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CO_2ReMoVe

Possible impacts of captured CO_2 stream impurities on transport infrastructure and geological storage formations

Current understanding and implications for EU legislation

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Abstract

At present, European regulation does not specify in quantitative terms a legal composition of a captured CO_2 stream. This report aims to provide an overview of the current state regulation regarding the presence of impurities in captured CO_2 streams, and their potential impacts on transport infrastructure and storage formations. It concludes that although impurities in the CO_2 stream may have impacts on storage efficiency and the porosity of storage reservoirs, if deemed necessary, advice on setting quantitative limits on the presence of a number of impurities for the purposes of safe and efficient storage cannot yet be given. A potential best practice emerging from literature regarding storage capacity could include that the amount of non-condensable gases in the CO_2 stream should not exceed 4% by volume. This figure is understood to reflect an optimum balance between gas conditioning costs and the costs of compression. Further work is recommended that assesses the interaction between the CO_2 purity requirements between the different stages of the CCS chain.

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Summary

Demonstrating the safe and permanent storage of CO_2 in geological storage complexes is important for realising CO_2 capture and storage (CCS). Ongoing research is targeted towards improving understanding of storage integrity issues, focusing on migration processes of the injected CO_2, wellhead integrity, fault reactivation and the occurrence of surface deformations. In addition, the chemical composition of the CO_2 stream can potentially affect the chemistry in the geological storage reservoir. This report aims to provide an overview of the current state regulation regarding the presence of impurities in captured CO_2 streams, and their potential impacts on transport infrastructure and storage formations.

CO_2 streams from all capture processes will contain variable levels of impurities. It is possible to remove such impurities using gas cleaning techniques, however this will increase the overall cost of CCS projects. If left untreated, certain impurities can to some extent change the physical behaviour of the bulk gas, which need to be taken into account in the design of the compression and transport system. Furthermore, there has been a limited amount of research conducted on the potential effects of impurities on storage efficiency and storage integrity.

At present, European regulation does not set quantitative limits on the composition of a captured CO_2 stream, but places the responsibility of the competent authority to determine an acceptable CO_2 stream composition on a case-by-case basis. Although the impacts of impurities on the transport system are relatively well understood, and health and safety issues can be overcome through risk assessment, the limited understanding on the impacts of impurities on storage integrity may cause difficulties in assessing the compositional requirements and laying those down in legislation.

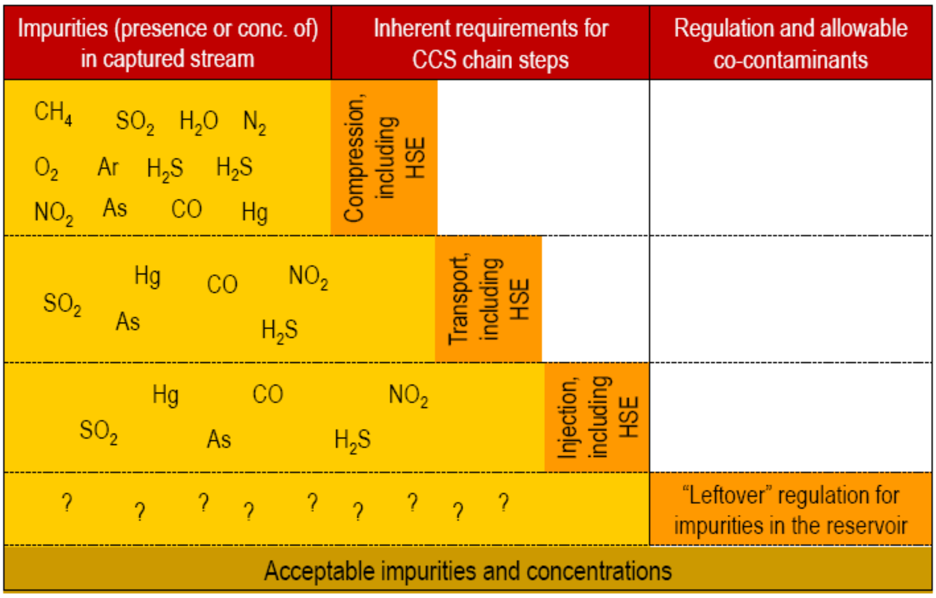
'Impurities', 'contaminants' or 'other components' in CO_2 streams can include nitrogen (N_2), oxygen (O_2) and water (H_2O), but also air pollutants such as sulphur and nitrogen oxides (SO_x and NO_x), particulates, hydrochloric acid (HCl), hydrogen fluorides (HF), mercury, other metals and trace organic and inorganic contaminants. The types of impurities that may be present in a CO_2 stream destined for CO_2 storage depends on fuel type, the nature of the process and the application of capture and separation technologies. For instance, oxyfuel processes may lead to a certain oxygen concentration in the CO_2 stream.

Literature indicates that impurities in the CO_2 stream could have an impact on storage efficiency and the porosity of storage reservoirs. Sulphur dioxides (SO_x) in the CO_2 stream, and the subsequent formation of sulphuric acids in the well appear to lead to increased geochemical activity over pure CO_2. Effects could go two ways: SO_x could accelerate mineralisation of CO_2 reducing the possibility of CO_2 leakage, but it has also been argued that it could negatively affect the cap rock and well closing infrastructure. The role of other impurities is even less clear at this point. A best practice that is suggested by literature regarding storage capacity could include that the amount of non-condensable gases in the CO_2 stream should not exceed 4% by volume, reflecting a balance between gas conditioning costs and the costs of compression.

Impurities can affect the economics of transport, because higher volumes of gas need to be transported, and liquefying a multiphase mixture is more costly. In addition to economic

considerations, removal of impurities may be required by existing health and safety legislation related to the compression, transport and injection of CO_2. Such economic and HSE requirements leave operators with inherent incentives to reduce or remove impurities to the extent necessary to operate economically and legally, making additional legislation unnecessary.

Figure S.1 gives an overview of those impurities that have to be removed or significantly reduced in a CO_2 stream for economically viable and safe operation of compression, transport and injection (top three yellow bars). It also highlights that when existing legislation already regulates impurities, or when there is an inherent incentive to remove or reduce contaminants at a particular stage in the CCS chain, there may be no need for additional regulation of the CO_2 stream at later stages.



Figuur S.1 ***A conceptual diagram illustrating different CCS chain step requirements for the reduction of impurities in the CO_2 stream. It also illustrates the uncertainties around the impacts of impurities in the geological storage reservoir.***

There are more uncertainties and less economic incentives around the role of impurities once the CO_2 stream is injected underground (Figure S.1, lowest yellow bar). In addition, from a storage perspective, the issue of impurities need to be viewed in connection to the compression, transport, injection and health and safety requirements earlier in the CCS chain in order not to over-regulate the CO_2 stream. If quantitative limits on the CO_2 stream composition are deemed necessary in the future, such legal provisions need to strike a balance between the economics of the entire CCS chain and protecting people and the environment.

