CO_2 QUALITY REQUIREMENT FOR A SYSTEM WITH CO_2 CAPTURE, TRANSPORT AND STORAGE

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Abstract

An important but not very well studied aspect in the analysis of a system with CO_2 capture-transport and storage is the quality requirements put on the captured CO_2, i.e. the concentration limits for the non-CO_2 components present in the stream sent to the storage site. This aspect could be seen as both an opportunity and a risk and could have a direct influence of the cost of CO_2 capture and storage:

- An opportunity to co-capture other main pollutants from power plant operations such as SO_x and store them together with the CO_2. Thereby, a concept with near zero emissions could be created and in addition costly and energy-demanding flue gas cleaning equipment could be excluded.
- A risk that components other than CO_2 in the captured stream could have a negative effect on the transport and storage system, both from a technical and environmental and health point of view, and therefore need to be removed. Stringent requirements are however likely to induce high costs for cleaning of CO_2.

A discussion on CO_2 purity/specification is presented for the CO_2 capture transport and storage system. A list of potential impurities in the captured CO_2 stream is provided for considerations to bring forward a practical CO_2 specification which could be used as a guideline for CO_2 capture, transport and storage, and acceptable for environmental regulations.

The results from this initial investigation show that further investigations of the CO_2 specification especially from transport, storage and environmental points of view is needed in order to understand the impacts and limitations of various impurities on different procedures of CO_2 capture and storage.

Introduction

The aim of CO_2 capture is to reduce the emissions of CO_2 and other pollutants from fossil fuel fired power plants. In order to achieve this aim, the capture process should provide a concentrated CO_2 stream for further transport and storage. The quality of the captured CO_2 stream technically depends on the fuel used, approaches used for the combustion and the capture process. The CO_2 quality requirements are defined by the limitations set by CO_2 transport, storage, safety and environmental regulations and the cost. There are generally no strong technical barriers to provide high purity of CO_2 from the flue gas of fossil fuel fired power plants, however high purity requirements are likely to induce additional costs and energy requirements resulting in a loss of power plant efficiency. It has been estimated in studies carried out by Vattenfall that a COE cost reduction of almost 10% could be achieved if the sulphur removal is left out of the oxyfuel process and SO_2 is co-captured with the CO_2. A study by IEA GHG found that the overall capture cost could be reduced by about 20% if H_2S is left in the captured CO_2 stream (IEA GHG, 2003).

It appears that not very much attention has been given to the topic of CO2 quality requirements, and above all, very few have tried to look at the entire chain and systematically investigate what the real requirements are from a CO_2 capture and storage perspective. The CO_2 specifications of relevance that exist today, are related to Enhanced Oil Recovery (EOR) projects, where the main objective is to increase the oil recovery from old oil fields through injection of CO_2. These existing specifications mainly appear to be related to concerns associated with transport of CO_2 and the effects on the oil extraction process (miscibility with oil). In addition, the present knowledge and experience in this field are mainly based on CO_2 that has been extracted from natural sources, with a slightly different composition than in the case where CO_2 is captured from a power plant. A systematic analysis of the requirements is therefore needed, taking into account both the components present, the concentration levels and possible effects from interactions between the different components. Therefore, it was decided at Vattenfall to go through with a systematic approach to:

1) Evaluate possible components present in the captured CO_2 stream and their approximate concentration levels when applying a minimum level of gas purification equipment in the power plant with CO_2 capture (a “worst case” scenario). The capture options assumed where post combustion capture with MEA absorption, IGCC with pre-combustion capture and oxyfuel (or O_2/CO_2 recycle) combustion applied to the utilization of a German lignite coal. Later, two additional cases with sulphur removal to “conventional” levels were added to the pre-combustion IGCC case and the oxyfuel case.

2) Summarize the present knowledge of what components could be of concern and for what reason, and when possible, identify a maximum acceptable concentration level. This analysis was performed for CO_2 compression, pipeline transport in supercritical phase or ship transport in liquid phase, storage in a deep laying saline aquifer or CO_2 storage in oil fields combined with EOR operation. Aspects related to environmental and health, as well as legal aspects related to the classification of the CO_2 was investigated.

