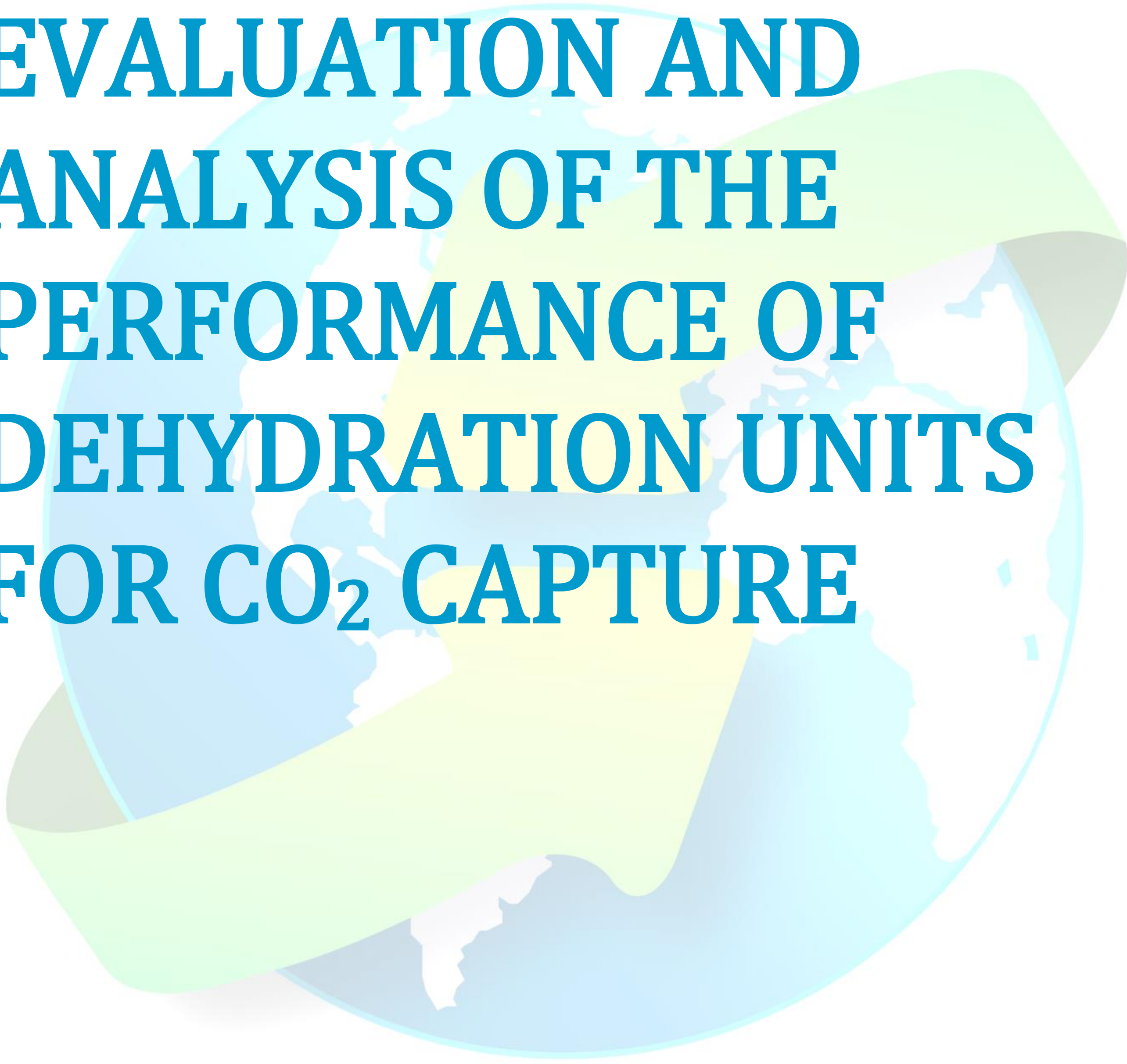

EVALUATION AND ANALYSIS OF THE PERFORMANCE OF DEHYDRATION UNITS FOR CO_2 CAPTURE

Report: 2014/04
April 2014

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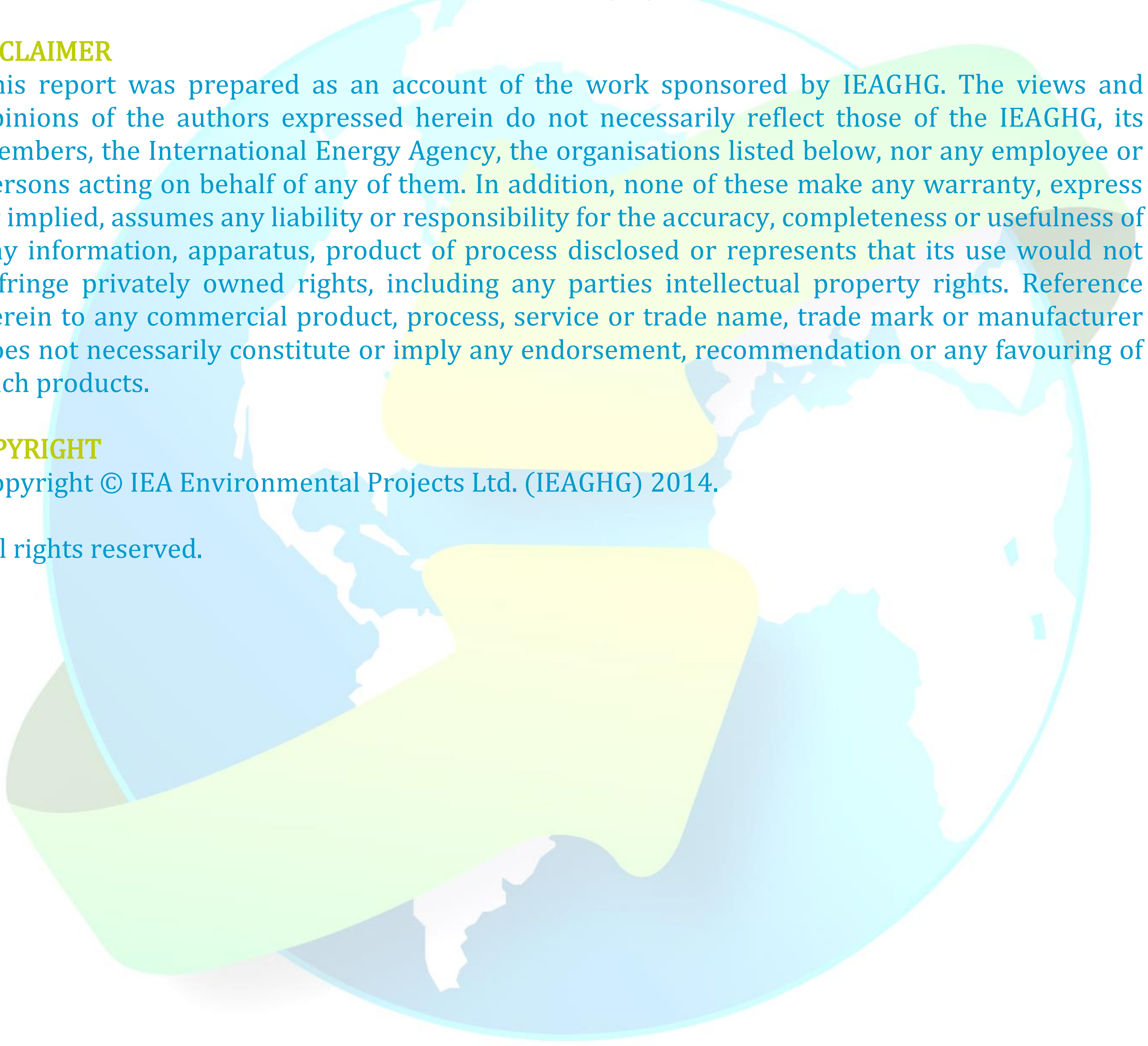

ACKNOWLEDGEMENTS AND CITATIONS

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EVALUATION AND ANALYSIS OF THE PERFORMANCE OF DEHYDRATION UNITS FOR CO_2 CAPTURE

Key Messages

- A number of suitable technologies for CO_2 dehydration exist. This study focusses on a comparison of molecular sieve and triethylene glycol (TEG) systems.
- Consideration of multiple dehydration technologies in series can be beneficial, e.g. a more basic technique can offload the main dehydration unit resulting in cost reduction.
- It is possible to protect dehydration systems that are sensitive towards certain impurities against degradation by using guard beds or additional upstream treatment.
- The minimum CAPEX and OPEX for both molecular sieve and TEG systems depend mainly on operating pressure and type of regeneration.
- In case of high inerts, the CAPEX will increase for both molecular sieve and TEG systems.
- Presence of NO_x, SO_x and H_2S leads to a 7% higher CAPEX but no significant difference in OPEX for molecular sieve systems. Currently, it is not possible to evaluate the effect of impurities on the costs of TEG systems.
- Due to lack of vendor support, the information on costs and operation is somewhat preliminary, fragmentary and uncertain. Re-engagement of vendors will be a priority for future projects and studies.

Background to the Study

The dehydration step is a small part within the full CO_2 capture and storage chain yet this unit plays an important role in maintaining the integrity of the system. In the past, this step usually appeared as a black box process, with little information available on its detailed design. However, the conventional drying technologies face a number of challenges that need consideration before full-scale deployment. These include, for example, the effect of impurities in the captured CO_2 stream on the dehydration process.

IEAGHG commissioned AMEC to carry out this study in order to examine the characteristics of the various drying processes and their integration into the CCS system.

Scope of Work

The scope of work for this study comprises four main elements:

1) Evaluation and characterisation of processes for the dehydration of captured CO_2
2) Preparation of guidance on the selection of processes to match the various requirements for water dryness of CO_2
3) Evaluation of methods for monitoring and management of water dryness
4) Analysis of future drying technology developments

AMEC used information available from the different capture processes to produce a set of dehydration feed gas compositions. Base case data represent the minimum and normal impurity levels. Water content of saturated gas depends on the temperature and pressure of the gas stream. Several test cases consider higher levels of impurities and inerts.

This study investigates three different moisture levels: 550 ppmv (typically used in pipeline systems that experience relatively high ambient temperatures), 50 ppmv and < 10 ppmv (typically required where downstream processing involves low temperature or cryogenic conditions).

AMEC considered two different CO_2 flow rates: 2 million te/year (typical amount of CO_2 captured from a 1 GW_e gas-fired power plant with at least 85% capture rate), and 4.5 million te/year (typical mass flow for a 1 GW_e coal-fired power plant with at least 85% capture rate).

The contractor asked the vendors to provide economic and technical data, including the maximum rate achievable for a single dehydration train.

Findings of the Study

Background issues

Due to the lack of vendor engagement, many of the conclusions presented are of a preliminary nature. This is why re-engagement of the package vendors is important for future activities.

Dehydration media vendors assisted with estimates of the number of beds and bed size. They were also able to help with information on the effects of impurities on the molecular sieve adsorbent and the role of side reactions.

Important background issues relevant to the full CCS chain are the following:

- The presence of inerts and impurities can lead to significant changes in the CO_2 physical properties. In addition, impurities can affect the desiccant and lead to higher rates of corrosion. These changes need further understanding and quantification.
- The adequate modelling of physical properties of CO_2 containing inerts and impurities requires new or modified equations of state.
- Water ice, hydrates or liquid CO_2 can form, when cooling wet CO_2 gas below certain limits of pressure and temperature. Figure 1 shows the crossover region of hydrate, water ice and liquid CO_2 formation for selected temperature and pressure conditions.

- There is a wide range in dry CO_2 moisture specifications used for pipelines in the literature. These specifications influence the selection of the appropriate dehydration technique.

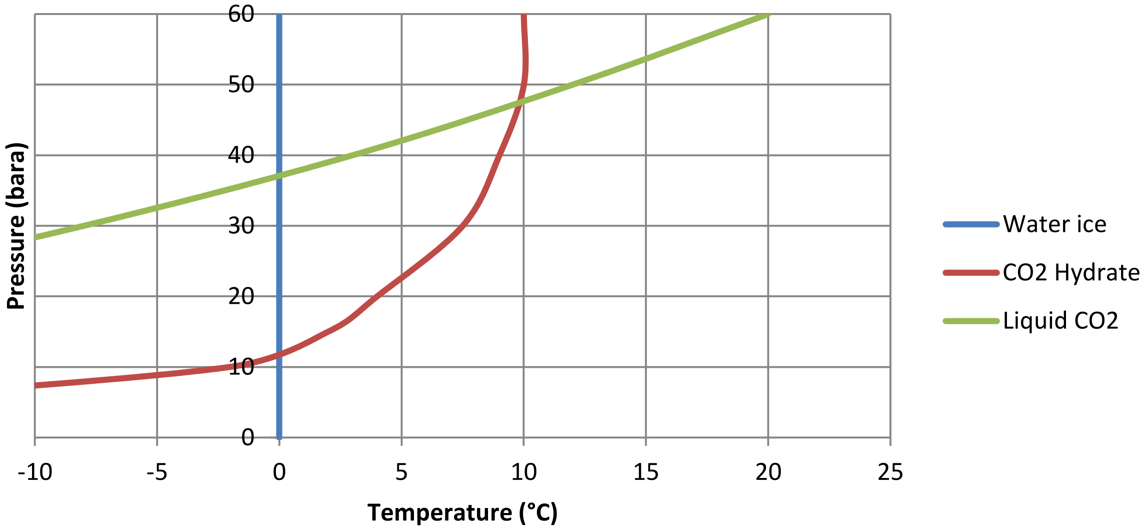

Figure 1 - Combined hydrate/water ice/liquid CO_2 plot

In the case of solid desiccant systems, the following approaches are helpful for dealing with impurities:

- Additional amounts of desiccant can cater for the effects of impurities
- Use of an acid resistant desiccant, which can better withstand the impurities
- Applying guard beds (e.g. activated alumina or silica gel that can tolerate acidic impurities)

In the case of liquid desiccants, impurities can form solids, cause foaming or react with the desiccant to build corrosive products. The below mentioned measurements can assist with addressing these issues:

- In-line filtration
- High-efficiency column internals
- Anti-foam
- Degradation/corrosion inhibitors

It is important to know and consider the specific impurities and their normal and maximum concentrations during design. Sometimes the levels of impurities are not acceptable, because of either their damaging effects or the increase in necessary dehydration media volume. In this case, removal of the impurities in a separate upstream process is an option.

