO_2 is likely to require a departure from traditional amine systems, which form heat stable salts from residual SO_2 not removed by upstream SO_2 scrubbers. The situation is complicated further by the prospect that the need to capture CO_2 could lead to altogether new approaches for the capture of traditional pollutants. Potassium carbonate-based sorbents, for example, are much more tolerant of sulphur and nitrogen oxides than amines – enzyme-based capture systems are generally not tolerant of those gases. This process variability by type of power generation and by type of control system requires that co-capture and storage be considered independently for each major method of power generation.

The National Institute for Occupational Safety and Health (NIOSH) US Department of Health and Human Services, is the federal agency responsible for conducting research and making recommendations for the prevention of work-related injury and illness in the USA. NIOSH has established short-term Recommended Exposure Limits (REL) for CO_2 (30,000 ppm, 15 minute average), SO_2 (5 ppm, 15 minute average), and H_2S (10 ppm, 10 minute average). For some chemicals, NIOSH identifies an additional concentration at which the material is 'immediately dangerous to life or health (IDLH)'. For CO_2, the IDLH concentration is 40,000 ppm. For SO_2 and H_2S, the IDLH is 100 ppm. In addition to being harmful to breathe, H_2S is flammable (auto-ignition temperature = 250°C) and is explosive in concentrations between 4% and 44% in air (NIOSH, 2005).

Coal characteristics are another important consideration at the capture site. Table 1 presents coal properties for a typical bituminous coal and subbituminous coal mined in the USA. The approximate proportion of captured gases can be estimated by assuming that all carbon, sulphur, and nitrogen compound emissions are captured. Sulphur compounds are assumed to be completely unabated, except for the co-capture process, and NOx is assumed to be reduced by highly cost-effective measures, such as low NOx burners. Since sulphur can vary in form, depending on the type of generation, both SO_2 and H_2S values are estimated, although both would not

Table 1 Properties of coals used in IECM simulations (IECM Model, Carnegie Mellon University, Ver. 5.2.2)

Coal properties	Bituminous, Illinois No 6	Subbituminous, Powder River Basin
Moisture, %	3.0	30.2
Sulphur, %	3.3	0.4
Hydrogen, %	4.2	3.3
Carbon, %	61.2	48.2
Nitrogen, %	1.2	0.7
Oxygen, %	6.0	11.9
Ash, %	11.0	5.3
Heating value, HHV, kJ/kg	25,353	19,399

Table 2 Potential emissions from example coals

Emission rates	Bituminous	Subbituminous
CO_2, $kgCO_2/GJ$	88.6	91.1
SO_2, $kgSO_2/GJ$	2.6	0.4
H_2S, kgH_2S/GJ	1.4	0.2
NOx, kgNOx/GJ	0.1	0.09
CO_2, m^3/GJ	45.2	46.5
SO_2, m^3/GJ	0.9	0.13
H_2S, m^3/GJ	0.9	0.13
Weight ratio		
$CO_2:SO_2$	34.5	238.7
$CO_2/:_2S$	65.0	449.4
Volume ratio		
$CO_2:SO_2$	50.2	347.2
$CO_2:H_2S$	50.2	347.2
Percentage of total CO_2 and pollutant		
by weight		
SO_2	2.8	0.4
H_2S	1.5	0.2
NOx	0.1	0.1
by volume		
SO_2	2.0	0.3
H_2S	2.0	0.3
NOx	0.2	0.1

be emitted in significant amounts from the same source. Table 2 presents various ways to consider the relative impact of co-capturing sulphur and/or nitrogen compounds with CO_2 emissions (such as by weight, volume, and as a percentage of combined emissions). For example, with the higher sulphur bituminous coal assumed for analysis, co-captured SO_2 or H_2S would constitute 2% of the combined volume of gases (at standard conditions), and co-captured NOx would constitute 0.2% of the combined volume. Percentages are somewhat lower for the subbituminous coal assumed for analysis because of its lower sulphur content, and inherently lower NOx emissions.

Air pollution control and application of CCS at an *existing* coal-fired power plant present different considerations from a green field application. First, the vast majority of existing coal-fired power plants are based on PC technology. Even though one IGCC in the USA used some components of an existing PC unit, widescale reconfiguration of PC plants to IGCC systems is not likely. That limits the possible retrofit CCS configurations to traditional post-combustion arrangements and oxyfuel systems. A second consideration is the presence of existing control technology. For example, in the USA the units most amenable to CCS retrofit are likely to be the units that became operational after 1980, because they have a significant useful life remaining. Generally these units are equipped with SO_2 and NOx controls. The presence of existing control equipment could limit the economic savings possible via co-capture of CO_2 and other pollutants, such as SO_2 or NOx.

