Good plant design and operation for onshore carbon capture installations and onshore pipelines

GOOD PLANT DESIGN AND OPERATION FOR ONSHORE CARBON CAPTURE INSTALLATIONS AND ONSHORE PIPELINES

A Recommended Practice Guidance Document

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FOREWORD

In 2006, the Department of Business, Enterprise and Regulatory Reform (formerly the DTi and now within the Department of Energy and Climate Change) asked the Health and Safety Executive (HSE) to determine if there were any health and safety concerns relating to the deployment of large scale carbon capture and storage (CCS) technology in the UK.

The HSE carried out a significant review of all aspects of the carbon capture and storage chain from the various capture technologies through to the injection points on the offshore platforms. Part of this process involved approaching the Energy Institute (EI) and jointly organising a number of workshops to identify the key areas for development. The workshops identified a number of areas which it believed merited greater attention.

These concerns can be split into two broad subject areas:

1. Modelling the dispersion of any leak of carbon dioxide appropriately, and

2. Ensuring good practice from industrial gases sectors is fed into the UK CCS industry and is adequate and appropriate for this new industry.

Modelling the dispersion of carbon dioxide

The HSE was concerned that the commercial models available to model the dispersion of gases were not validated for carbon dioxide which has particular thermodynamic properties. As a result, any dispersion modelling using these commercial models may not be accurate and without any validation of the models, it would be impossible to use them with any confidence. In identifying this as a need for development, the HSE and EI set about establishing a joint industry group to develop guidelines on 'Hazard analysis for onshore carbon capture installations and onshore pipelines'.

Ensuring good practices are used in the CCS industry

Carbon dioxide has particular properties which affect the choice of materials and plant design. Although many of these issues are well understood by the industrial gases sector, they are not 'business as usual' for the CCS industry. For example, elastomers are commonly used in seals in the power generation and oil and gas industry, but cannot be used for carbon dioxide as they explode when rapidly depressurised.

In response to the concerns raised by the HSE, the Energy Institute (EI) formed an industry group to work with the HSE to resolve the issues raised. The work forms two discrete documents: (Document 1) *Technical guidance on hazard analysis for onshore carbon capture installations and onshore pipelines*; and (Document 2) *Good plant design and operation for onshore carbon capture installations and onshore pipelines*.

This document is intended for guidance only and is intended to improve the industry's knowledge, to assist developers and operators to carry out hazard analysis, and procure and manage their plant safely. While every reasonable care has been taken to ensure the accuracy and relevance of its contents, the EI, its sponsoring companies, section writers and the working group members listed in the Acknowledgements who have contributed to its preparation, cannot accept any responsibility for any action taken, or not taken, on the basis of this information. The Energy Institute shall not be liable to any person for any loss or damage which may arise from the use of any of the information contained in any of its publications.

This publication will be reviewed in the future and it would be of considerable assistance for any subsequent revision if users would send comments or suggestions for improvements to:

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The project was coordinated by Isabelle McKenzie, CCS Technical Manager, Energy Institute.

1 INTRODUCTION

This section explains who this publication is intended for, what this publication covers, what it does not cover and why it has been produced.

Who is *Good plant design and operation for onshore carbon capture installations and onshore pipelines for*?

This publication provides information for:

- Project engineers and managers who are procuring new CCS installations and pipelines.
- Engineering designers involved in the design of CCS installations.
- CCS industry participants who wish to widen their knowledge of CCS technology and the properties of carbon dioxide.

What does this publication cover?

This publication provides information on:

- CCS technology options.
- The extent and scale of developing CCS technology options.
- The fundamental properties of carbon dioxide and the impact that has on plant design, operation and safety including catastrophic loss of high inventory equipment such as transmission pipelines.
- Some design and operational considerations for onshore installations.
- Some design and operational considerations for onshore pipelines.

Why the need for this publication?

This publication has been prepared to:

- Provide a basic guide for participants involved in the CCS industry.
- Communicate existing knowledge on plant design and operation from the industrial gases sector into the CCS sector and identify the limitations of such knowledge for CCS applications.
- Communicate existing knowledge on pipeline design and operation from the industrial gases sector into the CCS sector where applicable and identify areas of uncertainty where such knowledge cannot be applied with sufficient confidence considering the scale and nature of expected CCS operations in the future.
- Allow engineers and project managers involved in CCS projects to widen their knowledge base to ensure that procurement of equipment and operational guidelines are using the best available knowledge.

What does this publication not cover?

- This publication does not cover offshore installations or transportation to offshore installations via pipeline or ship.
- This publication does not cover onshore transportation by tanker or any onshore related infrastructure for onward ship transport.
- This publication only examines plant design and operational issues relating to carbon dioxide and provides no guidance on other materials routinely found within CCS installations such as amines, oxygen or ammonia.

- CCS research and technology application is multiplying rapidly at the present time; this means that some of the information contained within this report will be superseded by later research and we would encourage all participants within the CCS industry to endeavour to keep abreast of CCS developments
- It does not provide an exhaustive guide to all aspects of CCS plant design and operation and is no substitute for employing competent engineers and suppliers
- This publication does not provide design and operating information for non-CCS related uses of carbon dioxide

Where can I find further information?

If what you are looking for is not outlined above, you might not find it within this publication. Other sources of information are listed in the References section.

2 OVERVIEW OF CARBON DIOXIDE

An overview of carbon dioxide – by the end of this section you will:

- understand the thermodynamics of carbon dioxide including understanding the implications of impurities on the underlying thermodynamics;
- understand the key properties of liquid carbon dioxide;
- understand the key properties of supercritical carbon dioxide;
- have an appreciation of some of the hazards of carbon dioxide;
- understand the implications of carbon dioxide and hydrocarbon mixtures, and
- understand how a 'boiling liquid expanding vapour explosion' (BLEVE) event could occur.

2.1 GENERAL PROPERTIES AND USES OF CARBON DIOXIDE

Carbon dioxide gas is found in small proportions in the atmosphere (about 385 ppmvd); it is assimilated by plants which in turn produce oxygen by photosynthesis. It is produced from the combustion of coal or hydrocarbons, the fermentation of liquids and the breathing of humans and animals. Humans exhale carbon dioxide at approximately 4,4 % v/v. Carbon dioxide is also found beneath the earth's surface, and emerges during volcanic activity, in hot springs and other places where the earth's crust is thin. It is found in lakes at depth under the sea[1], and comingled with oil and gas deposits.

Carbon dioxide comprises two oxygen atoms covalently bonded to a single carbon atom, with an O-C-O angle of 180°. As such it is very stable, no process other than photosynthesis having been discovered that is able effectively to reduce carbon dioxide to carbon monoxide. Carbon dioxide is not classified by the UN as toxic[2].

Carbon dioxide is widely used commercially. It is used in the chemicals processing industries to control reactor temperatures, to neutralise alkaline effluents and used under supercritical conditions for purifying or dying polymer, animal or vegetal fibres.

In the food and beverage industries, carbon dioxide is used for carbonation of fizzing beverages such as soft drinks, mineral water or beer, for packaging of foodstuffs, as a cryogenic fluid in chilling or freezing operations or as dry ice for temperature control during the distribution of foodstuffs. Caffeine is removed from coffee using supercritical carbon dioxide.

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[1] '*Lakes of CO_2 in the deep sea*', Kenneth Nealson, Department of Earth Sciences, University of Southern California, 19 September 2006.

[2] Globally Harmonised System of Classification and Labelling of Chemicals, 2007 part 3: Health Hazards.

In the medical field, carbon dioxide produces close-to-physiologic atmospheres for the operation of artificial organs. Carbon dioxide is used as a component in a mixture of oxygen or air as respiratory stimulant to promote deep breathing. It is also used for the surgical dilation by intra-abdominal insufflations.

Industrially, carbon dioxide is typically used for process control, examples of which include the use of carbon dioxide for red fume suppression during scrap and carbon charging, for nitrogen pick-up reduction during electric arc furnace tapping and for bottom stirring. In non-ferrous metallurgy, carbon dioxide is used for fume suppression during ladle transfer of matte (Cu/Ni production) or bullion (Zn/Pb production). Carbon dioxide is used to enhance the recovery of oil from wells where primary and secondary methods are no longer cost-effective on their own.

Carbon dioxide is also used as a fire extinguishant and as 'dry ice' for storage and other effects.

2.1.1 General thermodynamics

Physical properties of carbon dioxide

Pure carbon dioxide exhibits triple point behaviour dependent on the temperature and pressure, as shown in Figure 1:

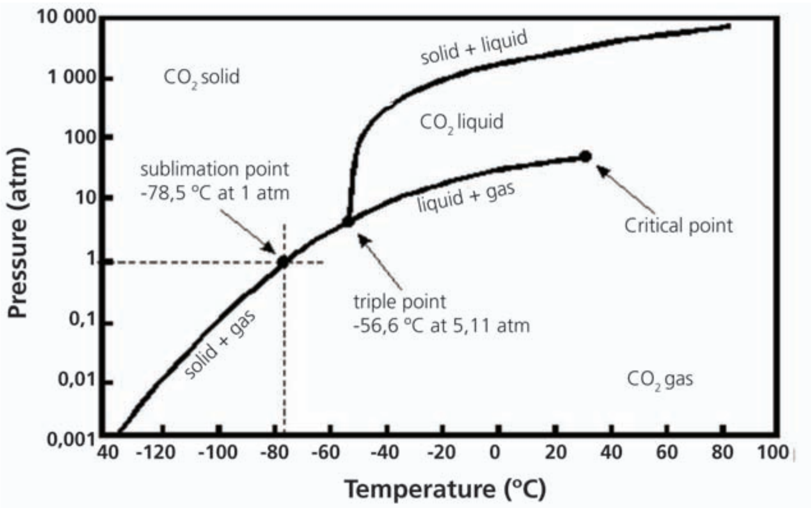

Figure 1 CO_2 Phase diagram

The triple point (at a pressure 5,11 bar and temperature of -56,7 °C) is defined as the temperature and pressure where three phases (gas, liquid and solid) can exist simultaneously in thermodynamic equilibrium. The solid-gas phase boundary is called the sublimation line, as a solid changing state directly into a gas is called sublimation. Physically, this boundary implies that the gas and solid can co-exist and transform back and forth without the presence of liquid as an intermediate phase.

Above the critical point (73,8 bar and 31,1 °C), the liquid and gas phases cannot exist as separate phases, and liquid phase carbon dioxide develops supercritical properties, where it has some characteristics of a gas and others of a liquid.

In the event of an uncontrolled release of carbon dioxide (e.g. damage to a pipe containing liquid carbon dioxide), a portion of the escaping fluid will quickly expand to carbon dioxide gas. The temperature of the released carbon dioxide gas will fall rapidly due to the pressure drop (Joule-Thompson effect – see later description), causing some of the released carbon dioxide to form carbon dioxide snow. As a result of the low temperature of the carbon dioxide, the surrounding air will also be cooled down, which will cause the water vapour in the air to condense locally, which will look like a thick fog. This will continue (to a greater or lesser extent) as long as there is cold carbon dioxide present (e.g. subliming 'snow').

A phase diagram, as shown in Figure 1, is a common way to represent the various phases of a substance and the conditions under which each phase exists. However, it tells us little regarding how the changes of state for carbon dioxide occur during a transient. The carbon dioxide pressure-enthalpy diagram (P-h), shown in Figure 2, or temperature- entropy (T-s) diagrams provide insight to the phase changes.

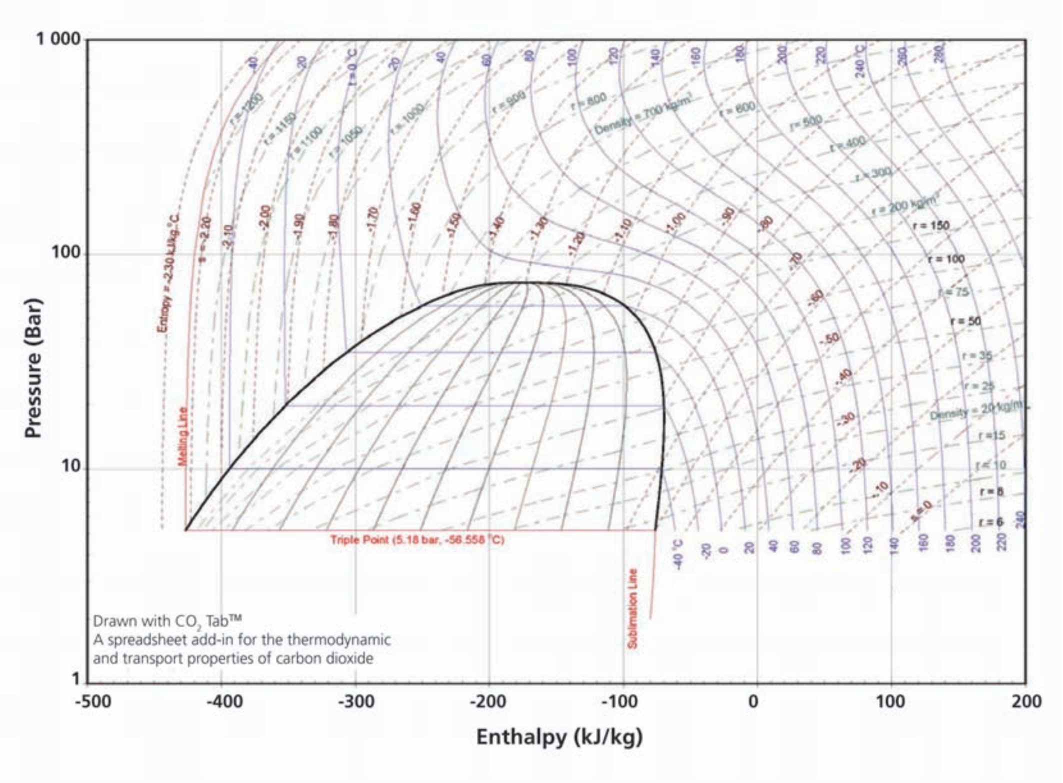

Figure 2 CO_2 pressure-enthalpy diagram

P-h and T-s diagrams can be used to examine phase changes, energy transfers, and density, pressure and temperature changes during depressurisation, e.g. for a leak of carbon dioxide from a vessel or a pipeline. In order to understand and interpret such a diagram some basic thermodynamic theory and terms need to be established.

The adiabatic (no heat exchanged) expansion of a gas may occur in a number of ways. The change in temperature experienced by the gas during expansion depends not only on the initial and final pressures, but also on the manner in which the expansion is carried out.

Isenthalpic expansion is a theoretical expansion which takes place without any change in enthalpy. In a free expansion, the gas does no work and absorbs no heat, so the internal energy is conserved. Expanded in this manner, the temperature of an ideal gas would remain constant, but the temperature of a real gas may either increase or decrease, depending on the initial temperature and pressure. This is called the Joule-Thompson effect. The amount by which the gas cools on expansion (measured in °C/bar) is called the Joule-Thompson coefficient, μ_{JT}. Carbon dioxide has a particularly high μ_{JT} compared with other gases, as shown in Table 1.

Table 1 Joule-Thompson coefficient for a number of gases

Gas	He	CO	H_2	O_2	N_2	CH_4	CO_2
μJ°C/bar[3]	−0,06	0,01	0,03	0,30	0,25	0,70	1,00

The value of μ_{JT} varies with the temperature of the carbon dioxide, as shown in Figure 3. The effect of higher pressures at 10°C is shown in Figure 4

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[3] Data from '*Basic Principles of Membrane Technology*' 2nd edition, May 1996, Marcel Mulder, ISBN 78-0-7923-4248-9 **NB. Reference temperature and pressure for these figures is not provided.**

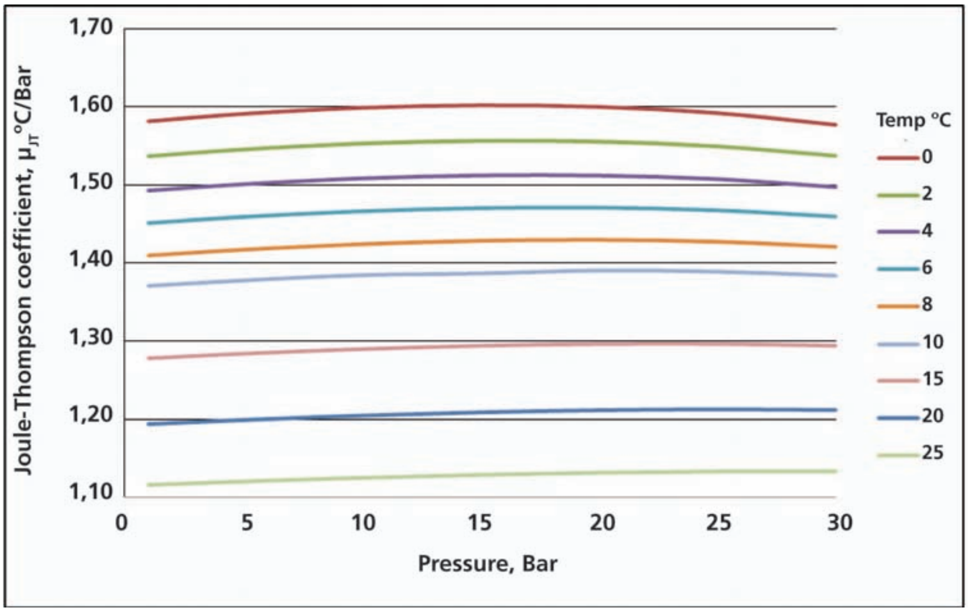

Figure 3 Changes in Joule-Thompson coefficient (μ_{JT}) for a number of different CO_2 temperatures and pressures

Positive or negative temperature change can occur during the Joule-Thompson process. Each real gas has a Joule-Thompson inversion temperature above which expansion at constant enthalpy causes the temperature to rise, and below which such expansion causes cooling. For carbon dioxide the inversion temperature, at atmospheric pressure, is 1 500K[4] (1 226,85 °C), which means that carbon dioxide gas always cools by isenthalpic expansion for all conditions relevant in CCS applications.

Isentropic expansion takes place if the expansion process is reversible, (meaning that the gas is in thermodynamic equilibrium at all times). In this scenario, the gas does positive work during the expansion, and its temperature decreases. Here, the temperature drop will be greater than for isenthalpic expansion.

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[4] Reference Perry's *Chemical Engineering Handbook*.

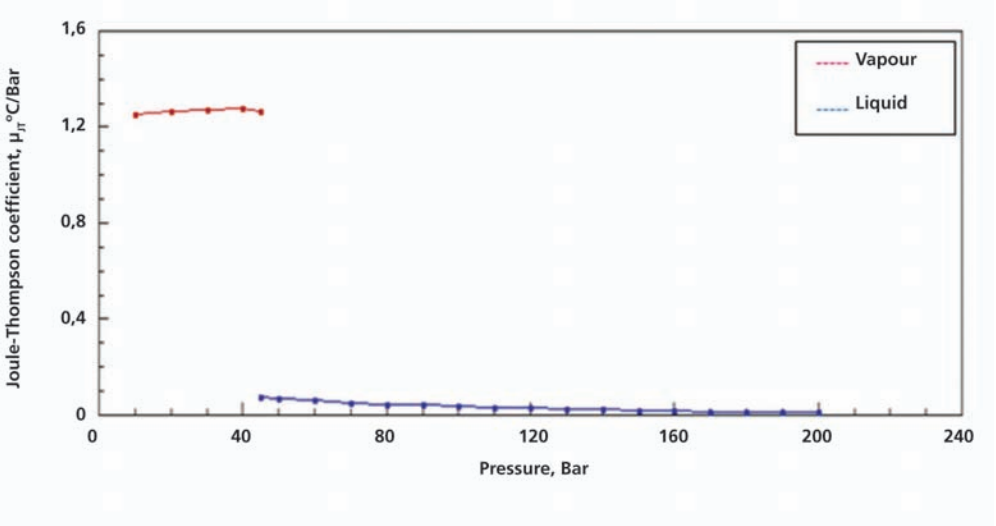

Figure 4 Changes in Joule-Thompson coefficient (μ_{JT}) for pure CO_2 at higher pressures at 10°C

Figure 5[5] shows the pressure-density behaviour of pure carbon dioxide during rapid decompression under ideal conditions from 130 bar (13,1 MPa) and 5 °C, and it can be seen that solid, liquid and gas phases are all present.

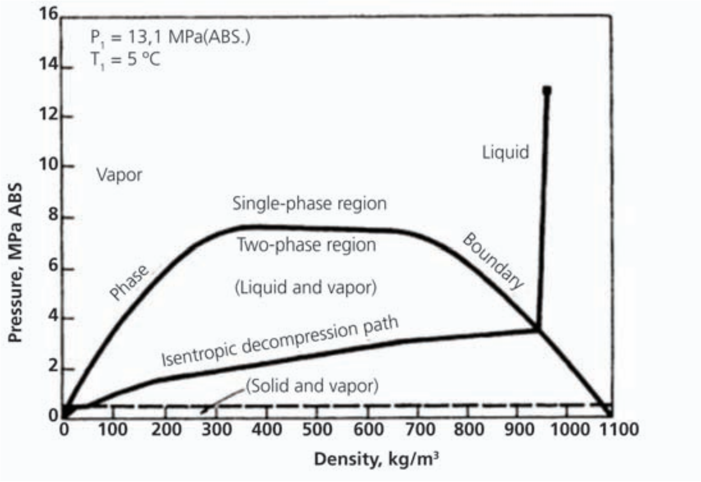

Figure 5 Pressure-density behaviour during rapid CO_2 decompression

Modelling[6] has indicated that impurities within the carbon dioxide will affect the critical point (see Figure 1), as Figure 6 shows (NB. The results shown are indicative only).

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[5] From '*Piping Design Handbook*', John McKetta, CRC Press, 1992.

[6] Reference Presentation by Julia Race, Newcastle University to Energy Institute, 24 July 2006.

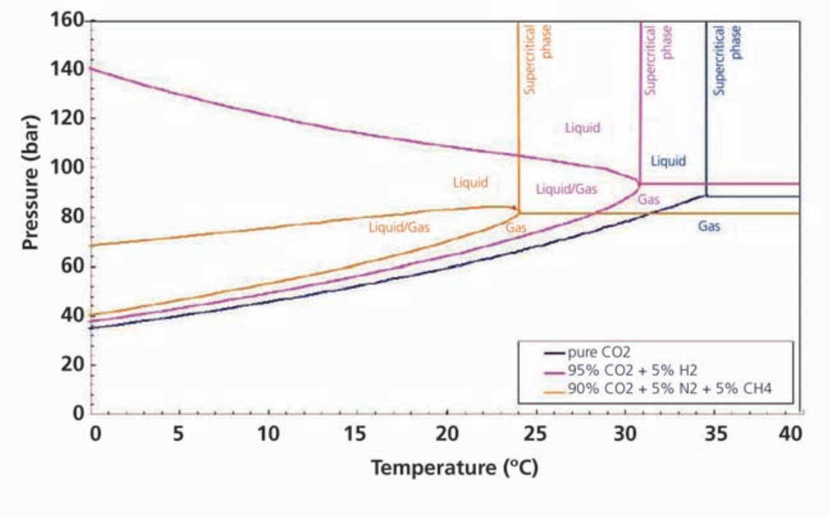

Figure 6 Effect of impurities on the critical point

Gaseous phase carbon dioxide

Carbon dioxide gas is colourless, heavier than air (1 521 times as heavy, with a density of about 1,98 g/litre), has a slightly irritating odour, and freezes at −78,5 °C to form carbon dioxide snow.

The effects of inhaling carbon dioxide and the limit values for working when there is carbon dioxide in the atmosphere are described in 2.4.1.

An escape of carbon dioxide gas, because it is heavier than air, will tend to accumulate in depressions in the ground and in basements or sumps. This accumulation can occur in low pressure carbon dioxide releases or where there is sufficient impingement on a high pressure release to remove the momentum[7]. The release will disperse as a result of air movements. Natural releases of carbon dioxide are often at low momentum (e.g. in Italy, Poland and USA). There have also been natural events leading to more hazardous accumulations of carbon dioxide, such as the incident at Lake Nyos in 1986, which is one of only three lakes in the world known to be saturated with carbon dioxide.

Models that assist in the prediction of this are described in EI document *Technical guidance on hazard analysis for onshore carbon capture installations and onshore pipelines*.

Corrosion potential

Carbon dioxide dissolves in water to form carbonic acid (H_2CO_3):

$$CO_2 + H_2O \rightarrow H_2CO_3 \rightarrow H^+ + HCO_3^{2-} \quad pKa = 6,35$$

$$HCO_{3^-} \rightarrow H+ + CO_3^{2-} \quad pKa = 10,25$$

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[7] Impingement will change the velocity of a jet and hence the source terms for the release. There are a few examples where it is possible to envisage a low momentum outcome. For example, a small high pressure leak from an underground pipeline, where the leak is insufficient to blow away the topsoil material. In this case, the soil will remove the momentum from a leak.

The solubility of carbon dioxide in water is 1,45 g/litre at 25 °C and 1 bar. Carbonic acid is relatively weak, and it is impossible to obtain pure carbonic acid at room temperatures. Whilst carbonic acid is described as weak, it still carries the potential to corrode carbon steel pipes:

$$2Fe + H_2CO_3 \rightarrow Fe_2CO_3 + H_2$$

This leaves the designer with the choice of either using a more costly pipe material, lining the inside of the pipe with a corrosion-resistant coating, or reducing the water to a level where significant corrosion will not take place.

There is also a hypothetical acid, orthocarbonic acid, H_4CO_4.

Liquid phase

Carbon dioxide cannot exist as a liquid at atmospheric pressure. At a pressure of anything above 5,11 bar(a) and at a temperature between −56,6 °C and 31,1 °C it becomes liquid (see Figure 1), and its density rises with temperature to 1 180 kg/m^3. The liquid/gas equivalent (1,013 bar and 15 °C (per kg of solid)) is 845 vol/vol.

Solid phase

If the temperature of liquid carbon dioxide drops below 56,6 °C it becomes solid (see Figure 1). Solid carbon dioxide usually has a snow-like appearance, and can be compressed into blocks to form 'dry ice'. Solid CO_2 will form in vessels/pipelines when conditions fall below the triple point and this may not be snow-like.

Dry ice manufacturing starts with liquid carbon dioxide held under pressure (about 21 bar) in bulk storage vessels. To begin making dry ice, the liquid CO_2, is expanded through a Joule-Thompson valve into an empty chamber where, under normal atmospheric pressure, it flashes into CO_2 gas. This change from liquid to gas causes the temperature to drop quickly. About 46 % of the gas will become carbon dioxide snow. The rest of the carbon dioxide gas is either released into the atmosphere or recovered to be used again. The carbon dioxide snow is then collected in a chamber where it is compressed into block, pellet or rice size pieces to meet customer’s requirements. The denser the dry ice is, the longer it will last, the easier it is to handle, and the better it will perform when blast cleaning, if it is to be used for this purpose.

Supercritical phase

Carbon dioxide above the critical point (in terms of both pressure and temperature) is described as being in the supercritical phase. The properties of supercritical fluids lie between those of gases and liquids; a supercritical fluid has densities similar to those of liquids, while the viscosities and diffusivities are closer to those of gases. A supercritical fluid can diffuse in a solid matrix faster than a liquid, yet possess a solvent strength to extract the solute from the solid matrix.

2.2 LIQUID CARBON DIOXIDE

In practical terms the majority of the carbon dioxide inventory in CCS applications will be in liquid form (i.e. sub-supercritical), since it will be at high pressure (>100 bar) and low temperature (<31 °C). Liquid carbon dioxide has a volume factor of 0,002542 compared to gaseous carbon dioxide at standard temperature and pressure, thus pipes to export it from the production site can be much smaller than had the carbon dioxide been transported as a gas.

2.2.1 Corrosion

Liquid carbon dioxide with no free water or impurities is not corrosive.

The previous section on corrosion was concerned with the dissolving of carbon dioxide in water. In a CCS context, the issue is dissolving water in liquid carbon dioxide. The difference is that if the fluid being considered is pure carbon dioxide, there is no potential for corrosion, as there are no loosely bonded oxygen atoms available to form oxides. If the carbon dioxide contains water, then the potential exists for the oxygen within the water to initiate corrosion.

Water will dissolve in liquid carbon dioxide, so the first priority for the process designer will be to ensure that the levels are such that no free water is present. If this is achieved and operating conditions are controlled, then carbon steel can be used with confidence.

There are a number of models that can be used to describe the solubility of water in carbon dioxide, and a number of these have been analysed with reference to experimental observations[8]. A graphical presentation of the conclusions of this for water-in-carbon dioxide is provided in Figure 7.

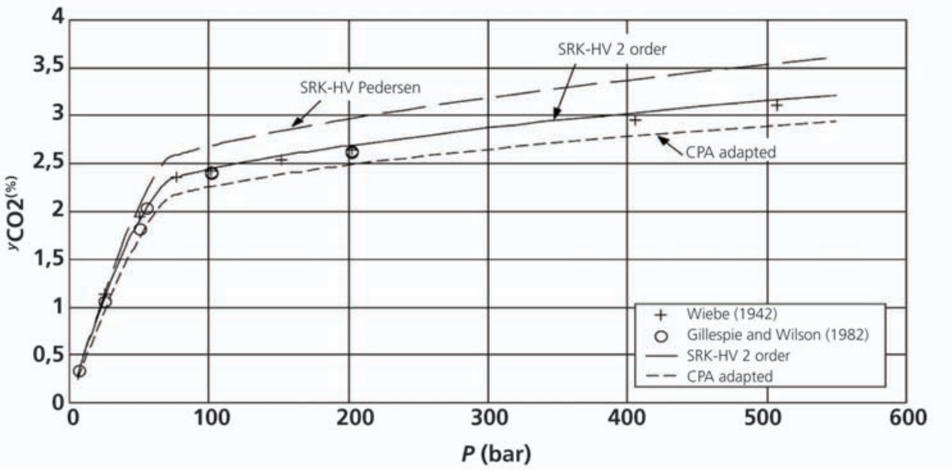

Figure 7 Solubility of H_2O in pure CO_2 at 30°C

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[8] '*Thermodynamic models for calculating mutual solubilities in H_2O-CO_2-CH_4 mixtures*' A. Austegard, M. J. Mølnvik, SINTEF Energy Research, Trondheim, Norway and E. Solbraa, G. De Koeijer, STATOIL Research and Technology, Trondheim, Norway, published by the Institution of Chemical Engineers, September 2006.

This would indicate that at pressures above about 80 bar range, there is reasonable confidence that whichever model one chooses to use, at least 2,1 vol % of water will dissolve in carbon dioxide at 30 °C (i.e. 21 000 ppmv). Thus anything less than this would not allow free water to appear, and corrosion of carbon steel pipes would not take place.

However, carbon dioxide forms hydrates with water ($CO_2.6H_2O$), and thus water that might normally be dissolved uniformly throughout a liquid can become concentrated at particular points. Hydrates are essentially small non polar molecules 'trapped' within hydrogen bonded water molecules. The carbon dioxide is not bonded to the water molecules, but supports the lattice structure surrounding it. Carbon dioxide is just one of many molecules able to form hydrates with water, and Figure 8 shows a Type 1 hydrate structure of the type exhibited by carbon dioxide. Physically, hydrates are solid, and have the appearance of ice.

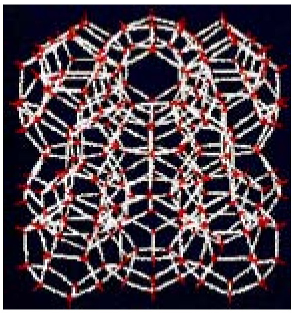

Figure 8 Type 1 clathrate structure, CO_2 hydrate

The generic diagram presented as Figure 9 explains where these are predicted to exist for pure carbon dioxide. The black squares show experimental data[9], and the lines of the carbon dioxide phase boundaries are calculated according to thermodynamic tables. The dark grey region (V-I-H) represents the conditions at which carbon dioxide hydrate is stable together with gaseous carbon dioxide and water ice.

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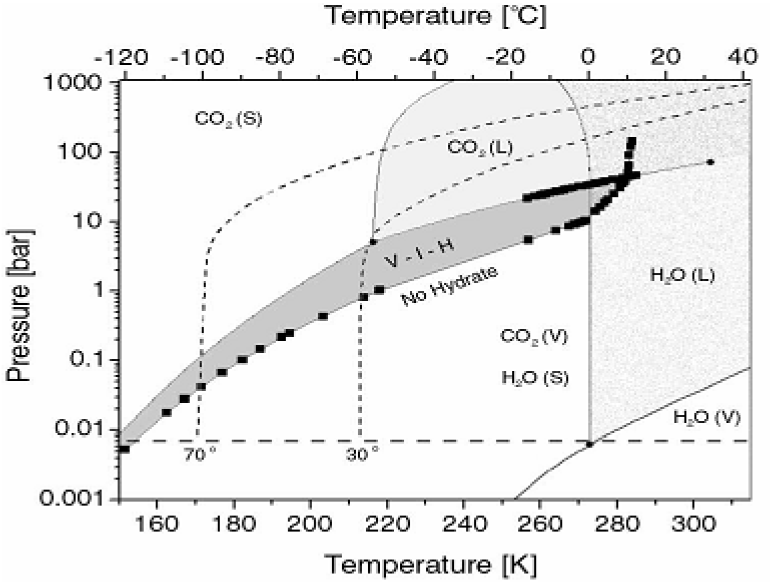
[9] '*Clathrate hydrates of natural gases*' 2nd edition, E D Sloan Jr, 1998.



Key

H	hydrate
I	water ice
L	liquid
S	solid
V	vapour

Figure 9 Hydrate diagram for pure CO_2

The potential for hydrate formation in liquid carbon dioxide is of particular importance when considering the corrosion potential of liquid carbon dioxide from CCS applications at low temperatures, such as will be experienced sub-sea. The variables in hydrate formation are temperature, pressure, gaseous contaminants within the carbon dioxide, and water concentration. It is possible for all of the water to be dissolved within the liquid carbon dioxide in the land-based sections of a CCS system (where the temperatures will probably be in the 10-25 °C range), but once the carbon dioxide reaches an equilibrium temperature at the bottom of the North Sea (around 4 °C), hydrates will form at some level of water content, providing the potential for pipe internal corrosion as free water appears.

Of the variables, the operator can exercise little control over temperature and limited control over pressure, but the system can be designed to deliver carbon dioxide with a controlled level of key contaminants, and a water content sufficiently low for hydrates not to form. Hydrates can be formed at temperatures both below and above 0 °C and become more stable with increasing pressure. Thus the design levels for impurities and in particular dissolved levels of water within the carbon dioxide must take into account the operating conditions across the entire pipeline and not just the onshore segment.

Experimental work and modelling[10] have been carried out to establish the hydrate stability zone, outside of which formation will not take place in pure carbon dioxide. The objective has been to establish the conditions under which hydrates can form under different conditions of temperature and pressure. These have concluded that at a pressure of up to 200 bar and down to 4 °C (typical conditions for a sub-North Sea pipe), provided the moisture content of the carbon dioxide is below 250 ppm, hydrates will not form. With this level of moisture, hydrates will also not form under choke conditions (assumed to be −2 °C and 50 bar).