Some of the dehydration techniques do not achieve low moisture levels, however they are straightforward, low cost processes, often required in a process anyway (such as compressor inter-stage cooling and knockout). This could offload the main dehydration unit, resulting in smaller, less costly dehydration systems.

Most of the liquid and solid desiccant systems investigated in this study are applicable for use with gaseous CO_2. The different processes and desiccants can achieve orders of magnitude different product moisture contents. Basic liquid desiccant systems can achieve 150 ppmv; enhanced liquid desiccant systems 30 ppmv. Solid desiccant systems can reach lower levels. Activated alumina and silica gel can get down to < 10 ppmv while molecular sieves can achieve 0.1 ppmv.

Technologies

The CO_2 streams produced by the various combustion and capture processes are of different quality, containing different types and concentrations of inerts and impurities. The list below explains the differences between the various CO_2 capture processes, which are relevant to dehydration:

- Post combustion capture delivers a water-saturated CO_2 rich gas from the stripper condenser at pressures just above atmospheric.
- Pre-combustion capture provides multi-stream CO_2 gases from the AGR unit at low pressure and medium pressure conditions.
    - The Rectisol process delivers dry CO_2 gas at < 1 ppmv moisture containing small levels of methanol. The gas does not require further drying and the methanol content will usually not condense out in the subsequent compression and/or cooling process.
    - The Selexol solution contains water, so the process supplies a water-saturated CO_2 gas. Selexol has a low vapour pressure so there is minimal contamination of the dry CO_2 stream. UOP advise that lower water levels of around 500 – 1000 ppmv are achievable, but only at pressures in excess of 10 barg with a purity of less than 98%.
- CO_2 rich gas from oxyfuel combustion will have a wide variation of composition and pressure dependent on the technology selected for the CO_2 processing unit (CPU). The gas entering the dehydration unit is water-saturated and contains inerts and other trace amounts of acidic components – mostly the residual NO_x from the selected NO_x-SO_x removal process upstream.

For post-combustion and pre-combustion capture, a variety of different dehydration pressures is possible. This depends on the available supply pressure and compressor interstage conditions. Oxyfuel cases span a range of pressures from 5 to 30 bara, dependent on the supply pressure and downstream processing requirements.

Information from both package vendors and media vendors centred around two basic process mediums: TEG and molecular sieves. Because of this, the study focusses on a discussion of these two media.

Selection of acid resistant molecular sieves (type 3A or 4A) is favourable for CO_2 streams with high levels of impurities (typically NO_x, SO_x and H_2S). The quantity of desiccant required is a function of the selected adsorption time, the number of beds in parallel and any margin added due to the presence of impurities. Low-pressure operation will require larger diameter beds and larger bed volumes to cater for the higher volume of gas and the increase in moisture content.

Media life of both molecular sieve and TEG varies between 2 and 4 years, typical are 3 years.

The maximum train size appears to vary considerably. For molecular sieve cases with feed gas at 30 bara and 30°C the range (from different vendors) varied between 300 and 600 te/hr. The limitations depend on several factors including the maximum vessel diameter, the capital cost of the vessel, the maximum number of beds of a certain size in parallel, the adsorption time of each bed and the regeneration rate. It is desirable to keep the bed size small to avoid the requirement for large volumes of desiccant and associated vessels. At a certain point, it is more practical to split the feed across an additional number of trains. Bed adsorption times of less than 6 hours are generally unattractive.

Preliminary estimates show that a TEG regeneration unit can handle the moisture of up to 3,500 te/hr of CO_2 rich gas, although this quantity would perhaps require multiple contactors.

Future expansion of capacity is possible for both molecular sieve and TEG systems if the original design allows for additional beds.

Costs

Data presented in this section is a combination of data received from different vendors (as part of this study), data from previous AMEC projects and AMEC modelling and cost estimation. The figures show the cost numbers as uninstalled equipment costs and in the form of cost indicators. A cost indicator of “1” represents the baseline. In general, the capital costs of dehydration equipment are a minor part of the overall costs for a CCS plant.

There is a wide spread in molecular sieve capital cost data from different vendors for a fixed operating pressure. Figure 2 plots the cost indicator against CO_2 flow rate and shows the maximum and minimum cost lines. The differences are due to several factors:

- The regeneration techniques proposed by different vendors. Atmospheric pressure regeneration with air will be less costly. The amount of equipment required is significantly lower than for a high-pressure regeneration using CO_2. The volume of CO_2 gas passing through the online bed is also lower, so smaller bed size results.
- Use of the CO_2 compression facility to provide the driving force for the regeneration gas results in less equipment for the dehydration package but larger compression and cooling equipment and higher compression costs.
- The materials of construction proposed.
- The number and size of the individual adsorption beds proposed.
- The number of parallel dehydration trains proposed.

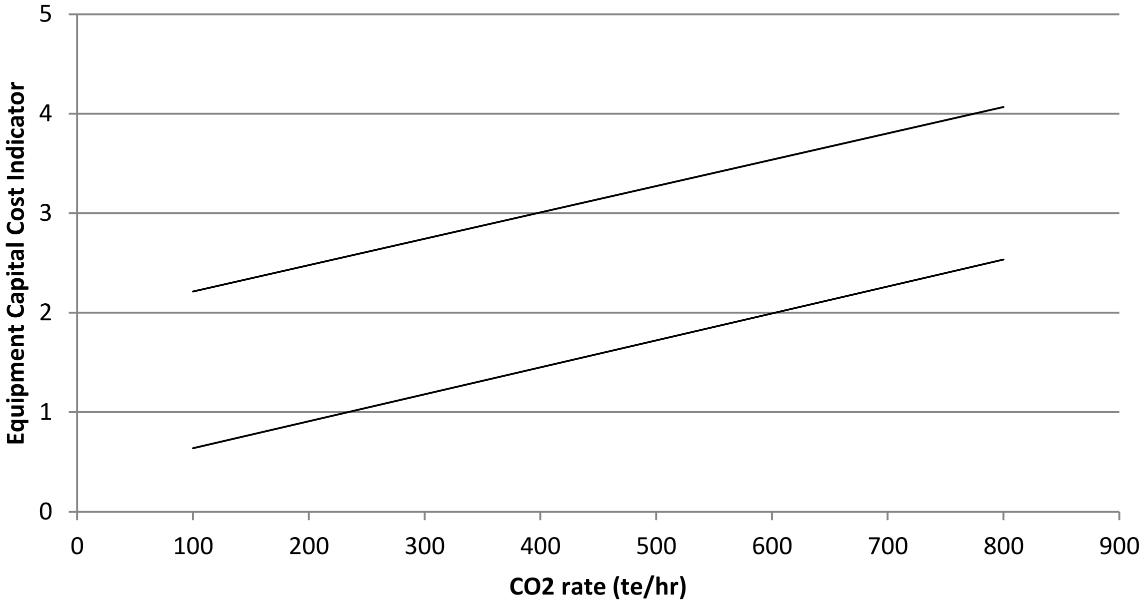

Figure 2 - CAPEX indicator for molecular sieve

Operating pressure has an effect on the equipment capital costs of molecular sieve systems. Limited available data indicates that equipment capital cost passes through a minimum. Figure 3 illustrates the qualitative relationship between the capital cost and the operating pressure for a molecular sieve system with a minimum at 25 – 30 bara. The actual location of the minimum is application specific and depends on:

- The same reasons that cause differences in capital cost (see above).
- The equipment design pressure (whether it is set to be 10% above the maximum operating pressure or designed for compressor settle out pressure on compressor trip).
- The type of regeneration and the extent of regeneration equipment.

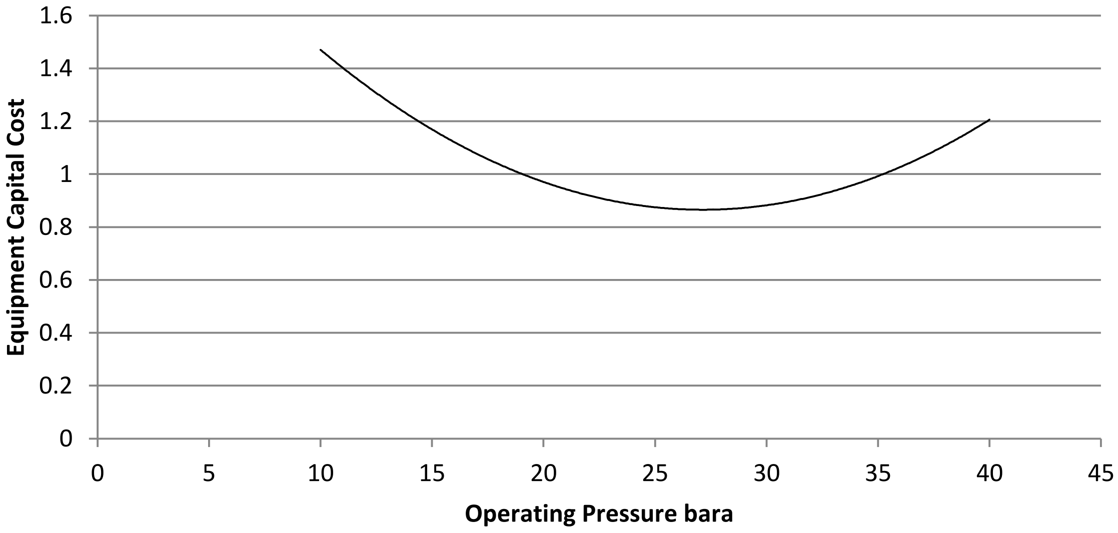

Figure 3 - CAPEX indicator for molecular sieve as function of operating pressure

There is no difference between the capital costs of the molecular sieve equipment for target moistures of 550 ppmv, 50 ppmv and < 10 ppmv. Media suppliers and package vendors all advised that it is normal to design for the removal of water from the gas stream to achieve < 1 ppmv, irrespective of the target moisture required. However, at lower target moisture, the cycle time of each bed becomes shorter.

Data on liquid desiccants, i.e. TEG, is lacking. The available data is for water-saturated raw gas at 30 bara and 30°C. The raw gas stream is relatively pure containing > 99% CO_2 with low levels of impurities. Target product moisture is 50 ppmv; the TEG process includes the use of stripping gas to increase the TEG concentration. Figure 4 shows the equipment capital cost indicator as a function of CO_2 flow rate. The line represents a maximum cost line.

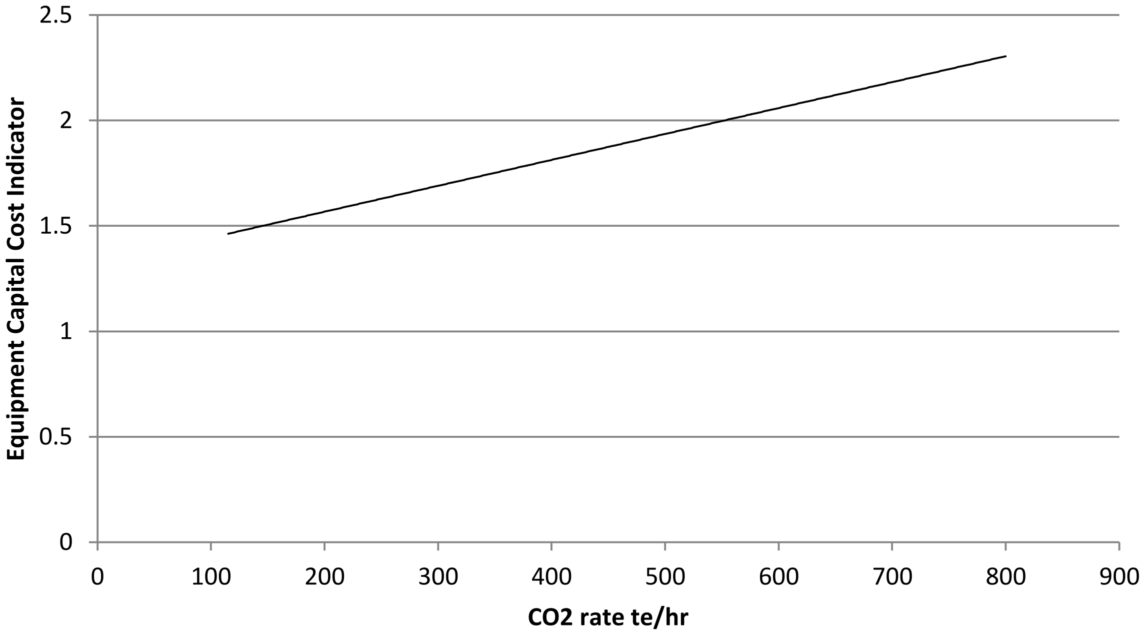

Figure 4 - CAPEX indicator for TEG

Higher levels of target product moisture (i.e. greater than 150 ppmv) will require only basic equipment; the stripper is not necessary. The cost for such a system will therefore be lower.