The form of future climate change legislation may have a major impact on how CCS investment decisions are resolved at existing power plants. For example, under a pure 'cap and trade' system, CCS technology would be retrofitted only when the levelised cost of CCS is lower than the projected allowance costs over the remaining life of the unit. However, it is possible that regulators will not rely on a pure cap and trade approach, but will also apply performance standards to existing power plants. Such standards would essentially mandate that the units install CO_2-reducing technology, or shut down. The leading climate legislative proposal in the USA in 2009 did precisely this for *new* power plants, but not for existing power plants. (The proposal can be found in section 116 of HR 2454, introduced May 15, 2009. It should be emphasised that HR 2454, at the date of writing, is only a bill and has not been enacted into law.) Under a mandated CCS scenario, the decision process for existing units becomes more complex, as electric power suppliers would have to consider how to generate adequate power to meet customer demand, given the large parasitic power requirements for CCS, space limitations at existing power plants, the cost and time required to construct additional power plants, and other factors. Additionally, legislators may determine that it is appropriate to subsidise CCS installations, either through tax incentives, or by recycling revenues generated by climate change mitigation legislation. These considerations might expand the types of existing power plants deemed appropriate for CCS retrofit. Gaining insight into this decision process is probably best provided by a set of case studies, examining the economics of retrofitting various categories of existing units, and considering alternative capture technologies, including co-capture of CO_2 and other pollutants.

2.2 Emerging capture technologies

A number of innovative technologies are being investigated for the capture of CO_2. For example, an overview of the US Department of Energy (DOE) 'existing plant' CO_2 capture R&D programme identified six membrane-based technology projects, five projects examining new post-combustion solvents (including oligomeric solvents and ionic liquid solvents), and twelve projects evaluating post-combustion sorbents (including zeolites, metal organic frameworks, and carbon sorbents) (Ciferno and others, 2009). Much of this research includes consideration of the effects of contaminant gases, such as NOx and SO_2. For example: membranes tend to be more tolerant of chemical contaminants than traditional solvents; research on metal organic framework sorbents is examining SO_x/NOx reactions during CO_2 compression, and some metal organic frameworks could be physically damaged by reactive species such as H_2S; and oxy-combustion research is considering more SO_2-tolerant metals for boiler construction. Approximately half of US coal-fired generating capacity is not equipped with SO_2 capture systems, and therefore might benefit from a co-capture process.

2.3 Potential economic savings

Savings in the capture process would vary with the type of power generation. For a combustion-based system (such as SCPC), either the SO_2 scrubber or both the SO_2 scrubber and selective catalytic reduction (SCR) system for NOx control could be eliminated. Conventional CO_2 removal technology (which uses amine solvents) would not operate properly due to build-up of heat stable salts, but one can assume that an SO_2, or SO_2 and NOx, tolerant CO_2 capture system could be developed. A slightly greater load would be placed on the CO_2 system, but the savings could be significant. This hypothesis can be quantitatively evaluated using the Integrated Environmental Control Model (IECM) developed by Carnegie Mellon University (available at www.iecm-online.com). Assuming a capture system with costs similar to current amine technology, the cost of SO_2 and post-combustion NOx control constitutes approximately 13% of the total cost of electricity for a CCS-equipped SCPC burning a 3% sulphur coal. For a subbituminous coal, the fraction of total cost is about 8%. (For a subbituminous system, the savings are less because there is less SO_2 to capture from the lower sulphur coal.) Only a portion of these costs could be avoided by a combined CO_2-SO_2-NOx capture system, because the combined capture system would cost a little more than a 'CO_2-only' system. Note that these percentages assume use of the relatively costly CCS systems currently available. If the CCS equipment costs were reduced significantly via research on new capture systems, the resulting potential savings of co-capture and storage expressed as a percentage of the cost of electricity would increase proportionately. Key inputs and outputs for the IECM simulation scenarios are presented in Table 3.

For a gasification-based power plant (such as IGCC), the mechanical trade-offs are different. In this case, one could assume capture of both H_2S and CO_2 by a Selexol process. Here, the primary savings available for sulphur are elimination of the Claus plant and tail gas clean-up system (and not the Selexol system used for H_2S), although there could be additional savings from capturing both CO_2 and H_2S in a single Selexol vessel. The IECM model assumes that regulatory requirements for NOx can be met without use of

Table 3 Results from IECM simulations

Scenario	Design	Fuel	Control equipment			Emissions, g/GJ		
			S	N	CO_2	SO_2	NOx	CO_2
1	SCPC	Bit	W-FGD	SCR	N	56	21	90,300
2	SCPC	Bit	W-FGD	SCR	Y	0.4	21	9030
3	SCPC	Sub	SDFF	SCR	N	33	21	90,300
4	SCPC	Sub	SDFF	SCR	Y	0	21	9030
5	IGCC	Bit	Selexol	Comb	N	54	8	86,000
6	IGCC	Bit	Selexol	Comb	Y	59	9	7310
	Capacity	Output	Heat rate	Cost of electricity		SO_2 cost	SCR cost	S&N cost
	MW net	GWh/y	kJ/kWh	\$/kW	\$/MWh	\$/MWh	\$/MWh	% of total
1	453	2979	9394	1708	63.4	9.46	2.49	18.8
2	342	2246	12,460	2876	120.0	12.55	3.30	13.2
3	463	3046	9483	1663	60.0	4.03	2.54	11.0
4	345	2274	12,702	2840	114.3	5.39	3.41	7.7
5	542	3560	10,437	2016	68.6	4.01	0	5.8
6	478	3147	12,259	2893	103.9	5.39	0	5.2