Consequences of hydrate formation on pipeline operation

It is necessary to avoid hydrate formation in carbon dioxide pipelines because there is a strong possibility of solid formation that could choke or even block flow. A piece of hydrate could lodge in a pipeline, restrict the flow and even set up a site for local erosion to start as a consequence. Because hydrates actually store water within the lattice, hydrates reduce the potential for corrosion to occur. Where storage of gaseous carbon dioxide is intended (e.g. within depressurised gas wells), the potential for the formation of gas hydrates needs to be considered within the overall system design, which will reflect on the specification for the admissible carbon dioxide.

2.2.2 Impact of impurities within liquid carbon dioxide

Carbon dioxide from carbon dioxide capture plants will generally not be pure, and some of the contaminants affect the properties of the liquid. Hydrogen, for instance, a possible contaminant from pre-combustion capture plants, affects the triple point (see the carbon dioxide phase diagram in Figure 1), and does not dissolve in the liquid until the pressure is quite high (>92 bar at 30 °C). Undissolved hydrogen would, for instance, cause a problem in carbon dioxide booster pumps, as two-phase flow would be experienced.

Figures 10 and 11 show the effect on density and viscosity respectively of a 2 mol % impurity of a number of contaminants on pure carbon dioxide at a pressure of 100 bara over the temperature range of 0 °C - 50 °C. These graphs have been compiled using the Peng Robinson equation of state and are for illustrative purposes only. These, and other properties, need to be confirmed by experiment, because equations of state, such as those of Peng Robinson are not always accurate, as Figure 12 (which also shows the change in the density of pure carbon dioxide with temperature according to the experimentally-derived Span-Wagner model) illustrates.

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[10] '*Effect of common impurities on the phase behaviour of carbon dioxide rich systems: Minimising the risk of hydrate formation and two-phase flow*', Chapoy, Burgass and Tohidi, Hydrafact/ Heriot-Watt University, Austell and Eickhoff, Progressive Energy, presented at the Oil and Gas Conference and Exhibition, Aberdeen, 8-11 September 2009.

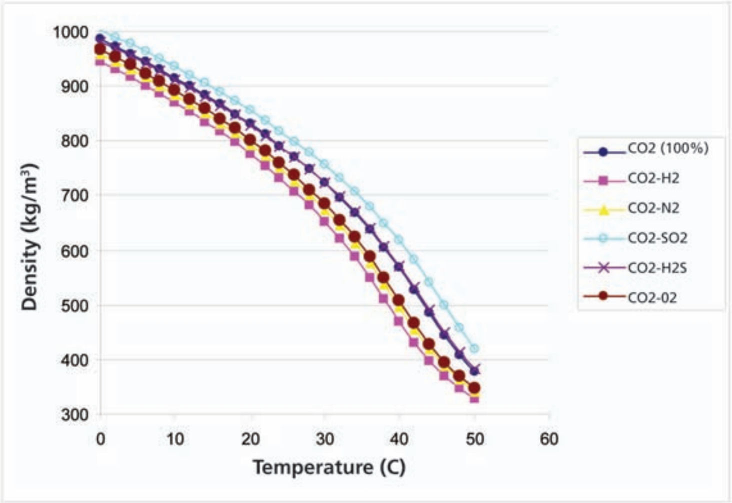

Figure 10 Effect of impurities on density of CO_2 with differences in temperature at a pressure of 100 bar

It may be seen in Figure 10 that H_2S has a minimal impact on density, whereas the effect of hydrogen is significant. In all cases except for SO_2 the effect is to reduce the density.

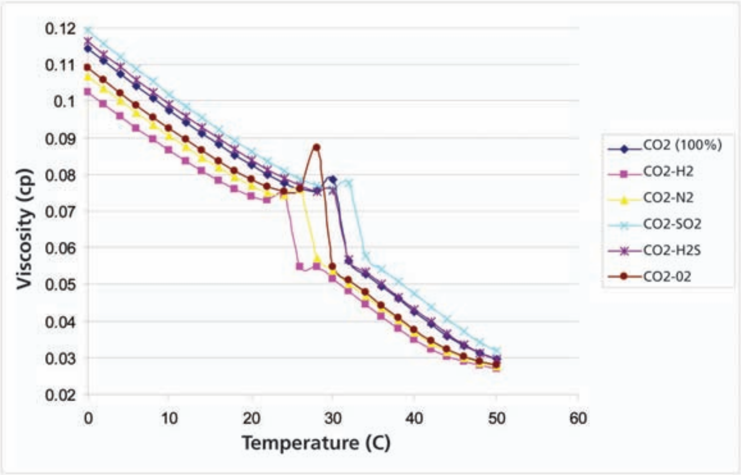

Figure 11 Effect of impurities on viscosity of CO_2 with changing temperature at a constant pressure of 100 bar

It may be seen in Figure 11, first, that H_2S has a minimal impact on viscosity, whereas the effect of hydrogen is significant, and second, that non-linearities appear in the 25 - 35 °C range, because the program used (ProMax) models the supercritical fluid as a vapour. This underlines the need to validate models with experimental measurements.

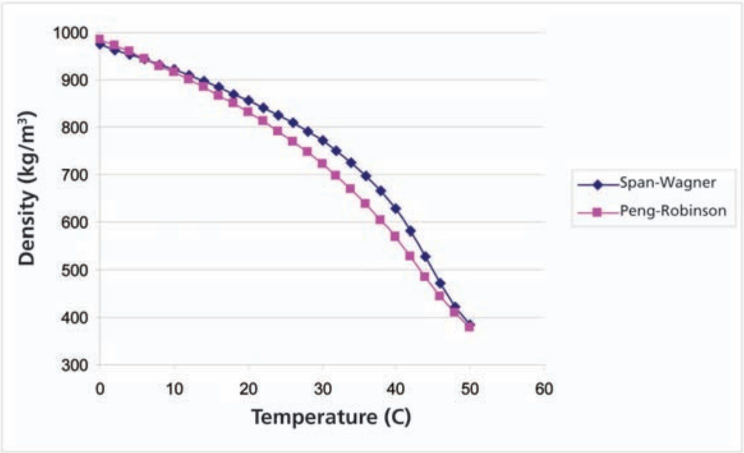

Figure 12 Effect of different models of equation of state on density of pure CO_2 at 100 bar

Graphs indicating the modelled effect (using ProMax) of impurities on the density of carbon dioxide with varying temperature and pressure at a fixed temperature of 4 °C are shown as Figures 13 and 14 respectively. Comparing this with the conclusion from Figure 10, it may be seen in Figure 11 that adding 2 mol% of H_2S has a minimal impact on density, whereas the effect of hydrogen is significant. In all cases except for SO_2 the effect is to reduce the density. The same conclusion may be drawn about viscosity from Figure 14.

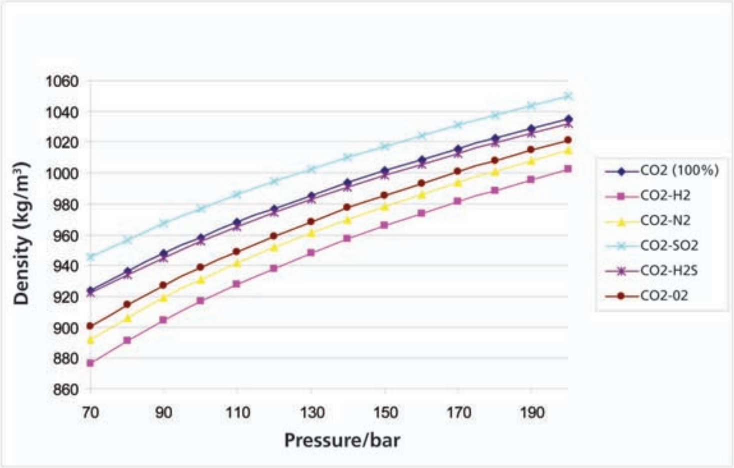

Figure 13 Effect of impurities on density of CO_2 with differences in pressure at 4 °C

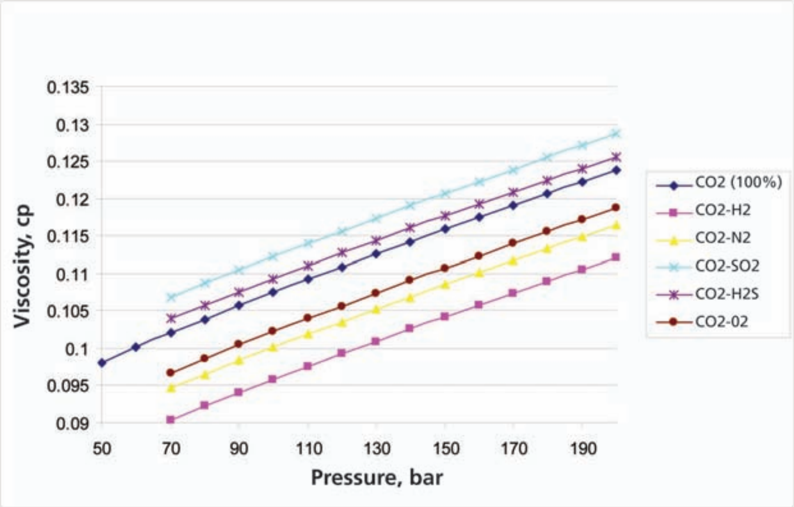

Figure 14 Effect of impurities on viscosity of CO_2 with differences in pressure at 4 °C

Figures 10 to 14 have modelled (using ProMax) the impact of a single impurity on the characteristics of pure carbon dioxide. Some work on the impact of multiple impurities has been carried out by Newcastle University[11], further to the work shown in Figure 5. Six different cases were examined (see Table 2), as being typical of some possible compositions of carbon dioxide (see Table 3, based on IPCC compositions) from the different processes. Table 3 also includes the Dynamis assumed carbon dioxide composition[12], which is intended to be a practical level which could reasonably be expected to be achieved for CCS. For comparison, Table 4 gives the standard grade purity for bulk liquid provided industrially[13].

Table 2 Case definition for reference 7

Fuel/capture route	Post-combustion	Pre-combustion	Oxy-fuel
Coal	Case 1	Case 3	Case 5
Natural Gas	Case 2	Case 4	Case 6

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[11] '*CO_2 Transport UKCCSC Progress Report*', Seevam, Race, Downie, Newcastle University, 2008.

[12] '*Towards hydrogen and electricity production with carbon dioxide capture and storage*' Dynamis project thematic priority : 6.1.3.2.4 '*Capture and sequestration of CO_2, associated with cleaner fossil fuels*', de Visser and Hendriks et al, Ecofys, July 2007.

[13] From '*Welcome to BOC Carbon Dioxide safety training program*', BOC National Training Center (http://boc3.bocgases.com/ntc/standards/CO2%20Safety.pdf).

The impact of modelling these impurities (using ProMax) on the phase envelope is shown in Figure 15, which also has the phase envelope for pure carbon dioxide included. It may be seen that the effect of the contaminants of cases 1 and 2 have little effect on the carbon dioxide, whereas those in case 3 have a significant impact, both in terms of the critical point, and opening up the phase envelope to a large two phase area containing liquid and gaseous carbon dioxide.

Table 3 Possible compositions of carbon dioxide based on IPCC

	Case 1	**Case 2**	**Case 3**	**Case 4**	**Case 5**	**Case 6**	**Dynamis**
SO_2	0,01	0,01			0,5	0,01	<0,01
NOx	0,01	0,01			0,01	0,01	<0,01
$N_2/Ar/O_2$	0,01	0,01	0,6	1,3	3,7	4,1	<4
H_2S			0,6	0,01			<0,02
H_2			2	1,0			with O_2
CO			0,4	0,04			<0,2
CH_4			0,01	2,0			<4
H_2O							<0,05

Table 4 Standard grade purity for bulk CO_2 liquid

Minimum purity (%)	99,9	Oxygen O_2	30
Inerts (ppmv)	1 000	Carbon Monoxide CO (ppmv)	10
Volatile Hydrocarbons (ppmv)	50	Nitrogen oxides NOx (ppmv)	5
Non-volatile hydrocarbons (ppmv)	10	Sulphur dioxide SO_2 (ppmv)	5
Water (ppmv)	32	Carbonyl sulphide COS (ppmv)	0,5
Ammonia NH3 (ppmv)	25	Hydrogen sulphide H_2S (ppmv)	0,5

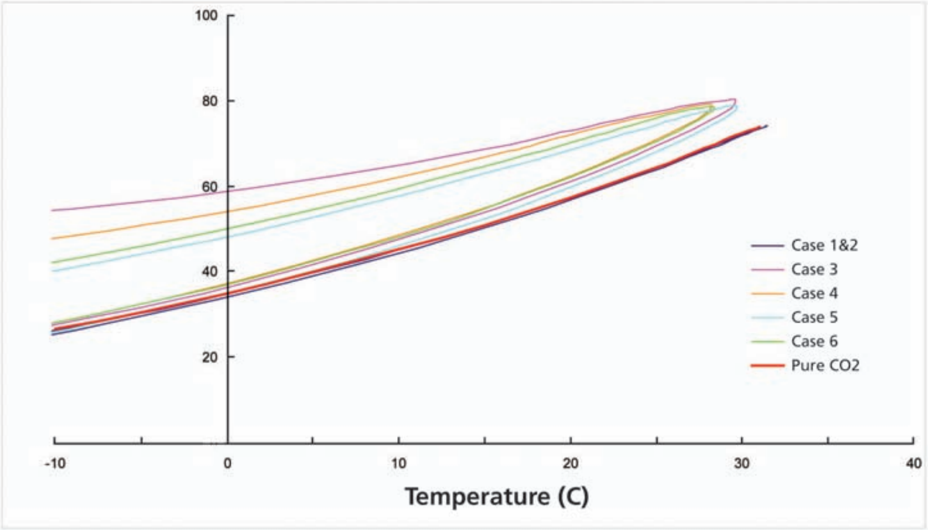

Figure 15 Impact of impurities from Table 3 on the properties of CO_2

The presence of impurities in the carbon dioxide will also affect the hydrate stability zone (described in 2.2.1), and specific analyses may be required for different levels of impurity in order to provide adequate confidence that hydrates will not form under the conditions of pressure and temperature being experienced. Of the mixtures analysed[14], the impurity with the greatest impact was hydrogen, but its impact (with other impurities) at 200 bar and 4 °C up to 2 vol% did not lead to hydrate formation at a moisture level of 250 ppmv. Under the same choking conditions (−2 °C and 50 bar), the conditions inside of the pipeline would be within the hydrate stability zone (i.e. hydrates could form), although the risk of blockage was considered to be low.

2.3 BEHAVIOUR IN THE SUPERCRITICAL REGION

Above its critical temperature (31,1 °C) and pressure (72,9 bar), carbon dioxide takes on the properties of a supercritical fluid (see definitions section 8.3). These properties include expanding to fill its container like a gas but with a density similar to that of a liquid. As it approaches the supercritical condition, the meniscus between liquid and gaseous carbon dioxide disappears.

Supercritical carbon dioxide with a high degree of purity is becoming an important commercial and industrial solvent due to its role in chemical extraction in addition to its low toxicity and relatively benign environmental impact. The solubility of solids in supercritical carbon dioxide can be 3-10 orders of magnitude higher than in liquid carbon dioxide.

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[14] '*Risk of hydrate formation in low water content CO_2 and rich CO_2 systems*', Prof. B. Tohidi, Hydrafact for Progressive Energy, carried out under the EC Dynamis Project, December 2008.

The relatively low temperature of the processes and the stability of carbon dioxide also allows most compounds to be extracted with little damage or denaturing. This is particularly useful when extracting volatile oils and fragrances for the perfumery industry. The amount of carbon dioxide used in these applications is very small compared to the volumes that will be produced during CCS, therefore little work has been carried out on the physics and impact of large releases of supercritical carbon dioxide.

For carbon capture and storage applications, none of the properties of supercritical carbon dioxide compared to those of liquid carbon dioxide can be considered as advantageous. Additionally, in order to maintain carbon dioxide in its supercritical phase, the temperature of the carbon dioxide would have to be maintained above 31,1 °C, which would be difficult for buried and sub-sea pipes. It is, however, likely that within the carbon dioxide capture plant itself (e.g. during compression), there will be some relatively small inventory of supercritical carbon dioxide.

Once in the injection well, the carbon dioxide will become heated as a result of the increased temperature of the earth’s crust. At normal hydrostatic pressures, and typical temperature gradients, the pressure increase is about 100 bar at 1 000 m depth increasing by around 100 bar for every additional 1 000 m depth. The temperature of the earth’s crust increases by about 30 °C for every 1 000 m, thus the carbon dioxide will not reach supercritical conditions for storage above about 800 m. Below that, temperatures are typically at around 90 °C at 2 000 m depth to 130 °C at 3 500 m depth.

2.4 HAZARDS OF CARBON DIOXIDE

This section will briefly look at some of the main hazards carbon dioxide presents and consider the implications.

2.4.1 Physiological effects of carbon dioxide

Carbon dioxide has two key physiological effects: it acts as an asphyxiant and also has toxicological effects. As stated in 2.1, carbon dioxide is present in the atmosphere at a concentration of approximately 0,03 %, and serves as an essential trigger in the human body for respiration. Carbon dioxide produced by the body exists at a slightly higher partial pressure than that inhaled, allowing the diffusion of carbon dioxide into the lungs ready for exhaling. However, when the concentration of carbon dioxide in the air is above the partial pressure (around 1,4 %), it alters the partial pressure of the carbon dioxide in the body so that carbon dioxide is not released from the blood and additional carbon dioxide is absorbed from the inhaled air. This increased level of carbon dioxide increases the acidity of the blood. In response to elevated carbon dioxide levels in the blood, the person is likely to begin to breathe more frequently and/or deeply as the respiratory system mechanisms react to stabilise this imbalance. If the person is in a high carbon dioxide atmosphere an increase in the depth or rate of breathing will only serve to worsen the situation as the victim takes in more and more carbon dioxide. The effect of carbon dioxide on the human body according to level of exposure is documented in Table 5. At concentrations of 1,5 % carbon dioxide humans are likely to suffer symptoms such as headaches, tiredness and increased breathing rate as carbon dioxide is absorbed into the bloodstream and increases its acidity. A further 5 % increase in carbon dioxide concentration can induce visual impairment and/or loss of consciousness. Above 10 % loss of consciousness can occur so rapidly that the person is unable to save themselves.

Table 5 Exposure reactions to carbon dioxide[15]

Concentration in air (% v/v)	**Effect**
1 %	Slight increase in breathing rate
2 %	Breathing rate increases to 50 % above normal level. Prolonged exposure can cause headache, tiredness
3 %	Breathing increases to twice normal rate and becomes laboured. Weak narcotic effect. Impaired hearing, headache, increase in blood pressure and pulse rate
4–5 %	Breathing increases to approximately four times normal rate; symptoms of intoxication become evident and slight choking may be felt
5–10 %	Characteristic sharp odour noticeable. Very laboured breathing, headache, visual impairment, and ringing in the ears. Judgment may be impaired, followed within minutes by loss of consciousness
10–15 %	Within a few minutes' exposure, dizziness, drowsiness, severe muscle twitching, unconsciousness.
17–30 %	Within one minute, loss of controlled and purposeful activity, unconsciousness, convulsions, coma, death.

The HSE has also published information in order to assess the risks associated with carbon dioxide which also considers the duration of exposure. Table 6 shows the specified level of toxicity (SLOT) and significant likelihood of death with a 50 % mortality rate (SLOD) levels determined by the HSE. These are derived from the SLOT dangerous toxic load (DTL).
$75\ 000\ \text{ppm}^8 \times 15\ \text{min} = 1,5 \times 10^{40}\ \text{ppm}^8.\text{min}$

And the SLOD DTL of

$100\ 000\ \text{ppm}^8 \times 15\ \text{min} = 1,5 \times 10^{41}\ \text{ppm}^8.\text{min}$

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[15] *Air Products and Chemicals, Inc* Safetygram-18 1993 andhttp://www.ptil.no/getfile.php/PDF/Ptil%20CCS%20CCS%202008.pdf Table 6.

Table 6 SLOD and SLOT values for CO_2

Exposure period (min)	CO_2 concentration (%) producing the	
	SLOT	SLOD
0,5	11,5	15,3
1	10,5	14,0
10	7,9	10,5
30	6,8	9,2
60	6,3	8,4
120	5,5	7,7

The UK HSE has described[16] SLOT and SLOD in the context of the provision of Land Use Planning. SLOT is described as:

— Severe distress to almost every one in the area.
— Substantial fraction of exposed population requiring medical attention.
— Some people seriously injured, requiring prolonged treatment.
— Highly susceptible people possibly being killed.

These criteria are fairly broad in scope, reflecting the fact that:

1. There is likely to be considerable variability in the responses of different individuals affected by a major accident.
2. There may be pockets of high and low concentrations of a toxic substance in the cloud release, so that not everyone will get exactly the same degree of exposure.
3. The available toxicity data are not usually adequate for predicting precise dose-response effects.

Importantly, the criteria are also relatively easy for non-scientists to understand in terms of the overall health impact.
SLOD is defined as the mortality of 50 % of an exposed population.

HSE is not the only body to provide guidance on exposure limits for carbon dioxide. The following table provides additional guidance on limits:

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[16] '*Assessment of the dangerous toxic load (DTL) for specified level of toxicity (SLOT) and significant likelihood of death (SLOD)*', Health and Safety Executive, 21 October 2008.

Table 7 International exposure limits[17]

Exposure time	**%CO_2**	**Comment**	**Reference**
10 hours	0,50 %	Time weighted average	NIOSH (US)
8 hours	0,50 %	Time weighted average	OSHA (US)
	0,50 %	Occupational long term exposure limit (LTEL)	COSHH HSE (UK)
60 minutes	4 %	Emergency exposure limit for submarine operations	USA Navy
	2,5 %	Emergency exposure limit for submarine operations	National (US) Research Council
	5 %	Suggested long term survivability exposure limit	HSE (UK)
	2 %	Maximum exposure limit	Compressed Gas Association 1990
20 minutes	3 %	Maximum exposure limit	Compressed Gas Association 1990
15 minutes	1,5 %	Occupational short term exposure limit (STEL)	COSHH HSE (UK)
	3 %	STEL	Federal occupational safety and health regulations (US)
10 minutes	4 %	Maximum exposure limit	Compressed Gas Association 1990
5 minutes	5 %	STEL	HSE (UK)
7 minutes	5 %	Maximum exposure limit	Compressed Gas Association 1990
	6 %	Maximum exposure limit	Compressed Gas Association 1990
3 minutes	7 %	Maximum exposure limit	Compressed Gas Association 1990
1 minute	15 %	Exposure limit	NORSOK (Norway)
< 1 minute	4 %	Maximum occupational exposure limit	Federal occupational safety and health regulations (US)

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[17] Table 6.3 published exposure limits, '*Mapping the potential HSE issues relating to large-scale capture, transport and storage of* CO_2' DNV Report 2008-1993.

2.4.2 Confined spaces

Since carbon dioxide has a higher molecular weight than air and is also typically processed at low temperatures as a liquid or dense gas, it will tend to sink and linger in confined spaces where the air is undisturbed. High concentrations of carbon dioxide can develop rapidly, even from a small leak, due to the large expansion ratio between the liquid and gas phases (see Figure 1). There have been several incidents where personnel have been asphyxiated/intoxicated due to incautious entering of confined spaces where carbon dioxide is present[18].

As a result of the asphyxiating/physiological hazard of carbon dioxide, unventilated areas should be minimised as far as possible by design (avoiding the construction of such areas by, for instance the inclusion of ventilation louvres at the base of all walls). Best practice in the industrial gases and nuclear industry includes either avoiding or controlling access to areas where a build-up of carbon dioxide is anticipated, and by installing detection equipment in enclosures where potential leak sources of carbon dioxide exist.

Where plant may be constructed indoors, plant designers must pay particular attention to suitable ventilation, which is modelled to ensure that there are no areas with poor air flow where appropriate. Operators should also include both fixed and portable detection around the plant as well as robust procedures to monitor the plant. Particular care should be taken in designing emergency procedures to take into account scenarios where the entire building may be at risk of hazardous concentrations of carbon dioxide.

2.4.3 Pressure and expansion ratio

The expansion ratio of carbon dioxide is significantly large such that high pressures can be generated very quickly. It has already been stated in 2.1.1 that one volume of liquid will yield approximately 845 volumes of gas. Systems must be designed to have capacity in order to accommodate the expansion of carbon dioxide and interrogated for any areas where liquid carbon dioxide may become trapped due to equipment isolation or other operational issues.

Plant design and relief devices will be discussed further in section 5.

Insufficient pressure protection or design can result in uncontrolled loss of containment which could lead to further hazards such as propelling vessel debris, cold embrittlement and or personnel hazard, or high carbon dioxide concentrations. Thorough Hazard and Operability (HAZOP) assessments pre-construction should ensure that these effects are considered in the design.

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[18] '*General hazards of carbon dioxide*', Health and Safety Executive, 13 August 2008.

2.4.4 Dispersion in open spaces

When high pressure carbon dioxide is released into the atmosphere during either a controlled or uncontrolled release, fog clouds can form. During a release, the rapid change in pressure can result in a significant drop in temperature. Where there is moisture in the air, this moisture will condense and/or freeze, causing a fog cloud. The extent and density of the fog cloud formed varies according to ambient conditions. These fog clouds reduce visibility and can make operating conditions more difficult. The concentration of carbon dioxide causing the water droplet fog may not be at concentrations that are harmful. Conversely, where there is low humidity in the atmosphere, the 'fog' cloud dimensions do not give an accurate indicator of the carbon dioxide hazard range and concentrations around the visible fogged area may be higher than is prudent.

This means that the visible plume created in humid atmospheres may provide some useful visual clues regarding a leak from the plant or pipeline, but must not be relied on as a suitable indicator of carbon dioxide concentrations. In addition, this 'fogging' presents its own hazards by reducing visibility so particular care must be taken when designing depressurisation systems to ensure that the potential fog created does not add a visibility hazard on site. The fogging must also be included within emergency operating procedures in the event of an accidental release.

Typical observations have been recorded, for illustrative purposes, in Table 8, where the leak considered is the escape of carbon dioxide from no greater than a hole with an equivalent size of 20 mm, and the loss of containment (LOC) assumes that a volume of approximately 120 tonnes of liquid carbon dioxide has been released.

Table 8 Observations on CO_2 releases at high relative humidity (>90 %)

Release type **Type of release**	**Release impinged**	**Released unimpinged**
Low pressure (<10 barg) CO_2 gas leak	Dense cloud	Momentum jet that disperses relatively quickly
High pressure (>100 barg) CO_2 liquid leak	Dense cloud/solid formation	Momentum jet that disperses relatively quickly/some solid formation may occur
Liquid CO_2 storage tank LOC above 10 bar	Dense cloud/solid formation	Momentum jet that disperses relatively quickly/some solid formation may occur

2.4.5 Low temperature effects

Solid carbon dioxide exists at −78 °C and as a result can cause cold burns when it comes into contact with the eyes or skin. As discussed earlier carbon dioxide sublimes and the vapours coming from dry ice (solid carbon dioxide) can be almost as cold.

If a mass of gaseous carbon dioxide experiences sudden depressurisation due to, for example, venting, it will cool rapidly as a result of the Joule Thompson effect. Contaminants in the carbon dioxide stream may 'freeze out' and carbon dioxide snow may also be formed. The resulting solids can cause blockages in process lines or plug valves which may cause system over-pressurisation.

The potentially low temperature at which carbon dioxide is handled or could become when depressurised also creates the need for using materials with guaranteed low temperature properties for vessels, pipes and fittings in order that they maintain their integrity. Materials change properties at low temperatures, and brittle rather than plastic properties tend to control failure mechanisms. Some materials such as aluminium become tougher at lower temperatures but many, including carbon steel, will become more brittle.

Plant must be designed for the range of operating temperatures that it will experience in service. Some equipment currently available is designed for low temperature operation such as cryogenic valves which are able to operate during low temperature conditions.

These low temperature effects must be included in plant specific risk assessment of hazards, where the risks from a failure scenario are compounded by additional material failure caused by the low temperatures (such as detection systems).

2.4.6 Elastomers

Most elastomers commonly used for seals in the power generation and oil and gas industries cannot be used for liquid carbon dioxide as it diffuses gradually into the molecular structure during pressurisation[19]. During a rapid depressurisation the gas expands within the structure and blistering or an explosive effect follows. Problems have been reported with the use of standard nitrile, polyethylene, some fluorelastomers, chloroprene and, to some extent, ethylene-propylene compounds.

Material selection for valves and seals is discussed in more detail in section 5.3.6, but it should be noted that all sealing materials selected for use within CCS plant should be tested for the exact composition (or range of composition) of the carbon dioxide and its impurities as well as the range of operating conditions. Very small changes in the sealing material can make a significant change to the performance of that material to carbon dioxide at the required temperatures and pressures. It is important, therefore to seek information from manufacturers regarding the testing that has been carried out on the sealing materials. For example, NORSOK M-710 is a standard test for qualifying seals for carbon dioxide service in the oil industry and is used to verify seals for specific operating conditions.

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[19] '*Handbook of speciality elastomers*' (ISBN 1574446762), Robert C. Klingender, CRC Press 2008, page 500.

2.4.7 Effect on internal coatings

Experimental work has been carried out[20] on epoxy (both force cured and fused), phenolic (both baked and fused), nylon-epoxy-amide (force cured), glass (fused) and vinyl (cemented) coatings/linings. This work showed that only the force cured epoxy coating gave rise to de-bonding after long term exposure testing to supercritical carbon dioxide. Fused epoxy was reported to show no adverse effect.

At the SACROC unit, powder applied phenolic epoxy and glass fibre reinforced epoxy have successfully been used to coat carbon steel pipe[21]. Where an internal coating is suggested for a particular application, the engineer should satisfy themselves that there is sufficient testing or evidence to support the long term suitability of the coating, as at present there is no significant body of evidence about the long term impact of carbon dioxide.

2.4.8 Lubricants

Petroleum based products will dissolve and some greases will decompose and create gum-like deposits or harden when in contact with liquid carbon dioxide, the main constituents dissolving and leaving behind the hard gum and wax additives of the grease. This can have a catastrophic effect on mechanical plant, for example, seized valve spindles and bearings that no longer rotate. There are specific lubricants and greases designed for carbon dioxide applications and these should be used.

2.4.9 Hydrate formation

If water is present in a carbon dioxide pipeline, even where there is no free water, carbon dioxide hydrate may form, as described earlier in 2.2.1. The consequence of hydrate formation may be a localised reduction in the hydraulic diameter of the pipeline, hence reduced transport capacity. In the worst case hydrate formation may cause blockage of the pipeline. During sudden changes in flow or pressure hydrates can also damage pipeline walls as they accelerate around small radius bends.

2.4.10 Carbon Dioxide BLEVE

A BLEVE is an explosion resulting from the failure of a container of liquid at a temperature significantly above its boiling point at normal atmospheric pressure. The term was first applied to steam explosions, but often and incorrectly, it is thought to relate only to flammable materials. BLEVEs involving non flammable liquids produce only two effects: blast due to the expansion of the vapour in the container combined with the flashing of the liquid, and fragmentation of the container (whether that container is a vessel or pipe).

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[20] '*Effect of supercritical carbon dioxide on construction materials*', Schremp and Roberson, Journal of the Society of Petroleum Engineers, June 1975.

[21] '*Pipeline design and construction, a practical approach*'. Mohitpour Golshan and Murray, ASME, 2003.

BLEVEs can be caused by a number of events e.g:

- an external fire;
- external impact;
- corrosion of the pressure containment;
- excessive internal pressure, and
- metallurgical failure of the pressure containment.

Guidelines for evaluating the characteristics of vapor cloud explosions, flash fires and BLEVEs[22] provides more information on how to evaluate the consequences of BLEVEs and gives further details of two known incidents where carbon dioxide BLEVEs resulted in the loss of life.

Much has been learned from similar incidents and this experience has been incorporated into design practices used by the industrial gases industry. One item worth repeating in this text is the issue of ice and hydrate formation. In one of the incidents described in the above book (Repcelak, Hungary, 2 January 1969), it is suspected that ice or hydrate formation caused the failure of a level instrument, which in turn resulted in the overfilling and eventual BLEVE of a vessel. This incident, together with operational experience of carbon dioxide liquefaction plant in the UK indicates that even with good control of moisture within a carbon dioxide process, regular blow down of instrument level legs and other 'stagnant' sections of a process plant are a necessary good practice to eliminate potential for ice and hydrate build-up in critical sections of a carbon dioxide process.

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[22] '*Guidelines for evaluating the characteristics of vapor cloud explosions, flash fires and BLEVE's*', ISBN 0-8169-0474-X, Centre for Chemical Process Safety of the American Institute of Chemical Engineers, 1994.

3 OVERVIEW OF CCS TECHNOLOGY

An overview of CCS technology – by the end of this section, you will:

- understand the different technology options for carbon dioxide capture;
- understand the options for transportation of carbon dioxide between the capture and storage sites, and
- understand the geological options for carbon dioxide storage.

3.1 INTRODUCTION

The capture and storage of carbon dioxide has been identified as one of the key technologies to address carbon dioxide emission reductions. Such schemes comprise three operating elements; capture, transportation and storage. The ongoing legacy of storage also requires measuring, monitoring and verification of the storage site, making a fourth longer term element.

There are currently three main technologies for the capture of carbon dioxide from coal fired power plant. These technologies are: post-combustion capture, which utilises a solvent that reacts with carbon dioxide and selectively removes it from the flue gas downstream of a traditional coal-fired boiler; oxyfuel combustion, which is based on the principle of combustion of coal in an oxygen rich nitrogen-free atmopshere; and pre-combustion capture, which uses the combustion of hydrogen rich (Syngas) fuel created from coal or natural gas when carbon dioxide is removed to power a gas turbine.

Capturing carbon dioxide from a gas stream is a proven technology. For over 80 years carbon dioxide has, as an acid gas, been removed routinely from natural gas sources or flue gases as a product stream either for chemical processes or food grade liquids or gases. Typically, the processes have occurred at small flow rates when compared to the large rates from power station emissions. The largest commercial plant is 1 million tonnes per year, where typically a 1 GW coal-fired station will emit around 7 million tonnes per year. The challenges for capture plant are one of scale and size for the plant itself, then integration of the capture processes to a power station, be it new-build or retrofit and economic impact.

There is already carbon dioxide transportation at the scale required for CCS projects. Carbon dioxide pipelines exist in the US, Canada, Algeria and in the Barents Sea. Predominantly, the transportation has been from point sources to oil fields where the carbon dioxide is used for enhanced oil recovery (EOR) rather than for the purpose of storage. Approximately 50 million tonnes/year is transported through 6 000 km of pipeline operating at pressures up to 172 bara and diameters of up to 900 mm. Ship and tanker transportation of carbon dioxide also occurs within the food industry, but not at the quantities required for fully commercial CCS projects because there is no market to transport such quantities at the present time.

Storage falls into two categories, storage where permanent long term storage of carbon dioxide is the sole purpose and secondly, storage (whether temporary or permanent) that results as a consequence of injection of carbon dioxide into an operating field. Storage may be temporary in the case of carbon dioxide injection for EOR, as some of the carbon dioxide will be extracted again with the hydrocarbon product. However, it can then be recovered and re-injected.

Overall, the integration of these elements is challenging but integrated schemes have been achieved, the issues are scale and cost alongside the safe, secure, sustained operation of each element.

3.2 CAPTURE TECHNOLOGY

3.2.1 Overview

Capture of carbon dioxide from flue gases and natural gas streams has already been implemented in many plants and is commonly used for medical and food carbon dioxide production as well as in a few instances for EOR. The technology has been deployed at what had been considered large scale, up to 1 million tonnes per year.