In case of high impurities:

- Increased oxygen levels have no effect on the molecular sieve equipment cost. However, oxygen can degrade TEG. It is not possible to evaluate the effect on TEG equipment capital cost because acceptable limits are unknown.
- The case with 100 ppmv NO_x, 100 ppmv SO_2 and 100 ppmv H_2S results in:
    - The use of an acid-resistant molecular sieve with an increase in media volume of ~ 5% and an increase in media cost of ~ 15%. Molecular sieve equipment capital cost will be ~ 7% higher.
    - Again, it is not possible to determine the effects on TEG equipment capital cost.

A clear recommendation is to discuss impurity issues with the vendor at an early stage, as an upstream removal might be advantageous or essential.

In case of high inerts content the cost of the equipment is higher per tonne of CO_2 present than for a low inerts gas. The reasons for this are:

- The increased volume of raw gas requires a larger diameter TEG contactor or larger diameter solid desiccant bed.
- The gas carries a higher amount of water. This extra amount of water needs removal. The circulation rate of TEG will therefore increase and the equipment in the TEG circulation loop will be larger. Similar, solid desiccant systems require larger media volumes to remove the increased amount of water.

Figure 5 presents the results of the operating cost estimation for the following cases:

- Molecular sieve at 265 te/hr – Options from two different vendors, one using low pressure regeneration with atmospheric air (minimum case) and another using CO_2 at pressure for regeneration (maximum case). Vendors advised to use a lifetime of 3 years for the molecular sieve.
- TEG at 265 te/hr – Only a single vendor has provided data. Lifetime of TEG desiccant can vary between 3 – 10 years, depending on the extent of impurities present. This study assumed a value of 3 years.

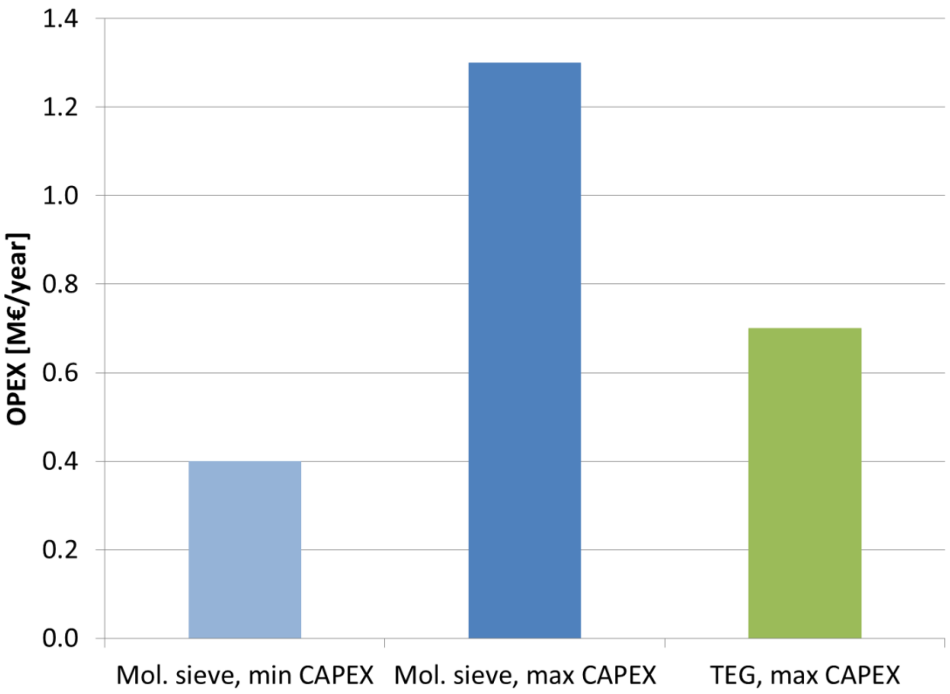

Figure 5 - OPEX estimates for different dehydration systems

Comparing data from the same vendor indicates that the TEG system annual operating cost is significantly lower than that for the molecular sieve package. However, the more basic molecular sieve package, from a different vendor, but for the same raw gas conditions, indicates that the annual operating costs can be significantly lower than those for a TEG system. Figure 6 shows estimated minimum operating costs for molecular sieve packages as a function of CO_2 flow rate.

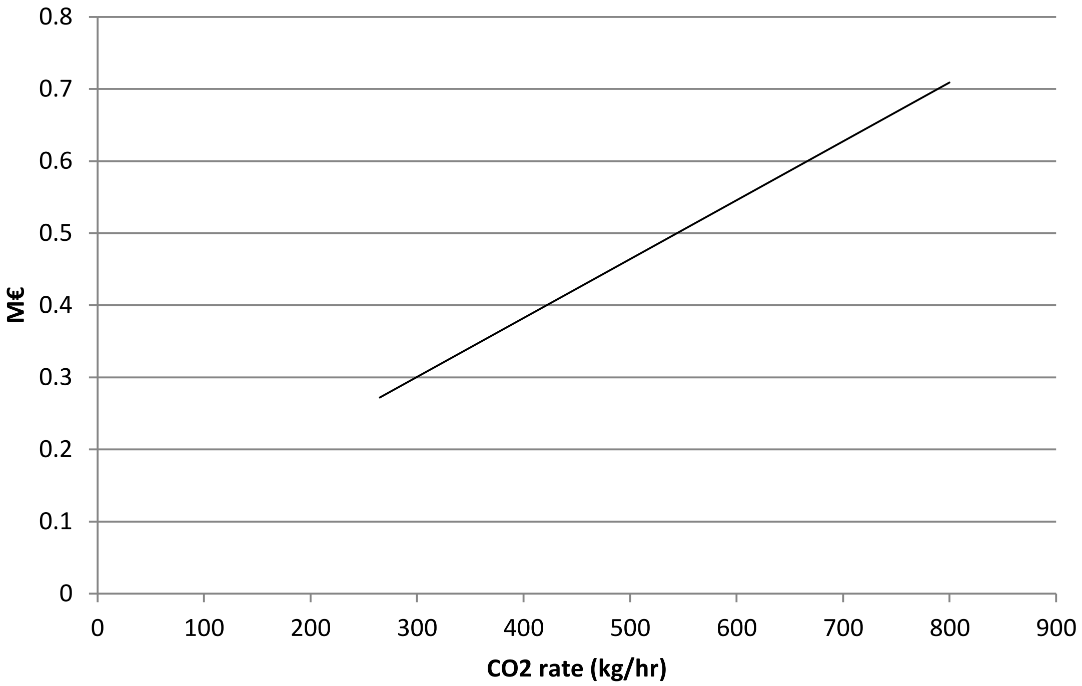

Figure 6 - OPEX for molecular sieve as function of CO_2 flow rate

The limited information available from vendors suggests that operating pressure has an effect on operating costs; the regeneration power consumption will pass through a minimum. The actual minimum pressure will vary for individual applications.

The vendor data also indicates that the effect of impurities on molecular sieve operating cost is insignificant. The increased bed volume results in higher capital cost, which impacts onto maintenance costs, taxes and insurance. Desiccant cost increases as well, but regeneration power consumption will be lower.

Selection

It is usually appropriate to consider combinations of different dehydration techniques to achieve the required target moisture content. Figure 7 illustrates the relative applicability ranges of the various dehydration technologies.

Under most circumstances, it is invariably cheaper to offload the final dehydration system by use of more basic techniques, if their application is feasible. In case of water-saturated, low-pressure gas it is beneficial to use the compression/cooling equipment (which is mandatory to reach the export conditions) to raise the pressure, knockout the condensed water and reduce the gas equilibrium moisture content as part of the normal compression process. This has the following effects:

- Minimisation of the moisture that enters the final dehydration package.
- Reduction of the actual volume of raw gas in the final dehydration plant, which results in smaller equipment.

The presence of certain impurities can physically damage molecular sieve desiccants. Installation of a short section of guard bed (containing silica gel or activated alumina) immediately above the molecular sieve bed can help avoiding deterioration. However, the guard bed will have a design life and once aging starts it will no longer offer protection to the molecular sieve.

Using multiple dehydration techniques in series is possible. For example, compression/cooling, followed by a TEG system, followed by molecular sieve polishing. The benefits of such systems depend on the individual process requirements. They can provide a higher level of product moisture integrity in the event of a malfunction. The extent of capital cost penalty is process specific.

In the event that a second molecular sieve dehydration train is necessary to process the gas, installing a TEG system upstream can offload the molecular sieve system. Smaller adsorber bed volumes and/or increased bed adsorption time will result.

For each specific application, a cost-benefit analysis is essential to determine the most cost effective option.

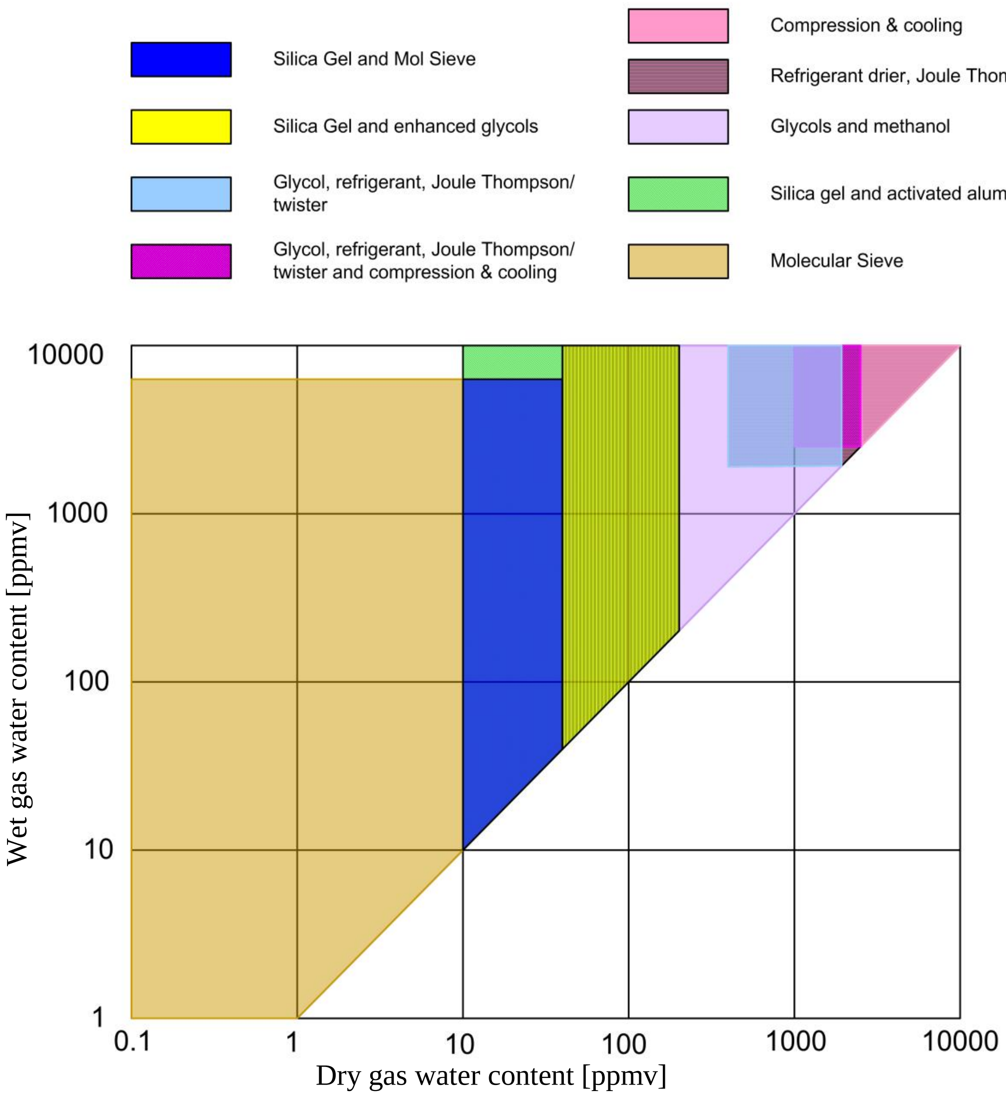

Figure 7 - Ranges of applicability of different dehydration technologies

The pressure for CO_2 dehydration depends on many considerations, including:

- Hydrate formation conditions
- Liquid CO_2 formation conditions
- Water solubility in CO_2
- Compressor interstage conditions
- Interstage cooling temperatures
- Minimum temperatures experienced at the point of dehydration and downstream
- CO_2 export pressure
- CO_2 supply pressure
- Downstream processing requirements (e.g. liquefaction or cryogenic processes)
- CAPEX/OPEX of dehydration equipment

Operation and monitoring

Monitoring of the drier performance ensures that water breakthrough does not occur. It is important to use a continuous monitoring system, because manual sampling and analysis will not be sufficient. The presence of CO_2 itself and the potential contaminants limit the number of available analysis techniques.

Many companies, which provide industrial moisture measuring instrumentation, declined to assist in this study. Participating vendors proposed a range of different physico-chemical measuring principles:

- Laser absorption spectroscopy
- Phosphorous pentoxide (P_2O_5) coated cell
- Quartz crystal cell
- Silicon sensor

As with the desiccants, impurities play an important role, so it is necessary to discuss the issue with the vendors to select the most appropriate technique and device.

The sampling system can significantly influence the overall performance and recovery time from upset conditions. Sampling usually involves pressure let-down and the related Joule Thomson chilling can result in condensation of any of the components present. Because this can affect both the analyser and the analysis result, vendors recommend sample heating systems. A reasonable response time is essential to ensure quick detection of off-spec product and remedial actions. To avoid damage or prolonged erroneous readings under upset conditions, the design of the sensor needs to consider these conditions.

