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# IMPACTS: Framework for risk assessment of CO2 transport

# and storage infrastructure

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#### Abstract

There is an urgent drive to implement Carbon Capture and Storage (CCS) on a commercial and global scale. This needs to be done in a demonstrably safe and responsible manner that gains widespread acceptance of stakeholders, most notably regulators and the public.

If inhaled in sufficiently high concentrations,  $CO_2$  can have toxicological effects on the human body. The hazardous aspects of  $CO_2$ , combined with the very large quantities that will be contained within CCS systems create the potential that a leak from a  $CO_2$  system could pose a major accident hazard.

The CO<sub>2</sub> stream from capture plants will not be 100% pure, but contain substances, referred to as stream impurities, such as CO,  $H_2O$ ,  $H_2S$ , NOx, SOx,  $O_2$  and  $H_2$  that, although in very low levels, can change the properties of the CO<sub>2</sub> stream and can change the likelihood and/or the consequences of CO<sub>2</sub> system leaks.

The IMPACTS project is concerned with the impact these impurities may have when present in  $CO_2$  transport and storage systems. The risks associated with  $CO_2$  captured as a result of CCS operations differ from those previously encountered either in Natural Gas pipelines or in pure  $CO_2$  pipelines (used in USA and elsewhere for enhanced oil recovery operations) in a number of ways, but particularly on account of the large volumes, high pressures and nature of the impurities involved. Established techniques can be used to determine the risks from events that would undermine the overall integrity derived from the design, manufacture, construction and operation of the infrastructure. Some of these techniques and the assessment thereof have been described, together with

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consequences that can be expected, based on industry experience with pipelines other than those transporting impure  $CO_2$ .

Some of the event types that can lead to a reduction in the level of safety of transport and storage of large volumes of impure  $CO_2$ , under high pressure, have been identified, and the associated risks described.

A significant amount of information, including guidelines, industry standards and legislation, exists worldwide and provides decision support for the design of pipelines carrying hazardous materials. This includes risk reduction measures, requirements for risk assessment, risk criteria and the need for further risk reduction. However, in most cases  $CO_2$  is not currently in the scope, but it is possible to apply many of the principles therein to pipelines containing  $CO_2$ , albeit with some caution.

In the absence of agreed guidance figures, reference is made to standards that could be used in system design to support a Safety Case to demonstrate that the risks are at an acceptable level. It would be hoped that these will serve to stimulate debate and provide a starting point from which an acceptable balance might be found between applying additional measures to improve safety by design, and providing projects that are affordable, at the same time allaying public concerns implicit in the introduction of new technologies. At the same time an ISO Standard for CCS is being produced, and this also attempts to provide necessary guidance for system designers.

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#### 1. Introduction

There is an urgent drive to implement Carbon Capture and Storage (CCS) on a commercial and global scale. This needs to be done in a demonstrably safe and responsible manner that gains widespread acceptance of stakeholders, most notably regulators and the public.

 $CO_2$  is a substance that has many everyday uses. However  $CO_2$ , if inhaled in sufficiently high concentrations, can have toxicological effects on the human body. The hazardous aspects of  $CO_2$ , combined with the very large quantities that will be contained within CCS systems, create the potential that a leak from a  $CO_2$  system could pose a major accident hazard (MAH) (i.e. a hazard that could pose significant harm to humans or the environment).

In addition, captured  $CO_2$  will not be 100% pure. The  $CO_2$  stream from capture plants will contain substances, referred to as stream impurities, such as CO, H<sub>2</sub>O, H<sub>2</sub>S, NOx, SOx, O<sub>2</sub> and H<sub>2</sub> that, although in very low levels, can change the properties of the  $CO_2$  stream and may therefore increase the risks associated with CCS operations. The effect these impurities may have on these risks, as well as methods for mitigation are the topics covered in this paper.

The EU FP7 project IMPACTS [1] was aimed at research into the impact of impurities in captured CO<sub>2</sub>, from power plants and other CO<sub>2</sub>-intensive industries, on CO<sub>2</sub> transport and storage. At the start of the project, the main uncertainties surrounding impurities in CO<sub>2</sub> transport and storage were related to the following areas:

- There was an incomplete understanding of the relation between impurities in the CO<sub>2</sub> and the properties of the mixture. Experimental data on mixture properties were incomplete; there was a need for verified property models that cover relevant mixtures of CO<sub>2</sub> and impurities;
- There was a limited understanding of the effect of impurities on materials, equipment, processes, operation and safety procedures;
- There was a need for a better understanding of the impact of impurities on storage integrity.

Knowledge about these issues is essential for safe and efficient transport and storage solutions for CCS.