A coal-fired power station produces about 743 g/kWh of carbon dioxide and a natural gas CCGT produces about 379 g/kWh[23]. Thus with 90 % capture, a 2 000 MW coal station would prduce 1 337 tonnes/hour (32 000 tonnes/day) of carbon dioxide, and a 930 MW natural gas CCGT would produce 317 tonnes/hour (7 613 tonnes/day of carbon dioxide).

Post-combustion capture of carbon dioxide involves the addition of a capture plant downstream of a traditional coal-fired boiler. Since the capture plant requires a low inlet SO_2 concentration, it would be fitted downstream of the flue gas desulphurisation (FGD) plant and may also include an additional SO_2 polishing unit to reduce the SO_2 concentration further. It is suitable for both retrofit and new-build applications.

Pre-combustion capture involves the capture of carbon dioxide from an integrated gasification combined cycle (IGCC) plant. In an IGCC plant, coal or natural gas is oxidised in an atmosphere in which there is a 'shortage' of oxygen (air) in a pressurised reactor. Reducing conditions are, therefore, maintained and a mixture of primarily carbon monoxide and hydrogen gas is produced. This product is called syngas. This carbon monoxide is then reacted with steam over a catalyst to produce carbon dioxide and more hydrogen. The carbon dioxide can then be removed via a solvent scrubbing process, leaving a gas which is predominantly hydrogen. The hydrogen is then diluted with steam or nitrogen and combusted in a combined cycle gas turbine (CCGT) to generate electricity. Pre-combustion can also be applied when using natural gas.

The basic principle of oxyfuel combustion is the combustion of fuel (usually coal) in an oxygen rich nitrogen-free atmosphere, thereby producing a flue gas which is predominantly carbon dioxide and water, SO_2, SO_3 and NOx having been reduced to acceptable levels. The carbon dioxide is conditioned to the required purity (through removal

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[23] '*Capturing CO_2*' IEA Greenhouse Gas R&D Programme May 2007.

of the water and other trace impurities) and then compressed and transported for storage. A proportion of the flue gas is re-circulated back to the boiler to control temperatures and flow rates. Oxyfuel firing can be suitable for both retrofit and new-build applications.

Typically, the capture processes are currently considered expensive to build and operate and are energy intensive. New technologies and improvements to existing ones are the subject of considerable research.

The list below sets out the processes and technologies of most interest at present:

New technologies such as ammonia-based processes may be significantly less energy intensive, whilst amine processes are improved. There is, therefore, a range of current technologies in addition to a number of processes that are developing and emerging. These include:

- Amine solvents:
  - ethanolamines;
  - hindered;
  - unhindered;
  - diamines, and
  - amino acids.
- Ammonia solvents:
  - aqueous, and
  - chilled.
- Physical solvents:
  - selexol, and
  - rectisol.
- Adsorption;
- Membranes;
- Sodium bicarbonate solvents;
- Ionic liquids;
- Potassium carbonate, and
- Cryogenic.

The more mature technologies are those that are amine-based, particularly ethanolamines, physical solvents and on a smaller scale, membranes. The above technologies are now described in more detail.

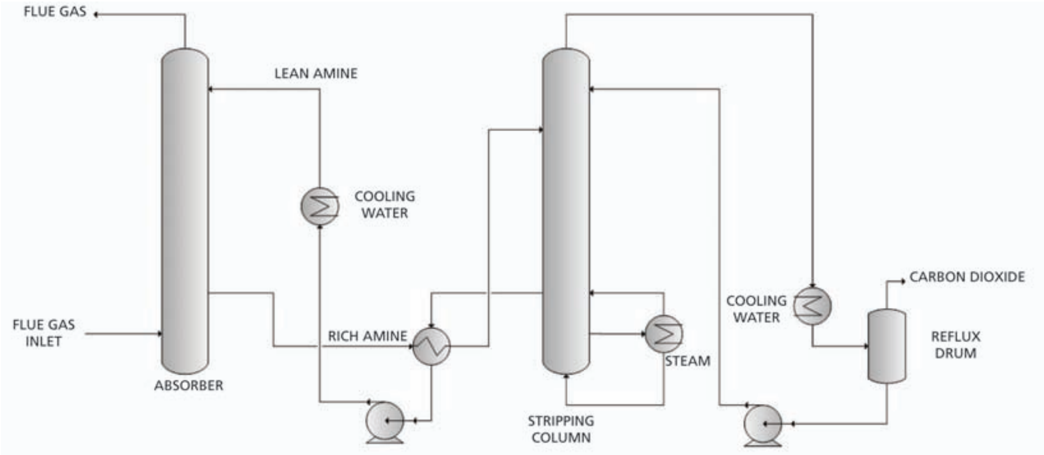

Figure 16 Example chemical absorption process

3.2.2 Absorption

Chemical absorption

Chemical absorption for removal of carbon dioxide, hydrogen sulphide and oxides of sulphur and nitrogen from gas mixtures is a well proven and mature technology. The energy industry has been utilising this simple technique for over 80 years to treat gas and flue gases. The process is essentially an absorber and a stripper, using heat to drive off the captured gas, Figure 16.

Feed gases to the unit are treated for contaminants, bulk sulphur and nitrous oxides are removed, cooled and then contacted with the chemical absorbent which is in the form of a solvent. The solvent traps the carbon dioxide by forming chemical bonds with it in a large absorber tower. Flue gas, stripped of the majority of carbon dioxide, vents from the absorber to the stack. The carbon dioxide rich amine is then processed in another tower which uses heat to strip the gas from the solvent. The carbon dioxide stream exits from the top of the stripper and is cooled to remove solvent and water vapours, which are returned to the regeneration column. The carbon dioxide that is captured is normally at a high purity and is then compressed, dehydrated and liquefied. The carbon dioxide lean amine is then re-circulated from the stripper to the absorber to capture more gas. Both the rich solvent travelling to the stripper column and the lean solvent travelling to the absorber pass through a heat exchanger where the hot lean solution is cooled by the rich solution.

The most common process uses ethanolamine derivatives (mono-, di-, tri- or methyl di-ethanol amines) as the solvent. Amines have a high affinity for acid gases and the absorption process is quick and efficient; capture rates in excess of 80% are typical. The solvent itself is an aqueous solution and may contain corrosion inhibitors in the mixture. The established processes are particularly heat intensive. The bulk solvent in the stripper is heated and the energy used is typically 30 % of an associated power station’s thermal output. More advanced processes are coming to commercial deployment using sterically hindered amines or amine blends which promise increased efficiency and lower energy requirements.

Ammonia systems typically work in a similar fashion using an absorber followed by a stripper. A key element with the use of ammonia is the vapour losses in both columns need to be controlled. Whilst some systems operate cold, some operate in an aqueous environment with ammonia vapour control equipment on the flue outlets. Ammonia systems may require a much lower thermal load of around 16-19 % of a power station's thermal output for example and may have smaller equipment, generally reducing capital and operational costs.

Inorganic solvents such as potassium carbonate or sodium carbonate are being examined as potential future absorbents. These have the advantage of requiring lower temperatures to release the bond between the carbon dioxide and the solvent, therefore less energy is needed, lowering the capture site energy load and the associated costs. The solvents may, however, have lower rates of reaction than amines.

Physical absorption

For higher concentration carbon dioxide streams, physical absorbents can be used. Here partial pressure rather than a chemical reaction holds the carbon dioxide in the absorbent. These processes are again mature technologies used for a number of years in the capture of acid gases. Rather than heat being required to strip the gas from the absorbent the process can be achieved by reducing the pressure adding further options to improve efficiency. Being partially dependent on pressure these solvent processes function better than amines in pressurised systems, and are commonly expected to be deployed with IGCC carbon capture enabled power systems.

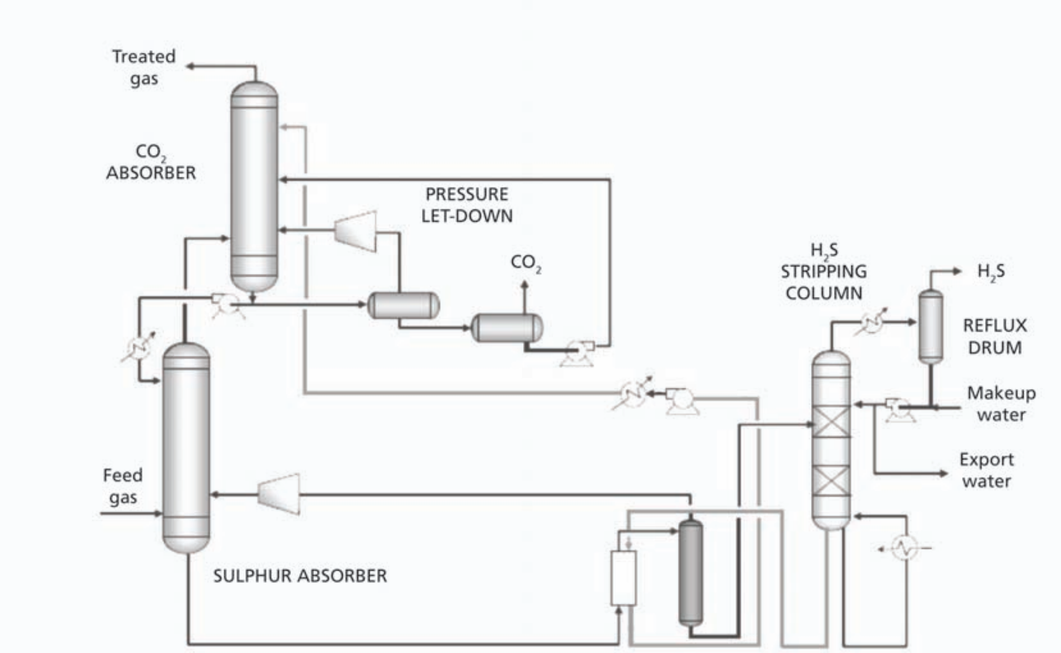

Figure 17 Example physical absorption process

3.2.3 Adsorption

Solid materials which have a porous surface or a granular structure often have very high surface areas. This makes the surface of the materials potentially a good adsorber of carbon dioxide from the flue gas. Typical examples of the materials used in adsorption include activated carbon (due to its extremely porous structure) and zeolites (which contain a microporous structure).

When the material has reached its maximum adsorption the carbon dioxide can then be stripped by change in pressure (pressure swing adsorption (PSA)), temperature (temperature swing adsorption (TSA)) or by applying a low electrical current across the material (electric swing adsorption (ESA)).

These methods may be more suitable to pre-combustion technology rather than post-combustion, but in most cases insufficient research has yet been undertaken to establish their efficiency at relatively low carbon dioxide concentrations.

3.2.4 Membrane separation

Selective gas membrane separation

A membrane that is selective for carbon dioxide must be used. Viable options for this are ceramic or polymeric membranes or a combination of the two. As the flue gas moves along the membrane the carbon dioxide passes through. The separated carbon dioxide is at a lower pressure than the flue gas and this drives the separation.

Gas absorption membranes

In this process, the micro-porous membrane is used to separate the flue gas and a liquid flow. Different from the gas separation membrane, it is the liquid flow on the other side of the membrane which separates the carbon dioxide from the flue gas. As the flue gas passes the membrane the carbon dioxide diffuses through and is absorbed by the liquid on the other side.

3.2.5 Cryogenics

For capture using cryogenics the carbon dioxide-rich stream is compressed, cooled and condensed, after the removal of water to avoid blockages. Impurities are removed either before the CO_2 becomes liquid (e.g. SO_2, boiling point −10 °C), or (e.g. hydrogen, boiling point −253 °C) as remnant gas after liquification. This technique is most applicable to pre-combustion capture and oxyfuel combustion and is used for streams which contain high concentrations of carbon dioxide. A large amount of energy is needed, however, to cool the stream. The process has the advantage of directly producing high pressure liquid carbon dioxide which requires little pre-treatment for onward transportation.

3.3 TRANSPORTATION

3.3.1 Overview

A key component of a CCS scheme which is often overlooked is the transportation system. Pipeline and ship transport are the only options for large scale transport of carbon dioxide. The principal method for transport of food and medical grade carbon dioxide is currently via road, although large consignments of carbon dioxide are sometimes transported by ship. While onshore pipeline transport of carbon dioxide is relatively mature, existing carbon dioxide transport by ship has not been established and may require significantly larger ships than currently exist for the purpose.

Existing carbon dioxide pipelines are mostly located in the United States and Canada, where predominantly natural sources of carbon dioxide are utilised in EOR schemes. Apart from a short length of pipe on the Sleipner project, the Snøhvit carbon dioxide pipeline in the North and Barents Sea are currently the only example of offshore carbon dioxide transport.

In total, around 6 000 km of pipelines have been laid since 1972. The carbon dioxide is transported in the dense or supercritical phase. Operating in this regime reduces viscosity and surface tension while increasing density. This is therefore the most efficient way of transporting carbon dioxide by pipeline.

Whilst the US and Canadian experience (see Figure 18) demonstrates that pipeline transportation of carbon dioxide is a proven technology, issues related to applying the technology in the context of CCS remain. These include:

- The transfer of US and Canadian experience into a global market.
- The application of the technology offshore and the associated consequences of reduced access.
- The transport of carbon dioxide from anthropogenic sources containing impurities and hence the need to define appropriate equations of state to describe the behaviour of the carbon dioxide stream.
- The higher population density found in other global locations including Europe and the associated health and safety implications of on-land pipeline routing.

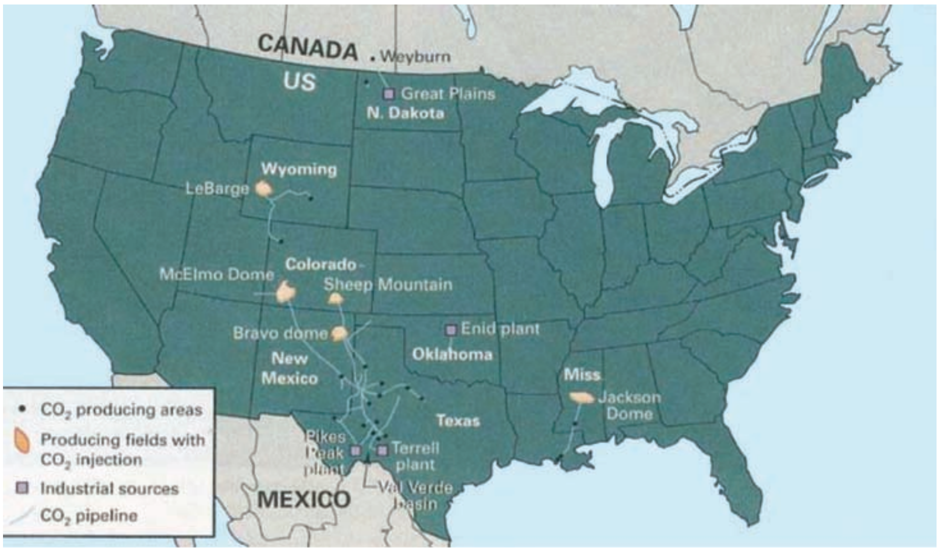

Figure 18 Illustration of the carbon dioxide pipeline network in North America

Detailed information on the design issues associated with carbon dioxide pipelines is set out in section 6.

3.4 STORAGE

3.4.1 Overview

After the capture and transportation of carbon dioxide it then must be stored. There are two main storage options for the UK and four main techniques to enable storage:

Carbon dioxide may be stored in:

- deep saline formations, and
- formations that contain hydrocarbons.

The storage may be:
via direct injection into a deep saline formation or depleted hydrocarbon formation:

- as a consequence of enhanced oil recovery;
- as a consequence of enhanced gas recovery, and/or
- for the purposes of enhanced coal bed methane production.

The availability of storage is determined mostly by geography, the proximity of an emitter to a potential sink and the nature of the site. Not all depleted hydrocarbon fields or EOR/enhanced gas recovery (EGR) schemes would be considered to be suitable storage sites.

Deep saline formations

Deep saline formations are geological formations located deep underground where highly saline water is present in porous rock formations. To get the carbon dioxide into the reservoir it is injected at pressure. This increases the 'pressure' within the reservoir which leads to a displacement of some of the *in situ* reservoir fluids which will offer resistance to movement.

Carbon dioxide is held in place in a storage reservoir through one or more of five basic trapping mechanisms: (1) stratigraphic, (2) structural, (3) residual, (4) solubility and (5) mineral trapping.

Initially, the dominant trapping mechanisms are stratigraphic or structural trapping or a combination of the two. Following injection and due to buoyancy forces carbon dioxide will rise to the top of the storage formation where it will be 'trapped' by an impermeable caprock which keeps the carbon dioxide within the reservoir. In structural trapping, impermeable rocks will contain the carbon dioxide within the reservoir as a result of faulting or some other geological mechanism where impermeable caprocks are juxtaposed over the more permeable reservoir rocks.

Residual trapping mechanisms generally dominate after injection ceases. Some carbon dioxide is trapped in pore spaces by the capillary pressure of water. Post injection, water from the surrounding rocks migrates back into the pore space containing the carbon dioxide which immobilises the carbon dioxide.

Over relatively short timescales carbon dioxide will dissolve into saline formation waters (solubility trapping). Carbon dioxide rich waters will be negatively buoyant and tend to sink to the base of the deep saline formation. Over much longer timescales the carbon dioxide may react chemically with the surrounding reservoir rocks to form stable minerals such as carbonates.

When storing carbon dioxide in deep saline formations, the most effective sites are those where the carbon dioxide becomes immobile. This happens when the carbon dioxide is: (1) trapped under a thick, seal of low permeability; (2) converted into solid minerals; (3) trapped through a combination of physical and chemical mechanisms.

These trapping mechanisms also apply in principle to carbon dioxide injection into hydrocarbon containing formations.

Abandoned oil and gas fields

Many abandoned oil and gas fields have very good potential for carbon dioxide storage as the hydrocarbons originally stored within the reservoirs did not escape into the atmosphere or overlying geological formations over millions of years prior to being extracted. They therefore provide a safe place to store the carbon dioxide without risking leakage into the atmosphere or overlying geological formations. A potential disadvantage, however, is that when hydrocarbon recovery was completed at these fields the production/monitoring wells were filled with mud-laden fluid and plugged with cement grout since it was not thought that one day they would be used as a storage facility for carbon dioxide. These man-made structures have the potential to provide preferential pathways for carbon dioxide leakage if their integrity is not maintained.

Enhanced oil recovery

There are two main methods of EOR which are thought to be suitable in the UK. Gravity stable gas injection typically takes place towards the end of a hydrocarbon field's working life and involves the injection of gas into a reservoir pushing the oil downwards through the reservoir towards production wells. It is anticipated that significant volumes of carbon dioxide would have to be injected relatively slowly to maintain a carbon dioxide front moving through the reservoir. An alternative variant on this process is the injection of alternating slugs of carbon dioxide and water into an oil reservoir. The carbon dioxide mixes with the oil, decreasing its viscosity and swelling it, and because it is lighter than water, it may rise through the reservoir. The following slug of water helps move the carbon dioxide/oil mixture towards production wells. In both cases, between 50-70% of carbon dioxide returns with the oil; however, this can be separated and re-injected into the hydrocarbon reservoir to minimise operational costs. The remaining carbon dioxide is trapped in the reservoir formation and may be considered as permanently stored.

When recovering oil, the displacement created by the carbon dioxide depends on the phase behaviour of the carbon dioxide and the crude oil mixtures. These are strongly dependent on reservoir temperature and pressure. Once oil recovery has ceased, the reservoirs are in principle available for further carbon dioxide storage.

EGR

As carbon dioxide is denser than natural gas, injecting carbon dioxide into the base of a gas field would result in natural gas rising through the reservoir. This has the potential to increase gas recovery rates. To date EGR has only been carried out at pilot scale.

Coal seams

There is thought to be limited quantifiable carbon dioxide storage potential in UK coal seams due to their low permeability. Furthermore, as coal is an important energy mineral in the UK its use for carbon dioxide storage would limit the potential for future mining or underground gasification of the coal in the future. To date small scale pilot investigations have been attempted to ascertain the potential for carbon dioxide storage within coal beds throughout the world. At present this is still considered to be an immature technology.

3.5 SUMMARY

There are three key technology types used for capturing carbon dioxide, each at varying scales of demonstration and maturity. The three process types are: (1) post-combustion capture; (2) pre-combustion capture and (3) oxyfuel combustion. Each option has its own technical complexities and currently demonstration projects using all three technologies are being developed (see next section).

Transportation of carbon dioxide already takes place in pipelines, tankers and by ship. Transportation in pipelines is at an equivalent scale, and there are limited examples of this type of pipelines. Tanker and ship transportation exists at smaller scale as there has been no demand for larger scale and without the experience of coupling a ship to an offshore injection point.

Storage is possible within deep saline formations, depleted oil and gas fields and also within coal seams. Carbon dioxide can also be used for enhanced oil and gas recovery, where carbon dioxide is immediately stored within the formation. Most of that carbon dioxide will emerge with the hydrocarbons and will be processed and re-injected. Further storage capacity may become available at the end of the field's life.

4 STATE OF THE ART FOR CCS COMPONENTS

State of the art for CCS technology components – by the end of this section, you will:

— understand the current application of different CCS technologies, including the scale at which they are employed and

— have an overview of some of the planned future CCS projects.

4.1 INTRODUCTION

As far back as 1992 and probably earlier, strategies were being discussed on how to deliver low emissions from the use of coal for power production. At that time the main emphasis was on low emissions of sulphur dioxide and nitrous oxides, and also, for the 'long term', carbon dioxide[24]. Over the past 17 years some of the components and technologies that were established then have been further developed, and other technologies that were at bench-scale have been brought to pilot-scale, with full-scale demonstration projects being planned. This chapter presents the current stage of development for the main components of the CCS chain using the best information publicly available at the time.

4.2 CARBON DIOXIDE CAPTURE

It has previously been explained (section 3.2, capture technology) that there are a number of different technologies capable of capturing carbon dioxide and that the more mature technologies are those that are amine-based, particularly alkanolamines, physical solvents and on a smaller scale, membranes. This section will address chemical solvents, and physical solvents, being those most appropriate to large-scale carbon dioxide removal. It will also include oxy-combustion and briefly consider membrane separation.

4.2.1 Chemical solvents

Chemical solvents described in section 3.2.2 are most appropriately employed where the partial pressure of the carbon dioxide in the gas being treated is low, a situation which is typical of post-combustion capture from pulverised fuel power stations, where the bulk of the flue gas is nitrogen from air. The same technology would also be used to remove the carbon dioxide from the flue gas of natural gas CCGT power stations, where the partial pressure of carbon dioxide is even lower.

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[24] 'CO_2 Abatement from power generation', CJ Bower, British Coal Corporation, CRE. Part of 'The future for coal in power generation - clean coal technologies and economics' St. Catherine's College, Oxford, 22-26 June 1992

This would not preclude the use of amines in pre-combustion applications: amine solvents have been used for sulphur removal on a number of IGCC projects (e.g. Puertollano, Buggenum), and some operators familiar with the amine plants are planning or constructing pilot plants to remove carbon dioxide from a slipstream of the syngas.

Development has been targeted at two principal chemical solvents, amines and ammonia, although applications for these developments are not confined to the power generation sector alone.

4.2.1.1 Amines

It would be wrong to claim that the list of amine-based plants extracting carbon dioxide is exhaustive, but the picture it is hoped to present is that this technology has been proven at scale sufficient for the demonstration projects that are currently planned in a number of different industrial and commercial contexts (the 1 000 tonnes of carbon dioxide a day recovery plant described below is approximately equivalent to the capture required for a 60 MW_e demonstration plant). There will be a step change in scale for commercial projects, which will have an electrical capacity in the hundreds not tens of megawatts.

Carbon dioxide for EOR

The largest carbon dioxide recovery plant in the world was the 1 000 tons/day (42 tons/hour) carbon dioxide technology plant at Lubbock, Texas (USA) which used the Fluor Daniel econamine process to remove carbon dioxide from the flue gas of a natural gas plant. The facility was designed to produce carbon dioxide for EOR at the nearby Garza field. This same process was also used on the 90 tons/day (3,75 tons/hour) N-Ren Southwest plant at Carlsbad New Mexico (USA)[25]. Mitchell Energy (Bridgeport, Texas, USA) also commissioned a 493 tons/day (20 tons/hour) econoamine plant for EOR. All three of these plants have now been shut down[26] following the collapse in the crude oil price in 1986[27].

Carbon dioxide for soda ash production

In 1976, the North American Chemical Company (Trona, California, USA) commissioned an amine-based 800 tonnes/day (33 tons/hour) carbon dioxide plant to carbonate brine to produce soda ash (Na_2CO_3), which is still operating today.

There is a smaller plant (300 tons/day, 12,5 tons/hour) producing soda ash from brine at Aua Pan in Botswana, which has been operational since 1991. Both of these use monoethanolamine (MEA) processes to strip the carbon dioxide from flue gases, the former from a gas engine, the latter from a coal-fired boiler.

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[25] '*Recovery of CO_2 from flue gases: commercial trends*', Chapel, Ernest, Mariz, Canadian Society of Chemical Engineers, October 1999.

[26] '*CO_2 capture – post combustion flue gas separation*', Module 2 from 'Building capacity for CO_2 capture and storage in the APEC Region' S. Wong, Asia-Pacific Economic Cooperation.

[27] '*Recovery of CO_2 from flue gases: commercial trends*', Process Engineer Magazine, December 28 2007.

Food grade carbon dioxide

Northeast Energy Associates (Bellingham Massachusetts, USA) commissioned an amine-based food-grade carbon dioxide plant in 1991, extracting 320 tons/day (13 tons/hour) from the flue gas of a natural gas-fired CCGT. The combined cycle output is 303 MW. Food-grade carbon dioxide (200 tons/day, 8,3 tons/hour) is also removed at the AES plant at the 320 MW Shady Point in Poteau (Oklahoma, USA), but from a coal-fired fluidised bed boiler. All of these use an inhibited monoethanolamine (MEA) process.

At Chiba, in Japan, Sumitomo Chemicals have extracted 165 tons/day (7 tons/hour) of food-grade carbon dioxide from gas boilers and an oil/coal boiler, using a Flour Daniel amine process since 1994: Prosint have used the same process to extract 90 tons/day (3,75 tons/hour) from a gas-fired boiler in Rio do Janerio since 1967.

In Australia, Liquid Air Australia have two 60 tonnes/day (2,5 tons/hour) MEA plants using a Dow design extracting carbon dioxide from a gas boiler to produce food-grade carbon dioxide, which has been in operation since about 1995.

YARA, in Norway, produce 425 000 tonnes/year of carbon dioxide. It is captured after reforming by absorption with water under high pressure.

Carbon dioxide for the manufacture of Urea

In Luzhou, Sichuan Province in China, the Luzhou Natural Gas Company is extracting 160 tons/day (6,7 tons/hour) of carbon dioxide from the reformer exhaust of the ammonia plant, making 150 000 tonnes a day of Urea and other fertilisers using an MEA technology supplied by Dow, who also supplied it to the Indo Gulf Fertilizer Company (Jagdishpur, Uttar Pradesh, India), where 150 tons/day (6,25 tons/hour) of carbon dioxide is extracted from the reformer exhaust.

Carbon dioxide for CCS

The most advanced amine plants with CCS in mind are probably those designed by Kepco. Since 1990 the Kansai Electric Power Company (KEPCO) working with Mitsubishi Heavy Industries (MHI) have been developing a carbon dioxide removal process to service coal-fired power stations. This was first tested at the Nanko power plant in Osaka. It was first used at commercial scale (160 tonnes/day, 6,7 tonnes/hour) in Kedah, Malaysia in October 1999 with a second plant (330 tonnes/day, 13,75 tonnes/hour) in operation from 2005 and a third in India (2 x 450 tonnes/day) starting up in 2006. An improved version of the technology, KM-CDR, was employed on a fertiliser plant in Abu Dhabi (400 tonnes/day, 16,7 tonnes/hour)[28]. Beyond this, it has recently been reported that MHI and Southern Company in USA are to launch jointly a 500 tonnes/day (21 tonnes/hour) carbon dioxide capture demonstration plant, at Plant Barry, a medium scale thermal power station in Alabama[29]. MHI also have a 10t CO_2/day (0,4 tonnes/hour) pilot plant extracting flue gas from J-POWER's Matsushima power plant at Saikai City, Nagasaki, Japan, which was started up in July 2006. The amine process is aimed at the post-combustion atmospheric market, and is not intended to separate H_2S and carbon dioxide[30], making it unsuitable for the IGCC market.

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[28] '*Development and improvement of CO_2 capture system*' Yagi, Mimura, and Yonekawa.

[29] '*Mitsubishi heavy to test CO_2 recovery from coal fired flue gas*', Steel Guru News, 27 May 2009.

[30] Telephone call Atsushi Kato (MHI)/Andy Brown (Progressive Energy), 22 June 2009.

Amine plants producing ~1 million tonnes CO_2/year (~115 tonnes/hour) are operating on CCS projects at Sleipner, I-n-Salah and Snøhvit (see 4.5.1).

SaskPower have constructed a 4 tonnes/day carbon dioxide removal plant at their 100MW Boundary Dam power plant, near Estevan, Saskatchewan, Canada (see Figure 19). This is eventually expected to capture about 1 million tonnes a year[31].

Another operational amine unit in Europe at the moment is the 24t CO_2/day at the 420MW power plant in Esbjerg, Denmark, operated by DONG Energy. This was built as part of the CASTOR project and started up in March of 2006. The power station with the carbon dioxide capture plant is shown in Figure 20.

Figure 19 The 4 tonnes/day CO_2 capture plant at Boundary Dam

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[31] '*Saskatchewan plans clean coal-carbon capture project*', Power Engineering International, 29 February 2008.

Figure 20 Esbjerg power plant with 24 tonnes/day CO_2 removal plant shown in red box

ENEL are expecting to have a 62t CO_2/day amine-based carbon dioxide removal plant operating on Unit 4 of the 4 x 660MWe Brindisi Sud power station operational in the autumn of 2009. This will process 10 000 Nm^3/h of flue gas, and extract 2,6 tonnes/hour of carbon dioxide[32]. ENEL are also planning a 600 000 Nm^3 /h demonstration plant for a 660 Mwe unit at the Torrevaldaliga Nord Power Station[33].

Carbon dioxide for other applications

The 180 MW Warrior Run power plant in Cumberland, Maryland (USA) captures 96 % of the carbon dioxide from its fluidised bed boilers for use in fire extinguishers and the manufacture of dry ice[34].

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[32] '*Advanced coal fired power plants equipped with post-combustion CO_2 capture systems at ENEL*', Rossi, Mallagge, November 2007.

[33] '*Ambiente, progetto pilota Eni-Enel a Brindisi per il trasporto della CO_2*', www.gazz.mezzagiorno.web, October 2008.

[34] '*Can carbon capture and storage save coal?*', Scientific American, 6 April 2009.

Table 9 Summary of maturity of chemical solvent CO_2 removal plants

Location	Capacity (tones/hour)	CO_2 use
Abu Dhabi	16,7	Fertiliser
Aua Pan (Botswana)	12,5	Soda Ash
Esbjerg (Denmark)	1	CCS
Indo Gulf Fertiliser (India)	6,5	Urea
I-n-Salah	115	CCS
Kedah (Malaysia)	13,75	CCS
Liquid Air (Australia)	2,5	Food grade CO_2
Lubbock (Texas)	42	EOR
Luzhou (China)	6,7	Urea
Mitchell Energy (Texas)	42	EOR
Nanko (Japan)	6,7	Urea
North American Chemical (California)	33	Soda Ash
Northeast Energy (Massachusetts)	13	Food grade CO_2
Rio de Janerio (Brazil)	7,75	Food grade CO_2
Shady Point	8,3	Food grade CO_2
Sleipner	115	CCS
Southeast (New Mexico)	3,75	EOR
Snøhvit	80	CCS
Sumitomo Chemicals (Japan)	7	Food grade CO_2
Warrior Run	4,5 (estimated)	Fire Extinguishers

By way of comparison, a 400 MW power station could produce 150-400 tonnes of CO_2 per hour, depending on the fuel available and technologies employed.

4.2.1.2 Ammonia

A number of companies are developing ammonia-based carbon dioxide removal technologies.

Alstom has developed their proprietary chilled ammonia process, setting the goal of making it commercial by 2011. In order to accomplish this, they have paired with American Electric Power (AEP) for two large-scale, testing and demonstration projects. The first phase of testing will be at the 1 480 MW Mountaineer plant, (New Haven) on a 30 MWth slipstream, and should capture up to 100 000 tons CO_2/year. Testing started in late 2008 and is projected to continue for a period of 12-18 months. For the second phase of this project, Alstom intends to move to a 200 MW demonstration on a 450 MW unit at the Northeastern power station, Oologah. The projected start-up date for this phase of demonstration is late 2011. In Europe, Alstom have constructed a chilled ammonia pilot unit on a 5 MW oil-fired auxiliary unit on E-ON's Karlshamn power station in Sweden, on which tests are being run in 2009[35].

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[35] '*Carbon capture in Karlehamn*', E-on Company Report 2008.

Alstom will also test the chilled ammonia process at the Technology Centre Mongstad, Norway. On behalf of the partners of the European CO_2 Technology Centre, Mongstad (TCM), StatoilHydro has signed an engineering, procurement and construction contract (EPC) with Alstom Nowary AS for a chilled ammonia (carbonate) carbon dioxide capture plant at TCM in Norway.

In 2008 HTC Purenergy commissioned a 50 MWth amine scrubbing facility at Searles Valley Minerals in Kansas, USA. The absorption columns are 14'6" ID (4,42 m) and 119' (36,2 m) high, and the stripper column is 12'6" ID (3,81 m) and 77' (23,5 m) high[36].

Figure 21 Columns at Searles Valley Minerals[37]

Powerspan also has an ammonia-based post-combustion capture process, called ECO_2 developed together with NETL. The ECO and Eco-SO_2 (no NOx control) processes, to which this is added, were first demonstrated on FirstEnergy's 413 MW RE Burger Plant in Ohio. The pilot scale testing of the ECO_2 process on a 1 Mwe slipstream, began in December 2008. This test is expected to capture 90 % of the carbon dioxide in the flue gas, which will amount to approximately 20 tons/day. The pilot has demonstrated up to 88 % carbon dioxide removal from an inlet concentration of 9,5%, equivalent to over 90 % from the design condition. Pilot testing is planned to continue to the end of 2009. They are also planning a commercial scale (120 MWe to capture 1 million tons/year, 110 tonnes/hour) demonstration, at Basin Electric Power Cooperative's Antelope Valley Station in North Dakota, which is scheduled to be online in 2012[38].

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[36] '*Capture ready coal plants*', M.Farley, Doosan Babcock energy, presented at I.Mech.E. 12November 2008.

[37] From www.htcpurenergy.com/co2info.

[38] E-mail from Stephanie Procopis (PowerSpan) to JAG Brown (Progressive Energy), 1 June 2009.

4.2.2 Physical solvents

4.2.2.1 DMEPEG

The most developed DMEPEG processes are those using Selexol, licensed by UoP. Selexol is being used on the 2 040 tonnes/day CVR Energy coal-to-ammonia plant in Kansas (see Figure 22). This produces about 128 tonnes/hour from the carbon dioxide flash drums, of which 18 % (23 tonnes/hour, or 10,5 MMSCFD or 297 000 Nm^3) is sent to the Urea plant[39], and was commissioned in July of 2000.