Maintenance frequency depends on the gas quality. In the event that a contamination incident occurs, cleaning of the sensor and associated lines will be necessary. Particulates are a particular issue for some types of device, such as the phosphorous pentoxide device, because they can block the capillary. Another issue are reactions at the cell surface that may cause contamination of the cell or formation of water and result in erroneous readings.

A number of two moisture analysis points is usually the minimum. If a fault develops at one location, then the second location will act as a backup. The analysis points are in different locations in the plant (one immediately after dehydration and another further downstream).

Operators should develop plans regarding what to do if off-spec gas has reached downstream equipment. The actual course of action depends on the extent of the moisture excursion and the conditions prevalent in the equipment at that time.

Further work

Several areas need additional work to enable a full and adequate consideration of dehydration processes and issues. This study identified the following key areas for further investigation:

- The effects of inerts and impurities on physical properties of CO_2, as both can cause significant changes in the phase envelop and saturated water content of CO_2.
- Modification of the related physical properties estimation methods and models.
- Clarification and quantification of the hydrate formation issue. One reference suggests limiting the water content to < 60% of saturation to avoid hydrate formation, but other references argue that the maximum amount of hydrates will be too small to cause operational problems in CCS applications.
- Re-engagement of vendors. Their opinions on CCS as a market have changed because of the cancellation of most major CCS projects and the DECC and NER300 competitions.
- Research on membranes for dehydration of supercritical CO_2.
- Development of acid resistant solid desiccants that can better deal with impurities. Vendors are currently working on this sensitive area of research, but are not willing to discuss it yet.

Expert Review Comments

Six reviewers from industry and governmental organisations submitted comments. In general, most reviewers felt that the report provides a good background on CO_2 dehydration options and the issues surrounding its application to CCS. The majority of the reviewers understood that the lack of vendor support affected the quality and quantity of information in the report. Comments included the request for more information in certain sections, especially on costs and detailed system design. Where possible, AMEC added clarification and technical detail, improved figures and carried out own estimations, e.g. providing a heat and mass balance for a TEG system.

Conclusions

The purpose of this study was to examine the characteristics of the various dehydration processes and their integration into CCS systems.

A number of suitable technologies for CO_2 dehydration already exist. Vendors quoted molecular sieve and TEG systems as the most likely technologies for implementation. However, due to lack of vendor support, the cost and operating information presented in this report is preliminary, fragmentary and associated with uncertainties.

Design and operation of dehydration units come along with several challenges. This study identified that it is usually beneficial in terms of economics to consider a series of dehydration techniques in order to offload the main system. Besides, application of guard beds and upstream treatment can offer protection for sensitive desiccants.

The minimum CAPEX and OPEX for both molecular sieve and TEG systems depend mainly on operating pressure and type of regeneration. For a fixed operating pressure, there is a wide spread in CAPEX data quoted by the vendors. In case of high inerts, the CAPEX will increase for both molecular sieve and TEG systems. Presence of impurities, such as NO_x, SO_x and H_2S, leads to a 7% higher CAPEX but no difference in OPEX for molecular sieve systems. At this time, it is not possible to evaluate the effect of impurities on the costs of TEG systems.

Areas requiring further work are, for example, the effect of inerts and impurities on the physical properties of the CO_2 stream. Some vendors indicated that interest in CCS projects might be limited in the near future, so it seems that re-engagement of the vendors will be a priority for any future projects and studies.

Recommendations

IEAGHG should track the research and project activities in this area. Maybe it will be possible to continue and expand on the existing study later, when vendors are willing to provide more involvement and information. In the meantime, it would be a good idea to engage the approached vendors in IEAGHG activities and networks related to CO_2 capture and transport.

	AMEC Contract No. 1853 **Client Contract Ref: IEA/CON/12/202**	
Document No. 1853-020-000-RPT-001		**Revision : A**

IEA GHG
Evaluation and Analysis of the Performance of Dehydration Units for CO_2 Capture

A	Final Report	JUW	15/11/13	LMS	12/12/13	JUW	12/12/13		
O2	Final Issue	JUW	25/10/13	Reviewed by client		Reviewed by client			
O1	Final Issue	JUW		Reviewed by client		Reviewed by client			
O	Post review Comments	JUW		Reviewed by client		Reviewed by client			
P	Preliminary	LMS	13/02/13	JUW	13/02/13	JUW	13/02/13		
Issue Rev	**Issue or Revision Description**	**Origin By**	**Date**	**Chkd By**	**Date**	**Appd By**	**Date**	**Appd By**	**Date**
		AMEC						**OTHER**	

Revision Changes Notice

Rev.	Location of Changes	Brief Description of Change

List of HOLDS

HOLD No.	Location of HOLD	Reason for HOLD

Table of Contents

Glossary of Terms

Abbreviation	Description
AGR	Acid Gas Removal
Ar	Argon
CAPEX	Capital Expenditure
CCS	Carbon Capture and Storage
CH_4	Methane
CO	Carbon Monoxide
CO_2	Carbon Dioxide
COS	Carbonyl Sulphide
CRDS	Cavity Ring Down Spectroscopy
DCC	Direct Contact Cooler
DEG	Di-ethylene glycol
DGA	Di-glycolamine
DIPA	Diiso-propylene
DRCF	Dual Refrigerant CO_2 Fractionation
EG	Ethylene glycol
H_2	Hydrogen
HCl	Hydrogen Chloride, Hydrochloric Acid
H_2O	Water
H_2S	Hydrogen Sulphide
IEAGHG	International Energy Agency Greenhouse Gas
LP	Low Pressure
MEA	Monoethanolamine
MM	Million
MP	Medium Pressure
MTZ	Mass Transfer Zone
N_2	Nitrogen
NaCl	Sodium Chloride
NH_3	Ammonia
NOx	Nitrogen Oxide Gases
O_2	Oxygen

OPEX	Operating Expenditure
PFD	Process Flow Diagrams
P_2O_5	Phosphorous Pentoxide
ppmv	Parts Per Million – Volume Basis
R&D	Research And Development
SCF	Standard Cubic Feet
SO_2	Sulphur Dioxide
TDLAS	Tune-able Diode Laser Absorption Spectroscopy
TEG	Tri-ethylene glycol
TREG	Tetra-ethylene glycol

Units of Measure

Where appropriate the report contains units of measure and as a default uses SI units. To avoid confusion with source material provided by references and vendors the units of measure in the original reference are used.

Care should be taken in using values in this report to ensure the correct units are being referenced.

Moisture Content

Throughout the report reference is made to dehydration levels in terms of water concentration or dew point. The following table should be considered as an approximation of water dew points in pure Carbon Dioxide gas at 1 atmosphere. It should be noted that pressure dew point values are different to those at atmospheric pressure.

Water, ppm v/v	Water, ppm w/w	Dew point °C
10	4.1	-60.5
20	8.2	-55.3
50	20	-47.9
100	41	-42.1
200	82	-35.9
500	205	-27.2
1000	409	-20.2
2000	818	-12.8

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- Systech Instruments Ltd
- AMCS
- Process Analyser Systems Ltd

1.0 Introduction

Within the full Carbon Capture and Storage (CCS) chain the dehydration step is a relatively minor part and has been treated as a black box process in the past, paying little attention to the details of its design. However, the conventional drying technologies face a number of challenges, which need to be addressed before full scale deployment. These include the effect of impurities in the captured CO_2 stream on the dehydration processes.

The IEA Greenhouse Gas R & D Programme (IEAGHG) has commissioned AMEC to carry out this study as part of the Research and Development (R&D) programme to examine the characteristics of the various drying processes and the way they can be best integrated into the CCS system.

1.1 Overview

The scope of work for this study comprises four main elements:

- Evaluation and characterisation of processes for the dehydration of captured CO_2 with potential for application in the emerging CCS industry.
- Preparation of guidance on the selection of processes to match the various requirements for water dryness of CO_2
- Evaluation of methods for the monitoring and management of water dryness of captured CO_2 including methods for responding to water content excursions outside normal limits.
- Analysis of future drying technology developments that might be applicable to the captured CO_2 and identification of research requirements.

It is required to evaluate dehydration processes that are able to reach water contents ranging from 600ppmv down to <10ppmv. Consideration is given to a range of flow rates, constraints on the pressures at which drying has to occur and the range of other substances in the CO_2 that might affect some drying processes.

2.0 Executive Summary

The purpose of the study is to examine the characteristics of the various dehydration processes and the way they can be best integrated into the CCS system.

Moisture in CO_2 can lead to corrosion and hydrate formation. It is necessary to dehydrate CO_2 streams prior to transporting the product in carbon steel pipelines.

Several different types of CO_2 capture processes exist. The type selected for use is dependent upon the basic type of combustion process in operation, e.g. coal or natural gas. The CO_2 produced by the various combustion and associated capture processes is of different quality, containing different inerts and impurities, with varying compositions and conditions. The dehydration process can be significantly affected by these differences; it was therefore necessary to consider the different types of capture process separately within this study.

The information from the different process capture types have been used to produce a set of dehydration feed gas compositions. Base case data represent the minimum / normal impurity levels. Water content of saturated gas is dependent upon the temperature/pressure of the gas stream. Test cases are used to consider the higher levels of impurities and inerts.

This study investigates three different moisture levels; 550 ppmv (typically used in pipeline systems where high ambient temperatures are experienced), 50 ppmv and < 10 ppmv (required where downstream processing involves cryogenic conditions)

Two different flow rates were considered; 2 million tonnes/year CO_2, which is typical for a 1 GW gas-fired power plant, and 4.5 million tonnes/year, typical of a 1GW bituminous coal-fired power plant. Vendors were also asked to advise the maximum rate achievable for a single dehydration train.

Pressure ranges for dehydration are based on the gas phase. Liquid and supercritical CO_2 are usually produced via the gas phase, so are not considered separately.

CO_2 background issues have been evaluated. The main conclusions are:

- Impurities and inerts can affect the vapour liquid equilibrium and properties of the CO2 stream. These effects are not well understood and further work is required.
- Impurities have a significant effect on the dehydration process, causing damage to solid desiccant media and processing issues with liquid desiccant.
- Wet, or near saturated, CO2 can form solid hydrates which can block lines and equipment.
- Liquid CO2 formation occurs within the potential range of conditions over which dehydration equipment may be installed.
- Wet CO2 causes corrosion in carbon steel and the effects can be significantly enhanced by the presence of impurities.
- Dehydration technology options were studied. Results indicate that:
    - Dehydration techniques exist which can be applied to CO2.
    - It is desirable to use the compressor inter-stage cooling and knockout to remove as much of the water as possible, thus offloading the dehydration unit.
    - It is necessary to consider CO2 liquefaction conditions, and conditions for hydrate formation in determining the possible points for location of a dehydration unit. They also limit the application of technologies which involve chilling of the CO2.
    - Liquid TEG desiccant systems can be used to dehydrate the CO2 to ~150 ppmv. Enhanced processes can be used to achieve lower levels of ~ 30 ppmv.
    - Solid desiccant systems can be used if significantly lower moisture contents are required; silica gel and activated alumina can achieve down to 10 ppmv and molecular sieve can achieve < 1 ppmv.

A chart is presented in Section 5.1 which indicates the moisture applicability ranges of different dehydration technologies. Selection criteria have also been developed to assist in selection of the appropriate location for dehydration processes.

Economic and technical data is presented for the TEG and molecular sieve dehydration units based on the limited vendor data available.

- Capital cost for molecular sieve packages passes through a minima when plotted against operating pressure.
- There is a wide spread in the equipment capital cost of solid adsorption type processes, depending on the type of process selected. A maximum and minimum capital cost indicator has been plotted against rate.
- Data for TEG systems is severely limited. A maximum equipment capital cost indicator has been plotted against rate.
- For a set flow rate, comparing data from the same vendor indicates that the TEG system operating cost is in the middle of the range of molecular sieve package operating costs.
- Estimated minimum total annual operating costs for molecular sieve packages are presented over a range of rates.

The drying unit is a critical piece of equipment for both safety and operational reasons. The drier performance should be monitored to ensure that water breakthrough does not occur; a continuous monitoring system is required. Vendors were requested to define the most appropriate analysis system. There appears to be equipment available to do the continuous moisture monitoring. However impurities must be considered in detail and the actual application fully discussed with the vendors to enable the most appropriate device to be selected.

Operational considerations have been discussed. At least two moisture analysis points are recommended; if a fault develops at one location then the second location will act as a backup. The analysis points should be located at different points in the plant: one immediately after dehydration and another further downstream, possibly located after compression, adjacent to the compression and conditioning plant boundary.

Further work has been identified as:

- The effects of inerts and impurities on the CO2 stream physical properties and the phase envelope.
- Generation of accurate physical property estimation methods to enable these physical properties to be adequately modelled.
- Engagement of dehydration vendors. Whilst several vendors (SPX Flow Technology, Frames Process Systems, Exterran (UK) Ltd, Zeochem AG, UOP Products Ltd, and Grace Materials Technologies) have assisted in this study, most others have been unable, or unwilling, to do so.

Technologies already exist which can carry out the CO_2 dehydration. Capital and operating information presented has associated uncertainties due to lack of vendor information. However, for a new CCS installation these uncertainties have little effect since the dehydration unit is a minor part of a large, high capital spend project.

3.0 Background Issues

The quality of the raw CO_2 gas is specific to the source of CO_2 (whether that is an industrial process, natural process or power plant) combined with the actual capture process used to concentrate the CO_2.