#### 2. Risk assessment methodologies of CCS

In line with most risk assessments of (stationary or mobile) installations containing (dangerous) chemicals the two main components considered to make up the risk are the (likelihood of a) hazard causing an installation to fail and the severity of the consequence such a failure may have. These are often combined into a risk matrix. Hazards with a high likelihood leading to severe consequences (which may be in terms of human life, costs or environmental pollution) represent a high risk. Methods to assess the risk therefore consist of methods to identify the hazards (and to estimate its likelihood), to determine relevant failure mode(s), and to assess the severity. Chains of hazard – failure mode – consequence are called Loss of Containment (LOC) scenarios. They are often visualised in so called bow ties. The knot of the bow tie represents the failure mode (e.g. pipe rupture). The left part of the bow tie contains the hazards that may directly or indirectly cause this failure; the right part contains the potential consequences. In a bow tie measures to prevent an LOC and measures to mitigate the consequences can be depicted as barriers.

The CO2RISKMAN Joint Industry Project (JIP) was initiated specifically to develop industry guidance that provides a reference source to assist the emerging CCS industry to appreciate, understand, communicate and manage the issues, challenges and potential hazards associated with handling CCS  $CO_2$  streams [2]. Recognising that the guidance needs to be readily accessible to a wide range of people with different backgrounds and requirements, the guidance has been developed into multi-level documents, ranging from level 1, consisting of a concise executive summary, to level 4, which is a 300 page, in-depth, knowledge source that is sub-divided to address each link of the CCS chain.

Lifecycle risk management for integrated CCS projects is the subject of a Technical Report [3] produced to support the production of an ISO Standard for CCS [4].

Specifically for off-shore pipelines, a novel scenario analysis framework has been created, called CASSIF [5]. CASSIF is based on the three major  $CO_2$  release scenarios (well, fault and seal) from where the relevant events and processes are identified and modelled. Expert opinion is a key value within these frameworks.

#### 3. Risks of CCS

A pipeline containing  $CO_2$  will be not be fundamentally different from a pipeline containing any other fluid. Therefore hazards affecting other pipelines may also affect  $CO_2$  pipelines. Statistically, the most common cause of damage to on-shore pipelines is that caused by third parties (TPD), typically hitting a buried section during earthmoving operations irrespective of the fluid being transported. Offshore pipelines are also potentially subject to damage as a result of TPD, where the main hazard is usually taken as anchor dropping or (more likely) dragging by shipping. There have been a small number of such incidents. In most cases the offshore pipelines have proved themselves resilient to third party interference. This is assisted by the concrete covering that is usually applied to ensure that the pipelines stay on the seabed, most notably during construction when the pipeline is filled only with air. Also as far as external corrosion is concerned the risks for  $CO_2$  pipelines are no different from other pipelines.

The specific properties of  $CO_2$  and the fact that, compared to natural gas, it is relatively unfamiliar to the designer, will mean that existing risk assessment processes should be applied with caution. Pure  $CO_2$  has quite well defined properties that can assist the designer in carrying out risk assessments. For instance a leakage may lead to a full rupture more easily in a  $CO_2$  pipeline than in pipelines carrying other gases or liquids. Because liquid  $CO_2$  escaping through a puncture in a pipeline will rapidly cool, as it expands, to about -80°C. At this temperature the pipeline and adjacent structural steel can become brittle, and will break more easily if it is impacted. Also blast damages from adjacent  $CO_2$ -pipelines may more easily cause damage because of the relatively high expansion coefficient of  $CO_2$ .

Although  $CO_2$  has some toxic properties, the dominant health effect will be asphyxiation as a result of the displacement of air. A release of  $CO_2$  will not have any adverse consequences for the environment.

# 4. Effect of impurities on risk of CCS

There is less history with impure  $CO_2$ , although considerable amounts of data derived from gas processing plants have also been used for enhanced oil recovery (EOR), for example the Canyon Reef, Weyburn, Val Verde and Bairoil pipelines.

With the introduction of impurities other risks for CCS emerge. In addition to the risks of pure  $CO_2$  (see above) there is the risk associated with the impurities themselves, as well as with the combination of  $CO_2$  and the various impurities. A list of potential impurities, as identified in another work package of the IMPACTS project, is shown in Table 1.