Bit	Illinois, No 6 bituminous coal, 3.25% S, 11,500 kJ as received
Sub	Wyoming Powder River Basin subbituminous coal, 0.4% S, 9284 kJ as received;
SCPC	500 MW gross supercritical power plant
IGCC	Integrated gasification combined cycle power plant, 630 MW gross capacity without CO_2 capture, 590 MW gross with CO_2 capture system
SDFF	spray dryer fabric filter control for SO_2 reduction
W-FGD	wet flue gas desulphurisation system for SO_2 reduction
SCR	selective catalytic reduction system for NOx control
Comb	NOx control via combustion modifications

SCR. Hence, although the total cost of sulphur control at the IGCC is about 5% of the cost of electricity, the savings estimated for co-capture of CO_2 and H_2S would be somewhat less. Additionally, the value of captured elemental sulphur is not inconsequential, and would be lost if a combined CO_2-H_2S system were employed. On the other hand, without the Claus plant, the facility would not need to manage concentrated H_2S, which presents a fire and explosion risk in concentrations of 4–44% in air.

An oxygen-fed SCPC system (oxyfuel) presents somewhat different issues regarding co-capture of CO_2 and traditional pollutants. An SO_2 control system may be necessary for a high sulphur coal in order to reduce furnace SO_2 to a level acceptable in a recirculating flue gas system, where pollutants tend to become highly concentrated. For a low sulphur coal, it may be possible to forgo an SO_2 capture system without damaging the boiler. Alternatively, for a fluidised bed combustion system with in-bed sulphur recovery, it may be possible to forgo a flue gas polishing system for additional SO_2 removal. These are appropriate systems for further analysis.

There are additional economic considerations related to co-capture and storage at existing power plants. A major barrier to retrofitting CO_2 capture systems at an existing unit is the large amount of water consumption needed for cooling CO_2-laden solvent after it has been heated to force the release of CO_2. It is roughly equivalent to the water consumption of the power plant before capture of CO_2. A second barrier is the space required for the capture and compression system. It is possible that co-capture can combine multiple capture systems within a single unit operation, and reduce the total space and water consumption of traditional approaches to capture CO_2, SO_2, and NOx. At present, the degree to which co-capture and storage can reduce overall water use and space requirements for multiple pollutant capture systems at a power plant is unknown, but it will be an important area for future research.

An additional issue which could be associated with oxyfuel systems relates to the composition of the captured gas mixture. Sass and others (2009) report that the captured gases could contain roughly 20% nitrogen. The presence of nitrogen would reduce the gas density, require additional compression, and could make the gas stream unacceptable in some pipelines or for EOR applications due to its reduced miscibility with oil.

2.4 Potential problems

Cost is the greatest barrier to use of CCS technology, with or without co-capture and storage. Important findings of this analysis are that co-capture presents a modest cost reduction *potential*, compared to the total cost of capture, when considering the relative costs of current technologies at new facilities. In addition, factors outside the scope of a generic cost analysis can be quite important, particularly for retrofit applications. These factors include land requirements and cooling water demand for pollution capture systems. As a result, the relative cost, land requirements, and water requirements (which are closely tied to parasitic power consumption) of currently available CO_2 capture technologies present barriers to co-capture. The broad slate of emerging capture technologies and those at the research stage will no doubt focus on these key parameters, and success could dramatically enhance the economic value of co-capture.

As noted above, current amine capture systems require low levels of SO_2 and NOx in the flue gas, in order to avoid the formation of heat stable salts, which consume the amine sorbent in a non-regenerative form. Similar problems could be associated with emerging control technologies which might be economically or environmentally attractive. For example, Haritos and others (2009) report that enzyme systems could act directly as a CO_2 sorbent, or reduce the relatively large parasitic power requirements needed to regenerate amine solvents. But enzymes can be sensitive to co-captured compounds (Haritos and others, 2009). Improved sorbents, or other capture media, which are tolerant of sulphur and nitrogen species in the treated gas stream are a key research need if co-capture is to be practical for traditional combustion systems.

3 Transport systems

There is no obvious benefit to transporting mixed gases, with the possible exception of reduced viscosity. Therefore, the discussion on transport will focus entirely on concerns and potential problems associated with transporting CO_2 with other gases, such as H_2S or SO_2.