Results

CO_2 capture process

The results from the capture process evaluation are presented in the left part of Table 1. The concentration of the components from the capture process is estimated based on calculations at a boundary which is defined by the stage in CO_2 compression just before liquefaction, that involves a maximum water removal by condensation through intercooling between the compression stages, but without non-condensable gas separation. In general, the composition and concentration of impurities in the captured CO_2 stream depend on fuel composition; combustion approach and CO_2 capture process. For some CO_2 capture processes, pre-treatment of flue gas may be required before the capture process. There is less dependence on fuel composition for post-combustion capture using the MEA process and for IGCC capture using the Selexol process. The H_2S level in IGCC capture is affected by the sulphur content of the fuel in the case of co-capture. Compared with post-combustion and IGCC, relatively high levels of impurities are expected in the captured CO_2 stream from oxyfuel combustion. On the other hand, a more complicated composition is generally found in the captured CO_2 stream from IGCC, in which there are many organic impurities such as various hydrocarbons and mercaptans.

Based on the physiochemical properties of the identified impurities, the components could be categorized into groups, see Table 1. These groups should be used for easy evaluation of the purification technologies and the concerns from compression, transport, storage, and environmental aspects for a given impurity component. The non-condensable gases could be removed through phase separation/distillation. Most of the water-soluble components should be removed through wet scrubbing processes and may only be a concern for some materials that are very sensitive to very low concentrations of these components. Some of the identified components are present in low concentrations, it may be commented whether these components should seriously be concerned, as their background concentrations in geological and environmental surroundings are likely to be much higher.

CO_2 compression

Main concerns related to the CO_2 compression train are operation in 2-phase flow, change in gas properties that might affect the efficiency of the compression process and conditions for phase transitions, hydrate formation and costs (corrosion). It is important to have an efficient dust and water droplet removal system before the compressors to avoid problems related to depositions on compressor blades, erosion, and corrosion.

CO_2 transport in pipeline and ship

Important for the transport conditions are the physical properties of CO_2. We can identify two technically different cases:

- Pipeline. In this case the CO_2 transport condition chosen is high pressure in the range of 10-15 MPa, a pressure well above the critical point. At ambient temperatures, the CO_2 here is in supercritical phase, or as dense phase liquid with similar behaviour, where it is liquid-like and can be pumped as a liquid but still is compressible and fills the room like a gas.
- Water carriers. Today, CO_2 is transported in moderate amounts by ship. In these, the CO_2 is transported in the liquid state to keep the pressure lower. Plans are discussed on new, larger CO_2 ships, 20 000 tonnes or more. If larger vessels and thus larger tanks are desired, a consequence is a wish to decrease the pressure further, which in turn will need a further decreased temperature, down to about –50°C.

Major identified factors of concern, with possible impact or to be avoided, for CO_2 transportation where other components may occur in the CO_2 stream, are summarized as follows:

- Water content
- Hydrate formation. CO_2, H_2S and CH_4 can form hydrates in presence of free water
- Corrosion. Existing CO_2 pipelines are made of carbon steel. CO_2 as well as other acidic components (e.g. SO_2, H_2S) form corrosive acids together with liquid water.
- Two-phase flow. If CO_2 is mixed with components with different physical properties, e.g. Ar, O_2, H_2, H_2S.
- Toxic components, in case of leakage

The different pattern of components from the three capture processes will have different pattern of impact on the transport part of the chain. Generally, the water content is a most important factor to keep controlled and at a low level, for a CO_2 transport system. If the supercritical/dense phase fluid CO_2 stream in pipeline transport is dry enough, the CO_2 itself as well as several other components cannot create corrosive acids. Pipeline transports are expected to be somewhat more tolerant to some degree of unwanted components, than the ship transport (tank transport) will be. The major identified difference in the ship case is the risk at low temperatures for hydrate formation between water content and CO_2, H_2S or methane.

CO_2 Storage in deep laying saline aquifers and depleted oil fields

Storing CO_2 together with other compounds has been investigated considering the possible impact on the storage reservoir, the cap rock, the injection facilities, and the use of CO_2 for Enhanced Oil Recovery (EOR), Table 1. The possibility of a leakage and geochemical reactions interfering with the injection of the captured gas stream are the main risks associated with geological storage. The leakage may be the result of a defect cap rock or poorly sealed well. Geochemical reactions between the gas stream components and the minerals and water present in the aquifer can cause problems during the operational phase, such as reduced permeability, increased pore pressures, corrosion and hydrate formation (in the injection facilities). The amount of chemical reactions that will occur in the aquifer will to a large extent depend on the specific composition of the storage rocks and conditions in the water such as redox potential, pH, buffering capacity etc..