1. Introduction

Carbon dioxide capture and storage (CCS) is a technology with the potential to make deep cuts in greenhouse gas emissions to mitigate climate change (IPCC, 2005; IEA, 2010). Demonstrating the safe and permanent storage of CO_2 in geological storage complexes is an important factor for substantiating the global potential of CCS.

CO_2-rock interactions are investigated with models and laboratory experiments using pure CO_2. However, as a consequence of the capture process, the CO_2 stream is likely to contain impurities, which may alter the behaviour of the stream through the compression, transport and storage elements of the CCS chain. Research on the effects of these impurities on the integrity of geological storage formations is limited.

The 'other components' or 'impurities' in CO_2 streams[1] can include nitrogen (N_2), oxygen (O_2) and water (H_2O), but also air pollutants such as sulphur and nitrogen oxides (SO_x and NO_x), particulates, hydrochloric acid (HCl), hydrogen fluoride (HF), mercury, other metals and trace organic and inorganic contaminants (IPCC, 2005). In addition small amounts of chemical solvents used in post-combustion capture may be present in the CO_2 stream (Visser et al., 2008). The removal of certain contaminants may be required for health, safety and environmental protection reasons, but also to ensure the effective transport and storage of the CO_2 stream.

However, without overlooking the importance of health, safety and the protection of the environment, the extent to which impurities must be removed from the CO_2 stream is also an economic issue. Reaching higher levels of CO_2 purity will involve a number of incremental gas treatment processes each incurring capital and operation costs, potentially increasing the energy penalty and reducing CO_2 avoidance. It is important that if deemed necessary, legal provisions regulating the maximum levels of impurities permitted in a captured CO_2 stream strikes a balance between the economics of the entire CCS chain and protecting people and the environment. In order to do this, policymakers need access to reliable scientific research, review existing regulation and consult a range of stakeholders.

This report aims first and foremost to provide an overview of the current understanding regarding impurities in captured CO_2 streams and the transport and storage impacts of those impurities. Second, the report will explore possible EU regulation on the topic. The report also presents a detailed literature review of the likely CO_2 stream composition from capture, requirements for transport, and interactions with storage reservoirs.

The implications of CO_2 stream composition on compression requirements, pipeline design and operation has been thoroughly researched and resulted in a number of recommendations, either for devising European regulations or to be used as standalone best practice documents (Visser et al., 2008; DNV, 2010). These results are discussed in section 2.

There is also a growing body of research focusing on gas-rock interactions with the presence of impurities in geological storage formations (Gunter et al., 2000; Knauss et al.,

[1] The term impurities will be used in this report.

2005: Xu et al., 2007; Jacquemet et al., 2009; Koenen, et al., 2010). This literature is reviewed and discussed in section 3 of this report.

It is currently unclear to what extent the information on storage integrity and impurities can be utilised to support competent authorities in determining an acceptable CO_2 composition from capture projects. At present, European regulation does not specify in quantitative terms a legal composition of a captured CO_2 stream, and it is unclear whether this will be altered in the future. Some of the impurities may be self-regulated by industry, as their presence affects the economics of compression or transport. However, for other substances, the lack of an agreed specification could lead to uncertainties for industrial stakeholders of CCS projects (Birat, 2010) and possibly for storage integrity concerns. Conclusions and recommendations for further research and other questions are discussed in section 4.

2. Impurities in capture, compression and transport

2.1. Impurities from capture installations

The nature and quantity of impurities present in a stream of captured CO_2 is dependent on the fuels used, the capture process (the type of solvent used) and any gas treatment steps either prior or subsequent to CO_2 capture (Visser et al., 2008). The composition of the resultant CO_2 stream is contingent on the associated capture processes, and distinct differences in CO_2 stream composition exist between the three main categories of post-combustion, pre-combustion or oxyfuel capture (Anheden et al., 2004). CO_2 capture from industrial process, such as blast furnaces or cement kilns present another level of complexity in the stream composition, as the potential suitability of different types of capture technologies, either based on chemical adsorption or physisorption is much less understood.

The composition of the captured CO_2 stream resulting from the post-combustion capture process is understood to contain fewer impurities as existing regulations, specifically the Industrial Emissions Directive[2], which requires sets Emission Limit values (ELVs) on sulphur dioxide (SO_2), nitrogen oxides (NO_x) and dust particles. The removal of these pollutants will precede the removal of CO_2 from the remaining flue gas passing. The CO_2 stream after the CO_2 capture process will contain small (up to 0.3% by volume each) amounts of nitrogen, oxygen, argon, water and, in some cases, very small amounts of ash, trace metals, SO_2 and NO_x (< 0.01% by volume each; ICF International, 2010). Furthermore, elevated levels of NO_x (50ppm) has been proven to cause significant degradation of the monoethalineamine (MEA)[3], the byproducts of which (such as alkalonamines, anionic heat stable salts and ammonia) will consequently reduce the efficiency of CO_2 removal (Pederson et al., 2010).

During pre-combustion capture, coal or biomass is gasified, resulting in a syngas composed of H_2 and CO, the latter which is converted to CO_2 through a water-gas shift process with the remaining hydrogen rich fuel used in a number of applications such as boilers, furnaces and gas turbines (Visser et al., 2007). The water gas shift process does result in a concentrated stream of CO_2 (>98%), however small amounts of hydrogen (H_2; 1.5%) and hydrogen sulphide (H_2S; ≈ 0.2%) may be present (ICF International, 2010). However, because gasification takes place in a reducing environment, no SO_2 or NO_x will be present in the captured CO_2 stream (Visser et al., 2007).

Dependent on feed composition and feed pressure, the purity of a CO_2 stream from an oxyfuel pulverized coal or natural gas installation can vary. The flue gas from an oxyfueled pulverized coal power plant contains approximately 63% CO_2, and thus needs to be purified (Pipitone & Bolland, 2009). The type and amounts of impurities present in the final CO_2 stream depends on the method of CO_2 purification. Incidental substances such as SO_x, NO_x, and Mercury (Hg), and significant amounts of nitrogen, argon and oxygen may be present in the captured CO_2 stream (ICF International, 2010). Oxyfuel combustion processes will also be regulated by the EU Large Combustion Plants Directive, which replaces restrictions on SO_2, NO_x and dust particles.

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[2] Directive 2010/75/EU).
[3] A common chemical solvent used in post-combustion capture systems.

In addition to CO_2 streams stemming from power generation processes, CO_2 capture processes may also be applied to industrial processes such as blast furnaces, cement kilns and certain parts of oil refineries. Capture techniques for these applications are currently in development, such as the oxyfuel cement kiln (IEA GHG, 2008) and the oxygen blast furnace with CO_2 capture. Even though at present it is still unclear which capture options are most suitable for various industrial processes, it is understood that high purity captured CO_2 streams can be achieved, albeit with additional energy and cost. Table 2.1 below provides an illustrative calculation of the compositions of CO_2 streams resulting from a range of capture processes from various installations.