Transport of large volumes of CO_2, such as the volume emitted from a power plant, will almost certainly be by pipeline. Mixed gases present three key issues for pipelines:

- The gases can have different phase characteristics (that is, existing as a liquid or a gas at a given temperature and pressure), which presents multiple problems for a pipeline.
- The contaminant gases, primarily H_2S and SO_2, pose greater health and safety concerns than CO_2 does.
- Other contaminants harmful to pipelines could be captured along with CO_2, nitrogen species, and sulphur species. For example, pipelines generally prohibit even small concentrations of water vapor or oxygen, due to concerns about corrosion. Contamination by water and oxygen are problematic for CO_2 pipelines, even without the co-capture of sulphur and nitrogen species.

In general, sulphur compounds do not present corrosion issues for steel pipelines if the gas is sufficiently free of water. Kinder Morgan has limited water content of CO_2 pipelines to 30 pounds of water per million cubic feet of gas (0.38 kg/million m^3), and oxygen content to 10 ppm, by weight (Havens, 2008). Water can also present problems for systems upstream of the pipeline, where hydrates can form and plug equipment. Svensson (2005) cites King as recommending a limit of 0.4 g/m^3 of gas, but it does not appear that the maximum practical tolerance for moisture has been clearly established for a CO_2 stream with multiple contaminants. This matter presents a useful area for further investigation. Moreover, most investigation has focused on H_2S, not SO_2. Moisture and SO_2 limits for pipelines with mixed fluids merit specific attention, and it may be useful to consider alternative alloys for SO_2-laden fluid streams. The issue of oxygen content in the fluid mixture should not be overlooked. Any significant infiltration of air into an oxy-combustion system, or the presence of excess oxygen to ensure complete combustion, would require oxygen scrubbing of the flue gas prior to transfer to a pipeline.

Perhaps the most relevant publications on managing mixtures of CO_2 and H_2S have been published by Bachu and Gunter (2005). They have described Canadian experiences of the capture and injection of CO_2 and H_2S from natural gas processing plants. These Canadian acid gas injection projects have been operated successfully for two decades, although at a smaller scale than a typical project for a coal-fired power plant. The authors emphasise the importance of avoiding a two-phase region for the captured gas mixture. During gas compression, operating with two phases can lead to cavitation, which can damage compressor hardware. Generally, corrosion is not a problem because the interstage cooling tends to dewater the gases. Interstage cooling is part of the compression needed to achieve the high pressures required for deep injection. CO_2 would combine with available water to form corrosive carbonic acid even without mixed gases, so it is essential to eliminate water from the gas stream in any event.

The Alberta Geological Survey website presents useful graphical information on the phase behaviour of CO_2, CH_4, H_2S, and a 50:50 mixture of CO_2 and H_2S, at a range of pressures and temperatures relevant to CO_2 capture, transport, and storage (Alberta Geological Survey, 2009). In general, somewhat higher operating temperatures (above 35°C) are necessary during compression of mixtures of CO_2 and H_2S to avoid formation of hydrates where there are significant amounts of water present in the mixed gas stream. CO_2 pipelines place moisture limits on transported gases to avoid corrosion problems, and typically operate at 14-20 MPa (compared with 4–8 MPa for natural gas pipelines) (Havens, 2008). Gas-phase operation would require compression-based systems instead of more efficient pump-based systems. Even when dealing with pure CO_2, a small change in working conditions when near the critical point (7.4 MPa and 31°C) can lead to large changes in density. For example, Svensson and others (2005) report that the density of CO_2 doubles for a decrease of 10°C for CO_2 initially at 47°C and maintained at a constant pressure of 9 MPa. Such a change would have an impact on the hydraulic properties of CO_2 in a pipeline. Hence, gas-phase transmission of CO_2, or CO_2 with other gas-phase compounds, is impractical. Sass and others (2009) note that for natural gas pipelines, the presence of even a small amount of heavier hydrocarbons will necessitate additional engineering analysis. They report that both fluid viscosity and fluid density vary with different concentrations of gases mixed with CO_2 at pipeline and injection well pressures, and that the resultant transport properties of mixed fluids can be difficult to predict over a wide range of conditions.

Various purity specifications for CO_2 transported by pipeline are available in the literature. For example, the Intergovernmental Panel on Climate Change (IPCC) reported a specification for delivery to the Canyon Reef Carriers pipeline that limited gas composition to $\leqslant$1500 ppm by weight of H_2S; and $\leqslant$1450 ppm by weight of total sulphur (IPCC, 2005). A separate specification, for a different Kinder Morgan pipeline, limited H_2S to $\leqslant$20 ppm, and total sulphur to $\leqslant$35 ppm (Svensson and others, 2005). The pipeline between Dakota Gasification's SNG facility and the Weyburn EOR field in Canada limits H_2S to 0.9%, by volume (9000 ppm) (Riley, 2003). Alberta acid gas injection systems transport mixtures of CO_2 and H_2S, which average about 50% H_2S, for distances of 100 m to 20 km (Bachu and Gunter, 2005). In addition to issues of corrosion and safety, the intended use of the CO_2 can influence the limits on permissible contaminants in a CO_2 pipeline. For CO_2 being transported for EOR use, the amount of nitrogen and hydrocarbons may be limited, and a minimal level of CO_2 (for example 95%) may be required to ensure minimum miscibility pressure.