The raw CO_2 stream may be cooled and washed, to remove impurities carried forward from either the source or carbon capture process. The CO_2 stream to be dried may therefore be at a range of different process conditions and compositions.

CO_2 quality affects the downstream process:

- The presence of water can lead to corrosion and hydrate formation.
- Impurities (such as H2S) and inerts can enhance corrosion, affect the vapour liquid equilibrium and the properties of the CO2 stream. They may also affect the dehydration process.

A brief summary of issues associated with CO_2 and its quality is given below.

3.1 Effects of Inerts / Impurities

- Impurities and inerts can have a significant effect on the properties of CO2:
- The presence of 3000 ppmv SO2 can reduce the dense phase density by around 14%.
- NO2, H2, N2 and H2S have effects on the CO2 VLE, critical point and density. Significant changes in the phase envelope appear to occur; H2 has a more marked effect than N2 and NO2. Studies[1] indicate that the CO2 phase envelope can be significantly affected by the presence of inerts; a pressure in excess of 80 Bara is required to fully condense CO2 gas containing 4% hydrogen at 5°C. It is postulated, for systems containing inerts / impurities, and H2 in particular, that two-phase regions may exist at pressures in excess of 120 Barg. This is significantly above the pure CO2 critical pressure and within the potential 'normal operating' pressure range for transport and storage.
- Other gases such as CH4 and N2 can dramatically reduce the saturated water content of CO2.

This has a direct impact on the dehydration equipment, and Joule Thomson cooling in particular. It is therefore important that inerts / impurities are quantified and controlled, and

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[1] 'DYNAMIS: Towards Hydrogen and Electricity Production with Carbon Dioxide Capture and Storage, D 3.1.3, DYNAMIS CO_2 Quality Recommendations', E de Visser, C Hendriks, July 2007

their effects fully understood; to date this has not been done and this may involve a large amount of work to obtain accurate physical properties.

The volumetric flow rate for a set quantity of low purity CO_2 gas can be significantly higher than for pure CO_2 gas. Thus high inerts content can result in larger, more expensive processing equipment and increased compression costs.

3.2 Corrosion

CO_2 forms carbonic acid in the presence of water. Carbonic acid is a weak acid (by definition it is only partly dissociated) with pH in the range of 3.3 to 3.7. Under high pressure conditions the degree of dissociation increases and the pH falls, as the acid becomes stronger. It has been reported that at room temperature and 50 atmospheres the pH was found to be 2.9[2]. Carbonic acid corrosion rates of mm/year occur in carbon steel.

Other acidic impurities, such as H_2S, NO_X, and SO_X cause corrosion. SO_2 and H_2S will form sulphuric acid in the presence of water and is corrosive to carbon steel. The presence of H_2S can accelerate the CO_2 corrosion rate. The effect of H_2S contamination on the CO_2 corrosion rate is illustrated in Figure 1.

Prevention of water dewing is therefore important to prevent / minimise corrosion from CO_2 as well as the impurities present. It should be noted that water removal does not prevent H_2S corrosion; H_2S reacts with carbon steel pipe work to form a thin surface layer of iron sulphide.

NACE Standards may be used to assist material selection. Steel pipelines will be used for CO_2; the option exists to use either carbon steel or stainless steel. Carbon steel is significantly cheaper and may be used in the presence of dry CO_2. Material selection is governed by the corrosion rate. The dryness level required is dependent upon the individual process conditions which may be present along the full length of the pipeline. The dew-point must be set at a margin below the lowest temperature experienced at the associated worst case pressure expected at any location. Care should be taken on initial commissioning and after any maintenance to ensure the system is dried adequately. Routine inspection and maintenance of the equipment and piping / pipelines is essential. Internal coatings must withstand the full range of expected process conditions and potential impurities.

A corrosion prevention, monitoring and control programme should be established. Internal and external corrosion may be prevented by use of coatings and cathodic protection. Consideration may also be given to chemical additives, but they should be selected with care to ensure that they do not cause additional problems or break the London Protocol (1996) (which allows incidental associated substances, but not addition of waste).

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[2] "Carbon Dioxide", Elton L Quinn and Charles L Jones, American Chemical Society, Monograph Series, New York, 1936. Page 117.

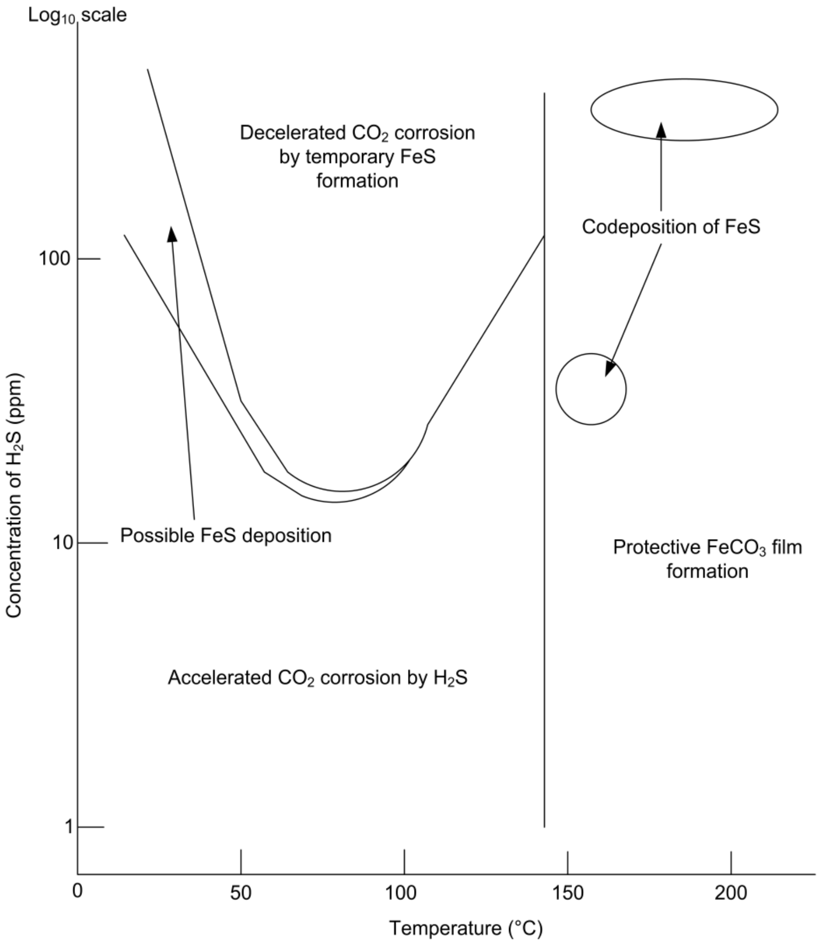

Figure for indication only – do not scale/read data

Figure 1 – Effect of H_2S Contamination on the CO_2 Corrosion Rate[3]

3.3 Hydrates/Solids

Hydrates are solid crystalline compounds which can form in the presence of both free and dissolved water. CO_2, in the presence of water, can form structure type I hydrates in pure CO_2 and structure type II hydrates in a gas mixture[4]. Hydrates can form in both vapour and liquid CO_2. The plots below indicate hydrate dissociation conditions[4,5] over a range of different temperatures and pressures for pure CO_2. Figure 2 and Figure 3 are associated with saturated pure CO_2; Figure 4 contains details of hydrate stability at different water contents[6]. Hydrates form at conditions above and to the left of the line.

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[3] "Engineering Standard for Corrosion Consideration in Material Selection", Dec 1997, IPS-E-TP-740, Iranian Ministry of Petroleum.

[4] 'Clathrate Hydrates of Natural Gases', E Dendy Sloan, Marcel Dekker, Inc, New York, 2nd Edition

[5] 'Carbon Dioxide', Elton L Quinn & Charles, L Jones, Reinhold Publishing Corporation, New York, 1936

[6] 'Rotating Equipment for Carbon Dioxide Capture and Storage', IEAGHG Report: 2010/07, September 2011

Hydrates may form prior to water dewing. It has been recommended that the water content selected be < 60% of saturation to avoid hydrate formation[7]. Other references suggest that the maximum amount of hydrates that can be formed with dissolved water in the CCS stream will be too small to cause operational problems[8].

CO_2 can react with impurities, such as ammonia, for example, to form ammonium carbamate / carbonate / bicarbonate solids. Both types of solids may block lines. Use of dry CO_2 prevents formation of these solids. Thermodynamic or kinetic inhibitor chemicals may be added to prevent hydrate formation.