Table 2.1 ***Calculated compositions of CO_2 streams from a range of capture processes (adapted from ICF International, 2010)***[4]

Component	Post combustion capture at subcritical pulverized coal plant (MEA)	Pre-combustion capture at coal IGCC plant (Selexol)	Oxy-fuel combustion at supercritical pulverised coal plant (Stack gas)	Cement plant (MEA)	Refinery stack (MEA)
Argon, Ar	22 ppmv	178 ppmv	3.7%	11 ppmv	38 ppmv
Arsenic, As	0.0055 ppmv	0.0033 ppmv	0.0085 ppmv	0.0029 ppmv	
Methane, CH_4		112 ppmv		0.026 ppmv	
Chlorine, Cl	0.85 ppmv	17.5 ppmv	0.14%	0.41 ppmv	0.4 ppmv
Carbon monoxide, CO		0.13%		1.2 ppmv	
Carbon dioxide, CO_2	99.7%	98.1%	88.4%	99.8%	99.6%
Carbonyl sulphide, COS		1.7 ppmv			
Hydrogen, H_2		1.5%			
Water, H_2O	640 ppmv	376 ppmv	640 ppmv	640 ppmv	640 ppmv
Hydrogen sulphide H_2S		0.17%			7.9 ppmv
Mercury, Hg	0.00069 ppmv	0.00068 ppmv	0.0035 ppmv	0.00073 ppmv	
Nitrogen, as N_2	0.18%	195 ppmv	2.8%	893 ppmv	0.29%
Ammonia, NH_3		38 ppmv			
Nitric oxides as NO_2	1.5 ppmv	11 ppmv	721 ppmv	0.86 ppmv	2.5 ppmv
Oxygen, O_2	61 ppmv		3.6%	35 ppmv	121 ppmv
Selenium, Se	0.017 ppmv	0.01 ppmv	0.026 ppmv	0.0088 ppmv	
Sulphur oxides, as SO_2	0.84 ppmv		1.3%	0.097 ppmv	1.3 ppmv

2.2. Potential impacts of impurities on compression and transport

The presence of non-condensable gases in the CO_2 stream increases the costs of compression and transport, while effectively reducing the storage capacity of geological formations (Yan et al., 2009). In addition, water and compounds such as hydrogen sulphide (H_2S) lead to corrosion of pipelines. Note that such processes have safety impacts but also affect the economics of compression and the transport process of a CCS project.

[4] Note that these concentrations refer to specific examples of modeled capture setups, and cannot be generalised to represent the different categories of capture processes in general.

2.2.1. Compression

Non-condensable gases in the CO_2 stream may include hydrogen (H_2), argon (Ar), nitrogen (N_2), oxygen (O_2) and methane (CH_4). These gases have a weak tendency to mix with other gases and dilute the CO_2, and complicate the phase change during compression. This means that higher pressures will be needed to avoid 2-phase flow (Visser et al., 2007: Anheden et al., 2004), leading to potentially substantial additional energy requirements. For example, 5% of H_2 present in the CO_2 stream composition represents an increase of 25% compression work (Austegard & Barrio, 2006). In the oxyfuel case in Table 2.1 above, approximately 8% of the stream is composed of Ar, O_2 and N_2, and this may require further gas conditioning prior to compression and transport.

2.2.2. Transport

Aside of the compression stage, non-condensable gases can also have an impact on CO_2 pipeline transport, both in terms of the volume available for CO_2, and the necessity for an increase in pressure to keep the CO_2 in dense phase[5]. For example, the volumetric capacity of a pipeline is decreased by 27% for a stream of CO_2 that contains 10% of hydrogen (Mohitpour, 2003). Yan et al., (2009), have evaluated the influence that various purities of CO_2 stemming from an oxyfuel capture installation may have on the costs of CO_2 transportation. Three purification scenarios were simulated resulting in CO_2 stream purities of 87%, 96% and 99%, with the remaining stream composition comprising of various amounts N_2, Ar and O_2. Although the lower purity CO_2 stream results in reduced capture costs (Δ2€/t CO_2 87-99%), the overall chain costs for the 87% purity stream were €2.5/t CO_2 higher than the 99% purity stream. The augmented costs of transporting the 87% CO_2 stream are affiliated to the additional 23% compression work to avoid 2-phase flow, and an incremental increase of approximately 100mm in pipeline diameter to compensate for lost volume due to the impurities. According to Yan et al., the 96% purity stream is understood represent the optimum cost balance in the CCS chain.

Impurities present in a CO_2 stream can also lead to corrosion and hydrate formation within a pipeline. Free water present in the CO_2 stream can react with small amounts of CO_2, H_2S and CH_4 and result in the formation of hydrates. Hydrates are solid crystalline compounds that can block the pipeline and potentially damage equipment (Carroll, 2003). Within carbon manganese steel pipes, (C-Mn) free water combined with the high CO_2 partial pressure can cause extreme corrosion rates, primarily due to the formation of carbonic acid. Sulphuric acids can also form if the stream is co-contaminated with H_2S or SO_2. Under laboratory conditions, Choi et al., (2010) recorded dramatically increased corrosion rates of carbon steel from 0.38 mm/yr to 5.6 mm/yr, after the addition of 1% SO_2 to water-saturated CO_2. The rate was increased again to 7 mm/yr with the addition of O_2. However, through sufficient dewatering of the CO_2 prior to transportation, corrosion can be almost entirely avoided[6].

[5] The most efficient for transportation.

[6] Corrosion rates are in the order of mm/y when free water is present, and can be reduced to the order of µm/y when dry CO_2 is transported (Seiersten, 2001).

Table 2.2 Descriptions and potential impacts of CO_2 and possible impurities for health and safety, compression and transport issues (adapted from DNV, 2010)

Component	Health and safety	Pipeline capacity	Water solubility	Hydrate formation	Materials	Fatigue	Fracture	Corrosion	Operations	Comment
CO_2	●	●	●	●	●	●	●	●	●	Non-flammable, colourless, no odour; low toxicity, heavier that air in the gaseous state
H_2O				●	●	●	●	●	●	Non-toxic; condensable; forms acids with CO_2, NO_x and SO_x, which have a corrosive impact on transport infrastructure
N_2		●	●							Non-toxic; stable
O_2		●	●					●		Non-toxic
H_2S	●	●			●	●	●	●		Flammable, strong odour, extremely toxic at low concentrations
H_2		●	●				●			Flammable, non-condensable at pipeline operating condition; impact on transport infrastructure through embrittlement
SO_2	●		●					●		Non-flammable, strong odour, toxic; forms sulphuric acid with water
NO_2	●		●					●		Non-flammable, toxic; forms nitric acid with water
CO	●		●							Flammable, toxic
CH_4+		●	●						●	Odourless, flammable
Amines	●									Potential occupational hazard with corrosive impact
Glycol	●							●		Potential occupational hazard

2.3. Regulation of captured CO_2 stream composition

A solitary piece of European regulation currently comments on the requirements for the composition of a captured stream of CO_2. The European Union Directive on the geological storage of CO_2[7], defines the CO_2 stream as 'a flow of substances that results from CO_2 capture processes.' The Directive also loosely defines the required stream composition that can be legally transported. Article 12(1) states in part:

'A CO_2 stream shall consist overwhelmingly of carbon dioxide. To this end, no waste or other matter may be added for the purpose of disposing of that waste or other matter.'