The most obvious health and safety concern regarding pipeline transport of CO_2 with other gases is the possibility of exposure of people to elevated concentrations of H_2S or SO_2, in the event of a leak or rupture of a pipeline. As noted in Chapter 2, the 10–15 minute average recommended exposure limits for are 5 ppm for SO_2 and 10 ppm for H_2S, as established by NIOSH. In contrast, the 15 minute average exposure limit for CO_2 is 30,000 ppm. Concentrations deemed 'immediately dangerous to life or health' are 100 ppm for SO_2 and H_2S, and 40,000 ppm for CO_2 (NIOSH, 2005). Additionally, although CO_2 and SO_2 are not flammable, H_2S is flammable or explosive at concentrations ranging from 4% to 44% in air. However, this is not a practical problem for power plants, because the concentration of H_2S in CO_2 would be below 4% (not counting the dynamic mixing with air of the highly pressurised fluid mixture in the event of a sudden release), but it could be an issue for other source categories, with a larger $H_2S{:}CO_2$ ratio. Clearly, relatively pure CO_2 presents a lesser risk than mixed gases unless the sulphur compounds are a very dilute portion of the mixed gas. The World Resources Institute's (WRI) report on CCS guidelines concluded that 'pipelines containing H_2S will require extra due diligence, particularly near populations.' WRI observes that the pipeline connecting the Dakota gasification plant in North Dakota to the Weyburn EOR field in Saskatchewan is a 'Type III' pipeline, requiring additional operational precautions compared to 'Type II' pipelines which restrict H_2S to less than 20 ppm, by weight (Forbes and others, 2008). Appropriate protocols and safety procedures would need to be developed for such pipelines because of limited experience with pipelines carrying SO_2 fluid mixtures under pressure.

In the USA, CO_2 pipeline safety is subject to regulation by the Department of Transportation, which groups CO_2 with 'hazardous materials', but which does not define CO_2 as a hazardous material (US Code of Federal Regulations, 2004a). In practical terms, this means that a higher level of pipeline inspection, and certain other more stringent rules typically reserved for hazardous materials, also apply to CO_2 pipelines, but the moniker of 'hazardous' is not attached to CO_2 (Doctor and Molburg, 2006). A specific concern with CO_2 pipelines is the dramatic cooling which can occur due to a leak, which can cause failures beyond the initial cause of the leak if the construction materials (for example, valve parts and 'O' rings) are not properly selected.

4 Injection and storage

Nearly pure CO_2 can behave in various ways in storage. For example, Benson and Cole (2008) report that as CO_2 goes into solution with brine, the weak acid can dissolve rock carbonates increasing porosity, while later reactions with feldspar can result in carbonate precipitates which decrease porosity. Hence, it is not surprising that mixtures of fluids with different acid complexes can lead to a variety of chemical reactions in differing types of formations, and at different concentrations within the same formation.

4.1 Modelling and experimental work on storage

Xu and others (2008) have used computer models to evaluate the effects of injecting mixed gases versus relatively pure CO_2 into sandstone formations. Modelling was selected rather than empirical observation due to the long time periods needed to observe significant change. Mixtures of 96.5% CO_2 and 3.5% SO_2, and 98.1% CO_2 and 1.9% H_2S (by weight) were assumed. Table 2 (on page 9) shows that an Illinois No 6 coal would yield comparable concentrations; however a Powder River Basin coal would yield about one-tenth of the concentrations due to its inherently low sulphur content. In general, Xu and others (2008) found that: 'the co-injection of H_2S, compared to injection of CO_2 alone, does not significantly affect pH distribution, mineral alteration, or CO_2 mineral sequestration. The co-injection of SO_2 results in a substantially different pH distribution and mineral alteration.' The changes projected for gases with SO_2 included a more strongly acidified zone near the simulated injection point, and precipitation of sulphates at a radial distance of 50–150 m. Carbonate precipitation is projected to occur beyond this more acidified zone. Ultimate carbonate precipitation (mineral trapping of the CO_2) is similar for both the nearly pure CO_2 simulation and the CO_2/SO_2 simulation, reaching maximum levels in about 10,000 y. Xu and others (2008) found that, for the conditions simulated, most SO_2 is converted to sulphate by alunite precipitation. H_2S converts to pyrite. Both the sulphur reactions occur in about 100 y, a much shorter period than carbonate reactions. Xu and others (2008) attributed this to the much lower amounts of sulphur injectate and the lower pH near the injection point. The SO_2 caused a projected increase in porosity from 0.3 to 0.43 after 100 y near the injection point. Porosity decreased at the acidification front, due to sulphate precipitation. However, porosity outside the more highly acidified zone was 0.28 for both the nearly pure CO_2 and the CO_2/SO_2 simulation, and was driven by carbonate precipitation.