Components in the gas stream that have been identified as critical for the storage process are H_2O, SO_2, NO, CO_2, H_2S, O_2, CH_4, HCN, Ar, N_2, H_2 and particulates. CO_2, SO_2, NO and H_2S are acid-forming compounds that may form corrosive acids in the presence of water. H_2O, H_2S and CH_4 are hydrate-forming compounds. Oxygen present in the gas stream may lead to changed redox conditions in the reservoir, which can cause precipitation reactions and reduce the permeability. Oxygen present can further, in the case of EOR, react exothermally with oil and cause overheating at the injection point. Particulates are critical to the reservoir since they can block pores near the injection well and reduce the permeability. When using the gas stream for EOR, it will also be important to look at the total concentration of components immiscible with oil (CH_4, Ar, N_2 and H_2). Toxic compounds, such as H_2S, COS, CO, SO_2 and NO_x are of concern for the EOR case as they are reproduced together with the oil at the pumping well when there is a break through of the CO_2 front. Sulphur components will also increase the sulphur content of the oil, which is a concern in cases when the raw oil has very low sulphur content.

Effects on environment and health

Components in the injected stream that need to be considered from an environmental point of view are CO_2, SO_2, H_2S, NO, and CO, since the concentrations of these compounds in some or all of the investigated cases, see Table 1, exceed occupational limit values and environmental quality standards. The limits and standards apply to a release to air and the components identified would add to the safety precautions already needed for transport and storage of pure CO_2. The injected gas might also contain a low concentration of mercury. The environmental benefits and risks of co-storing Hg and CO_2 could be argued.

Legal aspects

The legal implications associated with CO_2 purity levels are mainly related to safety requirements for workers, the public and the environment and the classification of CO_2 as waste and potentially hazardous waste. An assessment has been made if the CO_2 would be classified as hazardous waste according to today's EU regulation based on the estimated concentration levels in the CO_2 stream as given in Table 1. The regulation and classification of hazardous waste can be found in the directive on hazardous waste, (91/689/EEG). Because the CO_2 stream is not identified in the waste catalogue, the evaluation of the components has been made on the basis of available information on the substances as such, their levels as indicated and the properties listed in Annex III of the hazardous waste directive together with limit values in the waste catalogue and other provisions of the hazardous waste directive. The conclusion of this analysis is that CO_2 with the non-CO_2 component levels in Table 1 will not be regarded as hazardous waste according to the hazardous waste directive. However, as stated earlier, other restrictions could be placed upon the handling of the CO_2 stream from other perspectives, such as workers, the public and the environment.

Conclussions

CO_2 capture and compression

Excessively strict requirements on CO_2 quality should be avoided to reduce costs of CO_2 capture. From an engineering point of view, it would be fruitful to scan purification and dehydration technologies from an industrial and economic point of view, in order to find cost effective methods that may reach certain technical requirements well within reasonable economic limits. If this is found to be the case for dehydration, effective dehydration could be a key factor that could make restrictions on other chemical components less strict.

Some knowledge gaps related to CO_2 quality have been identified from capture point of view. Compared with CO_2 capture from post-combustion, there are more knowledge gaps on CO_2 capture from oxyfuel combustion and IGCC. A summary for the knowledge gaps is given as follows:

- The properties of CO_2 in a multi-component system especially under transition and supercritical conditions, need to be investigated in order to provide necessary data for the design and operation;
- The properties of non-condensable components in the captured CO_2 streams including conditions causing two-phase flow, the solubility in the CO_2 stream, and the selectivity during non-condensable separation;
- Detailed knowledge related to CO_2 purification processes with both high selectivity for impurities and high CO_2 recovery based on commercially available technologies;
- Practical operating data and experiences from large-scale gas processing systems applied for the CO_2 capture cases that are investigated in this study;
- Corrosion behaviour of the CO_2 stream under various operating conditions in order to provide a guideline for the materials used for the components of the gas processing systems

CO_2 transport by pipeline and ship

A conclusion is that technically and economically efficient, industrial methods to avoid the water content should be searched, as well as or alternatively methods to use inhibitors that can eliminate the effect of the water content, such as corrosion etc. In parallel, more knowledge is needed on which water levels that are true limits, and not only available practice for present, especially for the ship transport case.