Although clearly prohibiting the co-disposal of waste gases in a CO_2 stream, the Directive does not set absolute quantitative restrictions on the substances that compose the CO_2 stream, but uses qualitative criteria. The Directive does recognize that the CO_2 stream may contain incidental associated substances from the capture process, or substances used for monitoring and verification purposes, however all incidental or added substances must be below levels that would:

[7] Directive 2009/13/EC – henceforth referred to as 'the Directive'.

a) *'adversely affect the integrity of the storage site or the relevant transport infrastructure;*
b) *pose a significant risk to the environment or human health; or*
c) *breach the requirements of applicable Community legislation.'*

To meet the above criteria, operators are required to carry out a risk assessment in respect of the stream composition and maintain a register of the quantity, properties and composition of streams injected (UCL, 2010). However with reference to point "a)" above, questions can be raised regarding how various compositions of CO_2 streams may affect the integrity of the storage site. It is currently unclear whether sufficient information exists to allow a well-informed decision about the level of impurities that can be injected into a storage site.

In legal terms, the use of qualitative criteria for a gaseous stream composition (which can be quite easily quantified) seems inappropriate, as the term 'overwhelmingly' used in Article 12(1) could be interpreted differently between operators. The term 'overwhelmingly' was initially utilized in the London Protocol, the first international marine-environment protection instrument that permits the offshore geological storage of CO_2 (Holwerda, 2011). In the Directive, the formula that CO_2 streams "consist overwhelmingly of carbon dioxide" was chosen as it allows for a case-by-case assessment of the levels of impurities, recognizing the natural variation in storage site characteristics and different transport constructions[8].

Brockett (2009) informs that during the drafting of the Directive, the European Parliament's Environment Committee had proposed an amendment to the Directive, calling for a CO_2 concentration of ≥95% and above, and the elimination of H_2S and SO_2. This amendment was not adopted, on the basis that certain applications of CCS, particularly for the cement and steel industry[9], may have considerable problems reaching such levels of CO_2 purity. Furthermore the complete removal of H_2S and SO_2 is potentially impossible.

The Commission has produced guidance on the practical applications of the qualitative criteria outlined in Article 12 of the Directive[10]. It is also expected that documents specifying the Best Available Techniques (BAT) will be developed for capture installations, and these documents would include CO_2 compositions (Brockett, 2009). The Directive, including the provisions of Article 12, will also be reviewed and modified if required in 2015.

2.4. Recommendations on the CO_2 stream composition

The European DYNAMIS project has assessed the requirements for CO_2 stream composition in terms of health and safety, and the durability of the transport network (Visser et al., 2007). With exemption of the CO_2 purity levels suitable for use in enhanced oil recovery operations, the impact of impurities on geological storage formation or the behaviour of the CO_2 plume was not covered. Nevertheless, in order to best inform policymakers on any necessary regulatory requirements on CO_2 purity for storage, an

8 *International Marine Regulation*, supra note 22, at 4506.
9 CCS applications in many industrial sectors, particularly the steel and cement sectors, are currently in the early stages of development. There is not sufficient information on the CO_2 reduction potential of such industrial process with CCS, and the costs associated with such applications are uncertain.
10 See - http://ec.europa.eu/clima/policies/lowcarbon/docs/gd2_en.pdf.

assessment of the whole CCS chain is necessary. The compositional demands of CO_2 for storage cannot be viewed in isolation from compression, transport and safety.

In terms of transporting a CO_2 stream in a safe way, substantial amounts of impurities present in the stream may influence the impacts of a pipeline leakage or rupture (IPCC, 2005). Furthermore, in addition to the dangers of a sudden high concentrated release of CO_2, compounds such as CO, SO_2 and H_2S which may also be present in the stream are toxic by nature. Visser et al. (2007) used a set of calculations based on European Short Term Exposure Limits (STEL) to determine the maximum recommended concentrations of H_2S, CO, SO_2 and NO_2 in pipelines. A precautionary multiplication safety factor of 5 was used, justified on the basis of uncertainties in the diffusion patterns and possible synergetic effects between the various purities.

The DYNAMIS project also sets recommended technical limits for impurities in the CO_2 stream. The formation of hydrates and subsequent corrosion of the pipeline, and the reduced pipeline capacity for CO_2 are raised as the main negative impacts brought about by the presence of impurities in the CO_2 stream. The recommended composition of a CO_2 stream for efficient and safe transportation from the DYNAMIS project is presented in Table 2.4.

Table 2.3 Recommendations for CO_2 composition for safe transport (adapted from Visser et al., 2007)

Component	concentration	Limitation
H_2O	500 ppm	Technical: below solubility limit of H_2O in CO_2
H_2S	200 ppm	Health and safety considerations
CO	2000 ppm	Health and safety consideration
O_2	< 4%	Precautionary due to unknown effects underground
CH_4	< 4%	Methane affects the solubility of water
N_2	< 4%	Non-condensable gas effect storage/transport capacity
Ar	< 4%	Non-condensable gas effect storage/transport capacity
H_2	< 4%	Non-condensable gas effect storage/transport capacity/ economic reasons (energy content)
SO_X	100 ppm	Health and safety considerations
NO_X	100 ppm	Health and safety considerations
CO_2	>95.5%	Balanced with other compounds

All recommendations made by Visser et al., (2007) are based on criteria focusing on health and safety, and the efficient transport of CO_2 in pipelines. To date, there have been no specific recommendations presented to European regulators based on foreseen impacts of impurities on long-term geological storage formations. There have been however, a number of scientific investigations completed to attempt to explore, and if possible quantify such impacts. The results of such investigations are documented in section 3 of this report.

3. Current understanding on the impact of impurities on CO_2 gas-rock interactions

According to the IPCC (2005), there are three main geochemical trapping processes that can occur at different times during the storage process: solubility trapping, ionic trapping and mineral trapping. Before moving directly to the impacts of impurities on gas-rock interaction, it's important to cover the basic aspects of geochemical trapping of CO_2.

3.1. Geochemical trapping of CO_2

Saline reservoirs in sedimentary basins can provide suitable geological formations for the safe storage of supercritical CO_2 (; IPCC, 2005; Gaus, 2010). The salinity of water present in such formations is understood to range from 5,000 to over 350,000 mg/L, and the majority are not considered potable given the presence of dissolved toxic materials, organic and/or inorganic components naturally occurring radioactive material as well as the high salinity itself (Kharaka & Hanor, 2007). The conditions found with such formations are the result of various hydrogeochemical processes including mixing, dissolution/precipitation of minerals, bacterial activity and interactions with organic material. The injection of CO_2 into subsurface geological formations may induce a number additional geochemical processes, potentially altering the chemical reactivity of the system (Gaus, 2010).