Figure 22 The CVR Energy Ammonia plant

4.2.2.2 Methanol

The most developed methanol process is Rectisol, jointly developed by Lurgi and Linde.

The Rectisol process (chilled methanol) is used at the Great Plains Synfuels Plant to capture 4,5 million tonnes/year of carbon dioxide (520 tonnes/hour), of which 3 million tonnes/year are exported[40] to the Weyburn project for EOR applications. The syngas is manufactured from lignitic coal in Lurgi gasifiers principally to produce 130 million scf/day (3,65 million Nm^3) of synthetic natural gas.

The largest Rectisol plant currently in operation is a coal-to-liquids operation for the Shenhua Group Corporation Limited in the Shenfu Dongsheng coalfield area[41] of Inner Mongolia (China), which started up in 2007. The feed gas flow rate of this plant is

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[39] '*Synthethis gas purification in gasification to ammonia/urea complex*', presented at the GTC in 2004, and e-mail Vanheertum (UOP)/Brown (Progressive Energy), 23 June 2009.

[40] '*Ongoing CO_2 capital and transport costs*', G. Loop, Dakota Gasification Conference, May 2008.

[41] '*Shenhua Group – present and future*', www.iea.org/textbase/work/2004/coal/ShenhuaEng.pdf

24 200 kmol/hr (equivalent to 1 065 tonnes/hour) at 34 bara with carbon dioxide component removed from 42 % to 2 %. Linde Engineering is currently commissioning a Rectisol plant in China for a coal-to-liquid gasification project that removes 240 000 Nm^3/hr of carbon dioxide (445 tones/hour) from a shifted feed gas. This plant represents the largest Rectisol unit designed by Linde to date.

It should be noted that a standard Rectisol only makes about 60 % of the carbon dioxide available as product, and that modifications would be required to capture closer to 100 % for CCS schemes[42].

This process is used at the Pernis refinery (127 MW IGCC project) in the Netherlands operated by Shell Gasification Solutions. The Pernis plant is the first IGCC facility equipped with carbon dioxide separation, although 50% of the separated carbon dioxide is currently vented; the other 50% (300 000 tonnes/year) is distributed to greenhouse operators where the carbon dioxide is naturally sequestered via photosynthesis. Thanks to this arrangement, Pernis could be considered the only sequestration-ready IGCC plant in the world.

4.2.3 Oxy-combustion

By burning fuel in an oxygen atmosphere, oxy-combustion is designed to produce a flue gas that is high enough in carbon dioxide that little further processing is necessary before it can be compressed and exported from the power station site.

A 30 MWth pilot plant to demonstrate the oxy-combustion of coal started in September of 2008 at the Vattenfall power station at Schwarze Pumpe, Brandenberg, Germany. This is one of the largest of its kind in the world, and is intended to validate and support the technical concept as a precursor to a 200 – 300 Mwe demonstration plant generating 'near zero CO_2' electricity under commercial conditions by 2015 or earlier. This plant is designed to capture 75 000 tonnes/year of carbon dioxide (i.e. about 10 tonnes/hour), which will be transported by lorry to a depleted gas field at Aultmark for storage[43]. This storage location is about 200 km from the power station site: storage depth will be 3 km under the surface[44].

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[42] E-mails du Val (BOC Linde)/Brown (Progressive Energy), 10 and 11 June 2009.

[43] '*The pathway to zero emission and the role of demonstration*', Nick Otter, Alstom Power systems, presented at I.Mech.E. 12 November 2008.

[44] '*Worlds first carbon capture pilot fires up clean-coal advocates*', Alok Jha, Guardian, 5 September 2008.

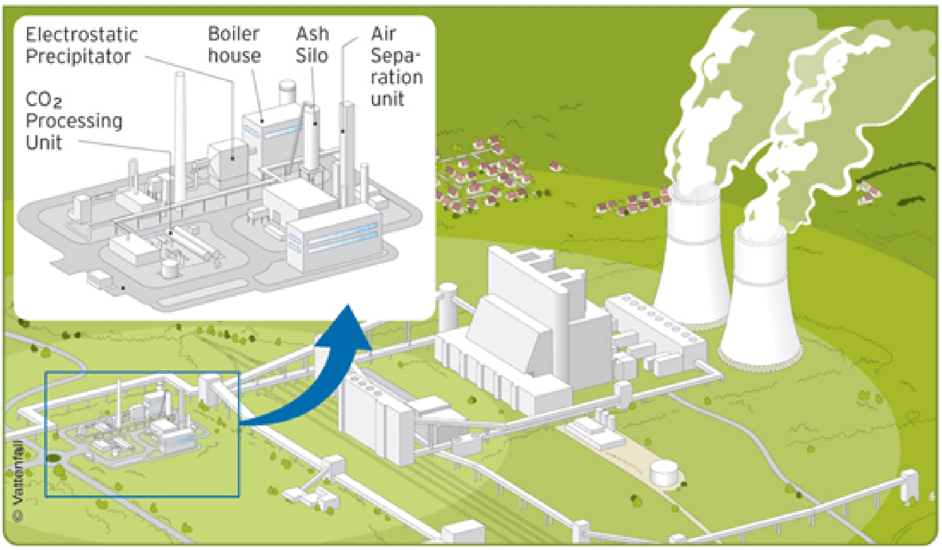

Figure 23 The 30MWth Oxy-combustion pilot plant at Schwarze Pumpe

Doosan Babcock are converting their 40 MWth burner rig at Renfrew to demonstrate an oxyfuel coal burner, coupled with flue gas recycling. The rig will help to demonstrate flame stability, emissions, flame shape, efficiency and to supply information on the heat transfer characteristics. It is hoped to also assist with understanding start-up and shut-down, transition from air to oxygen and load changes. Commissioning is expected in 2009[45].

The largest oxyfuel project presently being progressed is the 30 Mwe bituminous coal power station retrofit at Callide A at Biloea in Australia, which will be commissioning in 2010. This project includes CO_2 capture and storage, which will be in the depleted gas fields of the Dennison Trough geological formation, 350 km from the power station. The aim is to capture 90 % of the CO_2 over a five-year pilot period.

4.2.4 Membrane separation

Membrane separation has principally been developed to separate carbon dioxide from natural gas, because the carbon dioxide content of natural gas is a specified maximum figure for most pipeline systems, typically <1 %. However, for ammonia production the carbon dioxide content must be reduced to 10ppm, and many of the processes described above become costly when this more stringent criterion is required.

The economic comparison between membrane systems and the competing technologies would suggest that membranes are most cost-competitive where the partial pressure of carbon dioxide is high (10 % - 70 %), or where low flow rates are encountered.[46]

Commercial applications have demonstrated feed conditions between 400 psig and 1 400 psig (27 to 97 bar) with carbon dioxide levels from 3 up to ~70 % and feed flow rates from 5 MMSCFD (14,00 Nm^3/day) to 250 MMSCFD (7 million Nm^3/day) with future plans for producing twice that throughput[47].

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[45] '*Capture ready coal plants*', M.Farley, Doosan Babcock energy, presented at I.Mech.E. 12 November 2008.

[46] '*Polymetric membranes to separate CO_2 from natural gas mixtures – a review*', Sridar, Smitha, Aminabhavi, Separation and Purification Reviews, 36:2, 2007.

[47] '*SeparexTM membrane systems*', UOP, 1999.

4.3 CARBON DIOXIDE COMPRESSION

There are a number of different compressor types that can be used for carbon dioxide compression for bulk transport. The incentive is to transport the carbon dioxide in dense phase, which, for the pure gas, implies a pressure of above 73,8 bara, although the density of liquid carbon dioxide is very similar, which could allow pressures as low as 34,85 bara at 0°C (section 2 explains the impact of impurities on these figures).

4.3.1 Axial compressors

Axial compressors are appropriate for compressing carbon dioxide in the gaseous phase, and are available from a number of different suppliers. Axial compressors alone are suitable up to about 6 bar and 1,3 Mm^3/hour. For pressures higher than this an axial/radial compressor would be used, and pressures of up to 16 bar would be possible. An axial/radial compressor has a number of axial stages followed by a number of radial stages mounted on a single shaft.

4.3.2 Centrifugal compressors

Integrally geared types of compressor are ideal for handling a gas which has such extreme volume ratios as carbon dioxide, because each pinion speed can be optimised to maximise stage performance and hence minimise the overall power requirement. In this design, the compressor gearbox can be arranged with up to four pinion shafts (i.e. eight stages) driven from a single centrally-mounted bull wheel, as shown illustratively in Figure 24.

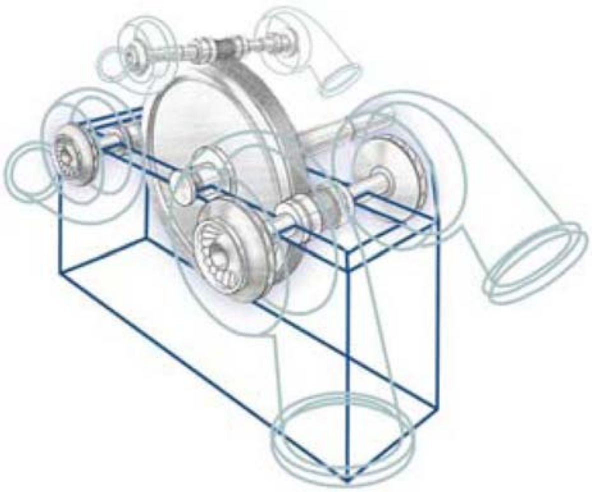

Figure 24 Integrally geared compressor concept

The integrally geared, centrifugal compressor for carbon dioxide is provided with inter-stage cooling and condensate removal from the wet stages; provision can also be made for dehydration during compression to meet pipeline material constraints, as well as avoiding hydrate formation in sub-sea pipelines (see section 2). The machine shown in Figure 25 is one of three MAN Turbo carbon dioxide compressors installed at the Dakota Gasification facility in Beulah, N. Dakota which probably represent the most advanced carbon dioxide compressors in the world. The Beulah facility has been operating continuously since 1997, initially with two compressors and then a third machine was commissioned in 2007 to increase the EOR injection rate. Each machine is designed for operating pressures up to 215 bar with a motor rating of ~14,7 MW; however due to the increased pipeline pressure-drop with three compressors operating, a pumping station has been introduced roughly midway in the pipeline to Weyburn. Suction flow rates of up to 350 000 m^3/hour are available[48]. This equates to 650 tonnes/hour[49].

Figure 25 Integrally geared compressor for Weyburn Project

Table 10 gives MAN's references for large-scale CO_2 compressors of the sort that would be supplied for CCS applications.

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[48] Information and figures provided by MAN Turbo: e-mail Allen (MAN)/Brown (Progressive Energy) 10 June 2009.

[49] Assuming pure CO_2 at an inlet temperature of 40 °C.

Table 10[50] MAN Turbo references for large-scale CO_2 compressors

Location	Type	Mass flow of CO_2	Pressure	Stages
North Dakota	RG80-8	126 tonnes/hour	187bara	8
Azot Nowomoskowsk (Russia)	RG56-10	46,8 tonnes/hour	200bara	10
Duslo (Slovakia)	RG40-8	28,8 tonnes/hour	150bara	8
Grodno Azot (Czech Republic)	RG56-8	57,6 tonnes/hour	150bara	8

Siemens also make internally geared compressors up to 480 000 Nm^3/hour (890 tonnes/hour) at pressures up to 100 bar.

4.3.3 Reciprocating compressors

Reciprocating compressors fall into two types, piston and diaphragm:

4.3.3.1 Piston compressors

Because of its high Joule Thompson coefficient (μ_{JT}, see section 2.1.1), carbon dioxide is used as a refrigerant gas, where it is known as R744. Piston compressors are frequently used in refrigerant applications, where the pressure to which the carbon dioxide has to be compressed is medium (up to about 40 bar). They are also used in the fertiliser industry, where single unit capacities of up to 30 000Nm^3/hour (55 tonnes/hour) at pressures up to 320 bar are available[51].

4.3.3.2 Diaphragm compressors

These pumps use diaphragms made from durable metal or a PTFE sandwich, and have the advantage that they are hermetically tight. The pressure range goes up to 1 200 bar with volumes up to 14 m^3/hour (for liquid carbon dioxide at 40 °C this equates to 2,6 kg/hour). Another advantage is that because of their linear pump characteristics, they can deliver high metering accuracy, making them suitable for re-injection (in an EOR context) or for boosting applications.

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[50] '*Innovative and proven CO_2 compression technology for CCS and EOR*', Habel, Wacker, SOGAT 2009, Abu Dhabi, March/April 2009.

[51] Data from Shenyang High Technical Import & Export Co. Ltd.

4.4 CARBON DIOXIDE TRANSPORT

Carbon dioxide can be transported between capture points and storage sites by pipe, by road tanker or by ship. It is likely that CCS logistics will develop into a combination of pipelines and ships for long distances, similar to the transportation of natural gas, and pipes and tankers for shorter distances, although with the major difference that natural gas is a product with high commercial value. Optimised transport solutions that dynamically follow volume developments are required. Fast-to-implement and low-CAPEX ship transport could be used to work in tandem with pipeline schemes.

4.4.1 Pipe transport

There are thousands of km of underground and overland pipelines carrying a large variety of substances. Some are explosive (natural gas, hydrogen), some are highly flammable (aviation fuel, petrol), some are relatively benign (water) and some pipes contain dangerous chemicals (ammonia, chlorine). In many ways, designing a pipe to carry carbon dioxide from a CCS facility is within current pipe design experience.

The first carbon dioxide pipeline to be constructed in the USA was in 1964[52], so experience in the construction and operation of carbon dioxide pipes stretches back over 45 years.

The longest impure carbon dioxide (96 % purity) pipe is the 205 mile (330 km) line between the Great Plains Synfuels Plant near Beulah in Dakota and the Weyburn oilfield in Saskatchewan (Canada). The pipeline has an internal diameter of 14" and 12" (355 mm and 305 mm) and is manufactured from carbon steel. The carbon dioxide is used for EOR to produce about 120 million barrels of oil. The carbon dioxide injection began in October 2000, and is expected to reach a rate of 95 million cubic feet/day[53] (2,69 million m^3/day, or 220 tonnes/hour).

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[52] '*CO_2 in the United states*' (Revised January 2008), CO2 Norway.

[53] '*Weyburn project plays double role*' FJ Schempf, September 1 2001.

Figure 26 CO_2 pipe at the Weyburn Oilfield[54]

Naturally occurring (relatively pure) carbon dioxide is piped considerable distances to oilfields for use in EOR applications. Each day, approximately 1,3 bn ft^3 (36,8 million m^3) is delivered through about 1 300 miles (2 100km) of pipelines from the McElmo and Bravo domes (among others) to the oilfields in the Permian Basin and the western mid-continent basin[55]. The Cortez pipeline, for instance, is 30” ID (760 mm) and 260 miles (418 km) long and constructed overland.

4.4.2 Carbon dioxide road tanker

Road tankers carrying carbon dioxide have been commonplace for over 40 years. Each tanker holds up to 20 tonnes of carbon dioxide. The operating pressure is between 17,5 and 20 barg, and the carbon dioxide is transported in insulated steel vessels/containers as liquid.

Generally this has been a safe method of transporting carbon dioxide. There have been a small number of incidents reported during loading/unloading over the years: at least one of these was fatal[56]. There do not appear to be any incidents during transit in the UK.

4.4.3 Ship transport

There is, according to some, no inherent difference between shipping carbon dioxide from shipping any other liquefied gas, such as LPG and LNG, and thus vessels used for CCS projects can either continue in the carbon dioxide trade or be converted to standard tanker grade[57]. There are no large carbon dioxide ships similar in scale to those used for LNG/LPG, as the current carbon dioxide market (without CCS) does not warrant their construction.

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[54] Photo courtesy of the Petroleum Technology Research Centre.

[55] Source: Kinder Morgan web site www.kne.com

[56] Berkeley Power Station Gloucestershire, circa. 1983.

[57] '*Benefits of CO_2 shipping*', A. Verder.

Large scale carbon dioxide shipping may be used to support the early CCS industry development as a transport enabler. In addition it could function as a feed-in to hub systems for transport from near-shore point sources. For the volumes and distances foreseen the optimal state of the carbon dioxide would be at a temperature of −55 °C and a pressure around 7 barg. This will give the carbon dioxide a high density (1 150 kg/m^3) thus giving highest possible transport efficiency. At the present time there are six ships in the range from 8 500 m^3 to 10 000 m^3 certified for carrying carbon dioxide in this condition and in large enough volumes. For transport distances up to 300 nautical miles one such vessel could under given conditions handle the carbon dioxide emissions from a coal-fired power plant with a net capacity of 300-400 MW producing two to three million tons carbon dioxide per year.

The Coral Carbonic (Figure 27) is the first purpose-built carbon dioxide tanker in the world, having a capacity of 1 250 m^3 (547 net tonne capacity), with all cargo transported in one tank. The maximum pressure is 18 barg and minimum temperature is −40 °C[58]. Its function is to distribute carbon dioxide for Linde from Finland to import terminals in Sweden and Latvia.

Over the past nearly twenty years a ship logistic system for industrial and food grade carbon dioxide has been developed and operated in Europe. Operationally, four ships between 800 and 1 250 m^3 distribute commercial grade carbon dioxide from production plants to import terminals as part of a market distribution system. An example of this is the 10 000 m^3 certified carbon dioxide gas carrier (see Figure 28). With an excellent safety and quality track record this supports the belief that marine carbon dioxide transport is technically proven.

Figure 27 MV Coral Carbonic

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[58] Anthony Veder Co, Fleet details.

Figure 28 The Norgas Napa

Because the transport of carbon dioxide by ship is similar to that of petrochemical gases and of LPG, it will grossly benefit from long-standing experience and from the existing regulatory framework. Currently the International Gas Carrier regulation (IGC Code) under the UN-IMO rules is being modified to include the transport of carbon dioxide. As an example of the industry's safety performance it has been estimated that more than 5 000 ship years have already been performed without a cargo related accident[59].

New ships are currently under design, where the response to specific CCS demands will be built in. For larger volumes over longer distances, gas carriers up to 30 000 - 40 000 m^3 could become economically feasible. Ship size, service speed, approach/de-approach times and loading and discharge times make up the key components of the round-trip time.

With LNG as the preferred fuel the total ship emissions would be significantly less than one percent of the transported volumes. Intermediate buffer storage of up to one-and-a-half times the ship tank size will be needed on at least the loading side, but possibly also on the discharge location as well. This storage would be orders of magnitude larger than current onshore tanked storage of carbon dioxide.

Offshore unloading of carbon dioxide is theoretically possible, but there remains a number of important issues to address, such as how the experience gained transferring oil from platform to tanker can be extended to transfer carbon dioxide in the other direction.

4.5 CARBON DIOXIDE STORAGE

Incentives to store carbon dioxide as a route to reducing the level of anthropomorphic carbon dioxide in the atmosphere, as opposed to using it as a working fluid for EOR operations, have only recently been formulated.

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[59] E-mail Neilson (Norgas)/Brown (Progressive Energy), 30 June 2009.

4.5.1 Deep saline formations

4.5.1.1 Sleipner

In 1996, Statoil and their licence partners started to inject 1 million tons of carbon dioxide per year into sands of the Utsira Formation at the Sleipner Field in the North Sea. The Sleipner West carbon dioxide facility comprises two main installations, the Sleipner B wellhead platform on the field and the Sleipner T treatment platform, adjacent to the Sleipner East facilities. Sleipner T is linked physically to the Sleipner A platform by a bridge. Other major component parts of the development include a 12,5 km flow line between the two. The wellhead platform is remotely operated from the Sleipner A control room via an umbilical line.

Amine scrubbing technology is used to remove carbon dioxide from high pressure natural gas. The carbon dioxide extracted is injected using a four-stage carbon dioxide injection compression system directly into the Utsira Formation 1 000 metres beneath the seabed. The Utsira Formation is a 200-250 m thick massive sandstone formation located at a depth of 800-1 000 m. It is estimated that the Utsira Formation is capable of storing up to 600 billion tonnes of carbon dioxide.

The carbon dioxide is injected into a small 'structural closure'; when the closure has been filled, the carbon dioxide is expected to spill towards the north, and thereafter to the northwest. This is the first case of industrial scale carbon dioxide storage in the world. As such, monitoring of the behaviour of the carbon dioxide storage facility was necessary, in part to validate the computer models on which the safety case had been built, and also to serve as a basis for the injection of carbon dioxide into other deep saline formations in the future. Statoil initiated and organised a multinational and multidisciplinary research project that collected relevant data, then modelled and verified the distribution of the carbon dioxide 'bubble' for three years, and developed and demonstrated prediction methods for the destiny of the carbon dioxide for many years into the future.

The project, which was co-funded under the EU Saline Aquifer CO_2 Storage(SACS) programme, has served as a test case for offshore underground carbon dioxide disposal in general, and for possible future use of the wide-spread Utsira Formation in particular.

3D seismic data covering the Sleipner East area has been used to map the Utsira Formation. The seismic response represents the changes in 'impedance' in the water-filled reservoir. The impedance is affected by the carbon dioxide injected into the reservoir, and is apparent on new seismic data produced. The presence of carbon dioxide and the movement of the carbon dioxide gas in the Utsira Formation reservoir can therefore be monitored by examination of later seismic data.

The computer predictions have been validated, giving confidence that the movement of carbon dioxide can be predicted with some confidence. Experiences gained have led to the production of a 'best practice' guide being published for the storage of carbon dioxide in deep saline formations[60].

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[60] '*Best practice for the storage of CO_2 in saline aquifers. Observations and guidelines from the SACA and CO2STORE projects*', European Commission, IEA Greeenhouse Gas R&D Programme, 2008.

4.5.1.2 Snøhvit

The Snøhvit field is located in the Barents Sea in the central part of the Hammerfest basin, at a sea depth of 310-340 metres. Snøhvit is a gas field with condensate and an underlying thin oil zone. The field comprises several discoveries and deposits in the Askeladd and Albatross structures in addition to Snøhvit, and will eventually comprise 19 production wells and one injection well for carbon dioxide.

The unprocessed product, containing a mixture of natural gas, carbon dioxide, natural gas liquids and condensate, is transported through a 143 km pipeline to the processing plant at Melkøya. The gas is processed and cooled down to liquid form (LNG), the carbon dioxide (found between 5 and 8 %) is separated out using an amine process, compressed, sent back to the field and re-injected in a deeper formation.

It is expected to store 700 000 tonnes/year of carbon dioxide at a depth of 2 600 m[61].

4.5.2 Gas formations

4.5.2.1 I-n-Salah

BP is using EOR technology in Algeria at the Rhourde El Baguel oilfield, which has been in production since the 1960s, but the difference with the gas re-injection projects at I-n-Salah is that, as a gas field, sequestration is motivated not by EOR, for there is no additional oil to recover, but simply to reduce greenhouse gas emissions.

The I-n-Salah gas project had a projected budget of about $3,5 bn which included laying a 520 km pipeline northwards from Krechba to Hassi R'mel, where existing gas pipelines connect to two subsea export pipelines to Europe and a natural gas liquefaction plant on the Algerian coast. I-n-Salah is expected to produce around 9 billion cubic metres of natural gas each year over its anticipated 20-year lifespan.

Like Sleipner, I-n-Salah, is a gas field in which the natural gas has a significant carbon dioxide content, frequently as high as 10 %. Europe, which sources around a third of its natural gas from Algeria, has required that this carbon dioxide content be scrubbed to a maximum of 0,3 % before it is delivered to its markets. In the past this would have been scrubbed and the carbon dioxide vented into the atmosphere. At I-n-Salah the decision was taken to scrub out the carbon dioxide using amines and to build two large compression trains at Krechba to prepare it for re-injection. The re-injection wells run vertically to a depth of more than 2 km, then horizontally for a further kilometre. The $50 m re-injection plant will give a net reduction of carbon dioxide emissions of about 1 million tons a year, or 17 m tons over the lifetime of the project.

Currently, I-n-Salah is the largest operational CCS project in the world (Weyburn being EOR).

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[61] Various web pages within the Statoil site http://www.statoil.com/statoilcom/snohvit/.

4.5.3 Carbon dioxide storage associated with EOR

EOR is a generic term for gaseous injection techniques for increasing the amount of hydrocarbons that can be recovered from an oil field. Using EOR techniques, up to about 60 % of the original oil in the reservoir can be extracted compared with only about 20 - 40 % using primary (oil under its own self-pressure) and secondary (injecting water) recovery. Nitrogen (e.g. at Cantarell in the Mexican Gulf) can be used, and so can methane from natural gas (e.g. Prudhoe Bay, Alaska), and so can carbon dioxide (examples being found in USA, Canada and Hungary).

Oil displacement by carbon dioxide injection relies on the phase behaviour of the mixtures of that gas and the crude, which are, in turn, strongly dependent on the reservoir temperature, pressure and crude oil composition. These mechanisms range from oil swelling and viscosity reduction for the injection of immiscible fluids (at low pressures) to completely miscible displacement in high-pressure applications. In these applications, more than half, and up to two-thirds of the injected carbon dioxide returns with the oil and is usually re-injected into the reservoir to minimise operating costs. The remainder is trapped in the oil reservoir by various means.

Worldwide there are an estimated 100 registered carbon dioxide floods that, in 2006, produced around 250 000 bpd of oil that would otherwise have been unrecoverable. There are currently 74 carbon dioxide – EOR projects operating in the USA (see Figure 18), however, most of these rely on naturally-occurring sources of carbon dioxide. The price of oil does not necessarily justify the processing of carbon dioxide from industrial processes (thus the closure of the Lubbock, Southwest and Mitchell Energy plants, as described in 4.2.1).

Thus over one third of the carbon dioxide injected remains trapped within the geological structure of the oilfield, making EOR an attractive option for storing carbon dioxide. This can be considered a mature technology, as it has been practised for over 45 years.

4.5.3.1 Weyburn

The Weyburn project is by far the largest carbon dioxide EOR project in the world at present. The oilfield was first discovered in 1954, covering an area of around 21 000 ha. It has around 960 active wells and produces about 19 300 barrels of oil/day, or 7 m barrels/year.

In October 2000, EnCana (one of the operators) began injecting significant amounts of carbon dioxide into the Williston Basin (part of the Weyburn oilfield) in order to boost oil production. The initial carbon dioxide injection rate was about 5 000 tonnes/day (2,7 million m^3/day). The carbon dioxide would otherwise have been vented to the atmosphere. The gas is from the Dakota Gasification Company Synfuels plant site in North Dakota (see 4.4.1).

It is estimated that 50 % of the carbon dioxide injected will be permanently sequestered in the oil that remains in the ground, the remainder coming to the surface with the produced oil. From here, the carbon dioxide is recovered, compressed and re-injected. Over the life of the project it is anticipated that some 20 Mt of carbon dioxide will be permanently sequestered.

During its life, through miscible or near-miscible displacement with carbon dioxide, the Weyburn project is expected to produce at least 122 million barrels of incremental oil, extending the life of the Weyburn field by approximately 20-25 years. It is estimated that ultimate oil recovery will increase to 34 %[62].

4.5.3.2 Abu Dhabi

In January of 2008, the state-owned Abu Dhabi Future Energy Company (ADFEC) joined with Hydrogen Energy (a joint venture between BP Alternative Energy and Rio Tinto) to develop hydrogen-fuelled power in the State[63]. The facility proposed will process around 100 MMSCFD of natural gas, producing hydrogen and carbon dioxide. The hydrogen will be used to generate 420 MW of low-carbon electricity from a CCGT and the carbon dioxide will be injected into oilfields where the carbon dioxide will be used instead of natural gas to maintain reservoir pressure. This carbon dioxide will be added to about 5 million tonnes/year (57 tonnes/hour) of carbon dioxide collected from a gas-fired power plant, an aluminium smelter and a steel mill[64]. The total project will collect carbon dioxide from a total of eight different sites, and will store some 15 million tonnes of carbon dioxide per year[65].

For Abu Dhabi, the world's fifth largest oil producer, the benefits of this scheme are obvious. A fully developed network could reduce Abu Dhabi's annual carbon dioxide emissions by up to 50 % while simultaneously increasing oil production up to 10% and also free up large quantities of natural gas currently re-injected into Abu Dhabi's oil reservoirs. At the same time 5 % of the state's power supplies are being met.

The project is expected to come on stream in 2013–2014.

4.5.3.3 Tjeldbergodden

Statoil, in partnership with Shell, has announced its intention to expand its huge methanol plant at Tjeldbergodden to power a new 860 MW gas-fired power station. It is planned that the resulting carbon dioxide should be captured, in this case piped offshore for EOR re-injection into the ageing Draugen and Heidrun oilfields.

4.5.4 Carbon dioxide storage in depleted gas reservoirs

4.5.4.1 Lacq

In June 2009 operation commenced at Total's integrated pilot demonstration carbon capture and storage facility at Lacq (near Pau) in South West France. This is one of the first fully operational CCS facilities in the world, demonstrating dedicated carbon capture storage from power generation (see Figure 29). This project will trial not only the retrofit of oxyfuel combustion technology to an existing 30 MWth gas fired boiler, but also onshore below ground storage. Carbon dioxide flu gas will be captured and compressed to 30 bar from a

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[62] '*Weyburn enhanced oil recovery project*' IEA Greenhouse Gas.

[63] '*Carbon technology boosts Abu Dhabi oil United Arab Emirates*': AME Info, May 12 2008.

[64] '*Masdar awards design contract for Abu Dhabi carbon capture and storage project to Mustang Engineering*', 18 November 2008

[65] '*BP in talks with Abu Dhabi on carbon-capture project (Update 2)*' Ayesha Daya, Bloomberg.com, 22 January 2009

40 tonnes/hour (60 bar, 450 °C) steam boiler, fuelled with gas from the Lacq reservoir. The carbon dioxide will be transported 27 km by pipeline to the nearby depleted Rousse gas field where it will be compressed further to 60 bar for injection 4 500 metres below the Pyrenees. The initial pressure of the Rousse reservoir was 480 bar, and it has now fallen to 30 bar. Approximately 150 000 tonnes of carbon dioxide will be captured over a two-year trial period (equating to about 8,5 tonnes/hour), during which time there will be both evaluation of the oxy-combustion capture process and monitoring of the storage location. Reservoir pressure after the two-year trial is expected to be 70 bar.

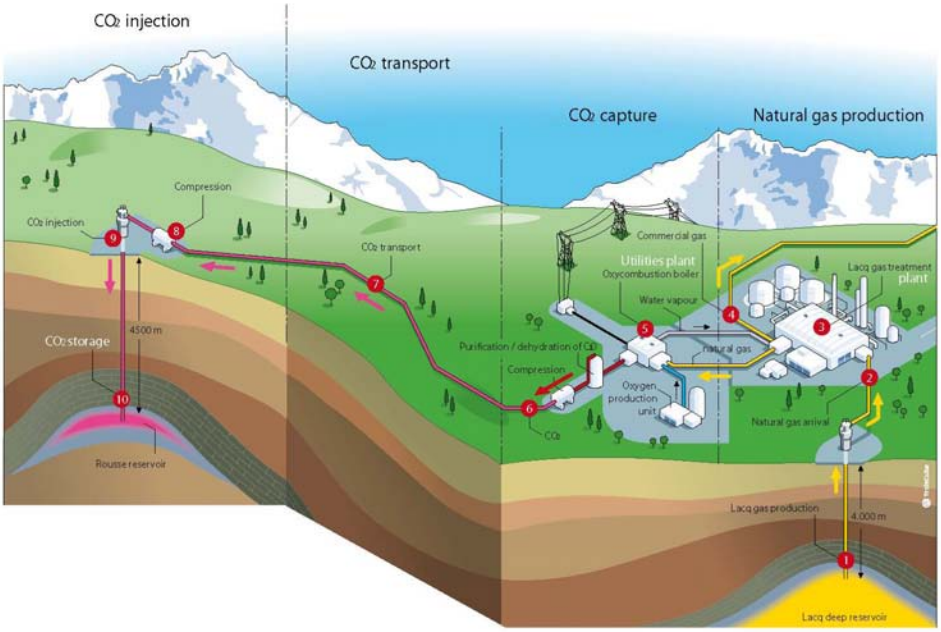

Figure 29 The Lacq project in South West France

Total is working in partnership with Alstom to convert and operate an existing boiler to the oxy-combustion process, and Air Liquide for the cryogenic separation of oxygen from air where the intention is also to demonstrate a 50 % cost saving versus other capture methods[66].

4.6 NEW CCS PROJECTS

A number of other projects are currently being formed to demonstrate the whole CCS chain, each claiming to be a 'world first'. A number are described below, but the details available at time of writing are limited.

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[66] E-mail Cook (Total)/Brown (Progressive Energy), 9 July 2009.

4.6.1 Australia – Gorgon

The Gorgon project starts with removing carbon dioxide from a natural gas deposit, prior to the production of LNG. Some of the carbon dioxide will be re-injected to increase yield, and some will be stored. The carbon dioxide disposal target is a saline formation in the Dupuy Formation located around 2 000 m beneath Barrow Island. The volume of reservoir carbon dioxide to be re-injected is about 100 MT. The proposed injection site was selected to maximise the carbon dioxide migration distance from major faults and limit environmental disturbance.

Once the carbon dioxide is injected into the subsurface, it will move through the host reservoir, driven by the injection pressure and buoyancy until it becomes trapped.

4.6.2 Australia – ZeroGen

In June of 2009, MHI signed a contract with the Queensland government to build a 530 MW IGCC plant with pre-combustion carbon dioxide capture and storage, scheduled to open in 2015. A smaller pilot plant had been planned, but confidence was sufficiently high that a decision was made to proceed directly to a commercial demonstration size. The cost of the project is estimated at $2,04 bn. The project would comprise MHI’s air-blown gasification system and would probably use the M701G2 gas turbine, which will handle high hydrogen fuels and deliver high efficiency. Underground carbon dioxide storage is planned.

4.6.3 Germany – Goldenbergwerk

Announced in August 2008, this would be a new IGCC power plant to be constructed in Hürth near Cologne and operated using domestic lignite with an estimated gross capacity of some 450 MW. Carbon dioxide removal would be pre-combustion. It could go on stream as early as 2014, with an investment of up to €2 bn. The carbon dioxide would be transported 530 km overland at 200 bar to a saline formation in the Schleswig-Holstein region.

4.6.4 The Netherlands – Magnum

The Nuon Magnum project is for a 1 200 MW multi-fuel power plant based on IGCC technology, building on experience gained on the Shell Demkolec power station at Buggenum. It is to be constructed at Eemshaven in the north of the Netherlands. This is described as a phased project, initially the CCGT islands using Mitsubishi equipment will be constructed, (operation 2011) then the gasification islands as 'carbon capture ready', and finally, the carbon dioxide will be captured pre-combustion and stored (operation 2015). The multi-fuels will include biomass. Ground preparation work on the site has commenced.

4.6.5 United Kingdom – Blyth

In 2007, RWE npower announced a feasibility study into the construction of a new 2 400 MW supercritical coal-fired power station at the site of the former Blyth Power Station in Northumbria. The new power station would be designed to be 'carbon capture ready' using post-combustion technology to enable CCS to be implemented once it had been proven. Facilities would also be included to allow biomass to be co-fired with coal. The station could be operational by 2014 and cost around £2 billion.