Xu and others' (2008) findings are also relevant to possible well bore reactions. In their simulations, 100 y after injection ceased, pH was roughly 4–5 for CO_2 only, and approximately 3.8–5 for the CO_2-H_2S mixture, for distances up to 100 m from the well bore. In contrast, the CO_2-SO_2 mixture was predicted to have a pH of 0 over the same distances. This suggests that CO_2-SO_2 mixtures may be much more aggressive in their interaction with well piping and the cements plugging the well after injection ceases, and may cause difficulties during a lengthy injection period. More research is warranted into these effects on materials, both for aqueous-phase reactions, and for formation water solvated in liquid or supercritical CO_2-SO_2 mixtures, as described by McGrail and others (2009).

Schaef and others (2009) exposed five different basalt rocks to CO_2 and CO_2/H_2S mixtures in laboratory experiments simulating deep geological conditions over periods of 6 to 45 months. Different basalts reacted differently to the CO_2 exposure conditions. Moreover, when H_2S was added, reactivity among the basalts changed dramatically. The authors concluded that 'reaction products in a CO_2/H_2S sequestration system are dependent on the type of geologic formation.' In general, they found that 'supercritical CO_2 injected into subsurface basalt formations is expected to dissolve into the formation waters, react with basalt, and subsequently precipitate as carbonates.'

Bacon and others (2009) reported results from numerical modelling of CO_2 and SO_2 into deep saline formations near the AEP Mountaineer power plant in West Virginia, USA. An injection period of 4 y and a recovery period of 100 y were simulated for a sandstone and a dolomite formation. The CO_2 led to dissolution of calcite and, to a lesser extent, dolomite. Co-capture and storage of SO_2 and CO_2 means that theoretically ferric iron in the formation could provide the oxygen needed to form sulphates from the SO_2, which could form precipitates and clog pores, thus reducing injectivity. For the simulation of a mixed fluid, 1% (by weight) SO_2 was assumed to be added to the CO_2 stream. The additional SO_2 led to a small increase in the amount of anhydrite already present in the formation, so the change did 'not result in significant changes in porosity or permeability near the well.'

Bachu and others (2008) offer an empirical view of formation chemistry, and the impact of acid gases. Acid gas injection into the Wabamun Group formation was started in 1994 and continues, with over 60,000 t of acid gas injected. The gases are primarily from 'sour' oil and natural gas processing plants and include relatively high (for example 50%) concentrations of H_2S. Formation water is almost stagnant for the reservoir studied. This means that movement of the injected gas is the result of injection pressure, for motion near the injection well, and buoyancy, since the injected gas is less dense than the brine in the formation even under liquefying pressure. Once outside the volume influenced by the injection well pressure, the migrating gas velocity is estimated to be 0.1–1 m/y. The authors conclude that the gas will almost certainly react and will be trapped prior to escaping the storage reservoir via natural migration, although that trapping process might take a very long time. The existence of wells into the formation is seen as a more probable means for possible leakage. The authors note that acid gases dissolve readily in the formation water, creating weak carbonic and sulphuric acids, and lower pH that accelerates water-rock reactions. Either rock dissolution or precipitation can occur, depending on local conditions, and these effect porosity in opposite ways. 'Dissolution of some of the rock matrix in carbonate strata, or of the carbonates surrounding the sand grains in sandstone units, results in lower injection pressures in the short term.' However, reduced injectivity could result from fines migration, precipitation, and other factors. At the time of the original paper little subsurface monitoring was required, so the ultimate fate of the injected gases was unknown.

In a separate analysis, Bachu and others (2008) reviewed the behaviour of mixed gases, including a mixed gas more closely analogous to gases from a coal gasification process (98% CO_2, 2% H_2S). In fresh water, H_2S solubility is roughly twice that of CO_2. The gas solubility seemed to increase with the volumetric fraction of H_2S, and the H_2S dissolved more readily than CO_2. As a result, CO_2 breakthrough occurred before that of H_2S in laboratory simulations, confirming a field observation in a depleted gas reservoir in Alberta. The implications for long-term risk profiles due to mixed-gas injection could be significantly different to those for pure CO_2 injection. It is generally assumed that solubility trapping due to CO_2 dissolution in aquifers would lower the long-term risks of CO_2 release. Using static solubility experiments, Bachu and others (2008) found that the volume of dissolved CO_2 decreased by 33% when the H_2S concentration increased from 0% to 50%. In an aquifer where H_2S tends to dissolve preferentially compared to CO_2, the presence of dissolved H_2S may result in larger quantities of CO_2 remaining in the supercritical/gas phase, thereby altering the leakage risks. Therefore, the long-term risk profile of mixed-gas injection could be significantly different from that for pure CO_2 injection if a large fraction of the injected gas were H_2S. However, changes in dissolved CO_2 should be much less than 33% for the range of concentrations likely from coal-based power plants.