Once injection has started, supercritical CO_2 and any other potential impurities will dissolve and interactions will occur between the injected stream and the well materials (Gaus, 2010). Although CO_2 alone is not reactive, once in contact with brine, carbonic acid (H_2CO_3) is formed, which dissociates in the brine. The formation of this acid reduces the pH of the brine, meaning that the brine becomes corrosive to well materials, rocks and pipelines (Gaus, 2010).

$$CO_2\,(g) + H_2O \leftrightarrow H_2CO_3 \leftrightarrow HCO_3^{-} + H^{+}$$

This reaction is then buffered through interactions with carbonate minerals present in the geological formation, the acidity of the brine will still be sufficient to react with other carbonate and silicate minerals (Gaus, 2010).

$$CaCO_3 + H^{+} \leftrightarrow Ca^{2+} + HCO_3$$

Dependent on the geology of the storage formation, the acid may react with calcium, magnesium and iron carbonates to form bicarbonate ions (IPCC, 2005). The trapping of CO_2 by dissolving it into the formation water is known as solubility trapping. Solubility trapping is understood to benefit the security of CO_2 storage because as CO_2 is dissolved, it no longer exists as a separate phase, losing the buoyant forces that can drive the CO_2 plume upwards. The process of solubility trapping is thought to be the dominant geochemical process during the first tens to hundreds of years after injection (IPCC, 2005).

The incorporation of the injected CO_2 into minerals due to chemical precipitation is termed mineral trapping, and this can be a rapid (a number of days) or a slow process (thousands of years) depending on the type of mineral (IPCC, 2005), but also on the in-situ temperature and pressure (Kaszuba et al., 2005). Examples of minerals that may precipitate in geological formations which contain clays and feldspars include, Dawsonite (from feldspar albite), siderite and dolomite (from the clay chlorite) (Gaus, 2010).

3.2. Dissolved gas-rock interactions and injectivity

Injectivity is the rate at which CO_2 can be injected into a given reservoir and the ability of the subsequent CO_2 plume to migrate away from the injection well (Kaldi and Gibson-Poole, 2008). There is a wide range of factors that determine the injectivity both anthropogenic, for example; wellbore design, injection rate and injection pressure, and natural; viscosity of in-situ fluid, stratigraphic architecture and the formation porosity and permeability characteristics (Soloman and Flach, 2010).

Permeability is one of the main controlling parameters of CO_2 storage in geological formations (van der Meer, 1995; Law and Bachu, 1996; Ennis-King and Paterson, 2001). If the formation permeability is insufficient, the low permeability will reduce injectivity with consequential negative impacts on overall CO_2 storage capacity. This could indicate that a potential storage location is not commercially viable. Although permeability can be tested prior to CO_2 injection, once injection has commenced, injectivity losses could arise from geochemical reactions between the CO_2 saturated formation water, but also from the presence of gaseous impurities in the CO_2 stream (Soloman and Flach, 2010).

Geochemical gas-rock interactions such as solubility trapping and mineralization are important for the permanent storage of the injected CO_2. However, although CO_2-saturated brine can initially cause increased porosity and permeability, insoluble reaction products will be precipitated downstream, potentially plugging pore throats and consequently reducing permeability (Soloman and Flach, 2010). According to Gaus et al., (2010), drastic permeability reductions due to minute amounts of dissolved minerals affecting the geometry of hydraulic capillaries are possible. To calculate the porosity change brought about by chemical precipitation, the balance between the space created by the dissolved mass and the space occupied by the precipitated minerals needs to be assessed (Gaus et al., 2010).

3.3. The impact of impurities on geological formations

3.3.1. Storage capacity

Impurities in a CO_2 stream, such as non-condensable gases, reduce the density of the gas stream. The lower density leads to a consequential drop in the total storage capacity of a storage reservoir. A less pure CO_2 stream would mean that storage locations would be expended at a faster rate, meaning that higher costs would be incurred both due to the physical pore space occupied, but also through the costs of more frequent re-mobilising of injection equipment, re-installation of sub-surface templates and conducting additional well characterizations. Overall, it is of course desirable to utilize geological storage space as efficiently as possible.

Yan et al., (2009) conducted a techno-economic assessment developing three CO_2 purification scenarios (87%, 96% and 99% CO_2), stemming from an oxyfuel combustion installation. As well as compression and transport costs, the effects of non-condensable gases (N_2, Ar and O_2) on storage capacity was also investigated. Figure 3.1 depicts the results of a simulation, highlighting the density changes of the three CO_2 streams as they are injected to various depths. The graph on the left is a simulation of injecting a stream of

CO_2 to a depth of 2000m, whereas on the rate the depth is 1000m, with corresponding values of the y-axis.

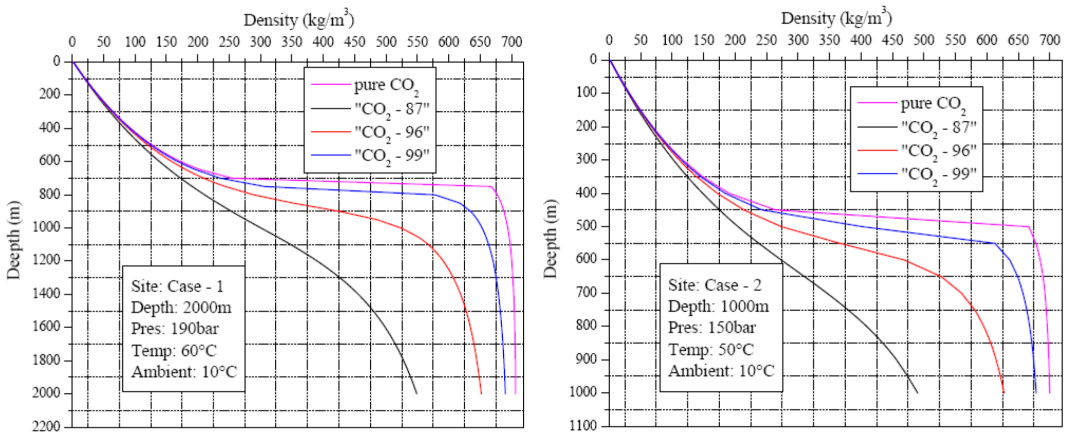

Figure 3.1 ***The density of CO_2 streams with different purities of CO_2 at different depths, pressures and temperatures (Yan et al., 2009)***