4.6.6 United Kingdom – Cockenzie

Scottish Power announced a feasibility study into converting Cockenzie and Longannet, its two largest power stations, to clean coal (supercritical) technology in 2007. The total generating capacity of the two stations is 3 390 MW and the new technology would see carbon dioxide emissions reductions of 20 % at both stations compared to the existing boilers, as a result of higher efficiency. Operation is expected to start in 2012. The stations will also be designed to incorporate carbon capture technology, which is being developed at Longannet. It is planned that the captured carbon dioxide would be used in Enhanced Coal-Bed Methane Recovery (allowing methane gas to be recovered from coal seams and the carbon dioxide to be stored).

4.6.7 United Kingdom – Eston Grange

The Eston Grange project is located in Teesside, UK, and is 850 MW. Carbon dioxide removal is described as around 85 %, and the intention would be to store this under the North Sea using a network developed by COOTS Ltd, which would also receive carbon dioxide from other producers in Teesside and the North East of England.

4.6.8 United Kingdom – Hatfield

In 2003 planning permission was granted for a major re-development of the Hatfield Colliery Site, which included permission to develop a new 900 MW IGCC power plant. A phased approach is planned, initially a 'capture ready' IGCC will be constructed and pre-combustion CCS added once commercial conditions are suitable and a disposal route is available. The plant is expected to begin operation at the end of 2011 and could be available for CCS by 2013.

4.6.9 United Kingdom – Kingsnorth

E.ON is proposing to construct two new 800 MW coal units at their Kingsnorth power station. By virtue of the use of higher levels of efficiency, these will reduce carbon dioxide emissions by approximately 20 % compared to the existing plant. It is proposed that the units would be built 'carbon capture ready'. Retrofitting with post-combustion capture would allow approximately 90 % of emissions to be captured and subsequently stored in depleted gas fields under the North Sea.

4.6.10 United Kingdom – Lynemouth

Lynemouth power station has 3 off 140 MW steam turbines. Rio Tinto Alcan are proposing an innovative retrofit option which involves conversion of one of the units into an IGCC with pre-combustion capture. The plant will capture around 2 255 million tonnes of carbon dioxide per year. The export pipeline will join the Teesside pipeline (see 4.6.7) and a common pipeline infrastructure will then transport carbon dioxide to the saline formation to be used as the primary store. This CCS project can be operating by 2015[67].

4.6.11 United Kingdom – Tilbury

In 2007, RWE npower announced plans for a 1 600 MW cleaner coal power station to replace the existing power station at Tilbury. Two new 800 MW supercritical coal-fired units would achieve a reduction in emissions of 22 % compared to the current power station as a result of the use of higher efficiency technology. It will be designed to be 'carbon capture ready' and will also include facilities to burn biomass. A feasibility study to explore developing the new station and to understand the CCS options for the site began in 2006.

4.6.12 United States of America – Carson (DF2)

The Carson Hydrogen Power Project would take petcoke from refineries in the LA Basin into a 450 MW IGCC facility with polygeneration, where 90 % of the carbon dioxide would be removed. Costs are estimated at about $2 bn, and about 4m tonnes/year of carbon dioxide will be captured, and probably used for EOR applications. An investment decision is expected in 2011.

The Gorgon project, being planned by Chevron, proposes to extract natural gas with a 10–15 % carbon dioxide content from a reservoir and liquefy it for export. The carbon dioxide extracted will be compressed and sent via a 12 km pipeline for storage in a saline formation.

4.7 CONCLUSIONS

In view of the foregoing sections, it can be concluded that: carbon dioxide capture and storage can be divided into a number of different steps with a number of technological options available for each of them. Each of these technological options is at a different stage of commercial development, and many are currently available at the sort of size that would be required for CCS projects.

There are large-scale examples of all parts of the CCS chain and a number of full size and pilot CCS projects under active development as well as numerous research programmes. As such, this area is constantly changing, with new experience and understanding developing.

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[67] '*Carbon capture and storage in North East England*', One North East, December 2009.

5 CARBON DIOXIDE PLANT DESIGN

Carbon dioxide plant operations and design issues – by the end of this section you will:

- understand materials of construction;
- understand plant design issues for carbon dioxide service;
- understand the implications of carbon steel embrittlement;
- be aware of the existing codes of practice for carbon dioxide in the industrial gases industry, and
- understand the recommendations on carbon dioxide leak detection.

5.1 INTRODUCTION

This section is intended to provide an overview of existing codes of practice and design consideration when designing and operating carbon dioxide producing facilities. It is envisaged that during the early stage of the industry's development carbon dioxide may be stored in large tanks and vessels and transported in relatively large quantities by road, rail or ship. With this in mind, considerable guidance is given on storage and handling of carbon dioxide in containers of varying size, which may be relevant to plant operation.

Current carbon dioxide sources

Most operational carbon dioxide plants capture carbon dioxide from industrial or natural sources, where it is then purified, compressed and often liquefied for transport by sea, rail or road. In the current carbon dioxide industry the most common sources of carbon dioxide are:

- Chemical processes (e.g. ammonia, hydrogen, ethylene oxide plants).
- Fermentation processes (e.g. ethanol plants).
- Carbon dioxide natural wells.

Carbon dioxide purification

Each feed gas source is unique and since the carbon dioxide plant is designed specifically to remove the impurities in the feed gas, each plant is also unique.

After the typical impurities in the feed gas have been determined, equipment to remove each impurity to meet the required specification is incorporated into the plant design. A quick synopsis of common removal equipment is listed below:

- Dryers – used to remove moisture from the carbon dioxide but could be used to remove some types of hydrocarbons depending on the bed media selected.
- Guard beds – used to remove a variety of trace impurities. Type of bed material selected will be dependent on the type of impurity that needs to be removed.
- Catalytic combustors – used to remove very large quantities of hydrocarbons by combusting the hydrocarbons with oxygen across a catalyst bed.
- Water wash columns – designed to remove water soluble impurities such as alcohols and amines by scrubbing the carbon dioxide with water.
- Permanganate towers – used to remove Nox or Sox by scrubbing the carbon dioxide feed gas with potassium permanganate.
- Sulphur removal/recovery systems – use different technologies including amines, depending on the sulphur compounds to be removed and their concentration in the carbon dioxide.

Non-condensable gases, such as nitrogen, are generally removed in the carbon dioxide liquefaction plant by distillation.

5.2 EXISTING GUIDANCE ON CARBON DIOXIDE FACILITY OPERATION AND DESIGN

There are a number of guidance documents relating to industrial scale gases industry facilities, as given in Table 11. The majority of these standards were designed for low pressure refrigerated carbon dioxide. However, these standards apply to CCS facilities whenever the pressure is below supercritical (73,8 bara) either through depressurisation for maintenance or by virtue of operating pressures in that stage of the plant.

Table 11 Guidance documents relating to large-scale facilities

ID	Title	Covers
BCGA Guidance Note GN10	Implementation of EIGA carbon dioxide standards: Revision 1: 2004	Standard published by the European Industrial Gases Association in response to recent quality incidents affecting bulk carbon dioxide are explained and guidance to their UK implementation is given.
IGC 66/08	Refrigerated CO_2 usage at users' premises	Requirements and practice for the design, construction, installation, operation and maintenance of CO_2 tanks between 1 and 100 tons at pressures between 10 and 25 bar.
IGC document 101/03/E	The carbon dioxide industry and the environment	Greenhouse effect, uses of CO_2 in industry.
IGC document 150/08/E	Code of practice: dry ice	Properties of dry ice: use in industry, requirements for dry ice in food applications, manufacture, storage and transport requirements of dry ice used in the food industry. Links to related European standards.
IGC document 24/08/E	Vacuum insulated cryogenic storage tank systems' pressure protection devices	Definitions of relief devices terminology, types of acceptable relief device for cryogenic service, sizing criteria for relief devices, installation of relief devices, vacuum insulated storage tanks, inspection requirements.
IGC document 119/04/E	Periodic inspection of static cryogenic vessels	Definitions: what is classified as cryogenic equipment, relevant legislation, materials selection, corrosion issues, insulation of vessels, inspection and testing thereof. (Includes a table comparing the testing intervals required, depending on the European country, common failure mechanisms, pressure relief devices, and a brief overview of incident statistics).
IGC document 07/03/E	Metering of cryogenic liquids	Metering system design including ancillary equipment required, maintenance, required operator training, types of flow meter, approval, calibration, handling transfer from cryogenic tankers.

ID	Title	Covers
BCGA code of practice CP 26	Bulk liquid carbon dioxide storage at users' premises	Hazards of CO_2 in industry; embrittlement, blockage formation, cryo burns etc. Layout and design features, access, testing and commissioning, operation and maintenance, training and protection of personnel.
CGA G6.7	G6.7 Safe handling of liquid carbon dioxide containers that have lost pressure	Guidance on the specialist techniques needed to recover from a situation in which solid carbon dioxide has formed within storage tanks and vessels.
IGC document 111/03/E	Environmental impacts of carbon dioxide and dry ice production	Not strictly relevant, but provides an insight into an industry that manages CO_2 in gas, solid and liquid states during processing. Useful as background reading only.

Further guidance is also available for smaller quantities of carbon dioxide, as given in Table 12.

Table 12 Guidance for CO_2 cylinders

ID	Title	Covers
IGC document 95/07/E	Avoidance of failure of CO and of CO/CO_2 mixtures cylinders	Past incidents where CO_2 cylinders have ruptured, material selection, inspection requirements.
IGC document 105/03/E	Odorising of CO_2 in fire fighting	Reasons and practical advice on what chemicals to add to CO_2 to give it an easily detectable odour for fire fighting systems only.
IGC document 83/08/E	Recommendations for safe filling of CO_2 cylinders and bundles	Filling of cylinders and bundles.
IGC document 64/05/E	Use of residual pressure valves	Details how to maintain positive pressure in cylinders and prevent ingress of moisture.

Additional relevant reference material may be found, examples of which are listed in Table 13.

Table 13 Additional reference material

ID	Title	Cover
BCGA code of Practice 25/2:	Revalidation of cryogenic static storage tanks	Static cryogenic storage tanks.
BCGA code of practice CP 32	Bulk liquid argon or nitrogen storage at production sites, Revision 1: 2002	Code of practice for liquid or nitrogen storage installations on storage sites where the storage installation is connected to the process plant.
BCGA code of practice CP 27	Transportable vacuum insulated containers of not more than 1 000 litres volume	Guidance for the minimum requirements for: general safety precautions, design and construction, operation, tank management and filling, transportation, in-service examination, modifications/repairs and records.
BCGA code of practice CP 28	Vacuum insulated tanks of not more than 1 000 litres volume which are static installations at user premises	Guidance for the minimum requirements for: general safety precautions, design and construction, operation, tank management and filling, transportation, in-service examination, modifications/repairs and records.
NFPA 55	Standard for the storage, use, and handling of compressed gases and cryogenic fluids in portable and stationary containers, cylinders and tanks	General guidance on the handling of compressed gases and cryogenic fluids.

5.3 PLANT DESIGN AND LAYOUT

5.3.1 Plot plan layout

5.3.1.1 General principles

The plot plan layout of a carbon dioxide installation should be sited to minimise the risk to personnel, local population and property from enriched carbon dioxide atmospheres. Consideration should be given to the location of any potentially hazardous processes in the vicinity, which could jeopardise the integrity of the installation.

An installation may, because of its size or strategic location, come within the scope of specific legislation for planning control. If so, the siting of any proposed installation will need to be discussed and agreed with the local authority and appropriate sections of the HSE in the UK or equivalent outside the UK.

Safety distances are defined as 'the minimum separation between a hazard source and an object (human, equipment or environment) which will mitigate the effect of a likely foreseeable incident and prevent a minor incident escalating into a larger incident'. IGC POC 75/07/E suggests a methodology for determination of safety distances based on assessment of frequencies and probabilities of exposure together with hazardous effects/consequences[68]. There are existing codes of practice for CO_2, (69).

The safety distances, described in the BCGA code of practice CP 26[69] are intended to protect personnel from the effects of cryogenic burns and provide a degree of protection for the installation against mechanical damage and fire. Even though these codes of practice refer to liquid storage, the principles can be applied to any large inventory of carbon dioxide on a CCS facility. If the quantities of carbon dioxide being processed increase, then the safety distances may have to be increased. A risk assessment may have to be carried out together with dispersion modelling to ensure that adequate measures have been taken.

One measure that may assist in mitigating the level of risk associated with the storage of larger quantities of carbon dioxide is the fitting of emergency shut-off valves (see section 6.7.7), which can even be installed internally to the tank itself.

CCS installations should be designed to avoid areas where carbon dioxide could collect such as inside buildings, below ground level, pits, ducts, un-trapped drains, cellars and other ground depressions. Where these features are unavoidable, confined space procedures must apply.

Due consideration should also be given to the possibility of the movement of vapour clouds, originating from discharge or venting, which could be a hazard. The prevailing wind directions and the topography need to be taken into account.

5.3.2 Safe entry to plant equipment

Whilst the primary design criteria are to eliminate confined space areas by removing enclosures, basements and other such confined areas, it is not always possible to remove them entirely. Where confined spaces are inevitable, both confined space procedures should be enforced during operation, but also the design of the enclosures and vessels should be such that the confined space can be vented thoroughly prior to entry.

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[68] IGC Doc 75/07/E.

[69] Appendix 2 of BCGA code of practice CP 26 '*Bulk liquid carbon dioxide storage at users' Premises*', Revision 2 : 2004.

5.3.2.1 Carbon dioxide storage tanks

CCS installations may have need for storage tanks where road tanker or ship based transportation solutions are chosen. In which case, BCGA code of practice CP 26 is applicable.

The foundations of any carbon dioxide tank (or vessel) should be designed to withstand safely the weight of the tank and its contents plus other possible loads resulting from wind, snow etc. Where liquid storage tanks are required to be installed in an elevated position, they should be supported by purpose-designed structures which can withstand or be protected from damage, e.g. by vehicle impact. Due consideration should be given to the possible impact of a leak accumulating in lower ground and increasing the risk to personnel in the vicinity.

Regular external visual inspection must be carried out by a competent person to confirm the satisfactory condition of a carbon dioxide vessel insulation, pipework, valves, controls and auxiliary equipment. A check on the refrigeration unit (if installed) should also be made whenever an abnormal pressure increase inside the vessel has occurred or excessive ice build-up is visible. When a carbon dioxide vessel is taken out of service, a competent person should endorse the further use of the vessel, taking into account the condition of the vessel, operating history and the degree and results of any previous examination(s).

The carbon dioxide vessel should also be examined periodically to determine its fitness for continued service; the requirements for and frequency of the examination are defined by a competent person. In addition, a competent person should revalidate the vessel design periodically, taking into account an assessment of design documentation, examination and service history records. Guidance on periodic revalidation is given in BCGA Code of Practice CP 25[70] (18).

The carbon dioxide vessel primary process isolation valve should be located as close as practicable to the vessel itself. Protection against over-pressure shall be installed between any two isolation valves where liquid or cold vapour can be trapped. A secondary means of isolation (required to prevent any large release of carbon dioxide should the primary isolation valve fail) should be provided for liquid lines greater than 8 mm nominal bore, or a liquid line where there is only one means of isolation between the vessel and atmosphere (such as liquid filling lines).

Each carbon dioxide vessel should be fitted with the following as a minimum:

— a maximum level indicator (e.g. dip pipe at the vessel termination of the vapour balance line, try-cock);
— an independent liquid contents' gauge, and
— a pressure gauge connected to the vapour space (to include under – as well as over-pressure alarms).

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[70] BCGA Code of Practice CP 25/2: *Revalidation of cryogenic static storage tanks*.

All carbon steel vessels should be fitted with alarms to warn of high or low pressure in the vessel.

Many factors determine whether a carbon dioxide tank needs to be bolted down. Where a horizontal vessel is secured by bolts, allowance must be made for expansion/contraction of the vessel as a result of changes of contents pressure and temperature.

Storage tank refrigeration units

The refrigeration system, where fitted, should be designed, manufactured and installed in accordance with all relevant regulations and industry codes of practice, e.g. BS EN 378[71].

5.3.2.2 *Carbon dioxide liquid transfer areas*

The liquid transfer area of a carbon dioxide facility should be designated a 'No Parking' area and should be level. A road tanker, when in position for filling from or discharging to the installation, should be in the open air and not be in a walled enclosure from which the escape of heavy vapour is restricted. Tankers should have easy access to and from the installation at all times. The liquid transfer area should normally be located adjacent to the fill coupling of the installation and be positioned in such a way that it facilitates the movement of the tanker in the case of an emergency.

Extended fill lines should not normally be fitted. Where there is no alternative then suitable additional gauges and valves should be installed. Extended filling connections should be limited to 10 m unobstructed walking distance. Greater distances will require special provisions.

Transfer of liquid with the tanker standing on public property is not recommended. However, if this cannot be avoided, the hazard zone should be clearly defined, using suitable notices during the transfer period. Access to this area during transfer shall be strictly controlled.

Fencing around a carbon dioxide installation should be provided unless there is adequate control to prevent access by unauthorised persons. On controlled sites with sufficient supervision, fencing is optional. The BCGA code of practice 26[72] gives details of what fence design should be applied.

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[71] BS EN 378-1:2008 Refrigerating systems and heat pumps. Safety and environmental requirements. Basic requirements, definitions, classification and selection criteria. BS EN 378-2:2008+A1:2009 Refrigerating systems and heat pumps. Safety and environmental requirements. Design, construction, testing, marking and documentation. BS EN 378-4:2008 BS EN 378-4:2008. Refrigerating systems and heat pumps. Safety and environmental requirements. Operation, maintenance, repair and recovery.

[72] Section 4.3.8 from BCGA Code of Practice CP 26 '*Bulk liquid carbon dioxide storage at users' premises*', Revision 2 : 2004.

5.3.3 Trapped liquid

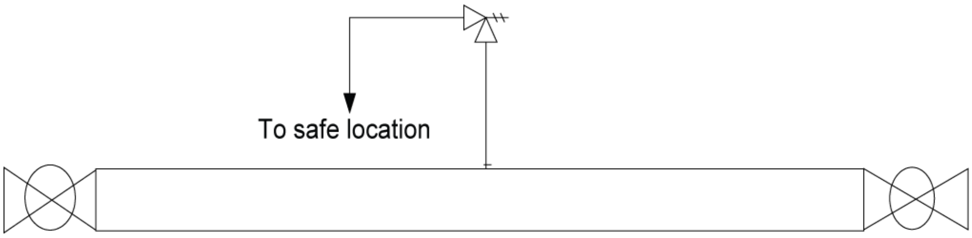

Figure 30 Thermal relief valve in carbon dioxide service

Consider the scenario in Figure 30, in which liquid carbon dioxide is trapped between two isolation valves. For any fluid an increase in the ambient temperature can lead to a reduction in density and expansion of the liquid. The thermal relief valve is designed to discharge the CO_2 in a controlled manner to a non hazardous location. Both BCGA (21) and EIGA (22) give guidance on the design of thermal relief valves in cryogenic service and the scenarios that should be considered. Care also has to be taken in the design of the relief path (e.g. avoiding the ingress of moisture to avoid freezing and/or potential blockage; because liquid carbon dioxide will become solid below 5,18 bar it could cause a blockage in the relief line).

Pressure-relief valves must be provided to prevent over-pressure, where this can occur, including situations where liquid can be trapped in piping or equipment.

5.3.4 Storage vessels

The BCGA code of practice 26 requires at least two pressure-relief valves to be fitted to the vessel in conjunction with a changeover valve, to ensure that two relief valves remain on-line during normal operation.

Bursting discs should not be used in carbon dioxide service, as their rupture leads to an uncontrolled release of gas, together with a complete de-pressurisation and solidification of the contents. Furthermore, any existing installations fitted with bursting discs should have these replaced with relief valves at the first practical opportunity when the vessel is de-pressurised.

The design of the changeover valve shall be such that the vessel is adequately protected at all times regardless of the position of the actuating device. The valve should be provided with a position indicator showing which relief devices are 'on-line'.

For sizing the relieving capacity of pressure-relief devices all operational conditions shall be considered on the basis that any refrigeration system has failed, including the following:

- Boil off due to ambient heat ingress, with conventional insulation degraded with age or loss of tank vacuum as appropriate.
- Energy input resulting from the normal operation, or failure of, a pumping system connected to the vessel/tank.
- Malfunction of any pressure raising system or any other foreseeable source of energy input into the vessel.

For conventional insulated tanks consideration shall also be given (when sizing relief devices), to the possibility of complete or partial fire engulfment of the vessel/tank. Safety relief systems should comply with BS EN 13648.

The installation should be designed to facilitate the regular inspection, testing and replacement of the relief valves.

5.3.5 Blow down and depressurisation of plant and equipment

Due to the large liquid to gas expansion factor of carbon dioxide, care must be taken in the design of any isolating valve. Carbon dioxide is not the only substance to have a large expansion ratio. Liquid natural gas (LNG) has an expansion ratio of 620 and there are well proven engineering practices in this area. Engineers should be mindful of this body of work when considering the management of pressure and expansion in carbon dioxide systems.

Figure 31 shows the modification required to a standard ball valve which is in carbon dioxide service, being used to isolate a pipe. Upon closing, the ball valve will trap a small amount of liquid carbon dioxide within its housing. The carbon dioxide will expand and the resulting pressure will exert a force so great that the ball valve will fail catastrophically. Cryogenic valves are designed with 'cavity pressure relief holes' so that the liquid is not trapped but can either expand back upstream into the pipeline from which it came or discharge to a safe location.

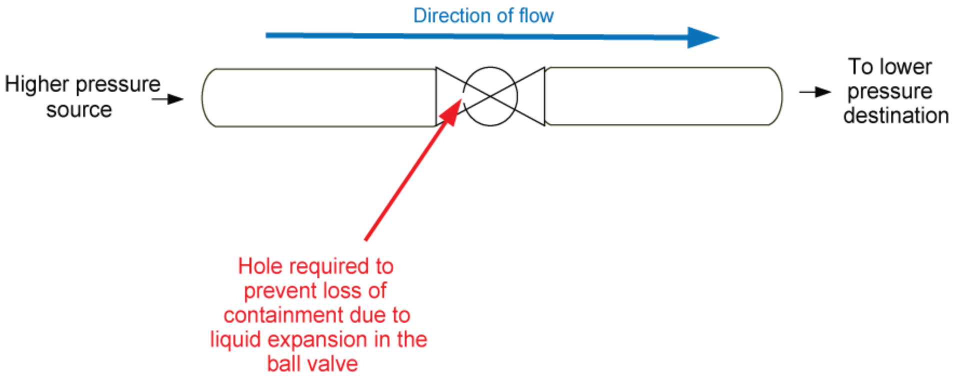

Figure 31 Illustration of the modification required to a standard ball valve for carbon dioxide service

In practical terms, this leads to carbon dioxide – specific valves being offered by suppliers, an example of which is shown in Figure 32[73]:

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[73] From presentation: '*Valve and seal selection for carbon dioxide*', Iain Symington, Flowserve.

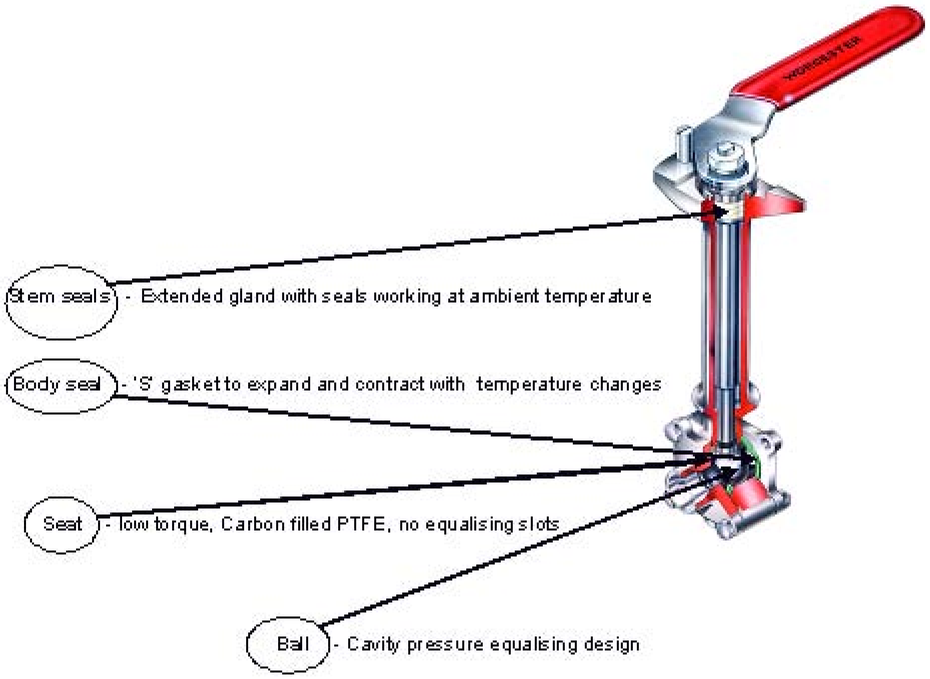

Figure 32 Cryogenic valve for liquid CO_2

Particular care needs to be taken when blowing down an installation which contains carbon dioxide, because it is important that rapid depressurisation to the triple point is avoided, such that the carbon dioxide forms a solid. Appropriate procedures that include monitoring of the pressure during blow down need to be established.

If liquid carbon dioxide is held within a static vessel it will tend to reach an equilibrium where the vapour phase at the top of the tank is just above boiling point and the liquid phase just below i.e. the liquid in the tank reaches its saturation point. If the pressure or temperature in the vessel is altered this equilibrium will reset. Industry tends to maintain the pressure of the vessel by drawing liquid from the bottom of the tank, thereby maintaining the vessel pressure and hence the condition of the carbon dioxide within.

Figure 33 shows how the temperature within the vessel would change with pressure because of the tendency to equilibrium. Figure 2 shows a section of the Mollier diagram for carbon dioxide from which the phase of carbon dioxide can be predicted if two thermodynamic properties are known. For example it can be seen that if the pressure is reduced below 7 barg the carbon dioxide within the tank will become solid.

Blow down should be from the liquid side of vessels and an uninsulated length of pipe is normally provided so that heat can be absorbed from the atmosphere to boil off the carbon dioxide to gas prior to its venting to atmosphere. If it is necessary to blow down vessels to atmospheric pressure, then this should take place slowly, so that rapid despressurisation of the vessel is prevented and thus solid formation, is also avoided. There is a danger that the blow down pipe itself can become plugged with solid, and the operator, observing that no further carbon dioxide is exiting the pipe, could believe that the vessel is drained. As the plug warms and subsequently melts, some or all of the remnant carbon dioxide could escape and either asphyxiate or harm personnel in the vicinity. For discussion of blow down in pipelines see section 6.7.

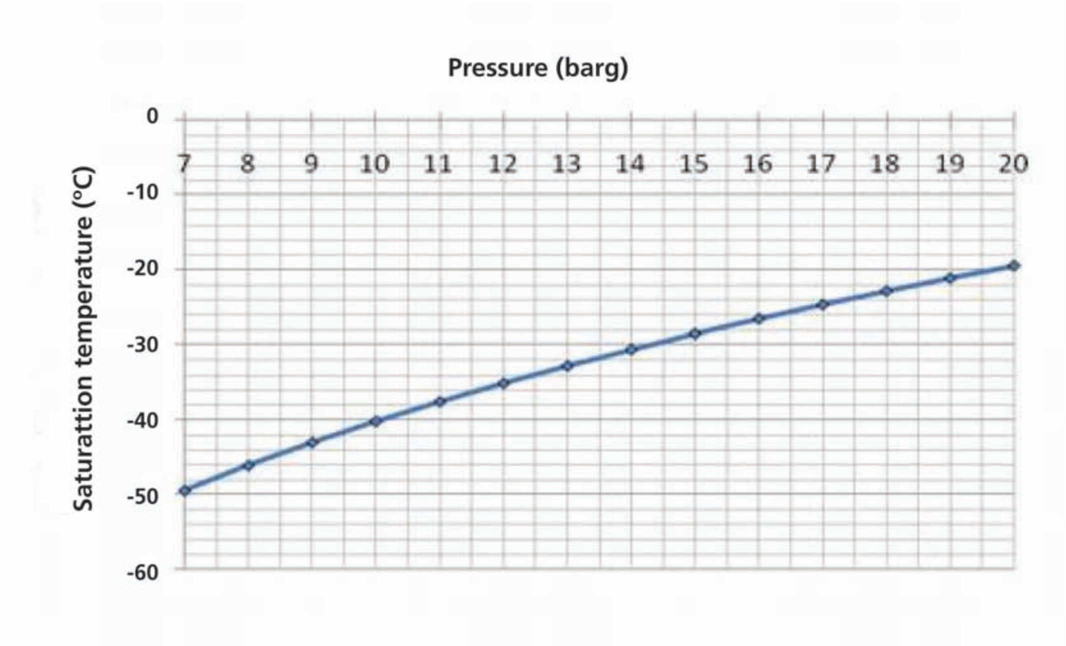

Figure 33 Variation of CO_2 saturation temperature with pressure

5.3.6 Selecting valves and seals for carbon dioxide service

The above text and Figure 32 indicate the importance of careful selection of valves for carbon dioxide applications. Apart from the need to avoid liquid carbon dioxide becoming trapped in the hole in the ball (as described in 5.3.3), the designer should be careful in the choice of materials for the rest of the components from which a valve is made up. Seal materials, gaskets and other non-metallic parts are common and made from a number of different materials. Dense phase carbon dioxide has desirable properties for transportation, but has implications for material selection (especially compared to low pressure liquid carbon dioxide). One of the industrial uses of supercritical or dense phase carbon dioxide is as a solvent; as such it can and does penetrate and saturate some non-metallic material. This causes problems for specific items such as seals, gaskets, instruments and valve bodies.

Seal and gasket materials

Non-metallic materials, for example elastomers or other polymers contain voids and rigid inclusions that are produced during manufacture. Fluids in contact with the material are absorbed and diffuse throughout the material. At high pressure the fluid remains as a liquid; when the pressure drops the fluid will expand to a gas which can cause mechanical damage such as extrusion and blistering and undergo rapid gas decompression, (RGD), often referred to as explosive decomposition (see later).

Table 14 gives broad guidelines on what is acceptable and what is not. This is a basic compatibility listing, intended to assist in the selection of products for use in a carbon dioxide gas system. Caution should be exercised and expert help sought from manufacturers of equipment – general data such as this cannot anticipate all conditions of concentration, temperature, humidity, impurities and aeration. The data shown here mainly concern high pressure applications at ambient temperature, and the safety aspect of material compatibility rather than product quality.

Whilst table 14 gives some guidance on general material compatibility of carbon dioxide, it is not sufficiently detailed to select materials for valves, seals and gaskets. Industry is carrying out some research into material selection for carbon dioxide service with a view to providing guidance on suitable materials. However, developers should satisfy themselves that the manufacturer of their valve, gasket or seal has tested the material performance for the range of operating conditions including operating aspects such as cycling as well as static conditions and the range of carbon dioxide composition for their particular project. Many of the non-metallic materials properties will change significantly with small changes in material composition. Thus even with general testing of material performance, CCS project developers will need to continue to satisfy themselves as to the performance of the chosen manufacturers' material for their exact project.

Table 14 General compatibility listing for valve materials used in CO_2 applications

Category	Material type	Usage	Comment
Metals	Aluminium	YES	
	Brass	YES	Only in dry service.
	Copper	YES	Only in dry service.
	Carbon steel	YES	Only in dry service. Some steels may become brittle below −20 °F (−28,9 °C).
	Stainless steel	YES	
	Monel	YES	
	Chrome/Moly	YES	
Plastics	Polytetrafluoroethylene (PTFE)	YES	
	Polychlorotrifluoroethylene (PCTFE)	YES	
	Vinylidene polyfluoride (PVDF) (KYNAR™)	YES	
	Polyamide (PA) (NYLON™)	YES	
	Polypropylene (PP)	YES	
	Ultra high molecular weight polyethylene (UHMWPE)	YES	
	Polyetheretherketone (PEEK)	YES	High temperature applications e.g. compressor valves.
Elastomers	Butyl (isobutene – isoprene) rubber (IIR)	NO	Significant swelling.
	Nitrile rubber (NBR)	NO	Significant swelling and loss of mass by extraction or chemical reaction.
	Chloroprene (CR)	NO	Significant swelling and loss of mass by extraction or chemical reaction.
	Chloroprene (CR)	NO	Significant swelling and loss of mass by extraction or chemical reaction.
	Chlorofluorocarbons (FKM) (VITON™)	NO	Significant swelling and loss of mass by extraction or chemical reaction.
	Silicon (Q)	YES	Acceptable, but expect strong rate of permeation.
	Ethylene – Propylene (EPDM)	YES	Acceptable, but expect swelling and significant loss of mass by extraction or chemical reaction.
Lubricants	Hydrocarbon based	YES	
	Fluorocarbon based	YES	

5.3.7 Materials of construction

Material compatibility issues

Wet carbon dioxide service

As has already been described in section 2 (section 2.2.1), corrosion becomes an important issue in wet carbon dioxide service, as the moisture and carbon dioxide combine to lower the pH of the moisture, creating a weak acid which is corrosive to carbon steel. Therefore, in wet carbon dioxide service, fibreglass, stainless steel and epoxy coated carbon steel are viable choices, for instance, for pipes, depending on the pressure. When using fibreglass or epoxy coating, it is important to ensure that the material choice is compatible with both the carbonic acid and the impurities that may be present in the feed gas. Yellow metals (copper, brass) are not suitable for wet carbon dioxide service.

Discharge piping on carbon dioxide compressors can be carbon steel if the gas is heated above the saturation point without developing excessive corrosion, but for suction piping, stainless steel is recommended, as the carbon dioxide has been cooled to saturation.

Feed gas impurities may also dictate the choice of materials used in construction. If chlorides are present in the feed gas, stress corrosion cracking can occur, even with stainless steel. Chlorides can also be present in the water used in water wash columns. Sulphurs can form a mild sulphuric acid in wet carbon dioxide, which can attack carbon steels. Depending on the impurities in the feed gas as well as the temperatures and pressures, more exotic metals may also be required such as titanium or nickel alloys.

Dry carbon dioxide service

Water and many of the feed gas impurities are removed in dryers. Carbon steel is the most commonly used material in dry carbon dioxide service.

Even for dry service, the tubing used for sampling carbon dioxide should not be yellow metal. These materials can absorb contaminants, such as H_2S. Sample tubing may be stainless steel or preferably can be one of the new coated stainless steels that are inert to sulphurs.

Hoses used for loading carbon dioxide can be braided stainless steel or rubber. When using rubber, it is important to ensure that the rubber is rated for liquid carbon dioxide use and is acceptable, for example, for food grade service. Some types of rubber decompose in carbon dioxide service, and some plasticiser/elastomers in rubber formulations can contaminate the carbon dioxide as an oil or a solid. Like valves and seals, materials selected for hoses should be verified to be suitable for the range of operating conditions and carbon dioxide composition at that application.[74]

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[74] For example, NORSOK M-710 is a standard test for qualifying seals for carbon dioxide service in the oil industry and is used to verify seals for specific operating conditions.

Gaskets

Gasket choice is by application. Gasket materials will have to meet certain pressure and temperature specifications depending on where they are used and the media they contact. In high temperature applications such as dryer regeneration or combustors, it is appropriate to use filled, spiral wound type gaskets. A competent manufacturer will advise on the most suitable materials. Figure 34[75] can be used as a preliminary guide and shows an example of the type of information available from manufacturers.