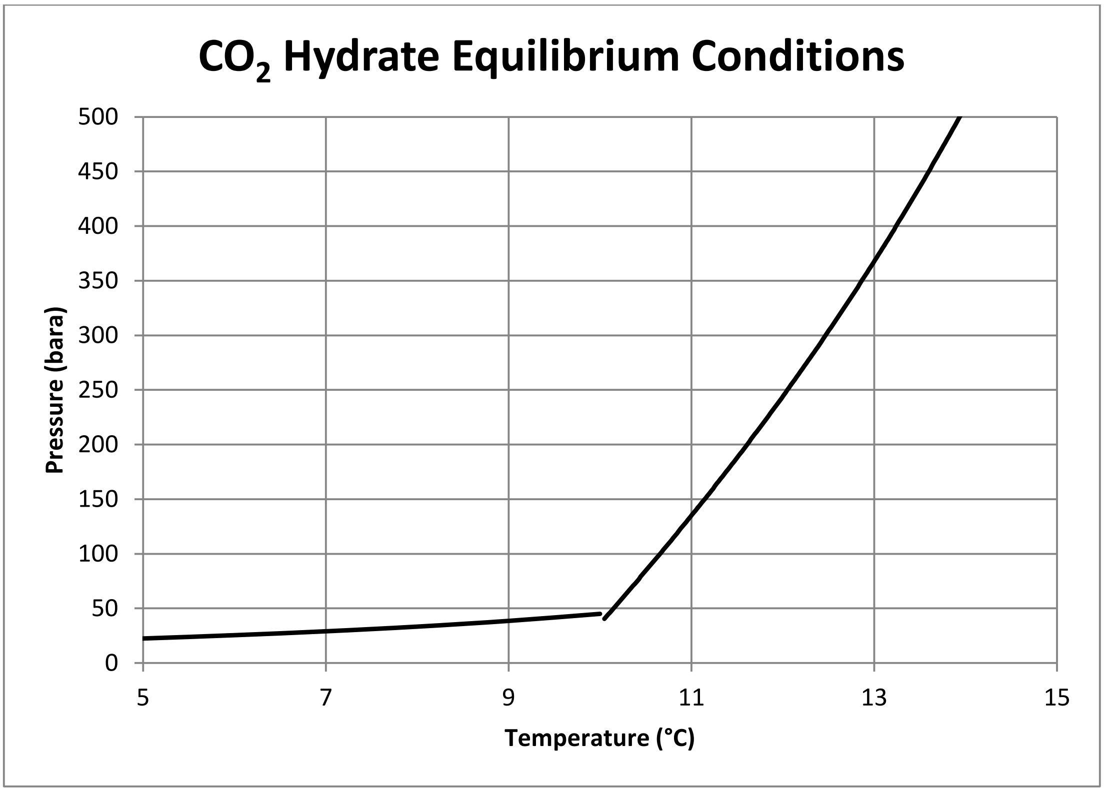

Figure 2 – CO_2 Hydrate Equilibrium Conditions

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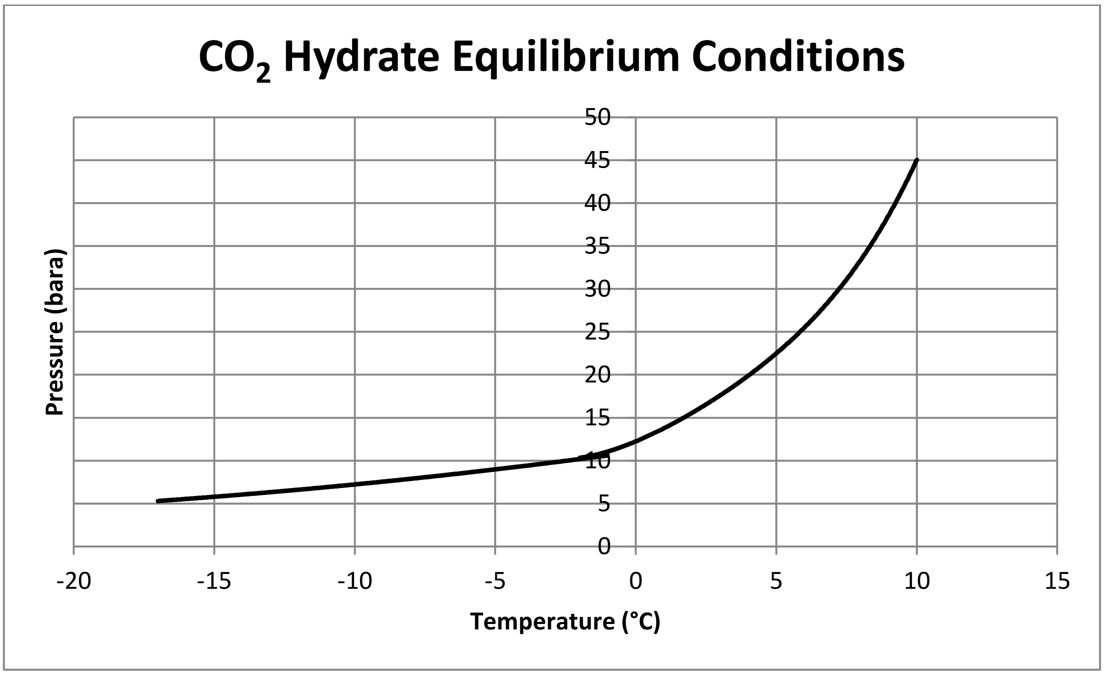
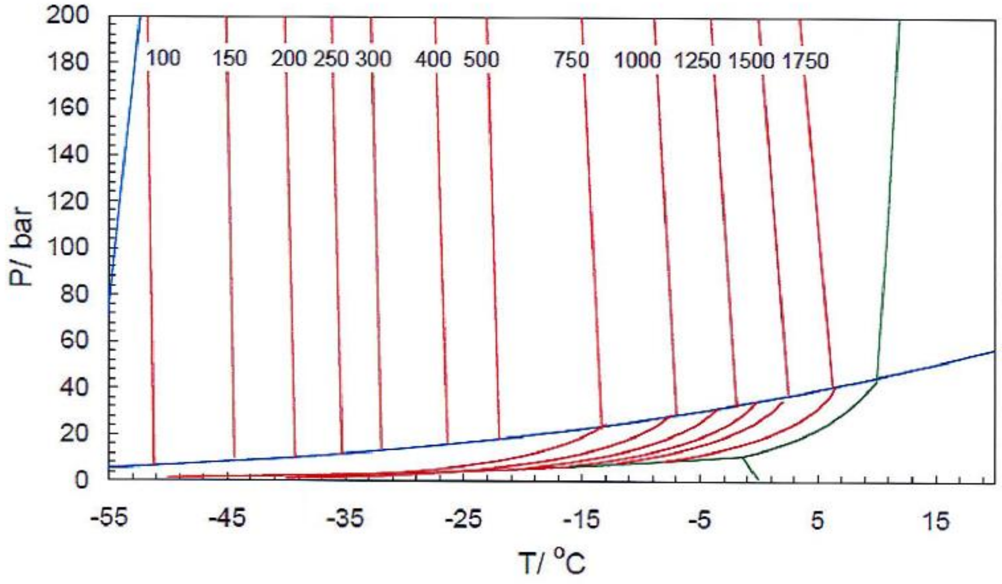
[7] 'DYNAMIS: Towards Hydrogen and Electricity Production with Carbon Dioxide Capture and Storage, D 3.1.3, DYNAMIS CO_2 Quality Recommendations', E de Visser, C Hendriks, July 2007.

[8] 'Technical and Economic Assessment of CO_2 Transportation', P Odru, et al, GHGT-8 Conference, June 2006.



Note: Information generated by AMEC CCS development project

Figure 3 – CO_2 Hydrate Equilibrium Conditions



Green lines: Hydrate stability of CO_2 in the presence distilled water or ice; Blue lines: VLE and SLE lines of pure CO_2; Red lines: Hydrate stability of CO_2 at fixed water content (Note in the vapour region, the water contents are (from left to right): 100, 150, 200, 250, 300 and 400 ppm)

Figure 4 - CO_2 Hydrate Equilibrium Conditions at Fixed Water Content

CO_2 hydrate kinetics are not as well understood as those of natural gas and CO_2 hydrate formation can occur at ambient temperatures at high pressures. Water removal will improve the situation but there is a need to clarify the maximum water concentration, below which hydrate formation is does not cause problems.

Hydrate formation conditions are also affected by the type and amount of impurities present. H_2S can also form hydrate solids in the presence of water at higher temperatures than required for CO_2.

A potential point of hydrate formation is upstream of the dehydration package, in the gas compression train within the suction and discharge coolers. The cooling medium supply temperature should be maintained at a margin above the hydrate formation temperature; adequate winterisation of exposed areas may be required. For air blast coolers, or gas-gas interchangers, the heat transfer wall temperature needs to be maintained at a margin above the hydrate formation temperature. Care is required to ensure that these tube temperatures are maintained during periods of turndown; under these conditions the wall temperature can approach that of the cooling medium

Liquid water also forms ice at 0ºC, thus a mixture of ice and hydrate can form.

3.4 CO_2 Liquid Formation

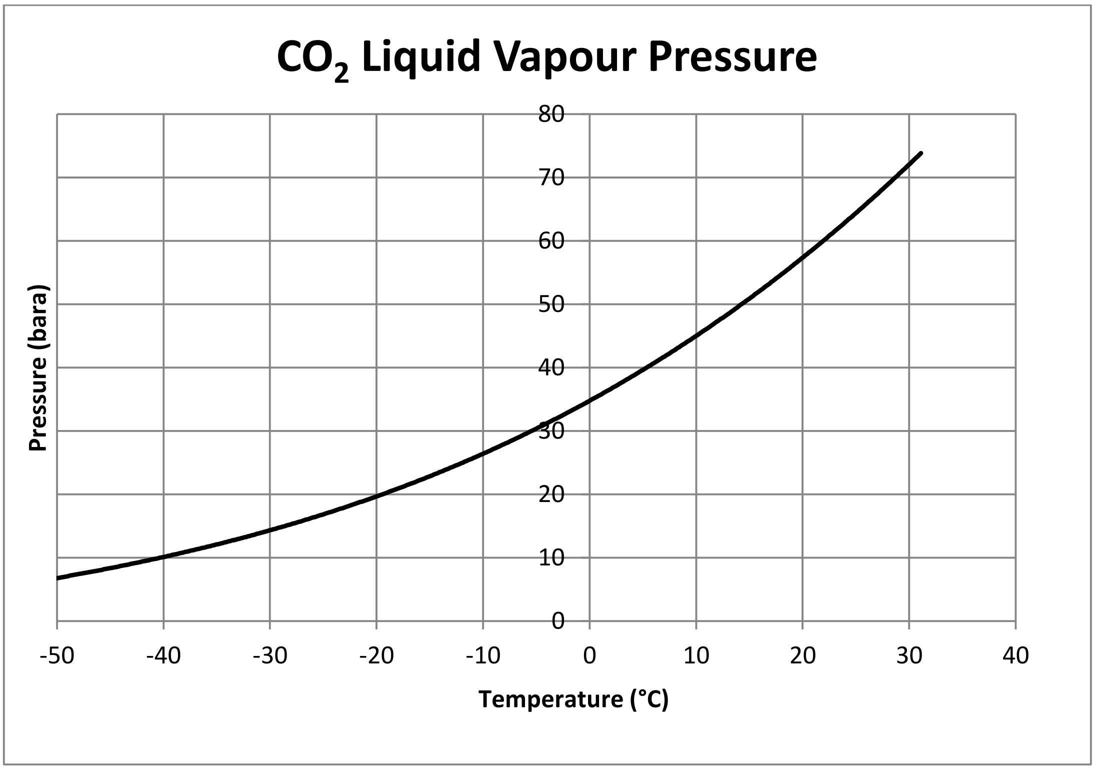
CO_2 gas liquid equilibrium data is shown in Figure 5.

Liquid CO_2 formation occurs within the same range of conditions as CO_2 hydrates formation. Liquid is undesirable in the gas processing units and may form a tighter limitation than hydrates under certain conditions.

3.5 Combined Hydrate / Water Ice / Liquid CO_2 Plot

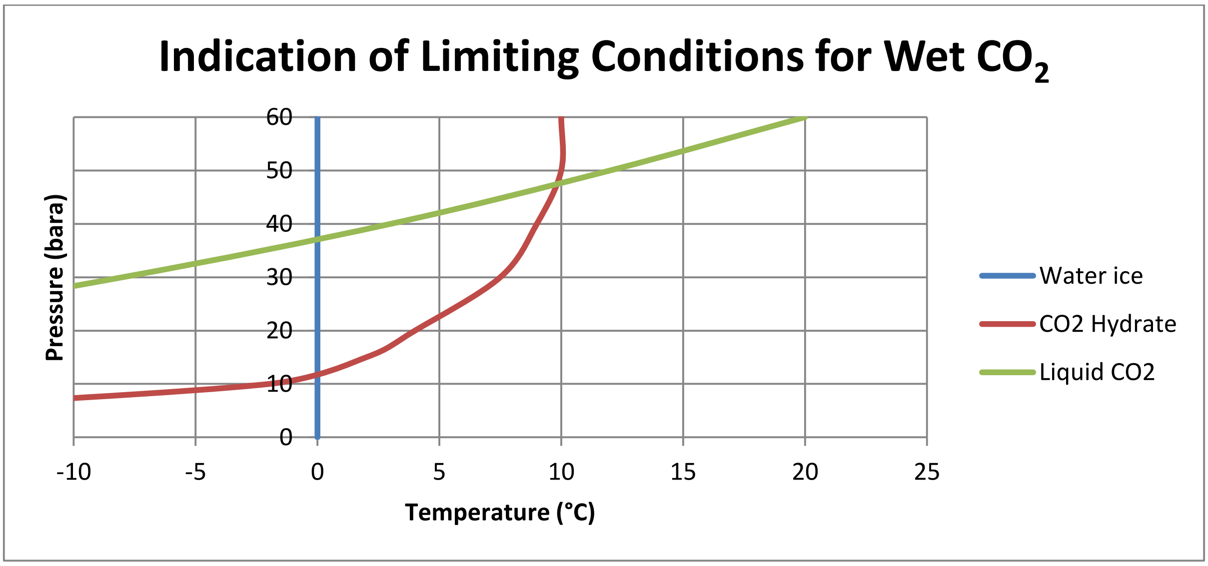
There is an area, within the normal range of compression conditions, at which the above plots cross and the limiting concern on cooling a saturated CO_2 stream changes from liquid CO_2 formation to hydrate formation to ice formation.

The above information is summarised onto a single plot, as shown in Figure 6, illustrating the allowable operating area. It is advisable to leave a significant margin between these boundary limits and the operating conditions



Note: Information generated by AMEC CCS development project

Figure 5 – CO_2 Liquid Vapour Pressure



Note: Information generated by AMEC CCS development project

Figure 6 – Combined Hydrate, Water Ice and Liquid CO_2 plot in Crossover Region

3.6 Moisture Specification in CO_2

It is necessary to reduce the moisture content to avoid issues with ice, hydrates and corrosion as well as to meet the CO_2 product specification. It is not the intention of this study to specify the moisture levels required. These are location and plant dependent and should be selected based on various considerations, which should include the following as a minimum:

- CO2 product specifications
- Corrosion due to presence of liquid water
- Hydrate formation due to the presence of water. References indicate that hydrates may form prior to water dewing. It has been recommended that the water content selected be < 60% of saturation to avoid hydrate formation
- Downstream conditions, for example chilled liquefaction of CO2 at subzero temperatures
- Minimum extreme ambient temperature over the range of operating pressures that the equipment will experience
- Turndown considerations, when equipment may be at lower temperatures
- Upset conditions
- Start-up conditions
- Shutdown conditions
- Standby conditions
- Blow-down conditions
- Commissioning activities
- Depressurisation of equipment and resulting low temperatures
- Variation in fluid composition
- Reliability of the dehydration equipment and likely excursions in the event of typical performance issues, for example foaming, etc
- Consequences of equipment or pipeline failure on safety and operation

The worst case operating conditions should be identified over the system operating range and target moisture values determined which include an adequate design margin to ensure that corrosion and / or hydrates do not occur. Management procedures can be used to limit / minimise some of the above concerns; if used they should be strictly adhered to.

3.7 Water Content of CO_2

The saturated water content of pure CO_2[9,10] is shown in Figure 7 and Figure 8.

Water solubility in CO_2 has a minimum inversion point which varies, depending upon temperature. The inversion occurs at around the CO_2 saturation point; liquid / supercritical CO_2 holds less water at low pressure than at high pressure. Gaseous CO_2 holds more water at lower pressure than at high pressure. Both liquid and gaseous CO_2 hold more water at higher temperatures.

It is important to ensure that the target product moisture content is carefully selected, giving due consideration to this information. Moisture content should be strictly controlled to ensure that free water does not occur at any point.

It is important to quantify the levels of inerts and impurities present since these have effects on the physical properties and behaviour of CO_2. Studies[9] indicate that the presence of 200 ppm H_2S in CO_2 has the effect of increasing the water solubility, therefore its effects on solubility can be ignored. However, the presence of 5% of methane in CO_2 results in a ~30% decrease in the water solubility values as indicated in Figure 9. This cannot be ignored.

3.8 Physical Property Estimation

CO_2 physical property estimation methods require to be validated over the range of conditions for which they are to be applied. They should be checked against verified data given in literature or determined experimentally. Physical properties can be significantly affected by impurities and inerts present in the raw gas, as discussed in Section 3.1; the phase envelope can be markedly changed.

Work needs to be carried out to adequately determine the effects of inerts and impurities on the CO_2 stream physical properties. Thereafter further work is required to generate accurate physical property estimation methods to enable these physical properties to be adequately modelled.