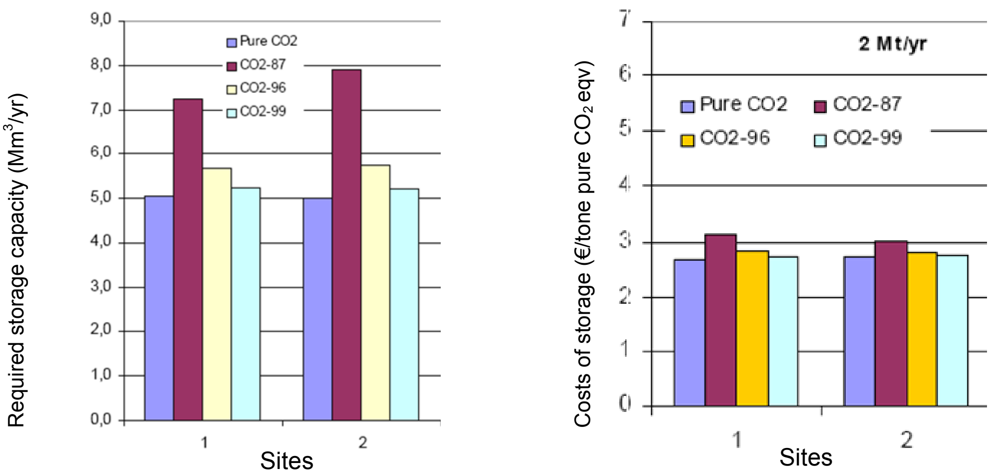

Figure 3.2 ***The required storage capacity (left) and associated costs (right) of CO_2 streams with different purities (Yan et al., 2009)***

In the assessment, three storage scenarios with altered depths and geothermal conditions were presented, of which two are presented in Figure 3.1. It is clear that according to Yan et al., (2009), the density of the CO_2 stream at both depths of 2000m and 1000m is directly affected by the increased presence of non-condensable gases. Given that additional amounts of a low purity CO_2 stream must be injected to achieve a specified level of CO_2 storage, the costs of storage are approximately €0.3/tonne of pure CO_2 equivalent higher than in the 99% CO_2 stream purity (Figure 3.2). The costs include the CAPEX, OPEX and annual amortisation, although it is unclear if the injection takes place on or offshore.

The presence of impurities may also have an impact on the solubility and subsequently the geochemical reactions. According to Jacquemet et al., (2009), if such reactions lead to change in porosity relative to the porosity prior to injection, the space volume of the storage would be modified as well. Reductions in the interfacial forces between the fluid and the rock brought about by impurities could consequently reduce the sealing capacity and the storage efficiency (Jaquement et al., 2009).

3.3.2. Induced porosity and permeability changes

As mentioned above, geochemical reaction between the CO_2 gas stream, in-situ brine and minerals in the storage formation can lead to problems during the operational phase, such as reduced permeability and increased pore pressures (Anheden et al., 2004). The blocking of fractures and pore spaces by mineral precipitation is a common feature in many geological settings (Emmanuel & Berkowitz, 2007). It is the growth in secondary minerals in the brine resulting from the precipitation process that are able to alter the geometry of the hydraulic capillaries. Impurities in the injected gas stream can have direct impacts on the intensity and/or nature of the gas-rock interactions, rapidly reducing the pH of the brine and potentially increasing dissolution of the host rock and precipitation of secondary minerals over time scales ranging from months to thousands of years (Anheden et al., 2004). However, it must also be raised that, depending on numerous in-situ conditions, modifications in permeability brought about by mineral reactions may actually aid the migration of CO_2 through the injection zone (ICF International, 2010).

If pure CO_2 is injected into a storage formation, once in contact with water a relatively weak carbonic acid (H_2CO_3) will be formed. However, if other compounds are co-injected with the supercritical CO_2, much stronger acids may develop. A number of the most potentially important acids and their relative acidity compared to carbonic acid have been calculated by ICF International (2010), and are presented in Table 3.1. The equilibrium constants used to develop the relative acidities have been calculated at 25ºC and at atmospheric pressure, and thus may vary given geological conditions.

Table 3.1 A range of acids and their relatively acidity compared to carbonic acid (adapted from ICF International, 2010)

Acid	Formula	Relative acidity
Hydrochloric acid	HCl	$2.3x(10)^{14}$
Sulphurous acid	H_2SO_3	$3.5x(10)^{4}$
Sulphuric acid	H_2SO_4	$2.8x(10)^{4}$
Carbonic acid	H_2CO_3	$1.0x(10)^{0}$
Nitrous acid	HNO_2	$1.0x(10)^{3}$

There are a limited number of studies that attempt to quantify the effects that stronger acids may have on the precipitation of minerals in geological formations. Knauss et al., (2005), coupled a chemical model with a simplified flow in a one dimensional (1D) simulation using the reactive transport code CRUNCH (Steefel, 2001; Steefel and MacQuarrie, 1996), in order to simulate the injection of CO_2 into a heterogeneous rock formation, calculating the mineralogical changes over the flow path of 1km. In addition to modelling the impact of the CO_2, the simulation, based on an injection period of 5 years, was run with the addition of small amounts of H_2S and SO_2. The amount of SO_2 added was sufficient to reduce the pH to 1, given the experimental reservoir conditions. The results suggest that the co-injection of H_2S should not adversely impact injection rates compared to pure CO_2. However if sulphur is able to oxidise to sulphate, which is highly probable given the abundance of oxidants such as water, a sulphuric acid will be formed. This strong acid reduced the pH in the testing domain, and consequently led to significant precipitation of calcite, dawsonite and anhydrite.

Further 1D reactive transport simulations made by Xu et al., (2007), using a different code called TOUGHREACT (Xu et al., 2004), focused on the injection of CO_2 in sandstone formations. The results of the simulation highlight the dominant geochemical impact of SO_2 compared to pure CO_2 or CO_2 and H_2S, supporting the findings of Knauss et al., (2005). In the case of co-injection of CO_2 and SO_2, 0.036 kg/s of SO_2[11] was injected with 1kg/s of CO_2, approximately 2.4% of the total injected material by mass[12]. The illustrative graph below displays the approximate pH values of the formation fluid 10 years after injection, also displaying the changes in pH in relation to the distance from the injection zone.

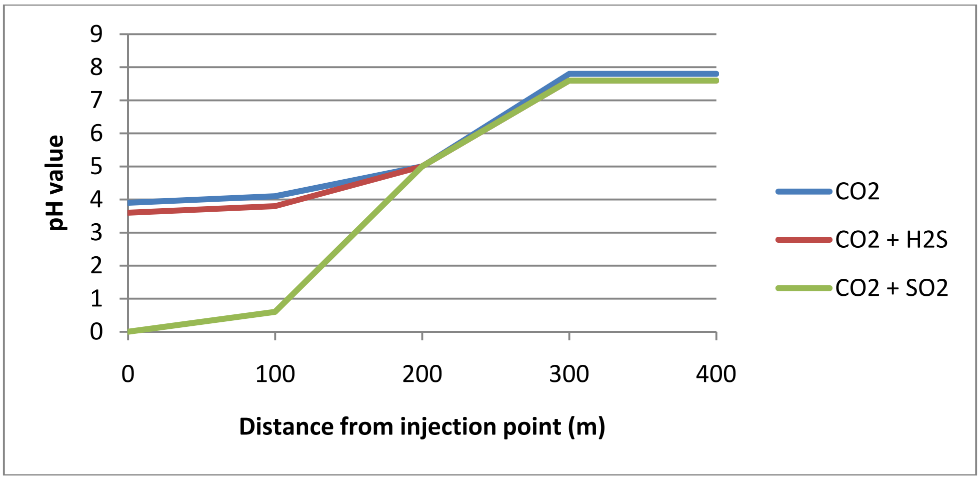

***Figure 3.3** Changes in the pH of formation fluid after injection of pure CO_2, and combinations of CO_2, H_2S and SO_2 (graph modified from Knauss et al. 2005)*