Dotontial immunity	Possible impacts						
Potential impurity	Health and Safety	Physical Properties	Chemical properties				
Amines*	Small	Small	Small				
Ammonia	Medium	Small	Small				
Ammonium salts	Small	Small	Medium with low water				
Antimony	Small	Small	Small				
Chlorine and chlorides	Medium	Small	Medium with low water				
Carbon monoxide	Medium	Small	Small				
Carbonyl sulphide	Medium	Small	Medium with low water				
C2+ compounds	Small	Small	Small				
Heavy Metals	Small	Small	Small				
Hydrogen	Small	Medium	Small (if low O2)				
Hydrogen cyanide	Medium	Small	Small				
Hydrogen fluoride	Small	Small	Medium with low water				
Hydrogen sulphide	Medium	Small	Medium with low water				
Methane	Small	Small	Medium with low water				
Methanol*	Small	Small	Small				
Nitrogen	Small	Significant	Small				
NOx and SOx	Medium	Small with low water	Small				
Oxygen	Small	Significant	Medium if low $H_2 \& H_2$				
Particulate	Small	Significant	Small				
Polyethylene Glycols*	Small	Small	Small				
Sulphur trioxide	Small	Small	Medium with low water				
Water	Small	Significant	Significant				
*Present as carry-over	r from 'wet' CO2 removal	processes					

Table 1 Summary of possible main impurities and their expected impacts

#### 4.1. Health and safety impacts of impurities

Although the risks associated with the impurities themselves have been briefly covered in the IMPACTS study they are not further considered in this article. In this study it is assumed that the recommendations by the "Dynamis team" were followed in which it was recommended that for health and safety, during transportation, levels should be set by design (of the capture plant and any subsequent processing) such that the impact of the  $CO_2$  should always dominate that of the impurity [6]. For environmental impact of impurities alone no further considerations is required as shown in [7].

This means only the combined effect of impurities and  $CO_2$  on the risk needs further investigation, i.e. the risk caused by the change in physical and chemical properties of the (impure)  $CO_2$  in the pipeline. Below the potential impacts of impurities with an impact other than 'small' are discussed, as well as potential mitigation measures.

#### 4.2. Water as an impurity

#### Impact

It is clear from Table 1 that the water content of the  $CO_2$  has a significant impact and that, if the water content is controlled to an acceptable level, many of the other potential hazards will not be present anymore.

The water content described in the original Dynamis documentation [6] considered only the potential for corrosion of carbon steel components within the transportation and injection infrastructure. This was based on the criterion that the concentration limit should prevent free water formation over the total pressure and temperature range of the CO<sub>2</sub> that is transported by pipeline. It was noted that, in a normal situation, when the CO<sub>2</sub> is transported above its critical pressure of 71.3 bar, the solubility of water is above 1300 ppm for a temperature range of  $-10^{\circ}$ C to  $+25^{\circ}$ C. A figure of <500ppm was considered to provide a sufficient margin for upset conditions. Subsequent work on the formation of CO<sub>2</sub> hydrates [21] indicated that the risk of hydrate formation in a pure liquid CO<sub>2</sub> stream at temperatures between  $-2^{\circ}$ C to  $+30^{\circ}$ C and pressures above 80 bar is unlikely if the water content is below 250ppm, but for a typical pre-combustion composition (95.8% CO<sub>2</sub>, 2% H<sub>2</sub>, 2% N<sub>2</sub>, 0.2% CO), some CO<sub>2</sub> hydrate may form at higher temperatures, thus an additional margin might be appropriate. The formation of CO<sub>2</sub> hydrates could lead to a partial blockage of the pipeline and increasing the load on the pump/compressor so that mass flow can be maintained.

Additional theoretical work on hydrate formation has been carried out [22]: a model based on equality of water fugacity in fluid and hydrate phase was used for the predictions of water content in equilibrium with hydrates. Whilst this model gave better accuracy in the overall temperature and pressure ranges of measurements than models found in the literature, it was not considered accurate enough to satisfy the requirements for  $CO_2$  transport. However, the simulation results showed that it is possible to form hydrate at a water content of 50 ppm if the temperature is low enough. The reference acknowledges that in order to verify the results and improve the model accuracy further, more experimental data over a larger temperature and pressure region would be required.

For CCS applications, a water content below 50 ppm is gaining widespread acceptance as a generalised limit to avoid  $CO_2$  hydrate formation at practicable operational temperatures. At this level, most of the other impacts greater than "Small" in Table 1 are reduced to levels the designer may consider to be very low.

In Table 2 mechanisms are suggested that have the potential to increase the risk to the transportation infrastructure from elevated water levels. If the water content is high enough, some acids may form directly (e.g.  $H_2CO_3$ ,  $H_2S.H_2O$  (hydrosulphuric acid), HONO (Nitrous acid),  $H_2SO_3$ ), potentially leading to corrosion of the carbon-steel of the pipeline, valve body, or pump casing, resulting in a loss of containment via a leak.