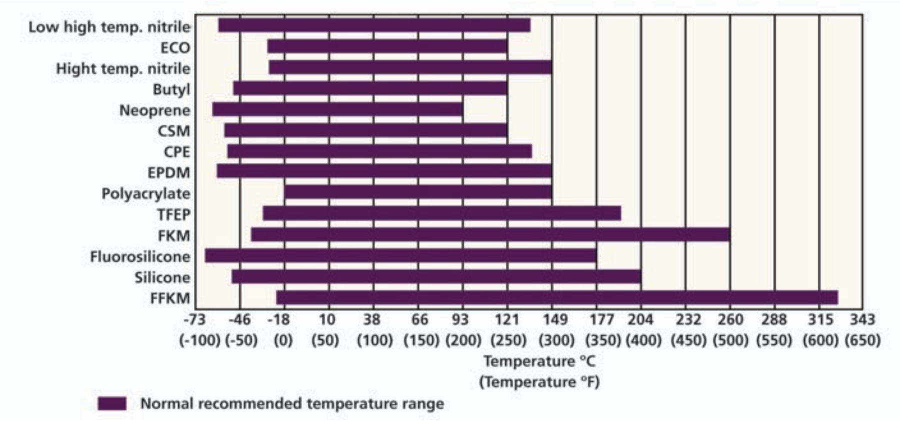

Figure 34 Temperature range of gasket materials

Pure PTFE is not suitable for liquid carbon dioxide applications, since it swells. A glass reinforced material is more suitable, as it does not exhibit this behaviour.

The problem with some gasket or seal materials is that of RGD (explosive decompression). Where liquid carbon dioxide is able to percolate into the structure of the elastomer, it can accumulate in voids. When the pressure is released the liquid carbon dioxide vaporises rapidly, leading to a sudden release of energy – explosive decompression. As the external pressure drops and the fluid nucleates to a gas in the voids, the voids inflate. This leads to high tensile stress and strains in the void walls. If the wall stress or strain is greater than the strength of the elastomer then elongation may occur, cracks initiate and propagate.

For multiple decompression applications, where pressure is cycled up and down, cracks can form and grow at stresses much lower than the break points. If the number of cycles is higher than the number of fatigue cycles to failure then cracks will grow and eventually the material will fail.

Figure 35 shows examples of this.

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[75] From presentation '*Valve and seal selection for carbon dioxide*', Iain Symington, Flowserve.

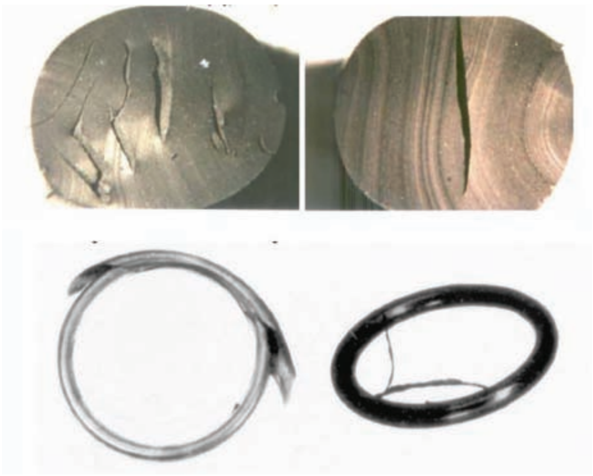

Figure 35 Examples of non-metallic material failure

One additional specification that is universal is to use a non-asbestos composite gasket.

Temperature issues

As shown in Figure 34, the material of construction chosen must also consider the temperature conditions for the service. Depending on pressure, liquid carbon dioxide is commonly found at temperatures between −12 °C and −40 °C. Low temperature carbon steel is suitable at temperatures down to −40 °C to −46 °C. Other carbon steels are susceptible to brittle fracture at temperatures below −28 °C.

High temperatures can also be problematic for carbon dioxide applications. Care must be taken when purchasing valves for dryers and adsorbers, which may be exposed to high temperatures during regeneration, to ensure that the seats are suitable for the maximum temperature to which they will be exposed.

Catalytic combustors operate at very high temperatures and with high levels of impurities. The materials used for the combustor system including heaters and heat exchangers need to be evaluated carefully. Depending on pressure and temperature, it may require the use of titanium, monel, high temperature stainless steel, chrome moly (Cr/Mo), or other alloys.

Pressure issues

The material of construction used must also consider the pressure of the system. For piping, the flange rating and the thickness of the piping need to be considered for the appropriate temperature, pressure and corrosion requirements of the system. Ensure that safety valves are set no higher than the pressure allowance for the piping in use.

5.3.8 Leak detection

The primary leak detection method in CCS installations is detection via sound and sight and operating staff can detect many leaks through careful onsite observation. Most high pressure leaks have a high sound volume due to the velocity of the jet. Many leaks will also be visible when the humidity in the atmosphere is reasonably high.

As a result, in general, fixed carbon dioxide gas detection sensors are not used in current production facilities in 'open' production areas. Note: in some jurisdictions, fixed carbon dioxide monitoring is mandatory (e.g. Hungary) and this guidance does not supersede guidance given by local health and safety authorities or local law. Fixed detection systems are more effective in confined spaces or enclosures. In open production areas personal portable units are widely available and often used.

Should leak detectors be required, there are several technologies available for carbon dioxide detection, and a careful choice must be made in order to ensure that the appropriate technique is applied. Responsible manufacturers are able to advise the operator which is the best for a particular application:

Infra red

Infra red sensors detect polarised bonds so are an ideal choice for carbon dioxide detection. Infra red sensors work on the principle that the beam of IR light will absorbed at specific wavelengths as it passes through a cloud of gas. The sensors cannot be poisoned and also have the advantage that they are not cross sensitive, that is the absorption caused by a C-O bond can be distinguished from that caused by a H-O bond.

Electrochemical detection

It is also possible to use electrochemical detection. In these sensors a REDOX reaction occurs and the resultant current is measured and then translated into a gas concentration. However electrochemical sensors can be poisoned.

5.3.9 Impingement on carbon steel equipment

Emission points from equipment such as bleed points and vents should be pointing away from carbon steel equipment. Failure to do so can result in cooling of the carbon steel below its nil ductility temperature at which point it may fail catastrophically.

Vents for blow down valves need to be designed from appropriate materials to prevent erosion from possible solid formation within the vent pipe. Solid formation will cause erosion in all materials, so either a regime of regular inspection/replacement must be instituted or a more robust material such as a stainless steel (with periodic inspection) could be used.

5.4 CONCLUSIONS

Many of the design principles which have been developed for the current carbon dioxide industry can be applied for CCS applications such as:

- Avoiding designing plant to have enclosed spaces, basements, hollows, bunded areas or dips.
- Where this is unavoidable, classifying all these areas as enclosed spaces and carrying out risk assessments to determine the appropriate mitigation and procedures.
- Staff are trained in leak detection (especially where sight and sound are used on open plant) whilst operating the plant.
- Avoiding the failure of materials (metals, seals, valves, gaskets, lubricants etc.) in service by ensuring that they are tested to meet the operating conditions in the particular application they will face (where no standard tests or guidance exists) such as:
  - impurities within the carbon dioxide stream;
  - operating pressures to which the materials will be subjected;
  - operating temperatures (particularly noting the conditions which can be extremely cold);
  - cycling of plant and its materials;

  - flow rates, and
  - whether wet or dry carbon dioxide is being processed and selecting materials appropriately for either condition.
- Recognising that in plant where you can get solid formation (e.g. in blow down lines), then material erosion may occur and materials should be designed to avoid this erosion or should be inspected and replaced regularly.
- Ensuring that impingement is avoided in areas where blow down is expected.
- Avoiding failure of ball valves caused by expansion of carbon dioxide.
- Reviewing existing codes of practice designed for the liquid carbon dioxide market and determining whether they provide useful guidance to your project's particular conditions.

The application of principles developed in the existing carbon dioxide operations provides a useful design starting point for demonstration sized projects, allowing designers to incorporate learning from the existing carbon dioxide applications.

From the experience and shared learning of the CCS demonstration projects, further codes of practice and design guides may be required to meet the needs of the scaled up full size industry, particularly with reference to higher pressures and quantities.

6 PIPELINE DESIGN AND OPERATION

Pipeline operation and design – by the end of this section you will:

- understand the current operating experience for carbon dioxide pipelines;
- have an appreciation of the codes and standards that already exist for carbon dioxide pipelines;
- understand the issues that are taken into account when designing a carbon dioxide pipeline;
- understand how the process conditions affect the pipeline design;
- appreciate how design of pipeline ensures controls to prevent fracture propagation;
- understand how pipelines are designed to ensure safe blow down and safe inventory control through emergency shut-off valves;
- understand how materials are selected for the pipeline design;
- understand key issues with pipeline operation, and
- understand how measurements are taken on a pipeline.

6.1 INTRODUCTION

The transportation of carbon dioxide is a common occurrence, predominantly on a small scale via road, rail or in some cases by sea. For large scale transportation pipelines are common with 6 000 km worldwide. It is when compared to hazardous liquid and natural gas lines a very small distance covered, however the pipelines have been in place since the 1970s. There is therefore a small body of evidence on the design and operation of carbon dioxide dedicated pipelines, with design information being more publicly available. The following section outlines general guidelines for consideration in designing onshore carbon dioxide pipelines. It only addresses issues which would be deviations from normal pipeline design. In particular, issues such as: leak detection; pipeline integrity monitoring; safety management systems; risk evaluation; route surveillance requirements; emergency response planning; operations and maintenance issues; and repair techniques are all adequately covered within current pipeline design practice.

This section does not cover issues around the use of odorants within carbon dioxide pipelines as it is not currently allowed under the OSPAR rules, nor European practice for high pressure natural gas pipelines. It also does not include issues of material standards for material selection. We note that there are various organisations which produce material standards test methodologies which may be of interest including ISO, DIN, API, ASTM, ASME and NORSOK.

6.2 CURRENT ACTIVITIES

6.2.1 Current context

The transferring of carbon dioxide outside of plant boundaries by pipelines is not currently practised in the UK although there are numerous sites routinely handling the material. The majority of carbon dioxide pipelines are to be found in North America feeding predominantly naturally occurring carbon dioxide to EOR schemes. Currently however there are over 6 000 km of carbon dioxide pipelines in the US and Canada, a further 90 km in Turkey and others in Algeria and Hungary. The process of transporting both gaseous and dense phase carbon dioxide, whilst less common in terms of both distance and operational year experience than other fluids, is reasonably established.

These 6 000 km of pipelines in no way implies the same maturity of operation and design that is seen in large natural gas pipelines and networks for example the US alone; has 490 000 km. However the design of such pipelines is not new and a certain level of maturity of design and engineering exists albeit within differing regulatory regimes. It is this experience that it is important to encapsulate in future projects.

Some estimates for CCS schemes in Europe alone range from 30 000 to 150 000 km[76] of new pipelines, more than a 10-fold increase in pipeline lengths compared to current world wide installations. This would also include considerable offshore pipelines and the experience so far is predominantly onshore with the exception of the Statoil Sleipner and Snøhvit projects in the North Sea.

6.2.2 Current experience

North America since 1972 has seen a number of carbon dioxide – EOR schemes arise; some are from man-made sources, but the majority of transported carbon dioxide is from naturally occurring gas fields along the mid-continental mountain ranges and Mississippi basin, Figure 18 and Table 15. The gas is transmitted in the 'dense-phase' or 'supercritical phase'; operating above critical pressure reduces viscosity and surface tension.

The current schemes are all EOR projects, as opposed to just sequestration so therefore the composition requirements are set for those schemes. In addition the sources are either gasification plants or natural sources with traces of hydrogen sulphide or hydrocarbons. As a result the content of hydrocarbons is typically higher than one would expect than from a combustion process on coal-fired power stations as they produce no hydrocarbons. The tightest specification is for water content given the risk of corrosion when free water is present in carbon dioxide.

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[76] '*Building the cost curves for CO_2 storage: European sector*' Report 2005/2 IEA GHG, UK.

Table 15 Major carbon dioxide pipelines[77]

Pipeline	**Location**	**Capacity** (Mt CO_2/y)	**Length** (km)	**Pressure** (bar)	**Year complete**	**Origin of CO_2**
Cortez	USA	193	808	186	1984	McElmo Dome
Sheep Mountain	USA	95	660	132		Sheep Mountain
Bravo	USA	73	350	165	1984	Bravo Dome
Canyon reef Carriers (SACROC)	USA	52	225	175	1972	Gasification
Val Verde	USA	25	130	-	1998	Val Verde Gas Plants
Bati Raman	Turkey	11	90	170	1983	Dodan field
Weyburn	USA and Canada	5	328	Up to 204	2000	Gasification

Typically entry into a pipeline system is controlled in terms of conditions, temperature and pressure as well as composition. For example the Canyon Reef project advises the following specification for carbon dioxide:

- 95 % mol carbon dioxide minimum;
- 0,489 g/m^3 (250ppm wt) water in the vapour phase, no free water;
- <1500 ppm (w/w) hydrogen sulphide;
- <1450 ppm (w/w) total sulphur;
- <4 % mole nitrogen;
- <5 % mole, <−28,9°c dew point for hydrocarbons;
- <10 ppm (w/w) oxygen;
- <4x10-5 l/m^3 glycol, no free liquid at pipeline conditions, and
- <48,9 °C temperature.

6.3 CODES AND STANDARDS

6.3.1 North American Regulation

Essentially the US and Canadian regulatory framework that governs carbon dioxide pipelines has been developed and deployed for a number of years. The design of such pipelines is essentially the same framework of standards as for a normal pipeline, although with some additional requirements. These codes are: for the US '49 CFR 195, *Transportation of hazardous liquids by pipeline*' and for Canada 'Z662-07, *Oil and gas pipeline systems*'. For gaseous carbon dioxide then 49 CFR 192 applies rather than the liquid specific 49 CFR[78] 195.

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[77] '*Special report on carbon capture and storage*', IPCC, 2005, UK .

[78] CFR – Code of Federal Regulation.

As part of the US code a number of established standards for API, ASME, ASTM and others are included, therefore becoming part of the regulation; this set in theory a hard standard on which to base design. The core standard is ASME B31.4 the code for liquid pipelines (see Figure 36). However evidence suggests that ASME B31.8 is also applied. This gas specific code is used to evaluate the safety issues around a gas pipeline, applying these rules to carbon dioxide liquid lines as the fluid transitions to gas on release.

6.3.2 European Regulations

In Europe the regulations around pipelines are well established, as are the design codes. These regulations do not consider carbon dioxide as a specific named substance in the prescriptive manner of the US federal regulations. This may require changes to the regulations; however in the UK the HSE have stated that from 2008 until the existing regulations are changed, carbon dioxide is to be considered a 'dangerous fluid' for the purposes of Pipeline Safety Regulations 1996 and a 'dangerous substance' for the purposes of control of major accident hazards (COMAH). Other current legislation in the UK also applies to CCS for pipelines. Specifically, compliance with the following regulations and requirements must be achieved including any regulations enacted under them:

— Construction (Design and Management) Regulations 2008;
— Control of Major Accident Hazards (Amendment) 2005;
— Deregulation (Pipe-lines) Order 1999;
— Electricity and Pipe-lines Works (Assessment of Environmental Effects) Regulations 1990 and amendments;
— Environmental Protection Act 1990;
— Health and Safety at Work etc Act 1974;
— Health and Safety at Work (Northern Ireland) Order 1978;
— Pipe-lines Act 1962;
— Pressure Equipment Regulations 1999;
— Pressure Systems Safety Regulations 2000, and
— Town and Country Planning Act 1990.

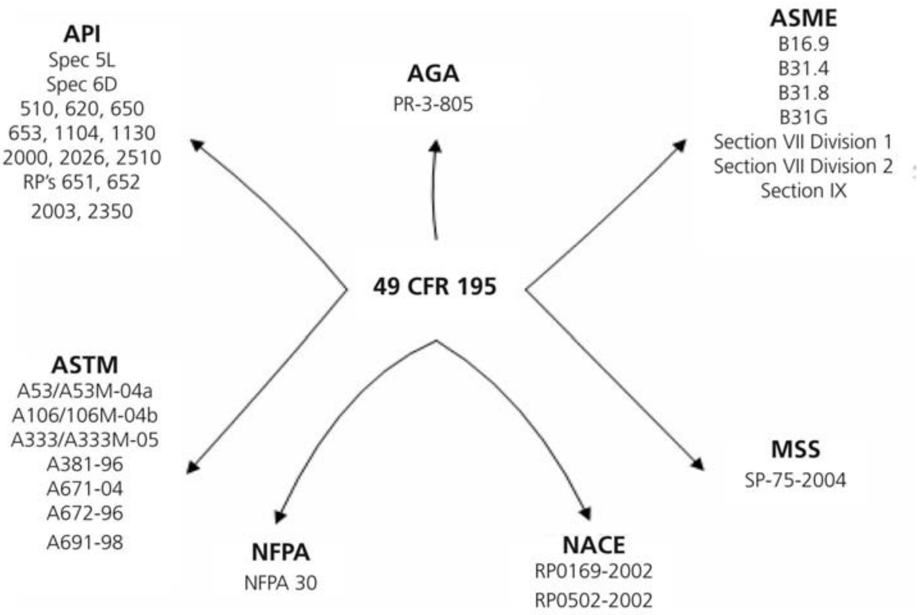

Figure 36 Prescribed standards and codes under 49 CFR 195

The European standard for pipelines is EN 14161 Petroleum and Natural Gas Industries – Pipeline Transportation Systems. In the UK the regulations and the HSE accept EN14161, however the HSE recommends that the code should be supported by good industry practice. Whilst the previous British Standard BS8010 has been replaced by EN 14161 it has become a published document BS PD 8010:2004 part1 '*Steel pipelines on land*' and part 2 '*Subsea pipelines*'. This covers EN14161 but encompasses good practice and a number of issues outside the cope of EN14161. Both standards, like the US regulations highlight a number of other standards that should be used in conjunction with the core code. Figures 37 and 38.

Under BS PD 8010:1 carbon dioxide is normally a Category C fluid, however once compressed and in a liquid state the categorisation changes to E, grouping it with ethylene and hydrogen. For a Category E fluid what amounts to a Quantitative Risk Assessment (QRA) is required. The code specifies separation distance parameters in most cases, but not for carbon dioxide therefore, until such guidance is provided, full dispersion models for carbon dioxide pipeline operation and leakage scenarios will be required as part of any pipeline design or design statement.

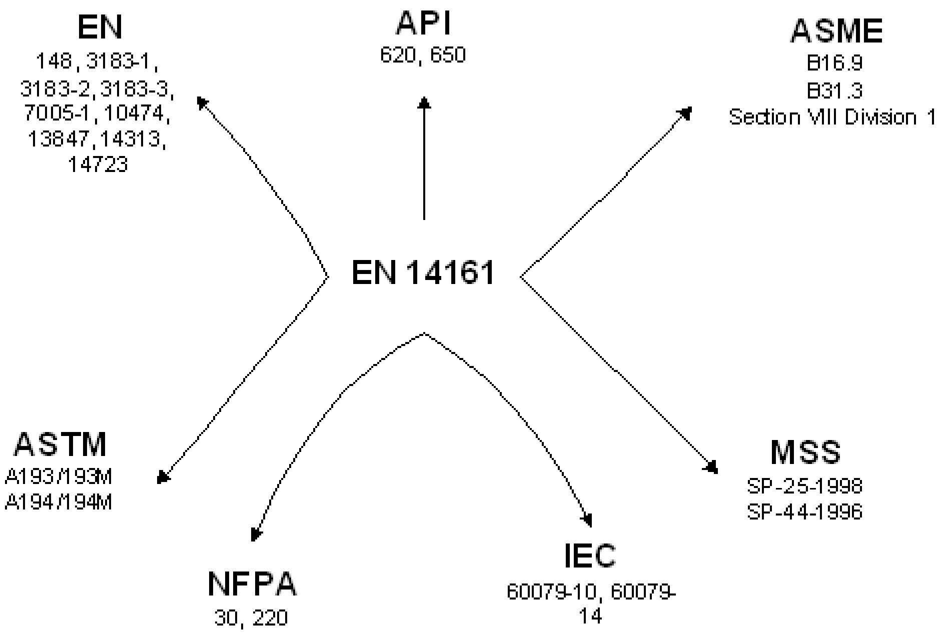

Figure 37 Standards associated with EN 14161

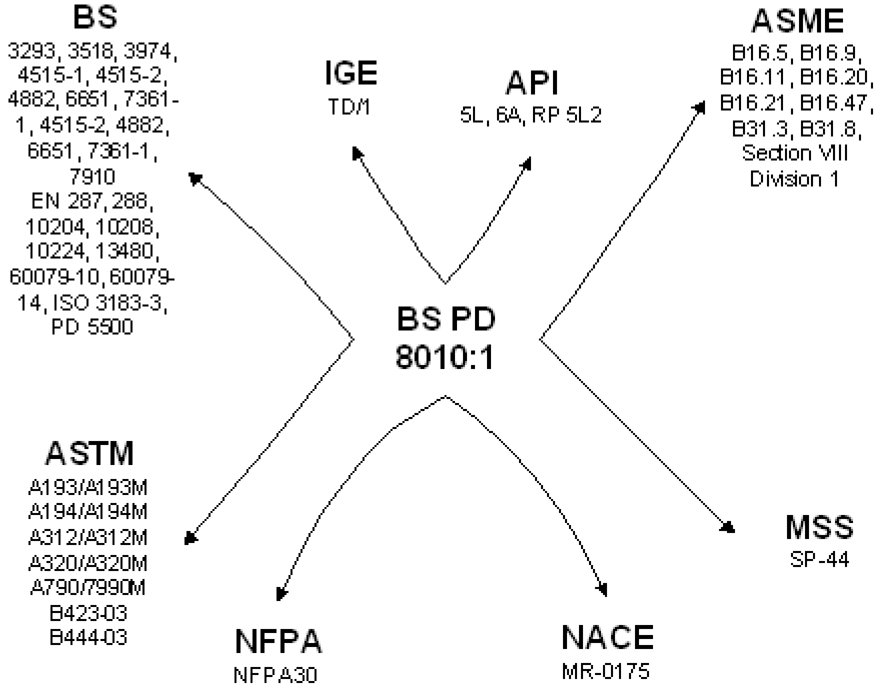

Figure 38 Standards associated with BS PD 8010 Part 1

6.3.3 Change of service

One issue that is considered in Europe is re-use of infrastructure. Whilst the North Sea has an abundance of infrastructure, previous carbon dioxide pipelines have been new builds. However the experience under US regulations considers this option. Within these regulations carbon dioxide as a supercritical fluid or liquid is covered under 49 CFR 195 and any pipe changing service is required to meet the regulations for the new service. For example a pipeline previously in gas service would be subject to 49 CFR 192 and ASME B31.8 a pipeline design code for gas. Changing to carbon dioxide liquid service changes the regulation to 49 CFR 195 and ASME B31.4 a design code for liquid pipelines. Within the regulations there exists a requirement that any pipeline changing service must meet all the requirements of the new applicable code. In Europe it would be logical to expect this practice to be replicated. In the UK for example PD 8010 would be applied to a gas pipeline that had previously been designed to IGE/TD/1, the Institute of Gas Engineers design standard for pipelines transporting natural gas in the UK.

6.4 DESIGN METHODOLOGY

6.4.1 Current design practice

The design of pipelines is well established in numerous text books, articles and standards and is a mature engineering subject. There are special considerations to be taken when considering carbon dioxide pipelines, but the basic pipeline engineering skills and techniques remain the same. For design there is a core of major factors that need to be considered that influence the design:

- fluid properties;
- environment;
- effects of temperature and pressure;
- design conditions;
- supply and demand magnitude/locations;
- codes and standards;
- route, topography and access;
- environmental impact;
- economics;
- hydrological impact;
- seismic and volcanic impacts;
- material;
- construction;
- commissioning;
- operation;
- protection, and
- integrity.

These factors are also given in a design process flow map in BS PD 8010-1, as shown in Figure 39 with each element examined in more detail within PD 8010.

It is not the intention of this guidance to provide detailed explanation or example of pipeline design. Therefore pipeline designers are recommended to specific texts and courses on the subject matter and to ensure that all pipeline design is executed by a suitably qualified and experienced person or organisation. The following sections examine carbon dioxide specific additions to normal pipeline design.

It should be noted that the subjects raised in this section are in addition to those you would normally consider for a pipeline. In effect the normal rules apply, whether they are regulations or standards. The codes, standards and regulations will dictate monitoring, leak detection, emergency planning requirements and such issues. Others such as general operations, maintenance and inspection are standard sound engineering practice. The key at least initially would be to utilise existing skills and subject matter experts and sound engineering practice and judgement.

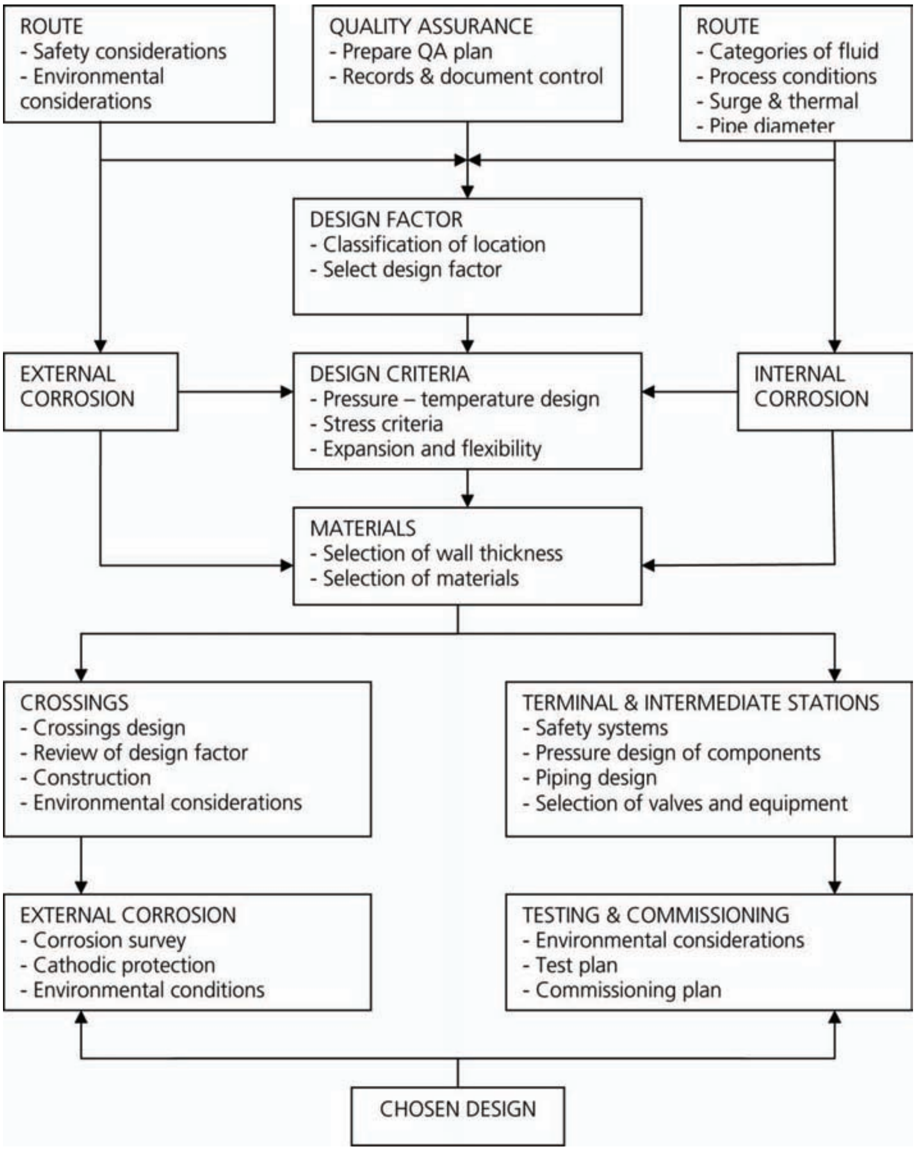

Figure 39 Pipeline design flow

6.4.2 Carbon dioxide specific design considerations

The following list highlights the critical issues that must be considered for all carbon dioxide pipelines[79,80].

- Process conditions:
  - properties;
  - operating conditions at entry and exit;
  - flow calculation method;
  - transient (surge) modelling;
  - flow characteristics, and
  - typical carbon dioxide compositions.
- Piping design:
  - fracture propagation;
  - blow down assembly design;
  - blow down rate basis and calculation;
  - linebreak controls;
  - pig trap;
  - depth of cover, and
  - routing topography.
- Safety and environmental:
  - ambient/ground temperature;
  - blow down rate basis and calculation;
  - dispersion pattern;
  - frequency and position of block valves;
  - leak detection systems, and
  - line inventory.
- Material selection:
  - pipeline materials;
  - carbon equivalent;
  - hardness value;
  - fracture strength;
  - valve, fitting and trim types;
  - seal, packing materials of construction, and
  - valve actuators.
- Cleaning and strength testing:
  - cleaning, and
  - hydrostatic testing/drying/dewatering.
- Construction techniques:
  - corrosion monitoring;
  - external corrosion;
  - fracture propagation;
  - special construction and welding, and
  - stress relief.

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[79] '*Pipeline design and construction: A practical approach*' Mohitpour M., 3e, ASME Press, New York, 2007.

[80] '*Carbon dioxide pipelines: A preliminary review of design and risks*' Barrie J. 7 th International Conference on Greenhouse Gas Technologies http://uregina.ca/ghgt7/PDF/papers/peer/126.pdf.

- Pipeline operation:
  - refrigeration effects during start-up/blow down;
  - start-up/shutdown methodology;
  - line pressuring;
  - requirement for blow down noise control;
  - environmental considerations;
  - operational problems, and
  - operational safety.
- Measurement:
  - custody transfer methods, and
  - moisture analysis.

6.5 PROCESS CONDITIONS

6.5.1 Properties of carbon dioxide related to pipeline design

When considering the physical properties of carbon dioxide it is important to understand the phase diagram first and the terminology. Figure 1 is an illustration of a phase diagram of carbon dioxide and shows the key points, critical and triple and the key area of interest, the supercritical region.

The properties of carbon dioxide are such that at supercritical conditions the density is relatively high but with a low viscosity, making it ideal for transportation. The properties of the supercritical region as a solvent also make it attractive for EOR, hence the infrastructure in North America, Figure 40 also shows the typical operating range of existing pipelines. The fluid properties during the transition down the pipeline also need careful consideration to ensure viscosity and density changes and their implications are considered.

Two-phase flow must be avoided, as should changes in the solubility of contaminants, so stable behaviour down the pipeline is critical. The prediction of properties is also key for the phase envelope, as a change in a contaminant may radically alter the phase diagram, in some cases depressing the phase boundary but in some cases increasing the pressures for phase change. This brings the operating pressure close to the phase change pressure with a changing temperature. Figure 40 shows the effect contaminants have on the phase envelope. The diagram shows nitrogen contamination of carbon dioxide at varying levels from 0,5 % to 10 % and the changes it makes to the envelope and critical points. If we take a comparison of 4 % nitrogen the critical point has shifted to 80 bar and is has a critical temperature below 30 °C. This potential change in phase boundaries must be carefully evaluated and defined as it will determine the minimum operating pressure of the pipeline to avoid two-phase flow.

The issue concerning properties is their prediction particularly when considering mixtures. Conventionally theses systems are modelled and as such modelling techniques use equations of state (EOS) to predict property data. In the absence of physical data caution must be used, however the current set of EOS are believed to be sufficient[81], although selection of an appropriate equation set is important.

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[81] '*Comparative study of equations of state (EOS) for CO_2 transportation in pipelines*', Li H & Yan J.

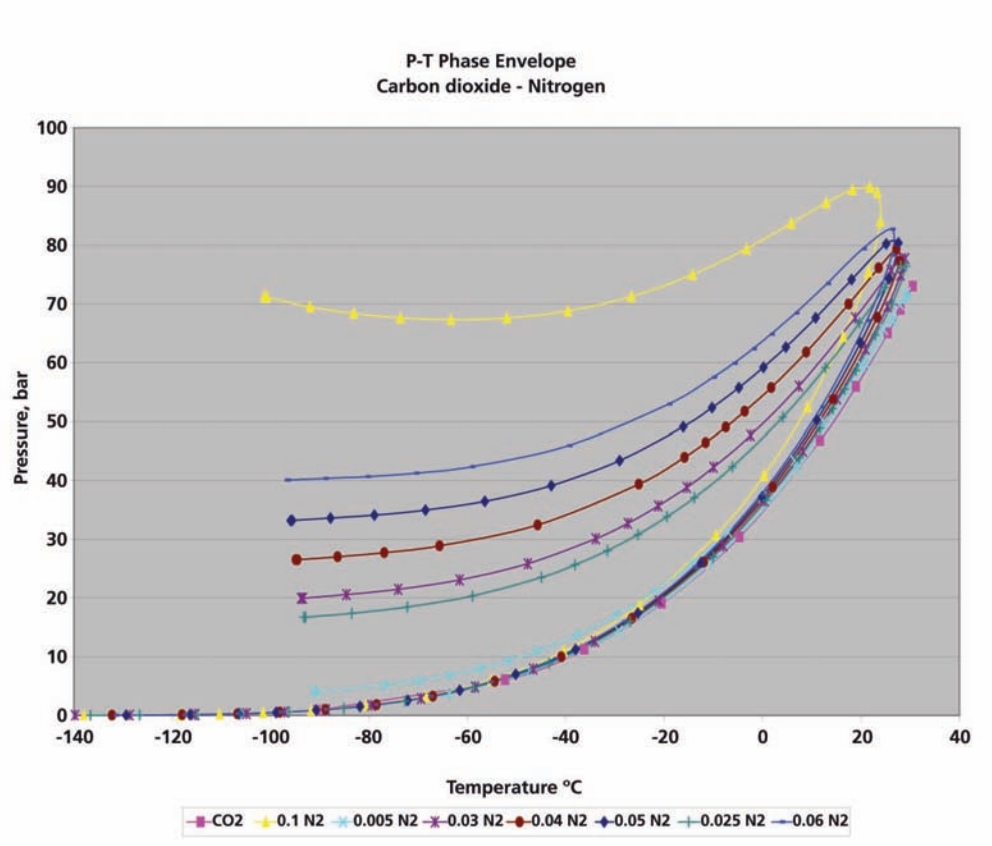

Figure 40 Phase envelope contaminant based deviations

6.5.2 Typical carbon dioxide compositions

The effect of contaminants on carbon dioxide is significant. Experience in the USA so far has been on carbon dioxide from either anthropogenic sources (25 %) or geological sources that are relatively clean (75 %). With anthropogenic sources there comes an increased number of contaminant possibilities, from the original source and the capturing and cleaning process. There will also be a need to consider the storage site requirements, and what is considered safe to transport. Therefore the range of contaminants needs to be understood as early as possible.

Table 16 shows a number of possible captured carbon dioxide mixtures from various processes.

In considering a carbon dioxide pipeline, particularly where there is more than one source, defining the range of the composition is a key component. For simple single source to single storage solutions the composition range will be defined by the emitter and the storage site acceptable limits.

The acceptable composition for carbon dioxide streams is not just set by the emitter or capture technology, but also by the other elements, particularly storage and transportation.

The following table indicates quoted compositions of carbon dioxide streams from the IPCC[82] and from the EU's Dynamis project[83].