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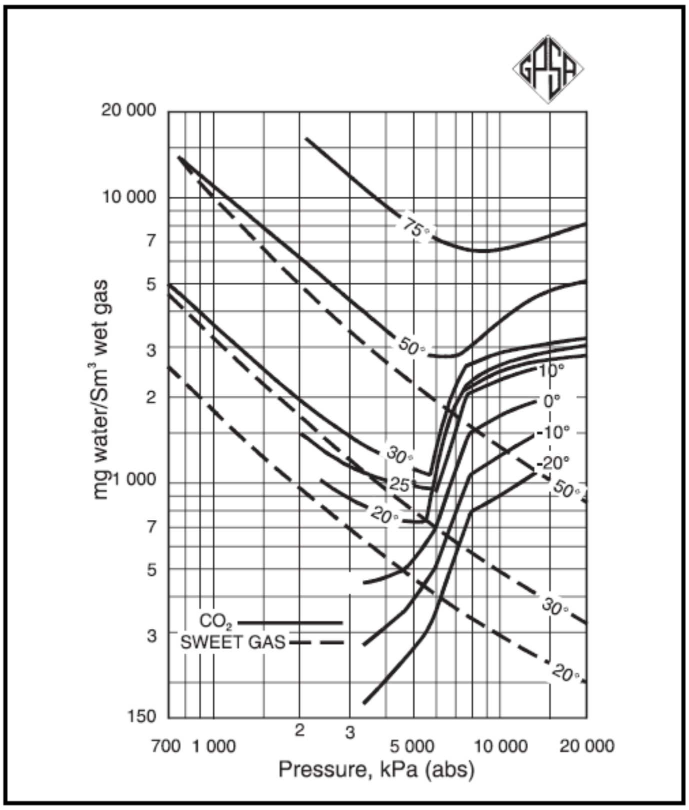
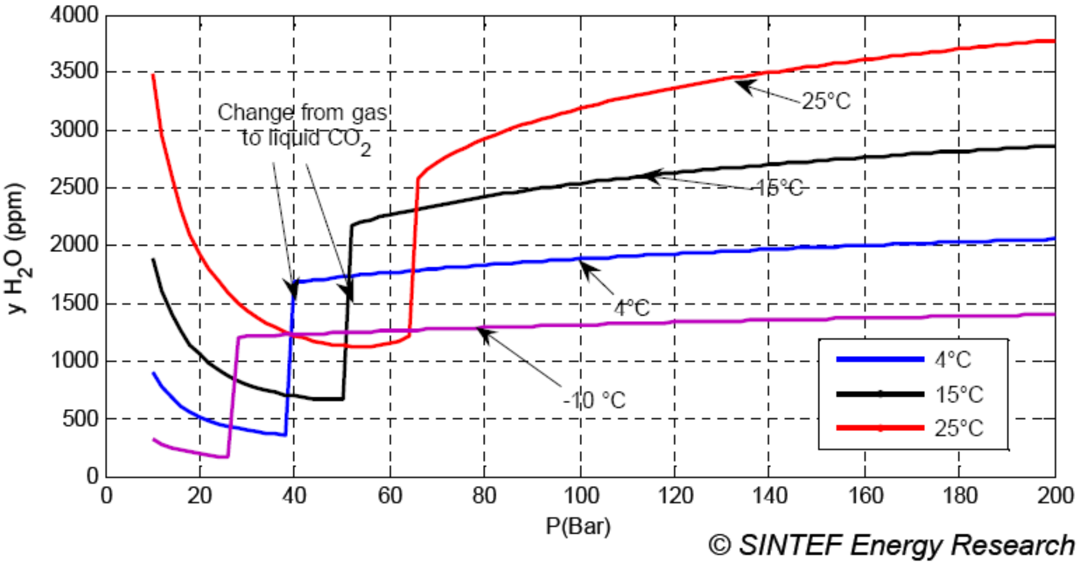
[9] GPSA Engineering Databook, 12th Edition, Section 20

[10] ‘DYNAMIS: Towards Hydrogen and Electricity Production with Carbon Dioxide Capture and Storage, D 3.1.3, DYNAMIS CO_2 Quality Recommendations’, E de Visser, C Hendriks, July 2007.



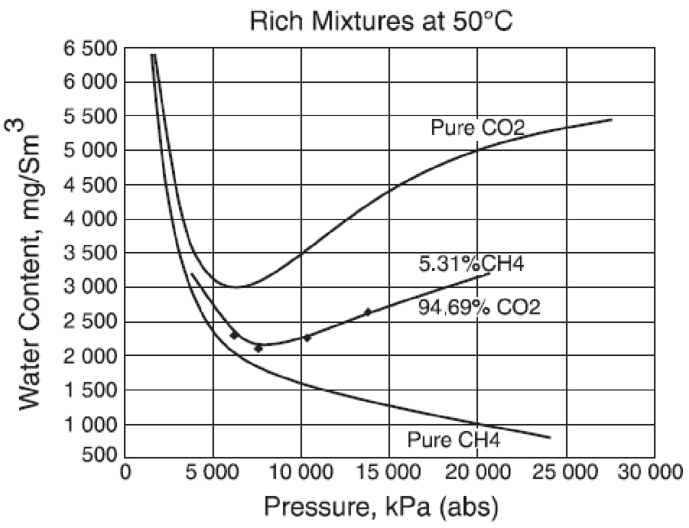
Reference: GPSA handbook 12th Edition

Figure 7 – Saturated Water Content of Pure CO_2



Reference: DYNAMIS: Towards Hydrogen and Electricity Production with Carbon Dioxide Capture and Storage, D 3.1.3, DYNAMIS CO_2 Quality Recommendations', E de Visser, C Hendriks, July 2007.

Figure 8 - Saturated Water Content of Pure CO_2



Reference: GPSA handbook 12th Edition

Figure 9 - Saturated Water Content of CO_2 Containing Methane

4.0 Description of Dehydration Technology Options

The dehydration unit is required to reduce the water vapour in CO_2 to less than the product target moisture specification. Low moisture content is critical in prevention / minimisation of both corrosion in carbon steel pipe work and hydrate formation. The selected process must therefore be robust and reliable while minimising the introduction of any additional impurities to the CO_2.

Several different types of dehydration techniques exist for drying of gases. Some of the techniques do not achieve low moisture levels, however they are straightforward, low cost processes, often required in a process anyway (such as compressor inter-stage cooling and knockout) so are important in offloading the dehydration unit, resulting in smaller, less costly dehydration systems.

4.1 Cooling

Cooling of the raw CO_2 gas stream will move the gas towards saturation due to the reduction in CO_2 water solubility with reduced temperature, as shown above. This allows water to be removed from the gas stream via a separator. Care needs to be taken to ensure that the water dew-point occurs without liquid CO_2 or hydrate formation occurring either at the chosen cooled temperature or on the cooling equipment tubes, which will be colder than the gas.

This technique is typically used in compression trains (where it is desirable to cool the gas prior to the next compression stage or subsequent processing activity) to improve compressor efficiency and / or reduce the size of subsequent equipment / compression stages. Cooling the gas to a set constant temperature as the pressure is stepwise increased at each compression stage will form liquid water at each stage which has to be removed. Once the inversion pressure point is passed then additional water will not be removed as higher pressure CO_2 can hold more water as its pressure is increased.

Inter-stage cooling of gas is not normally sufficient to achieve the required moisture content to minimise corrosion or hydrates. As shown in Figure 7 above, pure CO_2 gas, cooled to 30ºC, cannot achieve a moisture content below ~1100 mg water/Sm^3 of wet gas (or ~1430 ppmv water). Typical target moisture values in the literature are all significantly lower than this value; further processing is required to remove residual water. The technique, however, is acceptable for removal of the bulk of the moisture which was present in the feed raw gas.

Further cooling can be achieved by using a refrigerant. Moisture specifications required for this project could not be achieved using refrigeration alone; the hydrate formation region covers a large part of the zone in which a refrigeration package would be required to operate and liquid CO_2 formation needs to be avoided. Water ice formation should also be avoided. Refrigerated driers are available which may be used on low pressure CO_2 if:

- They were used in combination with another dehydration technique
- Higher target moisture levels were acceptable.

4.2 Joule Thomson Valve

Saturated gas at pressure (typically from a compressor delivery) is cooled and expanded across a Joule Thompson valve. CO_2 is subjected to adiabatic (Joule Thomson) cooling that accompanies the expansion of a real gas. When the gas reaches the saturation point the liquid condenses out. Care needs to be taken to ensure that the temperature / pressure combination is such that hydrates and / or liquid CO_2 / water ice do not form. If the water dew-point is reached first then liquid water will form which can be removed in a downstream separator.

Relatively large pressure drops are usually required for the Joule Thomson valve to operate effectively. The penalty for this large pressure drop is manifested in the form of a higher compressor discharge pressure and additional compressor power consumption.

The temperature achieved can be less than that achieved from simple cooling; therefore the saturated moisture content can be less than is achievable with simple cooling.

The Joule Thomson Valve is only likely to be acceptable as a standalone method of dehydration if the minimum temperature which can be experienced in the downstream equipment / pipe work is very high.

Severe valve wear can be experienced; frequent replacement of Joule Thomson let-down valves is to be expected.

4.3 Refrigeration

Saturated gas is cooled against product gas in a gas/gas heat exchanger, further cooled in a refrigerated exchanger and passes to a separator for water removal. Dried gas leaves the top of the separator, is warmed against incoming feed gas and leaves the drying unit.

Refrigerant gas is compressed, cooled / condensed and sent to the liquid receiver. Liquid is flashed across a valve, sent to the evaporator, where it is warmed / evaporated against the gas undergoing the drying operation and is then recompressed.

The same issues as occur with Joule Thomson cooling pertain to refrigerated cooling. If the CO_2 gas reaches its saturation point the liquid condenses out. Care needs to be taken to ensure that the temperature / pressure combination is such that hydrates and / or liquid CO_2 / water ice do not form. These effectively limit the allowed gas temperature, and therefore the amount of water which can be removed from the gas.

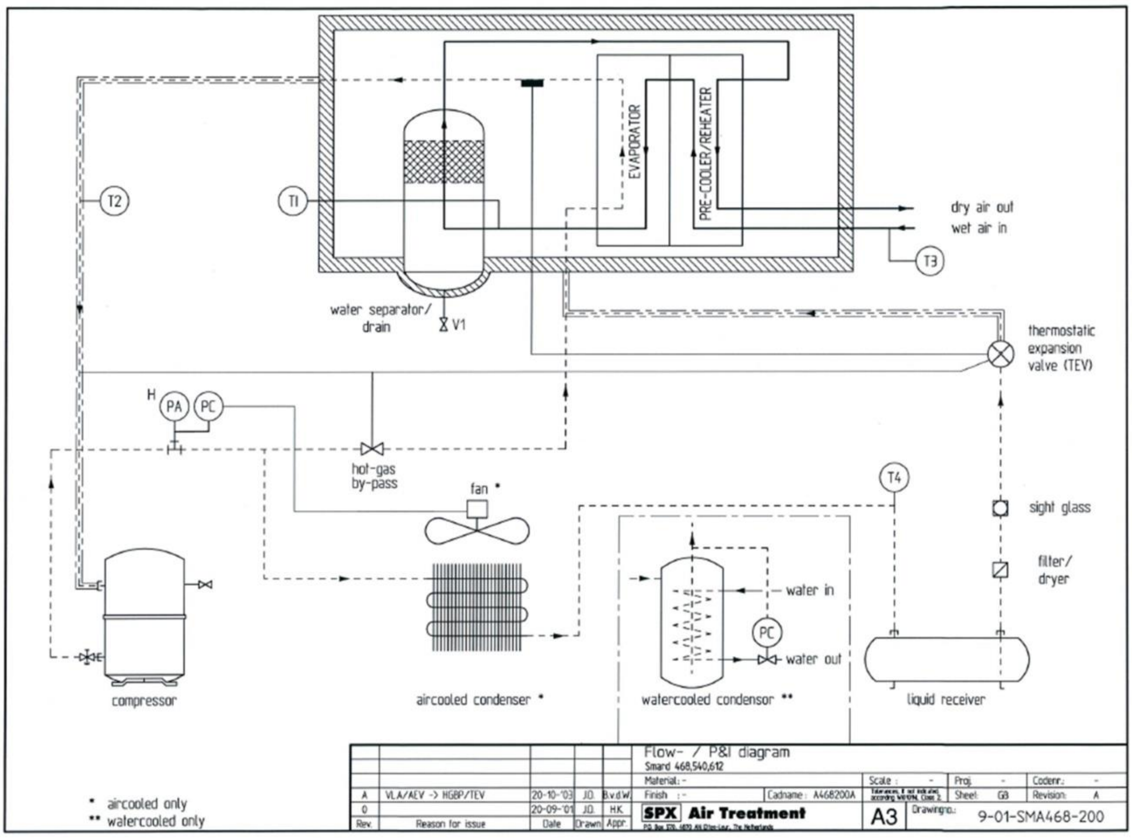
An example process is shown in Figure 10.

4.4 Turbo Expander

Saturated gas at pressure (typically from a compressor delivery) is cooled and expanded across a turbo expander, generating power. CO_2 is subjected to isentropic cooling that accompanies the expansion of a real gas. Significant chilling occurs on depressurisation, more than occurs with the Joule Thomson valve; higher outlet pressures may therefore be required to restrict the extent of cooling. When the gas reaches the saturation point the liquid condenses out. Care needs to be taken to ensure that the temperature / pressure combination is such that hydrates and / or liquid CO_2 / water ice do not form. If the water dew-point is reached first then liquid water will form which can be removed in a downstream separator.

Relatively large pressure drops are usually required to operate effectively. The penalty for this large pressure drop is manifested in the form of a higher compressor discharge pressure and additional compressor power consumption.

As for the Joule Thompson valve the temperature achieved can be less than that achieved from simple cooling, therefore the saturated moisture content can be less than is achievable with simple cooling.