Tab	le	2	Potential	levels	s of risk	c to	transportation	infrastructure	from e	levated	water	leve	ls
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Risk type
Ammonium nitrate formation and corrosion of carbon steel items
Chloride corrosion of carbon steel items
COS hydrolysis leading to formation of H <sub>2</sub> S
Hydrogen Fluoride formation and corrosion of carbon steel items
H <sub>2</sub> S leading to sulphide stress cracking of carbon steel components
Methane-induced raising of CO <sub>2</sub> hydrate formation temperature
Sufficient oxygen to lead to the formation of iron oxides on carbon steel components
Formation of sulphuric acid from SO3 and corrosion of carbon steel items
Formation of CO <sub>2</sub> hydrates at 0°C

#### Mitigation

A designer would need to satisfy himself that measures will be included either to minimise the risk of these mechanisms taking place, or to design the infrastructure to maintain its operational integrity following any degradation as a result.

The impacts of high water-in- $CO_2$  do not usually take place instantaneously, but rather over a period of hours or even days. This would give the pipeline operator time to alert errant producers or shut off the out-of-specification stream and only permit re-connection once the downstream operator is satisfied that the problem had been resolved in a satisfactory manner.

Also the formation of  $CO_2$  hydrates is not a rapid process. These hydrates grow slowly and would probably take several hours before they could become a restriction to flow or would cause local corrosion at a hydrate/carbon steel interface. The water can be re-absorbed back into the  $CO_2$  once the imbalance that led to the formation of the hydrate is reversed. The presence of H<sub>2</sub>S together with water can lead to sulphide stress cracking (SSC) of carbon steel components. SSC would unlikely be detected using an intelligent pig, because it takes place at an inter-granular scale. If there is a compelling case that SSC has taken place this would be a very serious situation, as no mitigation measures beyond replacing the pipeline have been suggested. Therefore preventive measures might be most appropriate. One could e.g.:

- eliminate completely all H<sub>2</sub>S, COS and any other species that could allow SSC to start and/or
- construct the pipeline from SSC-resistant steel (rated for sour service with adherence to NACE MR0175/ISO 15156 or NACE MR0103 or similar), such as a Duplex stainless steel, e.g. ASTM A240/A240M.

Strategies to minimise the risk of internal pipeline corrosion will include:

- Introducing a corrosion inhibitor into the CO<sub>2</sub> stream. Note that when adding corrosion inhibitors, care should be taken to ensure that compliance with the London Convention and London Protocol, as some chemicals may not be permitted for sub-sea CO<sub>2</sub> storage.
- Coating the internal surfaces of the pipeline with a suitable corrosion-resistant lining, with attention being given to the solubility of any lining in dense-phase CO<sub>2</sub>, and the potential for dense phase CO<sub>2</sub> to penetrate into the lining/steel interface and decompress explosively when the pressure of bulk of the fluid is reduced.
- Specifying materials which will limit corrosion to safe levels for the lifetime of the equipment, such as ASTM 304 and 316. However if a duplex steel is being specified to avoid SCC, then Duplex steels have far greater corrosion resistance than these.
- Specifying thick pipe and vessel walls with sufficient corrosion safety margin to minimise corrosive breach but be aware of the potential for corrosion products to cause downstream problems such as valve or formation pore blocking <sup>2</sup>.
- Apply active monitoring where necessary to replace corroded components before they cause Loss of Containment (LOC) events.

# 4.3. Hydrogen as an impurity

### Impact

Hydrogen, or any other species that affects the bubble point of the  $CO_2$ , may cause cavitation in the impellors of pumps, decreasing their efficiency and shortening the maintenance intervals between which components are inspected or replaced.

The presence of hydrogen can also lead to Hydrogen-Induced Stress Corrosion Cracking (HISCC), which can lead to rapid crack growth and ultimate failure of the pipeline, even in duplex stainless steels [8]. Under certain conditions hydrogen can degrade the fracture behaviour of most structural alloys, including many stainless steels, by causing brittle failure to occur. Even low concentrations of hydrogen in the fluid being transported can lead to embrittlement, caused by interface separation of grain boundaries [9].

# Mitigation

The presence of hydrogen in the  $CO_2$  is wasteful of energy and affects the bubble point. Neither of these affects the pipeline or even the injection infrastructure, but if it leads to cavitation in the impellors of pumps it will initiate local pitting, decreasing efficiency and threatening the integrity of the pump. Arguably, one could live with

 $<sup>^{2}</sup>$  Note that corrosion rates of carbon steel by a CO<sub>2</sub>/water mix can be quite rapid, and if the sacrificial wall approach were to be taken as a primary mitigation strategy, the designer may have to assume significant thinning, and apply generous margins.

shortening the maintenance intervals between which components are inspected or replaced, but it would be better to identify at what point in the chain the hydrogen level was increasing and notify the producer of the problem and allow him to bring his plant back into specification. If this is not possible to achieve quickly, then operations could continue and a commercial agreement sought with that producer which recognised the damage to downstream equipment.