As can be seen from Figure 3.3, the combination of CO_2 and SO_2 leads to a dramatically reduced pH within the first 200 metres from the injection point. The combination of CO_2 and H_2S has a relatively small impact on pH compared to the base case. The acidic conditions are caused by the formation of sulphuric acid (Knauss et al., 2005):

$$4SO_2 + 4H_2O \rightarrow 3H_2SO_4 + H_2S$$

The area of extreme acidity covers a radial distance of 100m from the point of injection. The lower pH due to the presence of SO_2 causes the rapid dissolution of calcite within the first 200m. The dissolution of calcite is followed by the precipitation of both minerals anhydrite and alunite, with the volume of precipitated minerals peaking at around 200m from the injection point. In terms of changes in porosity, the increased acidic conditions actually increased the porosity in the first 100m from the injection point. However, coinciding with the peak abundance of precipitated mineral, the porosity is lower than the base case at 200m 100 years after injection. Xu et al., (2007) suggest that small changes in porosity could result in a significant change in permeability, altering the flow pattern of the injected CO_2.

[11] This amount was chosen as it represents an average weight ratio of sulphur to carbon in a domestic coal fired power plant of 2.5:100 (Apps, 2006).
[12] A significant amount of H_2O was co-injected in addition to CO_2 in order to partly replicate the composition of the formation brine.

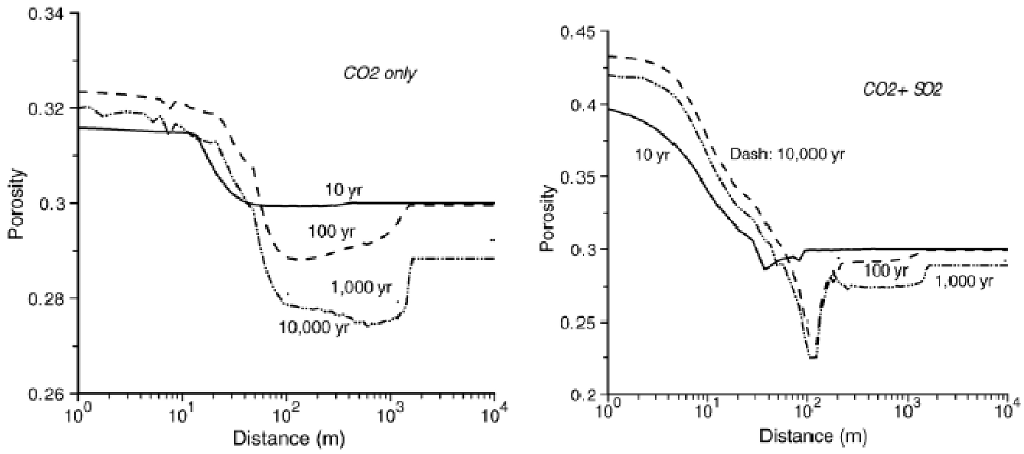

Figure 3.4 ***Modelled changes in porosity after injection of pure CO_2 (left) and a combination of CO_2 and SO_2***

Figure 3.4 (Xu et al., 2007), compares the modelled porosity changes between the base case (CO_2 only) and the combination of CO_2 and SO_2. At between 100 to 200m from the injection point, both scenarios display reduced porosity for all timeframes. It is also clear that in the case of CO_2 and SO_2, the minimum porosity reached at approximately 200m is approximately 0.07 pp lower than the control at 100 years. The reduced porosity in both cases coincides with the maximum precipitation of alunite.

Koenen et al., (2010) have also investigated the impact of impurities on a sandstone formation. The investigation involved the use of the geochemical modelling tool PHREEQC, which simulated the injection of CO_2 streams into a formation with the mineralogical composition of a potential Dutch CO_2 storage field. Three CO_2 composition scenarios were modelled; a pure CO_2 base case, and scenarios based on the expected compositions of captured CO_2 streams from pre-combustion and oxy-fuel technologies. The composition of the CO_2 streams from the pre-combustion and oxyfuel technologies are shown in table 3.2.

Table 3.2 ***The composition of CO_2 streams used in the modelling study of Koenen et al. (2010)***

Component	Pre-combustion (mole %)	Semi-purified oxyfuel (mole %)
CO_2	99.64	98.0
H_2S	0.00014	-
CO	0.03	0.005
O_2	0.0045	0.7
N_2	0.077	0.7
Ar	-	0.6
H_2	0.14	-
SO_2	-	0.007
NO_X	-	0.01

The results of the model experiment in all cases display a drop in pH due to the formation of acids. In the base case, the pH drops from 6.1 to 4.6 due to the formation of carbonic acid. In the semi-purified oxyfuel case, the formation of sulphuric and nitric acids (through the reaction between SO_2, NO_x, H_2S and water) leads to a slightly lower pH of 4.5. Given the small changes in pH, the difference in dissolution and consequently permeability is negligible. However, by increasing the concentrations of the impurities in the oxyfuel scenario tenfold, simulating an accumulation of impurities at the injection point, the pH drops to approximately 1.8. The acidification of the pore water led to a slightly higher calcite dissolution on the short term, though the porosity increase was negligible. Furthermore, the calcite dissolution also acts as a buffer, with the final pH raising again to 4.5. No precipitation of anhydrite ($CaSO_4$) was observed in this work, dissimilar to the results of Knauss et al., (2005) and Xu et al., (2007) covered above.

Of the main literature sources reviewed, there are a number of consistent findings. Dependent on reservoir geology, the co-injection of SO_2 with the CO_2 reduces the pH of the formation water to approximately 1, due to the formation of sulphuric acid. H_2S is seen to have a lesser impact on the creation of acidic conditions. With the co-injection of SO_2, a highly acidified zone forms within a radial distance of 200m from the injection point. In this acidic zone, rapid mineral dissolution of carbonate and silicate minerals may actually increase the porosity. At the edge of the injection zone (between 150-200m), the increased pH results in the precipitation of various secondary minerals, for example dawsonite, alunite, siderite and ankerite (dependent on the lithology of the formation). After approximately 100 years the level of precipitation is understood to reduce the porosity and potentially the permeability of the formation. A reduction in permeability could modify fluid flow, however this would not impact injectivity as the operational phase of the storage process would be complete.

4. Conclusion

Within the EU Directive on the geological storage of CO_2, the absence of quantitative requirements for the composition of a CO_2 can be attributed to a number of factors. Firstly, given that CCS is novel technology both in the power sector and industry, there is uncertainty regarding the composition of CO_2 streams that could be captured from currently unproven technologies. An eventual deployment of CCS may see a wide range of capture techniques being deployed, all resulting in heterogeneous gas stream compositions. In light of this, having a single purity requirement may incur significant economic penalties for certain technologies and hinder the development of CCS as a potential CO_2 abatement option both in the energy and industrial sector.