If capture will be made from a source where ship transport is a logistic option or a necessity, the conditions (temperature, pressure) at transport may be added to the factors of concern when choosing method for capture. The stream from the post-combustion process seems unproblematic in this aspect, but a preliminary conclusion is that the streams from primarily the IGCC process and secondly the oxyfuel process may be inferior alternatives in combination with ship transport; but at this moment the judgment is made without respect to total energy efficiency or total economy in the full chain. The picture may change if cleaning technologies are cheaper than the cost difference in capture technologies. In further studies, co-capture aspects of SO_2 and/or H_2S should be investigated more.

Storage

Before commencing a CO_2 storage operation with injection of impure CO_2 streams, several gaps in knowledge have to be addressed. This can be done through studies of analogue activities, computer modeling and practical simulations. However, it is very important to take into account the local conditions such as rock and water composition in the case of aquifer storage. Limit values for the possible components in the CO_2 gas stream have to be established for the case of saline aquifer storage, especially limits relating to the storage reservoir itself and to cap rock integrity. Limit values for the injection facilities are available for some components.

Environment and health aspects

At present, little is known about the risks of a leakage out of the reservoir and through the ground surface. The leakage rate and the concentration of different compounds released are also unknown. A dispersion model can be used to calculate the concentrations at different distances from the release point for different initial leakage concentrations. Concentrations for releases along a line can also be calculated in the dispersion model, which may be used to model diffuse leakages. A risk analysis and dispersion modeling of potential leakages will be required from authorities in order to get a permit for storing CO_2 and other components in the injected gas. Dispersion models are established and available but models for risk analyses and risk assessments need to be developed. The effects of a leakage to soil, groundwater and surface water must also be considered when evaluating the effects on ecosystems and human health. Research and modelling on the basis of local conditions must be undertaken in order to fill this knowledge gap. The potential long-term ecosystem impacts due to thousands of years of releases of the different injected gas components, relating to a slow leakage from the storage aquifer, must also be investigated.

Legal aspects

The analysis presented indicates that the CO_2 stream with the given concentration of components most likely will not be considered hazardous waste. If it would be considered hazardous waste, this would not as such render underground storage impossible, but there would most certainly be an acceptance problem. Member States of the EU are also allowed to introduce and maintain more stringent rules concerning the handling of waste, and it is therefore important to investigate the waste rules of each individual state where CO_2 is to be stored. Aspects related to storing CO_2 from different sources and with different levels of non-CO_2 components need also to be further considered.

References

1. IEA GHG, 2003, “Potential for improvements in Gasification Combined Cycle Power Generation with CO2 Capture” Report PH4/19 IEA GHG, Cheltenham, UK

Table 1 Critical components present in the CO_2 based on the components and concentrations as given by the CO_2 capture options in the left part of the table. The concentration of the components from the capture process is estimated at the boundary condition which is defined by the stage of CO2 compression before liquefaction, removal of non-condensable components and dehydration, with a maximum water removal by condensation through intercooling during the compression.
NA – not available = knowledge gap; C - critical; NC – not expected to be critical