Away from the pump the hydrogen would re-dissolve in the  $CO_2$  and be transported to the store. Were the hydrogen level to increase dramatically, there is an increased potential for HISCC in the pipeline material. Like SSC, HISCC would be unlikely to be detected using an intelligent pig, because it takes place at an inter-granular scale, hence no mitigation measures beyond replacing the pipeline have been suggested. This means use of HISSC-resistant steel as a construction material would be the preferred way to reduce this risk (e.g. ASME SA 106GrB or less commonly SA 333 Gr6, or some specific grades of A672).

#### 4.4. Nitrogen as an impurity

#### Impact

Nitrogen in the CO<sub>2</sub> has the following effects:

- It reduces the decompression velocity within the pipeline
- It can disproportionately lower the density, reducing the head in the injection well, and requiring more pump or compressor power to achieve injectivity.
- It can affect the bubble point, such that gaseous bubbles might form during pumping, resulting in cavitation damage to the impellor.
- Nitrogen within the CO<sub>2</sub> also elevates the minimum pressure for a two-phase state to occur: higher pressures or lower temperatures would be required to avoid this.

#### Mitigation

Pump impellor damage may require more frequent maintenance, or the operating conditions may have to be changed by increasing the pressure or reducing the temperature.

The presence of nitrogen as an impurity reduces the decompression velocity within the pipeline. This represents a risk against which the designer can provide some mitigation, which would be to increase the wall thickness of the pipeline, or change the material to steel with a higher fracture toughness. On-shore pipelines could have crack arrestors fitted to minimise the length over which a ductile fracture might run, and include automatically closing section valves to reduce the inventory of  $CO_2$  that might be discharged.

Fracture propagation control needs to be considered in pipelines conveying gaseous fluids, two phase fluids, dense phase fluids, or liquids with high vapour pressures. Propagating fractures are described as either brittle or ductile. Fracture propagation control of  $CO_2$  pipelines is achieved by ensuring that the toughness of the linepipe steel is sufficiently high to arrest propagating fractures.

Brittle propagating fractures are prevented by ensuring that the linepipe steel is operating on the 'upper shelf' (i.e. 85% shear area in a Dead Weight Tear Test (DWTT) at the minimum pipeline operating temperature). A brittle fracture will not propagate if the shear area measured in a DWTT is  $\geq$ 85% at the minimum design temperature [10]. Ductile propagating fractures are prevented by specifying a minimum toughness to ensure that a ductile fracture will arrest. If the required toughness is too high, mechanical crack arrestors may be applied, noting that these have limited effectiveness offshore.

Linepipe specifications and pipeline design codes specify toughness requirements in terms of the minimum shear area as measured in a DWTT to address the 'upper shelf' requirement. Brittle fracture propagation is not usually an issue in modern linepipe steel. A ductile fracture will not propagate if there is insufficient energy in the system to overcome the resistance to propagation. The resistance to a running fracture can be characterised by the Charpy-V notch (CVN) impact energy of the line pipe steel - although the relationship between CVN and fracture resistance becomes non-linear at high impact energies (when the full size impact energy exceeds approximately 100J) [11]. The toughness of modern, high quality linepipe steel is typically over 300 J (at 0°C), so specifying a minimum, average value of 250J simply represents "very tough" steel, and incurs no cost penalty [12]. Typical values for some steels commonly specified for  $CO_2$  pipelines are shown in Table 3.

API 5L	CVN absorbed energy (J) <sup>a</sup>		Notes
Steel	Minimum *	Typical	
X60	40		Considered an old specification, replaced by X65.
X65	40	235	In [13] it is shown that the DWTT energy of X70 is always lower than that for
X70	40	232	X70 at all temperatures.
X80	40	301.6	Figures are for -20°C from Figure 4 in [14]
X100	54	371	From Figure 11 in[15]

Table 3 Fracture Toughness values for some common pipeline steels

<sup>a</sup> From API Specification 5L/ISO3183

# 4.5. Oxygen as an impurity

# Impact

In addition to the potential of oxygen in the presence of water to lead to the formation of iron oxides on carbon steel components (see Table 2), oxygen has the very real potential to initiate the formation of sulphur-reducing bacteria (SRB) which can sour hydrocarbon formations were the  $CO_2$  to be used in Enhanced Oil Recovery (EOR) applications.