From another point of view, the implementation of multiple 'CO_2 purity classes' may obstruct the development of CO_2 transport networks and complicate the establishment of a 'captured carbon' commodity market (Paxton, 2011). It has been highlighted that if CCS is to significantly contribute to reducing CO_2 emissions in Europe, networks of pipelines carrying CO_2 from numerous installations will be required. Having some sort of minimum threshold or compositional ranges for impurities may then be required to facilitate the co-utilisation of transport and storage infrastructures. Furthermore, if Member States were to adopt divergent quantitative limits for impurities, this could impede cross-border trade of captured CO_2 and hamper the free movement of goods within Europe (Holwerda, 2011).

The second factor is the lack of understanding on the affects of impurities on various parts of the entire CCS chain. This is complicated by the multitude of possible interactions between the CO_2 stream and transport/storage equipment. Table 2.2 provides a useful overview of the potential impacts that impurities may have on CO_2 transport infrastructures, and also highlights health and safety concerns. However publicly available material covering the impacts of impurities on the storage of CO_2 appears limited.

The objective of this report has been to review current scientific literature regarding the implications of storing a CO_2 stream with the presence of impurities. Prior to the completion of this report, no publicly available review of this subject could be found.

4.1. Main findings

Capture processes rarely result in pure CO_2, which poses challenges for compression, transport and storage. Two possible impacts of impurities on CO_2 storage processes were identified:

- Non-condensable gases affecting storage capacity
- The formation of strong acids, which reduces the pH of the brine solution with possible affects on porosity and permeability

The presence of non-condensable gases such as H_2, Ar, N_2 and O_2 can significantly reduce the density of the CO_2 stream. In particular, captured CO_2 streams from oxyfuel capture technologies can contain relatively large percentages of non-condensable gases, up to approximately 10% depending on the conditioning processes deployed at the installation. For transport purposes, the incidence of non-condensable gases in the CO_2 stream would result in the requirement for additional compression work. Specifically for storage, the low density of the injected CO_2 stream would lead to the inefficient utilisation of pore space, reducing the amount of CO_2 that can be stored at a particular storage location. Therefore, there are economic reasons to partially remove certain contaminants in the CO_2 stream.

The presence of certain impurities such as H_2S, NO_x and SO_x, can increase the range and rate of geochemical reactions through the formation of hydrochloric, sulphuric and nitrous acids which reduce the pH of the formation water. From the scientific literature reviewed in this report, the presence of SO_2 and the formation of sulphuric acid, has the most potent effect at reducing the pH of the in-situ water (see Figure 3.3). The drop in pH results in an acidified radial zone of approximately 200m around the injection point, whereby the dissolution of carbonate material takes place. At the periphery of the acidified zone where the pH rises, the precipitation of secondary minerals is observed. The precipitation of such minerals is higher in the cases where SO_2 is co-injected with CO_2. After approximately 100 years, sufficient precipitation of secondary minerals may take place that can induce changes in porosity and permeability. However, no current scientific literature points towards the co-injection of SO_2 or H_2S leading to short-term (<10 years) porosity reduction that could hinder injectivity.

4.2. Implications for EU CO_2 storage legislation

This report has established that impurities in the CO_2 stream can have impacts on storage efficiency and the porosity of storage reservoirs, however it still remains a difficult task to recommend quantitative limits on the presence of impurities for the purposes of safe and efficient storage. Regarding storage capacity, work completed by Yan et al. (2009) supports previous recommendations by Visser et al, (2007), that the amount of non-condensable gases in the CO_2 stream should not exceed 4% by volume. This figure is understood to reflect an optimum balance between gas conditioning costs and the costs of compression.

In terms of the potential for impurities to induce changes in the porosity and injectivity of a storage site, the formation of acids from compounds such as SO_X, NO_x and H_2S are well understood. Moreover, work by Knauss et al., (2005), Xu et al., (2007) and Koenen et al., (2010) provide initial quantitative insights into the magnitude of porosity changes given different amounts of impurities. Further research should be targeted towards understanding the kinetics of diffusion and chemical reactions to assess if impurities may accumulate at the injection zone, and whether impurities may alter the integrity of the caprock and well cement (Koenen et al., 2010).

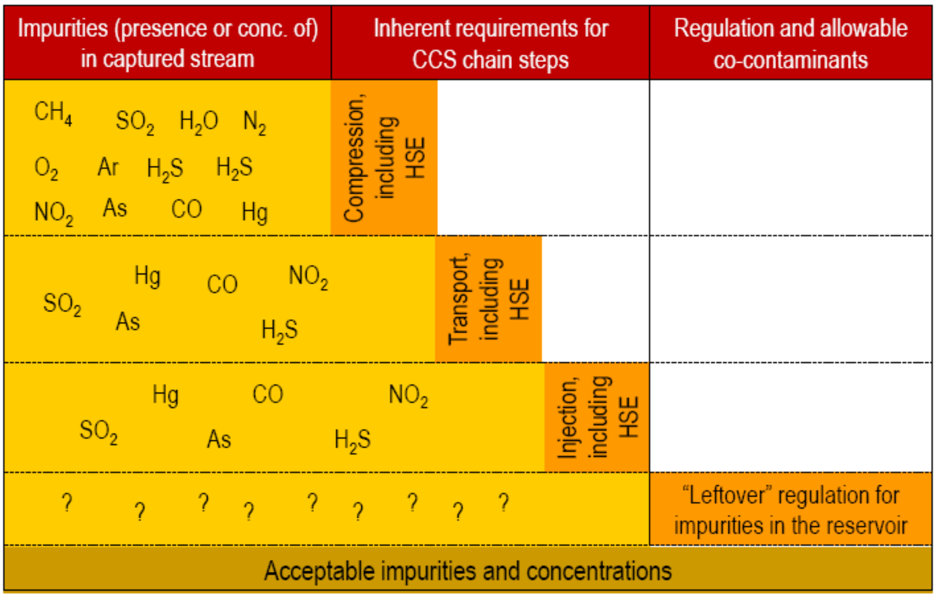

Figure 4.1 ***A conceptual diagram of possible CO_2 stream requirements at different stages of the CCS chain. It also illustrates the uncertainties around the impacts of impurities in the geological storage reservoir[13].***

As an extension of this report, it may be useful to question whether the development of storage specific legislation with regards to the possible impacts of impurities is necessary. As depicted in the conceptual diagram above, any CO_2 quality specifications for storage will be downstream from other purity requirements at different stages of the CCS chain such as compression and transport, as well as health and safety thresholds. One possibility is that upstream purity requirements render the development additional storage specific stream specifications as unnecessary.

In 2015, the European Commission shall review the Directive on the geological storage of CO_2, including an assessment of the provision on CO_2 stream acceptance and procedure referred to in Article 12 of the Directive. It is recommended that research on the behaviour of impurities in geological formations continues in order to provide further scientific findings to assist in the review process.

[13] Please note that this is a illustrative diagram and the presence of certain impurities may not be accurate for certain capture processes.

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