Table 16 Typical post capture composition for transportation

Component	**Post combustion**	**IGCC**	**Oxyfuel**	**Weyburn**	**Dynamis**	
CO_2				>95 %	>95 %	
N_2/Ar	1	0,03 - 0,06 %	4,1 %	<4 %	<4 % (for non-condensable gases)	<4 % for all non-condensable gases and hydrocarbons
O2					<4 % EOR 100 - 1 000 ppm	
Hydrocarbons	0	0,01 %		<5 %	Saline formation <4 % EOR <2 %	
H_2	0	0,8 - 2 %	0			
H_2O	0			<100 ppm	<500 ppm	
H_2S	0	0,01 - 0,6 %	0	<1450 ppmv	<200 ppmv	
CO	0	0,03 - 0,4 %			<2 000 ppmv	
Hg	0					
Sox	<0,01 %, <100 ppm	<0,01 %, <100 ppm	0,5 %		<100 ppm	
Nox	<0,01 %, <100 ppm	<0,01 %, <100 ppm	0,01 %			
Glycol						

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[82] '*Special report on carbon capture and storage*', IPCC, 2005, UK.

[83] '*Towards hydrogen and electricity production with carbon dioxide capture and storage*', de Visser et al. Dynamis Consortium, 2007.

6.5.3 Flow assurance

For CCS the guarantee of flow down the pipeline is essential to the producer; failure of flow will result in the producer stopping the capture process, unless there is intermediate storage, and incurring major costs and potentially some operational difficulties. The guarantee of flow, flow assurance, is a well established area of current pipeline engineering. This type of study examines network modelling, transient multiphase simulation and the effect of solids, carbon dioxide clathrates (hydrates) that may form. Flow assurance for carbon dioxide pipelines is critical given the integrated nature of the producer to storage site of CCS projects.

Critically the operating conditions at the entry and exit of the pipeline, and the pressure profile down the line need to be understood in detail, to ensure that two-phase flow does not occur. Modelling of the pipeline becomes critical to ensure that route changes in the hydraulic profile are understood and accounted for accurately in the design stage.

Therefore the flow assurance work must consider the following:

- Definition of design conditions:
  - design temperatures, and
  - design pressure.
- Definition of operating conditions:
  - temperature;
  - pressure;
  - flow;
  - composition, and
  - fluid velocity range.
- Suitable flow equation.
- Accurate compositional model for physical properties.
- Heat transfer with the environment.
- Elevation profile.
- Energy and momentum balance.
- Recompression distances.

The accurate modelling of the pipeline is fundamental. Unlike many transportable fluids, gas or liquids the transport pressures and temperatures for carbon dioxide exist close to the critical point. This is essentially a transitional area, where small changes in temperature or pressure make significant differences to viscosity, density and compressibility. Changes in temperature due to environment conditions can change the viscosity and density profile. Elevation changes can mean that the loss or gain in pressure over such changes can result in pressure drops equivalent to or higher than the frictional pressure drop. Therefore sudden changes in height need to be modelled carefully to ensure good flow conditions.

The flow over the course of the pipeline needs rigorous modelling, such as can be achieved using a current state of the art simulator like OLGA. The selection of a suitable flow equation is also important, with sources stating the AGA equation[84], Beggs and Brill with a Moody friction factor[85,86].

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[84] '*Unusual design factors for supercritical CO_2 pipeline*' Farris C, Energy Progress, Vol 3, 1983.

[85] '*Facilities, pipelines and measurement: A workbook for Engineers*', Brooks G.F. and Martinez J., ASME, New York.

[86] '*Pipeline design model addresses CO_2 challenging behaviour*' Hein M., Oil and Gas Journal, 1986.

6.5.4 Equation of state selection

In the absence of experimental data for compositions the modelling of transportation systems relies on equations of state to estimate thermodynamic and physical properties. Significant discussion on the subject has taken place in articles and conferences, however no consensus has been reached; a particularly good discussion of the issues is considered by Polytec[87] in 2008. Farris[88], King[89] and McCullough[90] all used Benedict-Webb-Rubin-Starling (BWRS), whereas Zhang[91] used Peng-Robinson with Boston Mathias modifications. Hein[92] also used Peng-Robinson as well as Soave-Redlich-Kwong (SRK). A comparative study work by Li and Yan[93] examined all of these equations and discovered that there is a significant impact on the properties and hence on pipeline design; Peng-Robinson also stated that without experimental data on the composition they considered it was not possible to validate the accuracy of the equations of state.

6.6 PIPING DESIGN

6.6.1 General considerations

The basic design of a carbon dioxide pipeline is no different from current design procedures, with added detail for certain areas of concern. The regulations and design guidance that currently exists is not only explicit in its coverage but also proven in the existing pipelines.

There are elements of pipeline design that do require special attention. Like many pipelines there are special needs based on the fluid. In the case of carbon dioxide the issues resolve around the nature of the dense phase fluid and operating close to the critical point. Some are design issues, some are preventative measures or engineering around anticipated problems, some will be operational requirements. For carbon dioxide the following design elements require special attention:

- Fracture propagation.
- Pipeline system factor.
- Design temperatures and pressure.
- Charpy impact testing test temperatures and energy values.
- DWTT testing.
- Linebreak controls:
  - online mass balancing;
  - flowrate rate of change, and/or
  - rate of change of falling line pressure.
- Blow down assembly design.
- SCADA system design and integrity.
- Blow down rate basis and calculation.
- Pigging system design.

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[87] '*State-of-the-art overview of CO_2 pipeline transport with relevance to offshore pipelines*' Oosterkamp A Ramsen J., Polytec, Norway, 2008.

[88] '*Unusual design factors for supercritical carbon dioxide pipelines*' Farris C., Energy Progress, 1983.

[89] '*Here are key design considerations for CO_2 pipelines*', King G., Oil and Gas Journal 1982.

[90] '*Central Basin pipeline: A CO_2 system in West Texas*', McCullough D., Energy Progress, 1986.

[91] '*Optimization of pipeline transport for CO_2 sequestration*', Zhang Z. Energy Conservation and Management, 2006.

[92] '*Pipeline design model addresses CO_2's challenging behaviour*', Hein M., Oil and Gas Journal, 1986.

[93] '*Comparative study of equations of state for predicting phase equilibrium and volume properties of CO_2 and CO_2 mixtures*', Li H. and Yan J., GHGT8, Trondheim, 2006.

- Depth of cover and impact protection.
- Routing topography.
- QA and inspection regime.
- Risk assessment.
- Pipeline cleanliness during construction.

6.6.2 Fracture propagation and control

An important part of any pipeline material selection is fracture control. Defined by Thomas[94] fracture control is "the rigorous application of those branches of engineering, management, manufacturing and operations technology dealing with the understanding and prevention of crack initiation and propagation leading to catastrophic failure." Therefore it is one of the main considerations in material selection and pipeline specifications.

Fracture control divides into two elements, fracture initiation control and fracture propagation control, where initiation are the events and conditions that contribute to the fracture occurring, and propagation control the elements that can be used to control or arrest a failure. Propagating fracture control is generally achieved by ensuring the toughness of the line pipe is sufficient to arrest the fracture and is of particular concern when transporting gases, two-phase fluids, dense-phase fluids or liquids with high vapour pressures. It is these two latter categories that are particularly relevant to carbon dioxide.

For carbon dioxide the high vapour pressure of the supercritical fluid means that a very large volume of gas can be produced when the pressure is lowered. In considering a rupture supercritical carbon dioxide will decompress rapidly as a liquid then transition across the phase boundary to produce two phases in the pipeline. The carbon dioxide now exits at the rupture point predominantly as gas. The pressure at which the transition occurs from liquid to gas, the saturation pressure, is the key to determining the toughness required to arrest a propagating ductile fracture.

The saturation pressure is also affected by the composition of the gas, and again the composition and modelling of the properties of the fluid are critical. The initial pressure and temperature will also affect the saturation pressure, the higher the initial conditions the steeper the decompression curve and higher saturation pressure.

A propagating ductile fracture can occur when the initial defect exceeds the critical size, in some cases it is possible that the fracture will run for a considerable length. The propagation occurs when the fracture velocity in the pipe is equal to or greater than the decompression velocity of the escaping gas. The typical method of control is through toughness however other factors may arrest the crack such as a girth welding on or ahead of the propagating crack. A simple method of arresting these cracks is the addition of crack arrestors. Risk assessment will alter the frequency fo crack arrestors.

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[94] '*Fracture control for marine structures*' Thomas J., Treatise on Material Science and Technology, Academic Press, New York, 1988.

In determining the fracture arrest conditions the criteria applied by Batelle[95] states that the ductile fracture does not propagate if the pipeline is designed according to the following:

$$3.33\frac{\sigma_d}{\sigma_f}) \frac{2}{\pi}\cos^{-1}\exp\left(\frac{-\pi E_N}{24}\right)$$

where

$$\sigma_d = \frac{P_d D}{2t}$$

$$E_N = \frac{EC_V}{A\sigma_f^2\left(\frac{Dt}{2}\right)}^{1/2}$$

where

A	is the area beneath Charpy notch, m2
Cv	is the material Charpy notch toughness, J
D	is the pipe outside diameter, m
E	is theYoung's modulus of elasticity, Pa
E_N	is the normalised toughness parameter
P_d	is the decompressed pressure, Pa
t	is the pipe wall thickness, m
σ_d	is the decompressed pipe hoop stress, Pa
σ_f	is the pipe steel flow stress = σy +68,95 Mpa
σy	is the yield stress, Mpa

The criterion essentially indicates that to avoid ductile fracture the pipe flow stress, σf, has to be equal to or greater than the decompressed hoop stress, σd, by a factor of 3,33. If this criterion is met then propagation of a ductile fracture should be avoided. To satisfy this condition pipe strength or wall thickness needs to be increased.

Considering the cost of pipe to meet the criterion Mohitpour[96] suggests that from an economic viewpoint the best option is to use lower grades of steel. Here, to avoid the risks, thicker wall pipe than normal would be required. However higher grade steels such as API 5L X80 – X100 are available that would be sufficient. Previous experience on North American pipelines has seen API 5L X65 – X70 used, and on existing projects crack arrestors have been installed on pipelines, as over long distances the increase in wall thickness or steel grade has proved costly. Crack arrestors as thick walled spools[97] or externally applied devices much like clock springs[98] increase the wall thickness to provide the necessary increase. The time line of construction for North American pipelines and the propensity for crack arrestors may be accredited to the lack of high toughness steels that are available today[99]. Whilst each pipeline is different and will require a full assessment the typical spacing distance for crack arrestors is 300-350 metres[100].

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[95] and [96] '*Pipeline design and construction: A practical approach*', Mohitpour M., 3e, ASME Press, New York, 2007.

[97] '*Challenges to the pipeline transportation of dense CO_2*' Bratfos H. et al, The Journal of Pipeline Engineering, 2007.

[98] '*Crack arrestors*' Brauer H., 4th International Conference on Pipeline Technology, Ostend, Belgium, 2004.

[99] '*Fracture propagation in CO_2 pipelines*' Cosham A. and Eiber R., The Journal of Pipeline Engineering, 2008.

[100] '*531 BCF of CO_2 through the CRC system*', Fesmire C., Eng Prog, December 1983.

A fuller consideration of fracture propagation issues, including initiating mechanisms for carbon dioxide pipelines can be gained from examining those references quoted herein and a detailed consideration, including worked examples is presented by Cosham[99] and Eiber.

6.7 BLOW DOWN

6.7.1 General

The blow down of any pressurised pipeline is a considerable undertaking given the physical impact of the process, the venting arrangement and the level to which cooling occurs within a pipeline.

Typically in the existing pipelines block valves would be placed every 20 miles (32 km)[101] and at each block valve blow down facilities are installed[102]. There are two reasons for this frequency. As with normal hydrocarbon or gas lines the partitioning of the line makes the line more manageable from both a safety and maintenance point of view. For maintenance or repair the section concerned can be isolated and depressurised without the whole line being emptied.

For safety the installation of block valves means that should a leak occur then the block valves can be closed, limiting the amount of gas released into the atmosphere; this is particularly a concern if a line is ruptured and is intended to limit the impact of such an event.

It should be noted that under PD8010-1 the frequency of block valves would be determined by a system safety evaluation. In addition for natural gas pipelines in the UK 16 km is the maximum distance between block valves on natural gas pipelines.

There are then two blow down states to consider, emergency and planned.

6.7.2 Blow down rate

Modelling the blow down rate is complex as the process of decompression and evolution of gas from dense phase liquid is initially non linear and involves complex fluid mechanics.

There are a number of arbitrary methods available such as the spill model suggested by Muhlbauer[103]. Here the highly volatile liquids are postulated to release initially as a liquid until the vapour interface establishes in the pipeline.

This spill model is believed to represent a conservative scenario where liquid and gas or aerosol mists are being emitted, which may form pools that continue to generate vapour. To achieve this the model considers that the fluid will vent at the much higher liquid flowrate for three minutes at the maximum allowable operating pressure, MAOP, followed by seven minutes at the vapour pressure at pipeline temperature, see Figure 41.

This is a gross oversimplification as admitted by Muhlbauer[103], but makes an initial assessment possible and allows consistency. For detailed assessments, full dispersion modelling of release scenarios should be carried out.

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[101] '*Pipeline design and construction: A practical approach*' Mohitpour M., 3e, ASME Press, New York, 2007.

[102] 32 km is the US standard for block valves, in the UK IGE/TD/1 for natural gas stipulates block valves every 16 km (10 miles). A risk assessment of the pipeline may suggest placements at different distances.

[103] '*Pipeline risk management manual*' Muhlbauer W. K., Gulf Publishing Company, Houston, 1996.

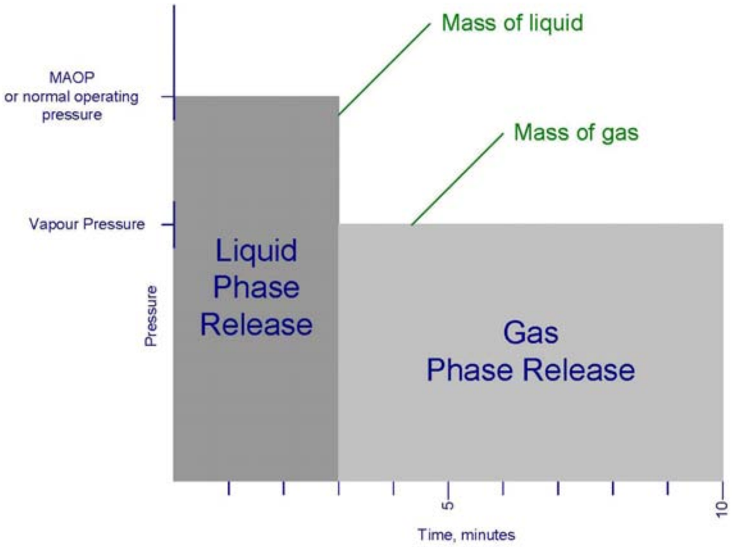

Figure 41 Spill model for two-phase releases

6.7.3 Planned depressurisation

Planned blow downs occur during maintenance, inspection and commissioning. Therefore ancillary equipment can be used and more importantly time can be taken to achieve the blow down. Experience in North American pipelines shows that for a typical 20 mile section of 20″ pipeline, blow downs are planned to take place over six to eight hours[104]. The typical assemblies, Figure 42, at the block valve include the primary block valve and a double seated ball valve with a pressurisation bypass. On a typical 20″ line the bridle is reduced to 8″ and isolated by double seated ball valves and the pressurisation section is further reduced to 3″ or 4″. The blow down valve is a 4″ globe valve and the process is regulated manually. Thermal relief devices should also be considered for lengths of blocked in pipeline sections.

The transition from liquid to gas occurs in the globe valve and because the gas velocities are high the valve seats may be liable to cutting. Therefore the valves are considered sacrificial[105]. If a blow down leg or vent downstream of the valve is installed it should also be specified for low temperature service. There are two critical elements in the blow down, firstly the release of the gas and second the temperature to which the blow down cools the pipe.

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[104] '*Pipeline design and construction: A practical approach*' Mohitpour M., 3e, ASME Press, New York, 2007.

[105] '*State-of-the-art overview of CO_2 pipeline transport with relevance to offshore pipelines*' Oosterkamp A Ramsen J., Polytec, Norway, 2008.

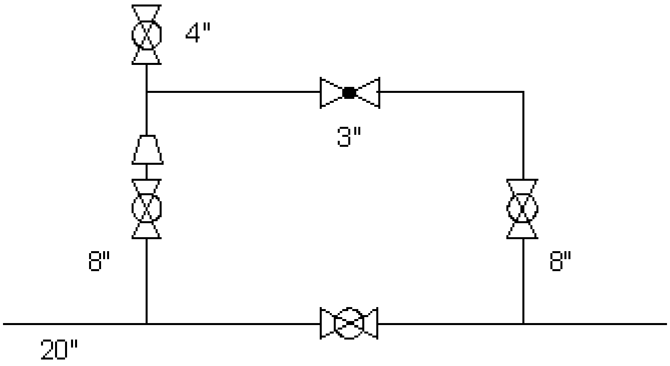

Figure 42 Typical blow down assembly

The blow down process will cool the contents of the pipe as the carbon dioxide expands which can have a detrimental effect on the line pipe material. Oosterkamp[105] presents an overview of blow down and discusses the results shown by Eagleton[106]. Here Eagleton compares theoretical calculation with actual observed calculation. The observed conditions from a 12 km 16" sectional blow down from 138 bara took five hours and showed that the temperature does not drop significantly until the saturation pressure is reached. From this point down to 20 bara the temperature falls to −2 °C, however from 20 bara to atmospheric the temperature rises again. Calculations in the same reference show a minimum temperature of −47 °C. This disparity serves to illustrate that careful modelling of such systems is required to determine the minimum temperature given the importance of these criteria on material selection.

The release of the gas is determined in this case by the discharge rate through the valve. During the transition to atmospheric pressure carbon dioxide solids can be expected to form, but have not been seen to cause blockages during venting. The weather conditions are also key as atmospheric conditions affect the heavy carbon dioxide gas' dispersion. Typically experience shows that carbon dioxide dispersion is depressed in situations with no wind, overcast skies or rain, with slightly increased ground level concentrations. Experience shows that whilst not critical the weather conditions impact on blow down dispersion, and that the minimum temperature can be controlled by slow depressurisation.

6.7.4 Emergency blow down

Emergency blow downs typically result from leaks or rupture of the pipeline and therefore very little control is possible. The extent of the blow down and the release volume of gas is effectively determined by the size of pipeline, the length to the next block valves and design of the remotely operated shut off valve (ROSOV) system.

Modelling of leaks and ruptures is critical, especially large bore failures, as it impacts on the safety issues of the pipeline and response plans, and greatly affects the planning and design elements of the project. The greater the threat from a rupture plume the further away from population centres a pipeline has to be. The dispersion from a volume

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[106] '*Transportation of carbon dioxide by pipeline*' Eagleton H.N. 8th International Pipeline Technology Exhibition and Conference, Houston 1980.

of pipeline also determines how far apart the block valves should be. For this reason the dispersion modelling of releases is important and needs to be accurate, and is discussed in a separate chapter. The issue has more importance in Europe given that population densities are generally higher than in the US or Canada.

The key issue to consider is finding the optimum segmented pipeline length between block valves that meets the requirements of the appropriate code or guidance.

6.7.5 Pigging

As with all pipelines there is a need to monitor integrity, or to clean the pipeline, and this is achieved using pigs, both 'utility' and 'intelligent'. The methodology of pigging a gas or liquid line is well established and carbon dioxide pipelines offer little change in that method. However there are issues that need to be considered in addition to the normal consideration on whether pigging is required.

Utility pigs used for scraping corrosion or other debris from a pipeline use polymers or rubbers in part or completely. When inserted in the pipeline the carbon dioxide can attack the material of construction causing it to swell possibly to the point where it will stick. In addition the carbon dioxide has low or no lubricating properties leading to increased wear of the elastomer components[107,108]. Experience in North America shows that the use of scraper pigs is redundant, unless there is an upset condition and water can enter the line.

The use of intelligent pigs for inspection purposes suffers the same generalised problems but added to this is the attack of carbon dioxide on the intelligent (e.g. sensors, processors, recorders) components. This can lead to any elastomers or seals becoming saturated and subject to deterioration and rapid gas (explosive) decompression destroying the pig. In fact Oosterkamp[105] indicates that it has been reported that by 2008 only two intelligent pig operations in North America had resulted in the expensive pig surviving.

The combination of friction wear and permeation leading to deterioration and failure of other components makes pigging a difficult operation and care should be taken to select an appropriate specialist.

A thorough internal and external inspection of the carbon dioxide pipeline soon after commissioning should be carried out to identify the 'installed' condition. These data will provide a baseline for future survey data. This survey is carried out through the use of intelligent pigs.

6.7.6 Line inventory and block valve location

The driver behind any rupture dispersion is effectively the pressure of the pipeline and the time it takes to depressurise. This time factor is dependent on the pipe volume to the next isolation in the line. Effectively the isolation block valves at the end of each section determine the volume, which in turn determines the size and duration 'foot print' of any dispersion. This dispersion model will determine the safety distances to occupied areas, which in turn pushes the pipeline route in order to maintain a safe distance.

This iterative process drives the provision of block valves; however there is a point at which increased numbers of block valves not only have an economic impact, but also a safety one. The more block valves there are means that the pipeline has an increasing number of potential failure points. As a guidance, 20 miles (32 km) seems to be a typical

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[107] '*A generalized overview of requirements for the design, construction, and operation of new pipelines for CO_2 sequestration*' Mohitpour M, The Journal of Pipeline Engineering, 2008.

[108] '*State-of-the-art overview of CO_2 pipeline transport with relevance to offshore pipelines*' Oosterkamp A Ramsen J., Polytec, Norway, 2008.

distance in North American pipelines. However BS PD 8010 and most codes are very specific, stating that isolation (block) valves to limit the inventory released should be spaced according to the outcome of full safety evaluations. It is worth noting that in the UK natural gas pipeline block valves are spaced at a maximum distance of 16 km. In addition block valves can be expected at major crossings such as rivers, rail lines and major roads.

In considering the positioning of block valves, a risk assessment has to be made regarding topography, operational access, security and proximity to normally occupied buildings.

6.7.7 Emergency shut-off valves (ESOV) [109]

6.7.7.1 Overview

As dense phase carbon dioxide will be classed as a 'dangerous fluid' under PSR96 regulations, an ESOV system will be required to prevent excessive inventory release, where directly connected to an offshore platform. For onshore pipelines it is also intended that ESOVs or remote operated shut-off valves (ROSOVs) are provided at the entry and exit of a pipeline and are considered where necessary following appropriate design and risk assessment to prevent excess flow and allow the pipeline system to be shut down quickly and safely to reduce the consequences of a pipeline failure caused by third party intervention, component failure or damage.

The ESOV shutdown system may also need to incorporate the requirements of a high moisture level trip system to guard against corrosion (subject to upstream process operations). Any ESOV trip system should satisfy the requirements of IEC61508 and be designed with an appropriate safety integrity level.

An ESOV can be automatic or manual in operation and is usually located on pipework leaving a production site. Depending on pipeline length and any spurs intermediate, ESOV installations can also be installed. The closure of the valve(s) can be initiated manually or automatically from a central control room or by automatic signals derived from high flowrate, low pressure, rate of decay of line pressure or online mass balance.

It may be acceptable for the emergency shut-off function to be incorporated into an existing control valve (subject to any safety integrity level assessment conditions or restrictions).

It is recommended that the technical requirements for a pipeline ESOV system are considered at the pipeline design stage and the specific project requirements included within the project process definition document and the process and instrumentation design.

6.7.7.2 Design considerations

Consideration of ESOVs should be compliant with recognised good practice such as those published by the HSE, HS(G) *Remotely operated shutoff valves for emergency isolation of hazardous substances*. The design and installation of ESOV systems, including pressure, flow, temperature switches and other devices, should take into account the following factors:

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[109] Whilst ESOV are mandatory on risers to offshore installations, they are not mandatory on onshore pipelines. However, they could form a risk management measure in mitigating against a large scale accidental inventory release.

- The quality and reliability of the devices.
- Failure modes and effects including, for example power failure, instrument gas failure and instrument circuit failure.
- Whether to use trips/and or alarms and in the case of the latter, the ability of the pipeline operator to respond.
- Fail safe requirements and consequence of failure considerations versus supply reliability concerns.
- The required safety integrity level of the system will require assessment and any requirements incorporated into the overall ESOV system design.
- The ability to test the installed system without interrupting the supply, for example by installation of duplicate systems or by-pass arrangements. Where a by-pass is installed, there need to be physical locks and management systems to ensure that the by-pass is only opened during specific periods during testing.
- Properties of the conveyed fluid.
- The valve and its actuating mechanism are required to be protected, so far as is reasonably practicable, against fire, explosion and impact. The aim is that under all foreseeable conditions the ESOV should be capable of closing. The extent of the protection system should at least cover the ESOV, its actuator and any other components required for fail-safe closure of the valve.
- The designer should ensure that the ESOV will at all times operate on demand or fail safe in the closed position, so minimising the possibility of an uncontrolled release of pipeline inventory. Once closed the ESOV should not be reopened until the safety of the installation and connected installations is assured.
- The ESOV should be capable of stopping the flow of the fluid within the pipeline. Minor leakage past the ESOV which cannot represent a threat to safety is acceptable.
- The ESOV should be a rapid acting isolation valve capable of being operated remotely by the emergency shutdown system or locally.
- The ESOV system must be designed such that once operated and shut it cannot automatically re-open. The ESOV should be designed to allow a means of manual repressurisation at a controlled rate.

6.7.7.3 *General principles of operation*

The ESOV system may be activated by one or a combination of the methods described below:

- On simple pipeline supply schemes where all services and instrumentation are available, then high flowrate and/or low pressure can be used as the tripping criteria. However the operational setpoint requires careful assessment, particularly if the pipeline operates with erratic flowrates and pressures. An incorrect or poorly chosen setpoint will cause spurious trips and disruption to the customer supply with a consequential impact on downstream and upstream operations.
- If the flowrate and pressure are constant, then either pressure or flow or a voting system from both could be used. This system would utilise the normal maximum flowrate or the normal minimum pressure and then apply a margin to remove the chance of spurious trips whilst ensuring that the real pipeline emergency excursion is catered for.
- A self-contained piece of equipment such as a 'Shafer valve'. The Shafer system measures the rate of change of falling pressure. This is a very accurate way of assessing a pipeline failure without causing spurious trips. The main reasons for choosing this unit is that it is 'stand alone' and can be used in remote locations and does not require the provision of any services except for a compressed instrument gas cylinder for actuation/motive power. This system would be chosen if the

pipeline supply flowrate and pressure were critical and very erratic with many and large deviations during normal operations This system can also be used to protect critical pipeline spurs or off-takes when looking at larger pipeline networks.

- Pipeline online mass balance. This type of system is particularly suited to complex pipeline networks. This system utilises flow and pressure inputs from all downstream consumer offtakes and compares the total against the flow and pressure at the inlet to the pipeline system. Should the difference (error) between the two be greater than a pre-determined setpoint the ESOV system would be operated and/or an alarm/s operated.

Note:

- The set point for these types of systems should be established as part of a 'modelling' exercise at the pipeline design stage. The flowrate and pressure under normal operation should be assessed and a margin over this applied to accommodate any normal deviations without making the pipeline system vulnerable.
- It should be noted that modelling the customer’s demand pattern is relatively simple for a single demand pipeline but can be very difficult in multiple demand grid systems where many individual process patterns can conspire to give a very wide set of possible conditions. Consideration should be given to tuning the system following commissioning taking account of accrued experience of the overall operational envelope.
- The response of the fluid to the shut-off system needs to be carefully considered. Dynamic analysis of the pipeline is recommended to avoid problems associated with sudden changes in momentum such as 'water hammer' effects.

6.7.8 Routing and topography

The primary factors of pipeline routing are well established as economic, technical and safety. The shortest route may not be acceptable and the avoidance of obstacles and environmental constraints needs also to be considered. For carbon dioxide pipelines these factors do not change. Codes such as BS PD 8010 and literature such as Mohitpour[110] go further in highlighting the detailed considerations at each step. The pipeline design factor chosen will also influence routing and proximity to normally occupied buildings under PD8010-1. The primary factors highlighted by PD 8010 are:

- Safety of the public and personnel.
- Content of the pipeline and operating conditions.
- Environmental impact.
- Terrain and subterranean conditions, including geotechnical and hydrographical conditions.
- Existing and future land use, including:
  - third-party activities;
  - agricultural practice, and
  - existing facilities and services.
- Permanent access.

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[110] '*Pipeline design and construction: A practical approach*' Mohitpour M., 3e, ASME Press, New York, 2007.

- Transport facilities and utility services.
- Construction, testing, operation and maintenance.
- Security.
- Proximity to other services.
- Crossings.
- Parallel encroachments.

Risk contours for the pipeline should be developed to determine safe limits and proximities as part of the design process. Routing of class E pipelines through class 3 areas of high population[111] should be avoided.

For carbon dioxide all of the above apply, but special attention must be paid to the topography of the route. The change in height and thus pressure of the pipeline needs to be carefully configured for hydraulic and pressure reasons. In addition the pipelines should be run such that the dispersion of any rupture or leakage plume should avoid the build-up of dangerous concentrations of the gas. As a gas, carbon dioxide is denser than air and a low momentum release or cloud of carbon dioxide can follow terrain changes and lead to an accumulation. Therefore the routing must also consider this possibility and where appropriate, deviate from areas that might see accumulation were there to be leaks. As with all elements of routing there is still an economic consideration as route change may add distance to the pipeline[112].

6.8 MATERIAL SELECTION

6.8.1 General materials of construction

The corrosion potential of carbon dioxide in hydrocarbon pipelines is a well-known issue. Where corrosion is likely, given the content of the carbon dioxide in the natural gas, the carbon dioxide is removed to avoid the issue. In the case of CCS the reverse is true. The main fluid is carbon dioxide and the contaminant is water. If free water were to form in a carbon dioxide pipeline then carbonic acid, H_2CO_3, will form and corrosion will occur. For long pipelines carbon steel is the only economic solution, however it is susceptible to corrosion. Specific issues for carbon dioxide are well known and include:

- pipeline materials;
- carbon equivalent;
- hardness value and fracture strength;
- valve, fitting, actuator and trim types;
- bends, and
- seal, gasket, packing materials of construction.

6.8.2 Pipeline material

The issue of corrosion has been studied extensively in laboratory tests and reported in a number of sources.

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[111] Class 3 locations are defined in PD 8010-1 as 'Central areas of towns and cities with a high population and building density, multi-storey buildings, dense traffic and numerous underground services'.

[112] '*Transmission of CO_2 – safety and economics considerations*' Gale J. Energy, 2004.

In the tests by Schremp and Roberson[113] six different compositions and three weld types were studied. The samples were full size X60 12" and 16" pipe sections that were exposed to a carbon dioxide mix consistent with real SACROC pipeline conditions. The stress tests were conducted at two conditions, the first at 138 bar and 22 °C for six weeks and then at 138 bar and 3 °C for four weeks. The chemical composition included 600-800 ppm of H_2S and 800 to 1 000 ppm of water. The water content is a third of the saturation value of 2 500 ppm at the operating conditions. As a result, it is now accepted that corrosion in carbon dioxide pipelines will not occur if the water content is kept less than 60 % of the saturation value[114]. The original test used a water content 20 times higher than specified for the SACROC line. The test concluded that corrosion did not occur, even at this elevated water content. The corrosion rate was determined at 0,02 Mpy (mili inch per year) or <0,5 µm/y. Operational experience showed that on the SACROC pipeline with a 50 ppm water content limit, after 12 years the corrosion rate was 0,25 to 2,5 µm/y[115,116].

Whilst care should be taken with regard to corrosion it is clear from continued operation that carbon steel is acceptable as a material for carbon dioxide pipelines. There have though been incidents with corrosion; SACROC reports[117] some issues, notably a corrosion incident in a spur line from a main pipeline. The area had free standing water remaining from a hydraulic test and so corrosion set in. Care must be taken not only to ensure a water content limit in the entry specification, but also the water introduced during testing, commissioning and maintenance events.

In specifying water content the industry accepted levels are conservatively specified as between 288 – 480 mg/m^3 [118]. In addition the presence of other additional 'acid gases' such as H_2S, SOx and NOx compounds needs to be considered. However Sox and Nox compounds will to some extent be subject to earlier restrictions in the capture stage and are unlikely to present themselves in the pipeline.

6.9 CONSTRUCTION TECHNIQUES

With the exception of fracture control and the material selection issues discussed earlier there are no fundamental changes to the way in which pipelines are constructed for carbon dioxide from other pipelines. The previous discussion on codes and standards cover the technical requirements and the application of existing legislation would cover all else.

Corrosion issues remain both internally and externally. Current best practice for cathodic protection and external corrosion should be followed. Typically in the US fusion bonded epoxy or polyurethane coatings are used. For a UK specific system use a good three layer coating system comprising a fusion bonded epoxy (FBE) base layer, adhesive layer and polyethene (PE) top coat. Field welded joints should be coated with a high integrity system such as multi layer shrink sleeves.

Cleaning and testing is an integral part of the start-up and operations of a pipeline. For carbon dioxide service there are subtle issues to be considered but in general the procedures and methods for these activities are unchanged.

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[113] '*Effect of supercritical carbon dioxide on construction materials*', Schremp F. and Roberson G. Society of Petroleum Engineers, 1978.

[114] 'Maintenance techniques proven on CO_2 line', Najera G., Oil and Gas Journal, 1986.

[115] '*Canyon Reef Carriers Inc, CO_2 pipeline description and 12 years of operation*', Gill T., ASME, 1985.

[116] '*Material selection for selection, transportation and disposal for CO_2*' Seiersten M., Corrosion 2001, 2001.

[117] '*Corrosion and operational problems, CO_2 project, SACROC Unit*' Newton L., Society of Petroleum Engineers, 1977.

[118] '*Pipeline design and construction: A practical approach*' Mohitpour M., 3e, ASME Press, New York, 2007.

The critical issue here is the testing. Pneumatic testing may not show leaks that carbon dioxide can penetrate so care must be taken to ensure the fitting and tightening of all components are correct. After a hydraulic test the water must be removed and is typically air dried to a dew point of −45 °C. Vacuum drying may have to be considered if the dew point is not attained through air drying alone.

There are some considerations when cleaning pipelines designed to carry CO_2. As discussed the scrapers or pigs are susceptible to swelling and other damage in carbon dioxide. Operational experience has shown that very little water or debris falls out of the carbon dioxide and indicates that the use of scrapers is redundant[119]. The pigging of pipelines is a fundamental practice, however, and should still be considered in line with the regulations and good practice from the oil and gas transmission sectors.

6.10 PIPELINE OPERATION

6.10.1 Key issues

Normal operation and start-up/shut-down does have a number of issues for consideration:

- refrigeration effects during start-up/blow down;
- line pressuring;
- requirement for blow down noise control;
- environmental considerations;
- operational problems;
- operational safety, and
- valve operation.

6.10.2 Start-up/shut-down refrigeration

The refrigeration effects of carbon dioxide have been previously discussed. For controlled blow down, a key operation and issue is avoiding the cooling effect of expanding gas when starting up. The norm is that the line is at first pressurised to 6,9 - 34,5 bar with dry air or nitrogen, before carbon dioxide is introduced. The carbon dioxide is introduced slowly, gradually displacing the air or nitrogen until the line is filled. The line is then pressurised. This is executed on a section by section basis until the line is completely full and ready for operation.