The petrochemical industry has imposed a limit of <10ppm O<sub>2</sub>-in-fluids used for injection into sub-surface strata [16], and this has proved effective in avoiding the souring of sweeter deposits. Work is currently in hand to examine the sensitivity of SRB formation to the level of O<sub>2</sub> in the injection fluid, but results have yet to appear. For the purposes of the IMPACTS project, the risk of SRB formation if the O<sub>2</sub> content is >10ppm will have to be assumed equal to 1 if the CO<sub>2</sub> is to be used in EOR operations. If the CO<sub>2</sub> is assumed to be stored in a saline aquifer, SRB may still be formed and could reduce store porosity, which may also, for the purposes of the IMPACTS project, be considered an unacceptable risk. The injection properties of the Ketzin saline aquifer have been degraded as a result of this mechanism [17].

#### Mitigation

Section 4.2 suggests mitigation options for corrosion resultant directly or indirectly from having oxygen in the  $CO_2$  stream. These do not provide mitigation from pore blocking or oil souring as a result of SRB formation. There seems little doubt that once the process that leads to SRB formation starts, there is little that can be done to slow or stop it, and the damage is significant and permanent. Although traditional chemical treatments can be effective in many cases they are not "worker friendly". Microbial Water Treatment (MWT) has been successfully piloted to Manage SRB activity at the Wilmington Oil Field in California in a 310,000 barrel per day MWT program [18]. Some work has also been carried out to consider the introduction of nitrate-reducing bacteria (NRB) into the SRB [19].

Mitigation options include:

- use of MWT techniques, possibly NRB, once these techniques have been proven.
- to divert the stream to a saline aquifer instead of using it for EOR: whilst this would not stop SRB from being produced in the aquifer, it would prevent souring of the oilfield, thus that revenue stream would be protected.
- having source one store, the impure CO<sub>2</sub> could be injected into another store. Whilst an expensive option (especially as the alternate store may also become blinded by SRB), this may be preferable to closing the CCS project.

#### 4.6. Oxygen together with hydrogen in the stream

### Impact

The potential impact of oxygen together with hydrogen theoretically exists if a stream of  $CO_2$  with a high (but within specification) level of oxygen impurity and another with a high (but within specification) level of hydrogen impurity, and both having a within-specification level of water content, combine to form a  $CO_2$  stream with an above-specification water content, as a result of the formation of water from the oxygen and hydrogen molecules.

Whilst such a situation may occur, the potential for the hydrogen and oxygen to combine to form water is considered to be low for the following reasons:

- Low partial pressures of oxygen and hydrogen in the inert gas stream.
- The initiating reactions between hydrogen and oxygen are endothermic and therefore slow at low temperatures.
- Small surface to volume ratio of a (long, large diameter) pipeline.

#### Mitigation

This has been classified as such a low risk that, for practical purposes, it can be ignored. However, were there to be some small increase in the overall water content, then the increase in the water content of the  $CO_2$  would be both detected and mitigated according to the procedures described in Section 4.2.

#### 4.7. Particulate material within the CO<sub>2</sub>

#### Impact

Particulate material could cause pore blocking in the storage strata, potentially reducing the capacity of the store. Particulate could also collect in depressed sections of the pipeline or accumulate at discontinuities, potentially restricting flow.

The presence of sulphur-containing species provides an environment from which elemental sulphur could be formed. This could also cause pore blocking. An accumulation in the pipeline could also restrict flow (increasing the pump/compressor load).

#### Mitigation

Once an amount of particulate sufficient to cause pore blocking has entered the storage strata there are no mitigating actions currently available to reverse or recover the situation. At which  $CO_2$  particulate content pore blocking might occur will be field-specific. The mitigation option is that the impure particulate-contaminated  $CO_2$  could be injected into another store, although this would be an expensive option (see also section 4.5).

Similarly, once an amount of sulphur sufficient to cause pore blocking has entered the storage strata there are no mitigating actions currently available to reverse or recover the situation. It may be possible to introduce an additive into the  $CO_2$  stream to reverse the sulphur deposition in the pipeline and carry it downstream in solution, but at the time of writing, no such technique would appear to have been proven commercially. It is possible to design the  $CO_2$  stripping or gas processing plant to reduce the amount of sulphur-containing species from which elemental sulphur could be formed, or to reduce the other species within the impurity mix that would also have to be present for sulphur to become deposited in elemental form. The easiest of these species to reduce is probably water.

4.8. Other impurities (ammonia and amines, chlorine/chlorides, CO and COS)

#### Impact

Ammonia (NH<sub>3</sub>) is the only impurity for which a significant increase in direct emissions compared to the non-CCS scenario is foreseen to occur [20]. The increase is predicted as a result of degradation of the amine-based solvents that are assumed in the current literature. Nevertheless, compared to the present-day level of emissions of NH<sub>3</sub> from the agricultural sector (around 3.5 million tonnes in the EU alone, or 94 % of the EU's total ammonia emissions), the magnitude of the expected NH<sub>3</sub> increase is relatively small. There is also ongoing research into the environmental fate of amine-based solvents (and their degradation products, including nitrosamines) following for example a release from  $CO_2$  capture processes. Nitrosamines and other amine-based compounds exhibit various toxic effects in the environment, and are potential carcinogens, may contaminate drinking water and have adverse effects on aquatic organisms. New solvents are under development, with potential to show less degradation.