Knauss and others (2005) reported that co-injecting large amounts of H_2S with CO_2 would not impact injectivity, but that co-injection of SO_2 could reduce injectivity if conditions favour sulphate precipitation.

Harju (2008) reported early results from a study of the Zama (Alberta) acid gas EOR/sequestration project. The multi-sponsor project is seeking to validate the storage of a CO_2/H_2S mixture in a depleted (carbonate) oil reservoir. The injected gases are 70% CO_2, 30% H_2S. Initial results echo the views of Bachu and others (2008) that the potential for migration to shallower strata, including potable ground water, is minimal because any leakage migration would require thousands of years, and be overtaken by 'dissolution, dispersion, and residual gas trapping along the migration pathway.'

The FutureGen Alliance has proposed co-capture and storage experiments to be conducted at the FutureGen facility. The Alliance conducted a simulation of co-capture and storage from the proposed facility to evaluate the potential environmental impacts of the experiments (FutureGen Alliance, 2006). Similar to the calculations in Chapter 2, the simulation assumed gasification of Illinois No 6 bituminous coal, resulting in a mixed fluid stream of about 2% H_2S and 98% CO_2. The analysis assumed a one week injection pulse of this mixture at an injection rate of 2.5 Mt/y. The simulation estimated concentrations of H_2S at the caprock seal to drop to about 100 ppm within one year after the pulse, and geochemical modelling did not indicate any changes in the starting partial pressure (concentration) of the H_2S due to dissolution or reactions with caprock minerals.

It is obvious that storing CO_2 and other gases will require more volume than the CO_2 alone. This volumetric imperative is not significant for trace gases, but would be significant if flue gases from traditional combustion were stored, due to the large volume of nitrogen present in flue gases. An evaluation of storage of oxy-combustion products concluded that the combustion products could contain 16–21% nitrogen (and 58–76% CO_2) (Sass and others, 2009). Moreover, the density of the injected gases could be significantly reduced by impurities, particularly nitrogen. Avoiding dual phase gas flow could require up to 20% greater compression than CO_2 alone, which also suggests a deeper injection formation to ensure dense-phase storage and minimal volumetric requirements. An example by Battelle (Bacon and others, 2009) cited a midwestern US location, which would be suitable for pure CO_2 at a depth of 800 m, but would require an injection depth of 1200–1500 m for the assumed oxy-combustion gases. An additional concern for nitrogen-rich mixed fluids is that nitrogen is inert and will not react with rock formations as CO_2 will. Over a long period of time, the lack of nitrogen reaction will result in a fluid mixture that is increasingly concentrated in nitrogen. The fluid could then shift to two phase, expand significantly, consume more reservoir space, and disperse the plume over a greater volume. This may increase the need for research to avoid the greater capture of nitrogen in the first place, or to remove nitrogen prior to injection in a manner that does not introduce unacceptable additional cost.

McGrail and others (2009) suggest that research has generally not addressed the behaviour of water bearing supercritical fluids. Understanding the behaviour of CO_2 dissolved in formation water is important, but it is also important to understand reactions involving the injected CO_2 mixture in its supercritical state, and mixed with formation water. One reason for this is that dissolved CO_2 tends to sink, whereas supercritical CO_2 tends to rise, where it could potentially reach and react with caprock. Corrosion principles differ for supercritical mixtures versus aqueous mixtures of gaseous CO_2. In laboratory experiments, McGrail and others (2009) found faster corrosion with the supercritical CO_2 than for aqueous CO_2 gas mixtures, and that addition of H_2S caused further acceleration. The H_2S/CO_2 mixture also reacted with reservoir rock, suggesting that supercritical mixtures could 'self seal' small fissures in caprock via mineralisation reactions producing precipitates. Current geological models do not address these reactions.

Use of CO_2 for beneficial purposes such as EOR, could benefit, or suffer, from the presence of contaminant gases. For example, Sass and others (2009) report that SO_2 is generally believed to be beneficial for EOR, while NOx is detrimental; but at expected power plant concentrations, neither is likely to affect recovery rates. On the other hand, high concentrations of nitrogen generally are prohibited in pipelines intended for

EOR because nitrogen can adversely impact the miscibility of CO_2 and oil, which can reduce oil recovery (Doctor and Molburg, 2006).