			Capture from														
			Oxyfuel		Post-combustion	IGCC		CO_2 Compression train	Transport		Storage				Environment, health		Hazardous waste
Case			CO_2/SO_2	CO_2+SO_2	MEA absorption	CO_2/H_2S	CO_2+H_2S		Pipeline	Ship	Ability to move oil ("EOR")	Injection equipment	Cap rock	reservoir	Risk transport	Risk storage	
Component	Type*	Unit	Concentration														
H_2O	1	vol%	0.14	0.14	0.14	0.14	0.14	C[a,c]	C[a, c]	C[a,c]	NC	C[a,c]	NC	NC	NC	NC	NC
CO_2	2	vol%	91	90	99.8	97.8	95.6										
SO_2	2	vol%	0.076	1.5	0.001	-	-	C[c]	NA	NA	NC**	C[a]	C[a]	C[a]	C[k]	C[i,k]	NC
NO	2? 3	vol%	0.25	0.24	0.002	unknown	unknown	NA	NA	NA	NC	C[a]	C[a]	C[a]	C[k]	C[i, l]	NC
H_2S	2	vol%	-	-	-	0.01	2.3	NA	C[c,k]/NC[o]	C[c,k]	NC**	C[a,c]	NC	NC	C[k]	C[i,k]	NC
HCl	2, W	ppmv	Trace	Trace	Trace	Trace	Trace	NC	NC	NC	NC	NC	NC	NC	NC	NC	NA
HF	2, W	ppmv	Trace	Trace	Trace	Trace	Trace	NC	NC	NC	NC	NC	NC	NC	NC	NC	NA
CO	2? 3?	ppmv	unknown	unknown	10	1700	1700	NA	NA	C [b]	NC	NC	NC	NC	C[k]	NC	NC
Ar	3	vol%	5.7	5.6	0.021	0.050	0.049	C[b]	C[b,r]	C[b,r]	C[d]	NC	NC	NC	NC	NC	NC
O_2	3	vol%	1.6	1.6	0.003	unknown	unknown	C[a,b]	C[a,b]	C[a,b]	C[p]	NC	C[e]	C[e]	NC	NC	NC
N_2	3	vol%	0.61	0.60	0.021	0.030	0.030	C[b]	NC	C[b]	C[d]	NC	NC	NC	NC	C[l]	NC
H_2	3	vol%	-	-	-	1.7	1.7	C[b]	C[b]	C[b]	C[d]	NC	NC	NC	NC	NC	NC
CH_4	3, 4	ppmv	-	-	-	350	350	C[c]	C[c]	C[b,c]	C[d]	C[c]	NC	NC	NC	NC	NC
Hydrocarbons	4	ppmv	-	-	30	unknown	unknown	NA	NC	NC	NA	NC	NC	NC	NA	NA	NA
HCN	4	ppmv	Trace	Trace	-	< 5	< 5	NC	NA	NA	NA	C[a]	NC	NC	C[k]	NC	NC
COS	4	ppmv	-	-	-	< 5	< 5	NC	NC	NA	NA	NA	NA	NA	NC	NC	NC
Mercaptanes	4	ppmv	-	-	-	220	220	NA	C[k, s]	C[k, s]	NA	NA	NA	NA	C[k,s]	C[k,s]	NC?
NH_3	5, W	ppmv	Trace	Trace	unknown	30	30	NC	NA	NA	NC	NC	NC	NC	NC	NC	NC
Hg	6	ppmv	Trace	Trace	Trace	Trace	Trace	NC	NC	NC	NC	NC	NC	NC	NC	C[k]	NA
Metals	6	ppm	Trace	Trace	Trace	Trace	Trace	NC	NC	NC	NC	NC	NC	NC	NC	NC	NA
Particulates	7	ppm	< 1	< 1	< 1	< 1	< 1	NC	NC	NC	NC	NC	NC	C[f]	NC	NC	NA
MEA	8, 4	ppm	-	-	unknown	-	-	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Selexol	8, 4	ppm	-	-	-	unknown	unknown	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA

Notations used in Table 1:
[a] - corrosion; [b] - two-phase flow and/or changes of properties; [c] – hydrate formation, dependent of water content; [d] – decreased miscibility; [e] - changed redox conditions; [f] - decreased permeability; [g] – asphyxiant; [h] – greenhouse gas; [i] – acidification; [k] – toxic; [l] – nutrient (eutrophication); [m] – flammable / explosive; [n] – ozon depletion, [o] – technically acceptable to at least 1 vol%; [p] - reacts with oil; [r] – volume efficiency; [s] – strong odour

*According to the physicochemical properties, the identified components could be categorized into following groups:
Group 1 - water; Group 2 - acidic components; Group 3 - non-condensable components; Group 4 - organic components; Group 5 - alkaline components; Group 6 - heavy metals; Group 7 - solid components; Group 8 - solvents and reagents; and Group W - water-soluble components.

** The components affect the purity of the extracted oil product

Afterword

As Europe's 5th largest energy company, Vattenfall has taken the strategic decision to play a leading role in the development of emission-free fossil-fuel based power generation and has started the project "Carbon-Dioxide Free Power Plant". The project deals with CO_2 capture, transport and storage, with main focus on lignite-fired power plants. The aim is to develop a commercially viable concept until 2015. Furthermore, Vattenfall is taking part in the development of CO_2 capture technologies as the coordinator of the EU Framework 6 project ENCAP (ENhanced CAPture of CO_2). Vattenfall is also a partner in the EU-projects CO2STORE and CASTOR.