Chlorine, some chlorides, carbon monoxide and COS can be responsible for various toxic effects in the environment, may contaminate drinking water and have adverse effects on aquatic organisms.

# Mitigation

It is difficult to mitigate against the possible impacts of significant amounts of other impurities, such as ammonia, chlorine, some chlorides, carbon monoxide and COS. Two options are available to the operator, one of which is to reduce or minimise these at source, and the other is to reduce the water content of the  $CO_2$ , without which these impurities have no direct impact on the infrastructure.

#### 5. Summary

Table 1 lists the impurities being considered by IMPACTS and ranked the potential impacts to aspects of health and safety, and adverse changes to the physical and chemical properties of the  $CO_2$ . Table 4 summarises those impurities which were assessed as having impacts other than small, together with the area where the impact might be experienced, the severity of this impact, possible mitigation measures other than improving the upstream processes to provide a lower level(s) of impurity.

Potential Level at which impact Area of impact Severity Mitigation measures impurity becomes unacceptable Ammonia Ammonia inhalation in the Medium/small No information available event of a leak Ammonium NH4OH formation and Depends on No information available, 1. Reduce water content in CO<sub>2</sub> 2. Corrosion-resistant steel (e.g. ASTM304, salts corrosion water content but only in the presence of but medium water 316) linepipe material Chlorine and Chlorine inhalation in the Medium No information available chlorides event of a leak Chloride corrosion Depends on No information available, 1. Reduce water content in CO2 water content but only in the presence of 2. Corrosion-resistant steel (e.g. ASTM304, but medium 316) linepipe material water Carbon CO inhalation in the event Medium No information available monoxide of a leak COS COS inhalation in the Medium No information available event of a leak COS hydrolysis/formation Depends on No information available, 1. Reduce water content in CO2 of H<sub>2</sub>S (leading to SSC, water content but only in the presence of 2. Corrosion-resistant steel (e.g. ASTM304, see below) if water present but medium water 316) linepipe material Hydrogen Operate at higher pressure or lower Bubble point change, Medium Dependent on pressure and possible cavitation damage temperature of impure CO<sub>2</sub> temperatures to pumps HISCC Medium No information available HISSC-resistant steel (e.g. ASME SA 106GrB, SA 333 Gr6, A672 (specific grades) Corrosion from water Medium Depends on: 1. Reduce other water content in CO<sub>2</sub> formation if O2 present 1. Water already in the CO2 2. Corrosion-resistant steel (e.g. ASTM304, (see below) 316) linepipe material 2. How much  $O_2$  is present Hydrogen HCN inhalation in the Medium No information available cvanide event of a leak Hydrogen Pipeline material corrosion No information available<sup>a</sup>, Depends on 1. Reduce water content in CO2 fluoride but only in the presence of water content 2. Corrosion-resistant steel (e.g. Monel but medium water. (NB. HF may form in alloy 400) preference to H<sub>2</sub>CO<sub>3</sub>) HCN inhalation in the Medium 200ppm (below STEL)<sup>b</sup> Hydrogen sulphide event of a leak Medium Operate at higher pressure or lower Bubble point change, Dependent on pressure and possible cavitation damage temperatures temperature of impure CO<sub>2</sub> to pumps SSC Depends on No information available. 1. Reduce water content in CO<sub>2</sub> water content but only in the presence of 2. Steel qualified for "Sour service" (e.g. Duplex, ASTM A240/A240M) linepipe but medium water material