6.10.3 Environmental considerations

Environmental considerations have been discussed elsewhere but it is critical that the environmental impact of operations is considered. This effectively relates to blow down and ensuring that correct location of the blow down point occurs, such that dispersing gas does not affect the local population adversely. Noise from the blow down also needs to be considered and controlled where necessary, for the safety of workers local to the blow down but also to the wider population.

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[119] '*Pipeline design and construction: A practical approach*' Mohitpour M., 3e, ASME Press, New York, 2007.

6.10.4 Operational problems

Operational problems are not necessarily reported in the public domain unless a release occurs so very little public information is available. One issue commonly referred to is pressure, often highlighted as needing special attention for transient issues or a general pressure profile along the line. Normal flow assurance techniques from the oil and gas industry would be transferable and careful consideration should be given to the mitigation measures that should be taken for carbon dioxide.

The operational problems most reported are safety incidents in the US for all pipelines to the PHMSA. In the period from 1986 to March 2008 there were 42[120] reported incidents to PHMSA, Figure 43. This relates to approximately 0,36 incidents/ 1 000 km/year, (assuming US pipeline distance average of 5 000 km over the period), compared to 2 447 incidents on the US gas transmission network or 488 000 km[121] or 0,22 incidents/1 000 km/year. In the period 1990-2001 the incident rate for natural gas was 0,17, for hazardous liquids it was 0,82[122], so the incident rate is still comparable and within the expected bounds for a hazardous liquid.

Another reference source for pipelines (although not specifically carbon dioxide) is CONCAWE. The data held by CONCAWE indicate a significant number of incidents relate to corrosion and third party intervention. Hence for carbon dioxide, systems drying is a critical aspect of design and operation as well as protection to prevent third party incidents (lay deeper, slabbing, thickwall etc.).

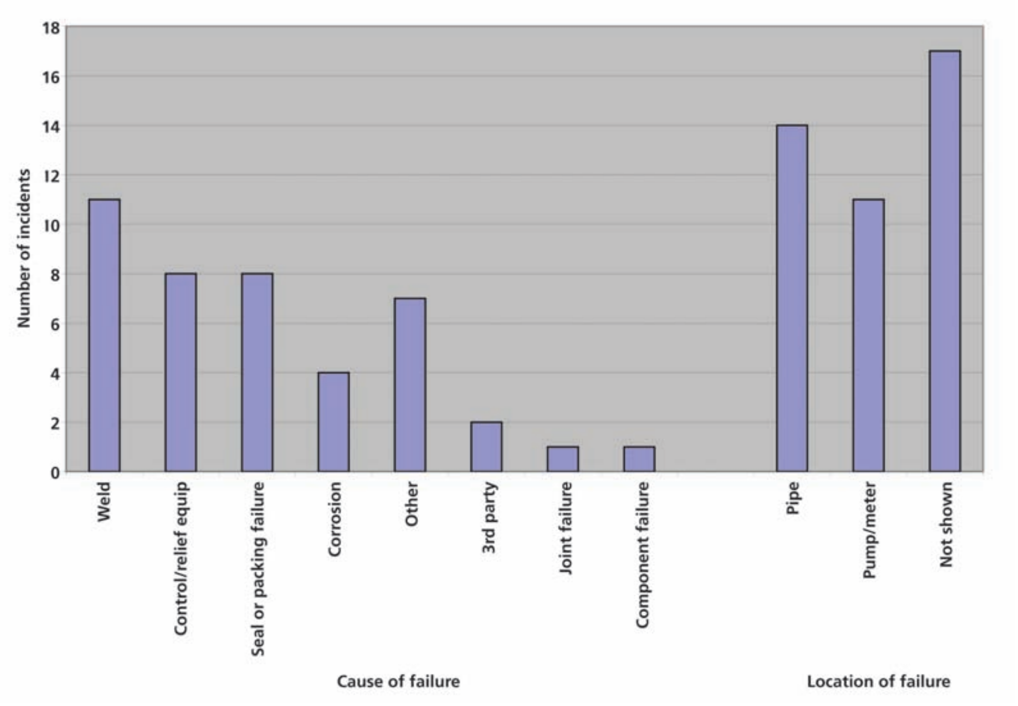

Figure 43 CO_2 pipeline incidents 1986-2008

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[120] http://www.phmsa.dot.gov/pipeline.

[121] http://www.eia.doe.gov/pub/oil_gas/natural_gas/analysis_publications/ngpipeline/

[122] '*Transmission of CO_2 – safety and economic considerations*' Gale J. and Davison J., Energy 29, 2004.

6.10.5 Operational safety

Safety issues are predominantly concerned with leaks and blow downs as covered in previous sections. There are two other operational issues to be considered. The first is valve operation where it is recommended that all valves are slow opening. This avoids damage to the valve and surging in the pipeline, this is particularly important for blow down valves.

Where pipe segments are above ground, thermal relief should be provided and the valve must be capable of seating under high carbon dioxide pressures. Current practice is not to work on pressurised pipelines and, where necessary, sections and valve bodies are blown down before removal of a valve or other equipment item.

6.11 FLOW MEASUREMENT

There are two elements to measurement, contaminants and flow. For flow measurement there are two types commonly used, vortex and orifice. Orifice meters, Figure 44, are generally used for custody transfer with incorporated flow computers, differential pressures and temperatures installed in accordance with BSEN 5167. The ability to carry out routine calibration work on the invoice meter should be included as part of the design i.e. (locked bypass or dual systems). Custody transfer measurement systems are installed in tandem for reliability and continuity. For normal flow measurement, vortex meters are used, Figure 45, with flow computers that do not rely on density correction. Density is computed from measured pressure and temperature, which is an important consideration where pressure and/or temperature are fluctuating or changing rapidly. In addition, density changes with impurities and this must be taken into account to ensure accurate measurement.

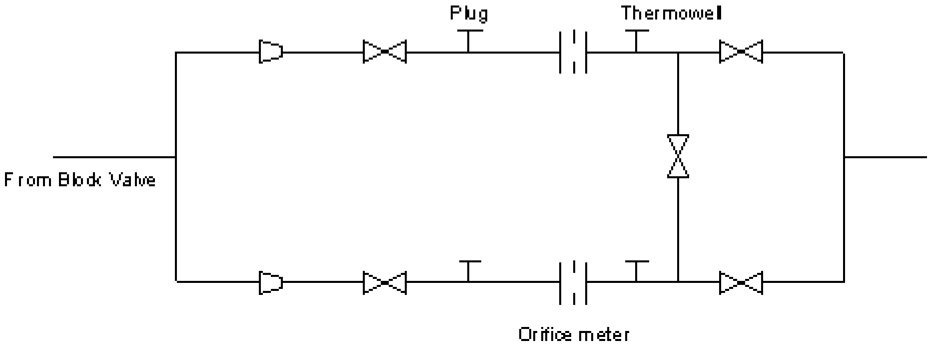

Figure 44 Typical orifice meter

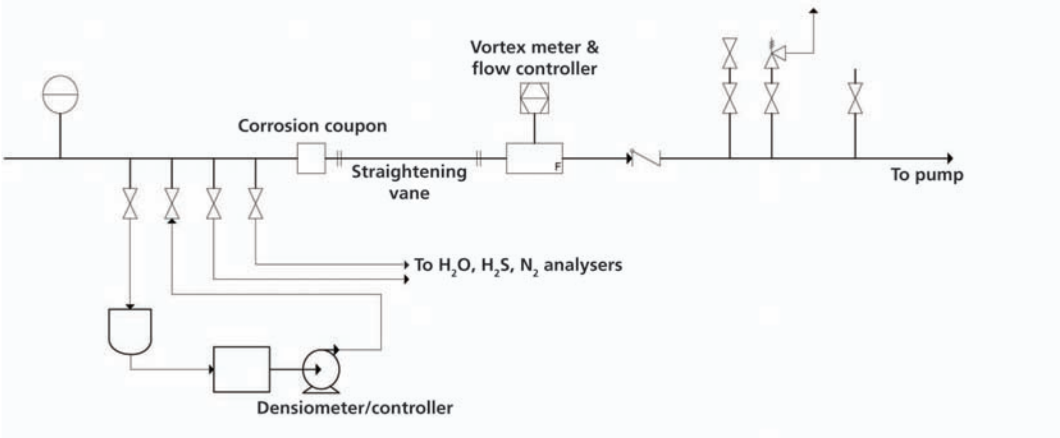

Figure 45 Typical vortex meter and contaminant analysis

Contaminant measurement is made typically at a metering station using analysers; the key contaminant is water. Experience has shown that the moisture analysers are good in service for 30-90 days depending on the water content.

Siting of meters should take into the likelihood of two-or multiphased flow as not all meters will be suitable at all locations or applications. Vendors should always be consulted to ensure applicability of any meter or metering type to the specific application and location.

Metering of carbon dioxide has been examined by TUVNEL, who produced a report *A study of measurement issues for carbon capture and storage (CCS)*, Report No:2009/54 April 2009, which provides a useful overview of metering issues. The importance of metering for the purposes of the EU emissions trading scheme needs to be considered carefully where accuracy is critical.

6.12 CONCLUSIONS

This section has discussed current experience and has drawn heavily from an already mature industry. It is clear from the experience in the US that design and regulation requirements are clear, but need enhancement to comply with other regional requirements. The following conclusions can be drawn from the section:

— Global CO_2 transportation by pipeline is a mature industry with 6 000km of pipelines up to 900mm diameter pipelines.
— Current pipeline experience is to the scale required for CCS systems.
— US and Canadian codes and standards are prescriptive and classify CO_2 pipelines in the same way as hydrocarbons.
— European regulations and standards allow for the design of CO_2 pipelines within current structures.
— Gaps in the knowledge do not prohibit design but are likely to lead to conservative design.
— UK specific regulations and guidance enable pipeline design to occur in the current frameworks with a mature established design methodology and risk assessment framework.
— The implications of impurities need to be understood in the design of a pipeline.

- Fracture propagation and control need to be considered and appropriately implemented.
- Blow down and emergency shut-down design is established both in industrial gases sectors and in pipeline transportation.
- Material selection is established with a significant body supporting the methodology. Some consideration must be given to the impact of impurities; however, they have been considered before.
- Pipeline operational issues are well understood and are shown to be consistent with the larger transportation systems.

7 SUMMARY AND RECOMMENDATIONS

7.1 SUMMARY

The primary objective of this guidance document is 'to improve the industry's knowledge, and to assist developers and operators to carry out hazard analysis, procure and manage their CCS plant safely'. It does not provide an exhaustive set of information on CCS issues and, by its very nature as an emerging area, research and knowledge is progressing at rapid speed. It is, therefore, important for participants in the CCS industry to keep abreast of research and developments in this sector.

7.1.1 Properties of carbon dioxide

Carbon dioxide is a clear odourless gas, slightly denser than air at atmospheric conditions. It can exist as a solid, liquid or gas. Above the critical point, it can no longer exist with separate gas and liquid phases and forms a supercritical fluid with some properties of a liquid and some of a gas. Carbon dioxide has a sublimation line, where at this boundary both gaseous and solid carbon dioxide can exist and transform between the two states without an intermediate liquid phase.

Carbon dioxide and some of the impurities found in CCS carbon dioxide streams can have:

- Physiological effects. Both asphyxiant and toxicological effects.
- Ability to accumulate in confined spaces being slightly denser than air.
- Large pressure expansion ratio when changing from liquid to gas.
- Low temperature conditions during the expansion from liquid to gas.
- Incompatibilities with some elastomers, internal coatings, lubricants and greases.
- Contain impurities that affect the fundamental physical properties such as the triple point, density etc. impacting on design. In some cases, the impurities themselves may have physiological effects (e.g. hydrogen sulphide).
- Corrosion can occur with some impurities such as water.
- With water within the stream, even if there is no free water, hydrates can be formed.
- Under certain conditions, it is possible to have a carbon dioxide BLEVE.

7.1.2 State of the art in CCS technology

There are a number of technological options for capturing and transporting carbon dioxide, through pre-combustion capture, post-combustion capture and oxyfuel technology. In the race to develop CCS, many companies are developing small scale and demonstration type projects. This allows real operating experience in CCS at the small to medium scale. It also allows the transfer of technology from allied industries at a similar scale of application into CCS.

In many cases there are examples of applications of similar scale to those of commercial CCS projects (e.g. compressors, rectisol carbon dioxide removal plants, EOR at Weyburn), and in others there are examples of applications at demonstration size (e.g. amine carbon dioxide removal plants). Coupled with the research work (e.g. oxyfuel burner rig testing), this is providing a baseline of knowledge for the increased development of commercial CCS projects. The challenge for the industry is to capitalise on the experience to date and as future demonstration plants start operating, recognising that there may be issues involved with scale up that may not, at first, be obvious.

Many parties have recognised the need to transfer information and to manage the scale up of technology sensibly. Existing knowledge sharing networks include CO_2NET, the IEA GHG and the sharing through the EU Demonstration projects programme. The plethora of demonstration projects and research also makes for inevitable overlap in research and some confused messages within the CCS industry as knowledge is rapidly overtaken. The industry does need to develop sensible standards to help CCS participants to avoid repeating design/operation mistakes. It also needs to focus on training new engineers entering the CCS field and in particular to help them recognise where their existing experience and training is useful and where it is not translatable (for example being an expert or experienced in designing a particular piece of equipment in another field does not necessarily translate into competence for CCS).

7.1.3 Onshore plant design and operation

The industrial gases industry provides useful experience of designing and operating carbon dioxide facilities. Many of the design principles which have been developed for the current carbon dioxide industry can be applied for CCS applications such as:

- Avoiding designing plant to have enclosed spaces, basements, hollows, bunded areas or dips.
- Where this is unavoidable, classifying all these areas as enclosed spaces and carrying out risk assessments to determine the appropriate mitigation and procedures.
- Carbon dioxide detection systems may not always be necessary in open production areas and may need further development to tangibly reduce risk. Staff training and operating procedures in leak detection can be an appropriate option.
- Avoiding the failure of materials (metals, seals, valves, gaskets, lubricants etc.) in service by ensuring that they are tested to meet the operating conditions in the particular application they will face (where no standard tests or guidance exists) such as:
    - impurities within the carbon dioxide stream;
    - operating pressures to which the materials will be subjected;
    - operating temperatures (particularly noting the conditions which can be extremely cold);
    - cycling of plant and its materials, and
    - whether you have wet or dry carbon dioxide and selecting materials appropriately for either condition.
- Recognising that in plant areas where solid formation is possible (e.g. in blow down lines), then material erosion may occur and materials should be designed to avoid this erosion or should be inspected and replaced regularly.
- External impingement is avoided in areas where blow down is expected.
- Avoiding failure of ball valves caused by expansion of liquid carbon dioxide.
- Reviewing existing codes of practice designed for the liquid carbon dioxide market and determining whether they provide useful guidance to your project’s particular conditions.

The application of principles developed in the existing carbon dioxide operations provides a useful design starting point for demonstration sized projects, allowing designers to incorporate learning from the existing carbon dioxide applications. At some stage, existing carbon dioxide standards will need to reviewed and systematically revised for the CCS industry to ensure that they cover the complete range of operating conditions encountered, including larger quantities.

From the experience and shared learning of the CCS demonstration projects, further codes of practice and design guides may be required to meet the needs of the scaled up full size industry, particularly with reference to higher pressures and quantities.

7.1.4 Onshore pipeline design and operation

Carbon dioxide pipelines are operating at the quantities and pressures expected for European CCS installations and can be considered a mature technology in the US/Canada. The hours of operation and pipeline lengths are not equivalent to the body of knowledge for natural gas, but there is no step change in scale of pipeline (in regard to quantity and pressure). US and Canadian design standards are prescriptive and classify carbon dioxide pipelines in the same way as hydrocarbons. UK and European regulations and standards allow for the design of carbon dioxide pipelines within current structures covering areas such as materials selection, blow down and emergency shutdown design. Gaps in knowledge do not prohibit design but are likely to lead to more conservative design.

The CCS industry would benefit from a consistent approach to gathering failure data of carbon dioxide pipelines to ensure that lessons are learnt across the industry, similar to the data gathering and dissemination carried out in the natural gas pipeline industry.

Fundamental to managing the hazards from a carbon dioxide pipeline is to:

- Carry out appropriate hazard analysis, including evaluating mitigation strategies.
- Carry out careful quality control of the carbon dioxide admitted to the pipeline systems, to avoid and/or minimise the impact of corrosion or hydrate formation.
- Recognise that the most appropriate form of large scale transportation over long distances will be in the liquid form (encompassing dense phase and up to supercritical).

7.2 RECOMMENDATIONS

7.2.1 Summary of hazards arising from carbon dioxide and its impurities and recommendations for their management

The fundamental properties of carbon dioxide, as well as impurities within the carbon dioxide stream result in hazards. The following table sets out a summary of the hazards and the key recommendations relating to those hazards.

Table 17 Summary of hazards arising from carbon dioxide and its impurities

Hazard	Recommendation
Physiological effect of carbon dioxide	Carbon dioxide has toxicological and asphyxiant properties. HSE has published SLOT/SLOD parameters for carbon dioxide and the occupational exposure limits. Exposure to carbon dioxide should be controlled to avoid exposure above the recommended limits.
Confined spaces	Hollows, basements, valleys or enclosed plant areas can become volumes in which carbon dioxide can accumulate. Where possible such spaces should be designed out, for example, by adding suitable ventilation or redesigning plot layout to remove low lying areas. Where it is impossible to design out confined spaces, classify and control accordingly with appropriate ventilation, monitoring, entry procedures and staff training.
Pressure expansion ratio	Ensure systems are designed to manage the significant pressure expansion ratio. Blow down systems must contain appropriate valves to clear any potential deadlegs within the system. Inappropriate design could lead to overpressure and catastrophic failure.
Low temperature effects	During planned and unplanned releases, the large expansion ratio gives rise to low temperatures. Where plant will be exposed to cold temperatures during routine operation, it must be designed for these temperatures. Where plant is not designed for low temperatures, embrittlement may occur. Low temperatures can also affect ancillary equipment such as temperature sensors.
Elastomers	Some seals are incompatible with carbon dioxide and fail catastrophically with carbon dioxide. Sealing materials should be selected with care and engineers should request evidence that the exact material supplied is suitable for the expected operating conditions and carbon dioxide composition for the project. Small changes in material composition can significantly affect performance and thus is it important to ensure that the exact composition of the seal is suitable.
Internal coatings	Some internal coatings debond with long term exposure to carbon dioxide. At present with the absence of a significant body of evidence, if an internal coating is planned, then the project engineers should satisfy themselves that suitable testing has been carried out to verify that the coating is suitable for carbon dioxide service.
Lubricants and greases	Some lubricants and greases are incompatible with carbon dioxide. Engineers should satisfy themselves that they have selected appropriate lubricants and greases for carbon dioxide service.

Hazard	**Recommendation**
Impurities	Impurities affect the fundamental properties of carbon dioxide by changing viscosity, density and critical and triple points. In some cases, the impurity may become the defining health and safety risk in a release (some carbon dioxide pipelines in the US have high levels of hydrogen sulphide which presents the greatest hazard). In other cases, a contaminant may cause problems such as two phase flow in pumps. As there are no standards on impurities in carbon dioxide, each project will have to evaluate the level of its own impurities and where necessary carry out tests to ascertain the impact of the impurities.
Corrosion	Carbon dioxide without any free water within it is not corrosive. Plant or pipeline in contact with wet carbon dioxide must be designed to resist the resultant carbonic acid. Where carbon dioxide is dry (i.e. with no free water and below the level where hydrates form) equipment can be designed using standard steels, provided that a robust process is put in place to prevent wet carbon dioxide entering that equipment.
Hydrate formation	Hydrate formation can occur where there is no free water within the carbon dioxide stream. Hydrate formation can cause solid formation, potentially resulting in blockages. The operating conditions across the entire process should be considered when designing the level of moisture content. For example, offshore pipelines which generally have lower temperatures will require lower levels of dissolved water to prevent hydrate formation. This may drive the specification for the carbon dioxide rather than the onshore pipeline conditions.
BLEVE	BLEVE can cause serious incidents and design and operation proceedings should give due consideration to this potential hazard.

7.2.2 Summary of recommendations on plant and pipeline design and operation

Table 18 Summary of recommendations on plant and pipeline design and operation

Hazard	**Recommendation**
Overall hazard management approach	This document recommends that competent engineering and the as low as reasonably practical (ALARP) approach to risk abatement and management and the proper consideration of all legislation, particularly COMAH, is the key to safe delivery of these projects.
Safety distances	Existing codes of practice from the industrial gases sector give guidance on applying appropriate safety distances for large inventories of carbon dioxide and these principles can be applied to CCS installations. Where installations have storage vessels and transfer stations (for example because they have tanker or ship transfer facilities), then the industrial gases codes of practice can be applied. Further work may be necessary on appropriate safety distance if inventories increase by an order of magnitude.
Thermal relief valves	Thermal relief valves should be designed to safely vent carbon dioxide in a controlled manner. The design should avoid ingress of moisture which could cause blockages due to low temperatures in the vent. In addition, valves must be provided to protect equipment against over pressure, which can occur if liquid becomes trapped in piping and equipment. Wherever blow down systems are designed, they must avoid impingement on nearby carbon steel equipment.
Blow down and emergency shut down on pipelines	Like installations, blow down and emergency shut down design is established for pipelines and suitable systems can be designed from existing regulations and guidance.
Isolating valves	The design of standard ball valves for isolating valves for carbon dioxide service requires modification to prevent small amounts of liquid becoming trapped in the housing which will expand and cause catastrophic failure of the valve. In other situations, where cryogenic conditions are found, there are specialist valves designed for operation under such conditions.
Blow down of vessels	Blow down of vessels must be controlled to avoid solid formation. In practice, this means that carbon dioxide should be drawn from the bottom of the tank and not the top of the tank. It should also be carried out slowly to prevent solid formation.
Material selection	Materials must be selected to operate at the full range of operating conditions encountered for the CCS plant operation and/or pipeline. As CCS plants are not yet standard installations with identical operating conditions and gas compositions, each developer will have to satisfy himself that all components and in particular elastomers, coatings, seals, gaskets, lubricants and greases are suitable.
Carbon dioxide quality	When specifying the carbon dioxide quality within the system, it must be considered across the entire chain from capture installation to the storage site to ensure that it meets the design and operating conditions of each element.

Hazard	**Recommendation**
Fracture propagation and control	For pipelines, material selection, design, construction and operation must take into account the potential for fracture propagation and its control.
Leak detection	Leak detection, is primarily through sight and sound, both on installations and for pipelines. Careful observation, including walking the pipeline line, allow small leaks to be detected. For example, localised ground freezing on a pipeline route would indicate a small leak. In some instances, hand held detection may also be useful. Fixed detection may be appropriate for confined spaces, if identified by a location specific risk assessment. There are a number of commercially available hand held and fixed carbon dioxide detection systems available.

CCS, at full scale and as a complete train, is novel and there are uncertainties surrounding the implementation and operation. But at demonstration – type scale, there is a significant body of knowledge – not complete or in many cases easily accessible – but giving many pointers as to the safe design and operation. Whilst robust design codes are not available, engineers must rely on the thorough application of existing knowledge from allied industries and other demonstration projects and trials as well as detailed evaluation of their particular project and its implications on key areas such as material selection. For each component and process, engineers should evaluate whether:

— It is suitable for the carbon dioxide stream in their project, the range of operating conditions and impurities.

— It takes into account the key hazards of carbon dioxide appropriately (e.g. does the blow down equipment design take into account temperature profile, pressure-expansion ratio etc..

— Is there any suitable experience from demonstration projects or research which could be applied here?

— Are there any allied industries which have design codes or experience which could be applied to this situation (e.g. LNG industry on pressure-expansion issues, industrial gases on carbon dioxide vents etc.)

— Is there anything novel which means testing of some sort is necessary? (e.g. project specific impurities and operating conditions requiring evidence that a particular seal will perform as expected, where applying material tests would be a suitable route forward to demonstrate suitability).

7.3 FURTHER WORK

This document identifies some areas of further work:

— Review of the existing industrial gases codes for carbon dioxide to improve their applicability to the CCS industry. This would encompass reviewing the codes to ensure they are relevant and to expand them where necessary to cover elements that are specific to CCS technology.

— Development of baseline information documents on CCS design and operation to allow knowledge transfer from other sectors and reduce accidents and incidents which could have been avoided if good practice was more widely shared.

- A failure rate database for CCS components to provide more detailed and up to date information on the likely failure modes of CCS components, equipment and pipelines to improve preventative measures and future design.
- A 'best practice' tool kit to help prospective CCS developers to use the good practices available for their project. This toolkit would include the following elements:
  - the scope of CCS facilities covering CCS installations and transportation;
  - sources of best practice within the CCS industry and in wider industrial practice;
  - identification of key participants and organisations, and
  - checklist to help participants evaluate the relevance, compatibility, practicality, transferability, repeatability, and maturity of best practice so that it can be used for that particular project.

8 GLOSSARY AND DEFINITION OF TERMS

Certain terms used within this document have specific meanings and these meanings have certain implications. Furthermore the terms 'dangerous fluid' and 'dangerous substance' have specific legislative impact. In addition the terminology of carbon dioxide phases is explained.

8.1 DANGEROUS SUBSTANCE

The term 'dangerous substance' is a term applied to substances as classified under the Dangerous Substances Directive (67/548/EEC)[123]. A substance that is considered a 'dangerous substance' falls into any of the following classes:

- explosives;
- oxidising agents;
- flammable substances or preparations;
- toxic substances or preparations;
- harmful substances or preparations;
- corrosive substances or preparations;
- irritants;
- sensitisers ;
- carcinogens;
- mutagens;
- substances or preparations that are toxic for reproduction, and
- substances or preparations that are dangerous for the environment.

General classification of carbon dioxide is that it is excluded from the list of toxic substances with exposure limits of 5 000 ppm time weighted average (TWA) and 30 000 ppm short term exposure limit (STEL) and is not listed as a dangerous substance under the directive. However carbon dioxide does have a known toxicity and is considered an asphyxiant but at high concentrations. There are two key definitions: the United Nations publishes model regulations[124] that classify substances that are transported, and this is the accepted classification that appears on material safety data sheets; the other is the UK Chemicals (Hazard Information and Packaging for Supply) (CHIP) Regulations[125] and supporting directive[126]. The definition of Toxic from the Chemicals (Hazard Information and Packaging for Supply) Regulations 2009[127] is:

"Substances and preparations which in low quantities cause death or acute or chronic damage to health when inhaled, swallowed or absorbed via the skin."

and the definition of toxic and non-toxic under the UN Recommendations on the Transport of Dangerous Goods Model Regulations[128] is:

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[123] http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CELEX:31967L0548:EN:NOT

[124] http://www.unece.org/trans/danger/publi/unrec/rev15/15files_e.html

[125] http://www.opsi.gov.uk/si/si2009/uksi_20090716_en_1

[126] http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CELEX:32006L0121:EN:NOT

[127] '*The Chemicals (Hazard Information and Packaging for Supply) Regulations, 2009*', Statutory Instrument No. 716.

[128] '*UN Recommendations on the Transport of Dangerous Goods, Model Regulations*', 15th Edition, 2007.

Division 2.3 *Toxic gases*
Gases which:

(i) are known to be so toxic or corrosive to humans as to pose a hazard to health; or
(ii) are presumed to be toxic or corrosive to humans because they have an LC50 value (as defined in section 2.6.2.1) equal to or less than 5 000 ml/m^3 (ppmv).

The UN classification of carbon dioxide is Division 2.2 – non-toxic gas and given the Chemicals (Hazard Information and Packaging for Supply) Regulations definition, carbon dioxide would not qualify as toxic. The United Nations has set out to harmonise such definitions internationally. The *Globally harmonized system of classification and labelling of chemicals* (2007) discusses the definition of 'toxic' material in Part 3: Health Hazards; this standard methodology of classification, like the transportation and CHIP regulations would indicate that carbon dioxide is not toxic.

The LC50 value for carbon dioxide is considered by the US National Institute of Occupational Safety and Health (NIOSH) to be 40 000 ppm[129], although some studies[130] indicate the value may be 100 000 ppm, far above the threshold required for the UN classification of toxic.

In the UK the HSE has stated[131] that carbon dioxide is to be considered a dangerous substance when considering carbon capture and storage schemes. This instruction automatically applies the requirements of the Seveso II directive[132] or in the UK the COMAH (Amendment) regulations[133] 2005. It should be noted that the current carbon dioxide production, storage and handling facilities of the industrial gases sector do not fall under COMAH.

However this document recommends, as with all hazards, debated or not, that competent engineering and the ALARP approach to risk abatement and management and the proper consideration of all legislation, particularly COMAH, is the key to safe delivery of these projects.

8.2 DANGEROUS FLUID

Like 'dangerous substance', 'dangerous fluid' also has a specific legislative meaning in terms of the Pipeline Safety Regulations 1996[134]. The term 'dangerous fluid' is used in the regulations to indicate that pipelines carrying a dangerous fluid are to be considered major accident hazard pipelines.

Dangerous fluids are described as:

- A fluid which:
  - is flammable in air;
  - has a boiling point below 5 °C, at 1 bar absolute, and
  - is, or is to be conveyed in, the pipeline as a liquid.

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[129] http://www.cdc.gov/niosh/idlh/124389.html NB. Described as the IDLH Level (Immediately Dangerous to Life or Health).

[130] ACGIH [1971]. Carbon dioxide. In: Documentation of the threshold limit values for substances in workroom air. 3rd ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists, p. 39.

[131] http://www.hse.gov.uk/carboncapture/partners.htm

[132] '*Directive on the control of major-accident hazards involving dangerous substances*' (96/82/EC).

[133] '*The Control of Major Accident Hazards (Amendment) Regulations 2005*' Statutory Instrument No. 1088.

[134] '*The Pipelines Safety Regulations 1996*', Statutory Instrument No. 825.

- A fluid which is flammable in air and is, or is to be conveyed in, the pipeline as a gas at above 8 bar absolute.
- A liquid which has a vapour pressure greater than 1,5 bar absolute when in equilibrium with its vapour at either the actual temperature of the liquid or at 20 °C.
- A toxic or very toxic fluid which:
  - is a gas at 20 °C and 1 bar absolute, and
  - is, or is to be, conveyed as a liquid or a gas.
- A toxic fluid which:
  - at 20 °C has a saturated vapour pressure greater than 0,4 bar, and
  - is, or is to be, conveyed in the pipeline as a liquid.
- Acrylonitrile.
- A very toxic fluid which:
  - at 20 °C has a saturated vapour pressure greater than 0,001 bar; or
  - is, or is to be, conveyed in the pipeline as a liquid at a pressure greater than 4,5 bar absolute.
- An oxidising fluid which is, or is to be, conveyed as a liquid.
- A fluid which reacts violently with water.
- For the purpose of this definition:
  - a liquid is oxidising, and
  - a fluid is toxic or very toxic, or reacts violently with water.
- Classified, pursuant to regulation 5 of the Chemicals (Hazard Information and Packaging for Supply) Regulations 2009, as, as the case may be, oxidising, toxic, very toxic or as reacting violently with water.

The above descriptions include carbon dioxide in a number of ways by being toxic and by the classification as a 'dangerous substance' under the CHIP regulations.

In considering this classification the implications are significant on the pipeline design process with specific criteria that must be met including emergency shut off valves, consideration of incident prevention, accident planning and specific planning and permitting requirements.

8.3 PHASES OF CARBON DIOXIDE

The phases of carbon dioxide are discussed at length through out this text. But the definition of supercritical and dense phase needs to be considered. Figure 1 shows the phase diagram for carbon dioxide. The fluid state above critical pressure is referred to as the dense phase, above both critical pressure and temperature, supercritical. Whilst the term supercritical is to specific conditions, dense phase is an umbrella terminology, and encompasses supercritical state and liquid state.

8.4 GLOSSARY OF TERMS

AGA:	American Gas Association
API:	American Petroleum Institute
ASME:	American Society of Mechanical Engineers
ASTM:	American Society for Testing and Materials
BCGA:	British Compressed Gases Association
BLEVE:	Boiling Liquid Expanding Vapour Explosion
CCGT:	Combined cycle gas turbine
CCS:	Carbon capture and storage
CFR:	Code of Federal Regulations
CGA:	Compressed Gas Association
CONCAWE:	Conservation of clean air and water in Europe
COSHH:	Control of substances hazardous to health
CR:	Chloroprene
Critical point:	the temperature and pressure point above which carbon dioxide gas and liquid phases cannot exist as separate phases
Cu:	Copper
DMEPEG:	Dimethyl Ether of Polyethylene Glycol
Dry ice:	solid carbon dioxide
DWTT:	Drop Weight Tear Testers
EAF:	Electric Arc Furnace
ECBMP:	Enhanced Coal Bed Methane Production
EGR:	Enhanced Gas Recovery
EIGA:	European Industrial Gases Association
EOR:	Enhanced Oil Recovery
EOS:	Equations of State
EPDM:	Ethylene-Propylene
ESOV:	Emergency Shut-off Valve
EU SACS:	European Union Saline Aquifer Carbon Dioxide Storage Programme
FGD:	Flue gas desulphurisation
FKM:	Chloroflurocarbons
HSE:	Health and Safety Executive
HSL:	Health and Safety Laboratory

IGCC:	Integrated gasification combined cycle
IGC Code:	International Gas Carrier Code
IIR:	Butyl isobutene isoprene rubber
IPCC:	Intergovernmental Panel on Climate Change
LNG:	Liquified Natural Gas
LOC:	Loss of Containment
LPG:	Liquified Petroleum Gas
MAOP:	Maximum allowable operating pressure
MMSCFD:	Million standard cubic feet per day
Mt:	Million tonnes
MW:	Megawatt
MWth:	Megawatt thermal
MSS:	Manufacturers Standardisation Society
NACE:	National Association of Corrosion Engineers
NBR:	Nitrile rubber
NFPA:	National Fire Protection Association
Ni:	Nickel
NIOSH:	National Institute for Occupational Safety and Health
NIST:	National Institute of Standards and Technology
NORSOK:	Norsk Sokkels Konkuranseposisjon – Standards developed by the Norwegian Technology Centre
OSHA:	Occupational Safety and Health Administration
PA:	Polyamide
Pb:	Lead
PCTFE:	Polychlorotrifluoroethylene
PEEK:	Polyetheretherketone
P-h diagram:	Pressure-enthalpy
PHMSA:	Pipelines and Hazardous Materials Safety Adminstration
PP:	Polypropylene
ppmvd:	Parts per million volumetric dry
PSR:	Pipeline Safety Regulations
PTFE:	Polytetrafluoroethylene
PVTF:	Vinylidene polyfluoride
QA:	Quality Assurance
REDOX:	Reduction-oxidisation reaction

RGD:	Rapid Gas Depressurisation
ROSOV:	Remotely Operated Shut Off Valve
SACROC:	Scurry Area Canyon Reef Operators Committee
SCADA:	Supervisory Control and Data Acquisition
SLOD:	Significant likelihood of death
SLOT:	Specified level of toxicity
***Sublimation point*:**	a temperature/pressure combination at which solid can vaporise directly into gas e.g. −78,5°C at 1atmosphere
Supercritical:	above the critical point where carbon dioxide has some characteristics of a gas and some of a liquid
Triple point:	the temperature & pressure where carbon dioxide exists as a gas, liquid and solid simultaneously
T-s diagram	Temperature-entropy diagram
UHMWPE	Ultra High Molecular Weight Polyethylene
UN-IMO	United Nations International Maritime Organisation
Zn	Zinc

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