4.2 Regulatory framework

Aside from the chemistry of co-capture and storage, there are significant issues related to the regulatory framework for managing the storage of gases that are predominantly CO_2, but which also include other compounds. On 25 July 2008, the US EPA proposed rules governing the injection of CO_2 into saline formations within the United States (US EPA, 2008). The EPA expressed the concern that 'there may be a risk that co-contaminants [hydrogen sulphide, sulphurous and nitrous oxides] in the CO_2 stream could endanger an underground source of drinking water (USDW) if the injectate migrates into a USDW' (US EPA, 2008). The proposed rule implied that low concentrations of impurities would be acceptable, but defined the 'carbon dioxide stream' to exclude hazardous wastes, as set forth under 40 CFR Part 261 (US Code of Federal Regulations, 2004b). Additionally, the EPA proposed rule raised the question: 'Is injected CO_2 considered a hazardous substance under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA)?' The proposed rule noted that CO_2 is not hazardous under CERCLA, but that the CO_2 stream could include other substances which are. For example, mercury is a defined hazardous waste, and SO_2 in injected gases could form sulphuric acid, which is also a hazardous waste (US EPA, 2008). Exactly how the USA ultimately addresses this issue will be decided by either a final rule under the UIC programme, or additional federal legislation.

Similarly, a 2006 amendment to the London Protocol, which is an international agreement for protecting the ocean environment, specifically allows CO_2 injection 'into a sub-seabed geological formation,' but only if the injections 'consist overwhelmingly of carbon dioxide. They may contain incidental associated substances derived from the source material and the capture and sequestration processes used.' The Protocol further requires that: 'no wastes or other matter are added for the purpose of disposing of those wastes or other matter' (UN IMO, 2006).

In 2009, the Parliament of the European Union adopted a Directive addressing geological storage of CO_2. The language notes that EU Directive 2008/1/EC 'further ensures that best available techniques to improve the composition of the CO_2 stream have to be established and applied.' Moreover, Article 12 of the Directive (*see box*) implies that the EU will limit the amount of non-CO_2 species that can be co-stored. The term 'incidental associated substances' may be further defined by subsequent EU guidelines (OJ, 2009).

Article 12

CO_2 stream acceptance criteria and procedure

1. A CO_2 stream shall consist overwhelmingly of carbon dioxide. To this end, no waste or other matter may be added for the purpose of disposing of that waste or other matter. However, a CO_2 stream may contain incidental associated substances from the source, capture or injection process and trace substances added to assist in monitoring and verifying CO_2 migration (OJ, 2009).

4.3 Potential benefits

The preceding discussion of the possible impacts of co-storage on storage reservoirs leads to few narrow certainties and many broad generalities which merit further research. Three types of benefits appear to be possible from injection of mixed gases, compared to relatively pure CO_2:

- Improved permeability of the storage reservoir, particularly near the injection point.
- Production of chemical precipitates which could 'self-seal' small fissures which would otherwise allow the stored gases to escape the intended containment region.
- Chemical reactions that reduce the mobilisation of harmful species contained in the formation zone prior to injection.

4.4 Potential problems

As is the case with potential reservoir benefits resulting from co-storage, potential problems with co-storage warrant further study. Potential problems tend to mimic the reverse of potential benefits: that is, geological chemistry which might reduce the porosity of the storage reservoir, interfere with beneficial uses like EOR, or increase the mobilisation of harmful species in the geological zone. Additionally, impurities can reduce the density of the injected gases, which can lead to the need for deeper injection depths to maintain dense phase fluids, increased buoyant forces on the caprock, greater storage volume requirements, and increased compression requirements due to the reduced 'static head' of the column of gases in the injection well. Finally, there is a realistic risk that the presence of additional gases in the CO_2 injection stream may trigger more stringent regulation of the injected gases than would apply to CO_2 alone, create potential liabilities under laws governing hazardous waste disposal, or provide a basis to prohibit the storage activity altogether.

5 Conclusions

The current state of science on the capture, transport, and storage of CO_2 mixed with other fluids does not support broad generalisations. The gases likely to be captured along with CO_2 vary significantly between traditional PC power plants, IGCC power plants, and oxyfuel power plants. Moreover, capture systems themselves, which can be adversely impacted by efforts to co-capture, are evolving over time. Pipelines can tolerate a large range of fluids, but pipeline owners may restrict gas composition depending on the end use for the dominant CO_2 gas (EOR versus saline storage), and on other factors. The greatest unknowns relate to the portion of CCS that is most remote from sensors: the storage media. There, the behaviour of mixed fluids, as compared to nearly pure CO_2, is known to vary by rock formation (for example, sandstone versus carbonate), trace materials within the formation, and distance from the point of injection. Indeed, it appears that mixed injectate could either enhance flow through small fractures in a formation (leading to undesired leakage of the CO_2 mixture beyond the intended containment volume), or have exactly the opposite effect and plug the fracture with precipitates, or have both effects at different distances from the injection well. More research is needed in all of these areas to determine even the most fundamental question: does co-capture and storage help or hurt the storage integrity of CO_2?

The potential economic savings of co-capture, as much as 13% of the total levelised cost of a CCS-equipped power plant, the potential for improved structure permeability, and the prospect of 'self-sealing' injectate, warrant further investigation of co-capture and storage options. Likewise, the potential for adverse impacts of mixed gas storage merit further investigation of possible adverse impacts of co-storage on the storage matrix and underground resources, including drinking water supplies.

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