Table 4 Summary of impurities and mitigation

Potential	Area of impact	Severity	Level at which impact	Mitigation measures
impurity	•	•	becomes unacceptable	~
Methane	Raises temperature at which CO <sub>2</sub> hydrates can	Depends on water content, but medium	Work not reported below 0.5vol% CH <sub>4</sub> <sup>c</sup>	
Nitrogen	Bubble point change, possible cavitation damage	Medium	Dependent on pressure and temperature of impure CO <sub>2</sub>	Operate at higher pressure or lower temperatures
	Increased risk of running ductile fracture following TPD	Significant	Dependent on pressure of impure $\text{CO}_2^{\ d}$	<ol> <li>Increase pipeline wall thickness</li> <li>Use steel with a higher Charpy V-notch energy</li> <li>Install crack arrestors (over-land</li> </ol>
	Taking up unnecessary	High	Dependent on specific Business Case	pipelines only) Utilise additional storage
NOx and SOx	NO, NO <sub>2</sub> , SO <sub>2</sub> inhalation in the event of a leak	Medium	100ppm <sup>b</sup>	
	Damage to store caprock integrity	Medium	200ppm °	Utilise additional storage
	Corrosion from $HNO_2$ or $H_2SO_3$ formation if water present (see below)	Medium	No information available	<ol> <li>Reduce other water content in CO<sub>2</sub></li> <li>Corrosion-resistant steel (e.g. ASTM304, 316) linepipe material</li> </ol>
	Corrosion from H <sub>2</sub> SO <sub>4</sub> and HNO <sub>3</sub> and elemental sulphur deposition in	Medium	Dependent on water content of impure $CO_2$ <sup>f</sup> (NB. No information available for	<ol> <li>Reduce water content of CO<sub>2</sub></li> <li>Corrosion-resistant steel (e.g. ASTM304, 316) linepipe material</li> </ol>
	pipeline: corrosion and pore blocking in store		levels other than 300ppm water, 350ppm $O_2$ , 100ppm $SO_2$ , 100ppm $NO_2$ and 100ppm $H_2S$ .	Utilise additional storage
Oxygen	Storage pore blockage by SRB, possible souring if used for EOR	Significant	>10ppm	<ol> <li>Utilise additional storage, abandon EOR operations or fit desulphurising plant to production platform</li> <li>Inject MWT e.g. NPR</li> </ol>
	Water formation if H <sub>2</sub> present (see below),	Medium	Depends on: 1. Water already in the CO <sub>2</sub> 2. How much H <sub>2</sub> is present	<ol> <li>Inject MW Fe.g. NKB</li> <li>Reduce H<sub>2</sub> content in CO<sub>2</sub></li> <li>Corrosion-resistant steel (e.g. ASTM304, 316) linenine material</li> </ol>
Particulate Sulphur trioxide	Storage pore blockage Corrosion from $H_2SO_4$ formation if water present (see below)	Significant Medium	Depends on store pore size No information available, but only in the presence of water	Utilise additional storage 1. Reduce water content in $CO_2$ 2. Corrosion-resistant steel (e.g. INCOLOY 25-6MO 825 and 020) linepipe material
Water	Generalised Corrosion	Significant	>200ppm <sup>b</sup>	Corrosion-resistant steel (e.g. ASTM304, 316) linepipe material
	Hydrate formation Corrosion from NH <sub>4</sub> OH formation, reaction with ammonium salts	Medium Medium	>50ppm <sup>g</sup> No information available, but only in the presence of water	<ol> <li>Reduce ammonia content in CO<sub>2</sub></li> <li>Corrosion-resistant steel (e.g. ASTM304, 316) linepipe material</li> </ol>
	Corrosion following reaction with chlorine or chloride formation	Medium	No information available, but only in the presence of water	
	COS hydrolysis/formation of $H_2S$ leading to SSC	Medium	No information available, but only in the presence of water	<ol> <li>Reduce COS content in CO<sub>2</sub></li> <li>Steel qualified for "Sour service"(e.g. Duplex, ASTM A240/A240M) linepipe material</li> </ol>
	Corrosion following HF formation	Medium	No information available, but only in the presence of water	<ol> <li>Reduce HF content in CO<sub>2</sub></li> <li>Corrosion-resistant steel (e.g. Monel alloy 400)</li> </ol>
	SSC following reaction with $H_2S$	Medium	No information available, but only in the presence of water	<ol> <li>Reduce H<sub>2</sub>S content in CO<sub>2</sub></li> <li>Steel qualified for "Sour service"(e.g. Duplex, ASTM A240/A240M) linepipe material</li> </ol>
	Methane-induced raising of CO <sub>2</sub> hydrate formation temperature	Depends on water content, but small	Work not reported below 0.5vol% $CH_4$ °	
	Corrosion from $H_2SO_4$ from $SO_3$	Medium	No information available, but only in the presence of	1. Reduce SO <sub>3</sub> content in CO <sub>2</sub> 2. Corrosion-resistant steel (e.g. INCOLOY

Potential	Area of impact	Severity	Level at which impact	Mitigation measures
impurity			becomes unacceptable	
			water	25-6MO, 825 and 020) linepipe material
<sup>a</sup> Table 3 of th	his document			

<sup>b</sup> EU Dynamis document 3.1.3 "CO<sub>2</sub> quality recommendations, 21<sup>st</sup> June 2007 [6]

<sup>c</sup> IMPACTS deliverable D23.1, Section A13 [24]

<sup>d</sup> IMPACTS deliverable D23.1, Section A14[24]

<sup>e</sup> IMPACTS deliverable D23.1, Section A15.3 [24]

<sup>f</sup> [23]

<sup>g</sup> Section 4.2 of this document.

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