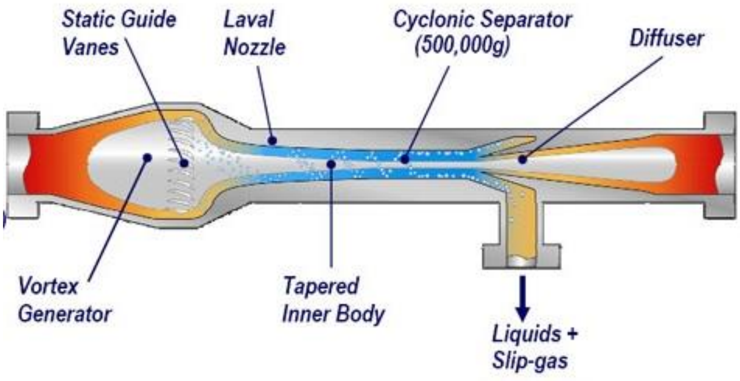
Reference: Supplied by SPX

Figure 10 – Typical Refrigeration Package

4.5 Supersonic Separators

Twister supersonic separators act by efficiently condensing and separating liquids from the gas stream. Saturated feed gas enters the unit. Static inlet guide vanes impart a concentric swirl. The saturated, swirling gas enters a Laval nozzle and the gas expands to supersonic velocity, resulting in low pressure and temperature. A liquid mist forms and condensed droplets, forced to the wall, are removed from the gas using a cyclonic co-axial separator. The separated streams are slowed down in separate diffusers. Slip gas, removed with the liquid stream, is separated and recombined with the main gas stream.

The pressure drops to around 30% of feed pressure in the nozzle, but after pressure recovery the pressure is approximately 75 - 80% of inlet pressure. Gas expansion in the nozzle is near isentropic. This low nozzle pressure / temperature enables more liquid condensation than would be achieved with a Joule-Thompson valve. However, care needs to be taken to ensure that the temperature / pressure combination through the device is such that hydrates and / or liquid CO_2 / water ice do not form. As for the Joule Thomson valve these relatively large pressure drops will incur increased compressor discharge pressure and increased compressor power. If used on the same duty as a Joule Thomson valve then a significantly lower overall pressure drop may be achievable for the same / lower moisture levels.



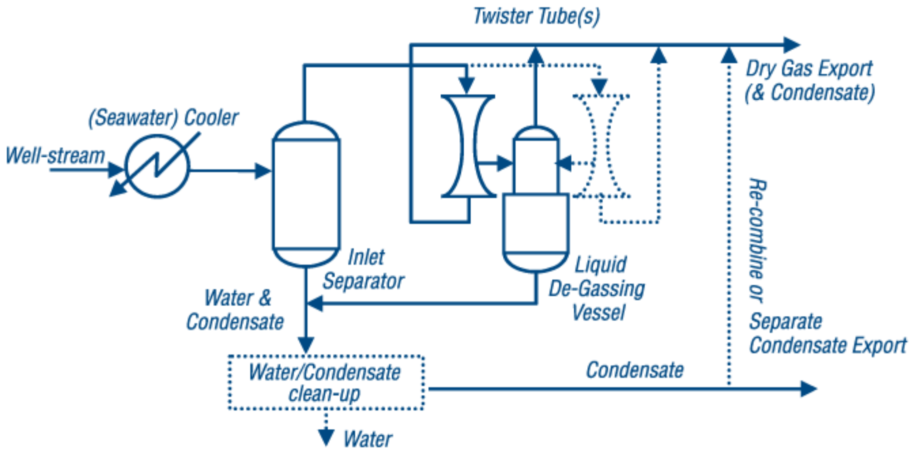
Reference: Twister BV, 2013, http://twisterbv.com/news/separation-goes-supersonic/

Figure 11 – Schematic of Twister Supersonic Separator

The Twister unit is compact and lightweight. Multiple units can be combined to achieve the required rate. The twister device is a fixed actual volumetric flow rate device in which the gas velocity at the throat of the inlet nozzle will always be Mach 1. Turndown can be achieved by adjusting the operating pressure or by taking individual twister tubes offline.

4.6 Supersonic Separators Combined with Hydrate Separation

The twister system can be used in combination with a hydrate separator (which is located downstream of the twister devices) to separate liquids and hydrates from the slip gas stream. The separator is based on a low temperature extraction technology with heating coils in the liquid section to melt the hydrates. Additional tangential inflow nozzles enable improved gas liquid separation efficiency: the vendor claims in excess of 99%. Gas is recombined with the main gas stream. Liquid is removed from the bottom of the vessel for disposal. Hydrate formation does not take place inside the Twister tubes due to the short residence time.



Reference: Twister BV, 2013, http://twisterbv.com/products-services/twister-supersonic-separator/system-design/

Figure 12 - Schematic of Twister Supersonic Separator on Hydrate Separation Duty

4.7 Continuous Liquid Circulation Systems

Dehydration takes place by absorption in which the gas is chemically absorbed into the liquid. Desirable properties for such absorbents include:

- High absorption efficiency, to minimise the required amount of solvent
- Low CO2 solubility, to minimise CO2 losses
- Non-corrosive and non-toxic
- Minimal processing problems
- Easy and economic regeneration
- No interaction with CO2
- Minimal reactions with impurities contained in the raw CO2 gas
- Low volatility at the process temperature, to minimise solvent vaporisation losses
- Low tendency to foam and emulsify
- Good thermal stability to prevent decomposition during regeneration

4.7.1 Absorbents

Several liquids are available for use as a dehydration medium from a variety of different vendors. Consideration should be given to CO_2 impurities as these may react with the absorbents to form undesirable products. Absorbents include:

- Glycol based systems, including ethylene glycol (EG), di-ethylene glycol (DEG), tri-ethylene glycol (TEG) and tetra-ethylene glycol (TREG). DEG may be used in colder duties below ~10°C, due to its lower viscosity, but TEG is more commonly used on natural gas systems and has been provided on CO2 duties in the past. TEG has high thermal stability, can be efficiently regenerated and concentrations of up to 99.99% TEG are achievable with enhanced processes. It has low vaporisation losses but is corrosive if contaminated or oxidised. The use of TEG is not advisable at high CO2 pressures since the TEG solubility in CO2 becomes high and subsequent losses of TEG are unacceptable. Pressure reduction prior to dehydration would be required followed by recompression, which is an expensive option. TREG has a lower vapour pressure which reduces glycol losses and may be considered where high feed gas temperatures (above 50°C) exist. However, it is more expensive and more viscous than the other glycols. Properties of the individual glycols are summarised elsewhere11. At supercritical conditions the CO2 density can approach that of TEG and carry TEG out of the contactor in the overhead stream.

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[11] 'Gas Purification', Arthur L Kohl, Richard B Nielsen, Gulf Publishing Company, 5th Edition, 1997, Chapter 11.

- Methanol based process. Methanol has a relatively high vapour pressure at normal process conditions so either chilled methanol or methanol recovery would be required to prevent high methanol losses into the product gas. Methanol has a high selectivity for CO2, especially at low temperatures so an alternative process may be more appropriate. Unfortunately, none of the methanol dehydration process vendors took part in the study.

- Glycerol, which has been used for supercritical CO2. The Glycerol Drying Process is used when high pressures (around critical or supercritical conditions) and non-idealities lead to excessive vapour phase glycol losses, making other processes uneconomical. CO2 solubility in glycerol is also lower than for glycols, so CO2 losses on flashing are reduced. The process is patented12 and licensed by Shell Oil Company and has been used to condition CO2 for EOR duties13,14. Product moisture levels of around 7 lb/MMscf (~150 ppmv) have been quoted. Glycerol has a low solubility in CO2. Desiccant losses to CO2 due to solubility are minimal. The regeneration temperatures required are lower than those for TEG systems; glycerol is thermally stable at such conditions so formation of degradation products is low. Glycerol is, however, very viscous and gas feed temperatures must be maintained above ~40°C.

The CO_2 dehydration solution preferred by the limited number of vendors who took part in the study is TEG. The selection of TEG rather than mono- or di-ethylene glycol is the preference of the technology vendor and mirrors the preference from the natural gas industry. Typically the glycols are all similar but the differentiator comes from the hygroscopicity and the system temperature. At cooler processes around freezing 10°C DEG is preferred due to the viscosity of the fluids, around 50°C TEG is preferred for the purposes of fugitive vapour losses. The basic process arrangement for the various liquid desiccants is generally similar. An example of the TEG process is provided below.

4.7.2 Typical Process Descriptions – TEG

Dehydration is by means of absorption. Water saturated CO_2 gas enters the bottom of the contactor via a vane-type inlet device, which ensures a good distribution of the gas across the column. A water scrubber section at the bottom of the contactor removes incidental liquid and solids carried over with the gas stream. Gas leaves the scrubber section and passes up through the contactor structured packing. Dry CO_2 gas, containing ~150 ppmv of water is normally expected in the product CO_2 gas, although the actual amount is sensitive to the feed gas temperature.

Lean glycol is fed to the distributor at the top of the contactor and the down flow of glycol is contacted with the gas at the surface of the structured packing. Water absorbs from the gas stream into the TEG. A high efficiency wire mist eliminator above the top distributor ensures an efficient removal of carryover droplets from the dried CO_2 gas. Glycol losses are thus reduced. Rich glycol is removed from the chimney tray and routed to the regeneration package for purification. The rich TEG is pre-heated in the reflux condenser in the top of the

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[12] 'Drying Substantially Supercritical CO2 with Glycerol' Z Diaz, J H Miller, Shell Oil Company, United States Patent number 4,478,612, dated 23rd October, 1984.

[13] 'CO2 Dehydration Scheme aids Hungarian EOR Project', G Udvardi, L Gerecs, Y Ouchi, F Nagakura, E A Thoes, C B Wallace, Oil & Gas Journal, 22nd October, 1990

[14] 'Use glycerol to dehydrate supercritical carbon dioxide', M Swadener, J Lundeen, K Fisher, C Beitler, Hydrocarbon processing, July 2011

reboiler still column then enters the flash vessel where three-phase separation of gas, TEG and condensate takes place. Flash gas is vented. The TEG may contain solids due to minor TEG degradation, corrosion or scaling; filters located downstream of the flash vessel remove these solids. Rich TEG is further heated in the lean/rich TEG exchanger. Pressure is dropped across the control valve and TEG is injected into the still column. The hot gas stream from the top of the still is cooled and condensed in the still reflux condenser. TEG is heated to ~204°C in the reboiler, where the remaining CO_2 and water are separated. Low pressure operation ensures that glycol degradation, due to high boiling temperature, is minimised.

TEG flows from the reboiler, through the stripping column, is cooled in the TEG/TEG heat exchanger and enters the surge drum. The lean TEG is further cooled in the trim cooler (to a temperature of ~5°C above the raw CO_2 gas inlet temperature) and pumped to the top of the contactor.

The system can typically turndown to ~10% of flow.

TEG losses into the CO_2 gas are estimated to be around 10-20 kg per million Sm^3 of gas for a well designed and operated system (they are very sensitive to pressure, temperature and contactor gas velocity). Entrained droplet losses are estimated to be around 5kg per million Sm^3 of gas.

The process generates a hot vapour off-gas stream from the reflux condenser and the flash drum at ~120 ºC, containing water (removed from the CO_2 gas), CO_2 (dissolved in the TEG) and small quantities of TEG. CO_2 lost to the overhead vapour stream is expected to be < 1% of feed gas. If this loss is unacceptable then water can be condensed out of the stream and the CO_2-rich gas recycled to the compressor suction for recovery.

Glycol make-up is added, as required, to the reboiler vessel. The expected lifetime of a TEG charge varies between 3 and 10 years, dependent upon the operating conditions and the levels of impurities present in the CO_2 gas. A potential operational life of up to 15 years is feasible, but vendors are not prepared to guarantee this lifetime.

Significant glycol losses can occur; excessive reboiler temperature will lead to glycol degradation. Excessive still top temperature can lead to loss of glycol in the tops vapour. CO_2 feed temperature is thus limited to ~ 30°C. Excessive contactor velocities lead to glycol loss to CO_2 due to carryover

4.7.3 Further Developments of the TEG Process

The above process is acceptable for higher moisture contents. However, to achieve < 150 ppmv water in the CO_2 requires a higher concentration of TEG. Variations on the basic process exist, and are typically focused on process efficiency savings, rather than additional dehydration.

In order to achieve the required glycol purity, the flash gas from the flash vessel is used as stripping gas in an additional stripping column. An outline arrangement is given in Figure 13. If there is insufficient flash gas to achieve the required glycol purity the quantity of flash gas can be supplemented by a small amount of dry product CO_2 gas, thus reducing the partial pressure of water vapour in the gas phase and further assisting in purifying the TEG. The stripping gas leaves the top of the stripper with the recovered water vapour and leaves with the vent gas from the top of the reflux column. Low pressure operation ensures that the additional stripping gas consumption is minimised. Moisture levels of ~30 ppmv are achievable in the product CO_2.

In the Drigas process licensed by Siirtec Nigi, the overhead vapour from the regenerator is cooled, dried and recycled to the stripping tower using a blower. Water is condensed out of the vent gas, and is collected in a separator. If higher concentrations are required then a second stage of absorption can be incorporated, fed by a small stream of lean TEG. TEG purity of up to 99.99% can be achieved leading to very low dew-points.

The DRIZO process is licensed by Prosernat. Water is stripped from the thermally regenerated TEG by a volatile hydrocarbon solvent. The regenerator overheads vapours are condensed in a 3-phase separator. Water is removed and the condensed solvent is re-circulated to the regenerator via a pump and heater. It gives an enhanced regeneration and very concentrated lean glycol.

The Coldfinger process is a licensed process, from Cormat, in which a heat exchanger, containing coolant, is located in the vapour space of the surge drum. A trough underneath the tube bundle collects and removes the condensed liquid, which contains a higher concentration of water. A higher concentration of TEG is thus present in the surge drum.

An additional regeneration, carried out under vacuum conditions can also give enhanced stripping against higher strength TEG.

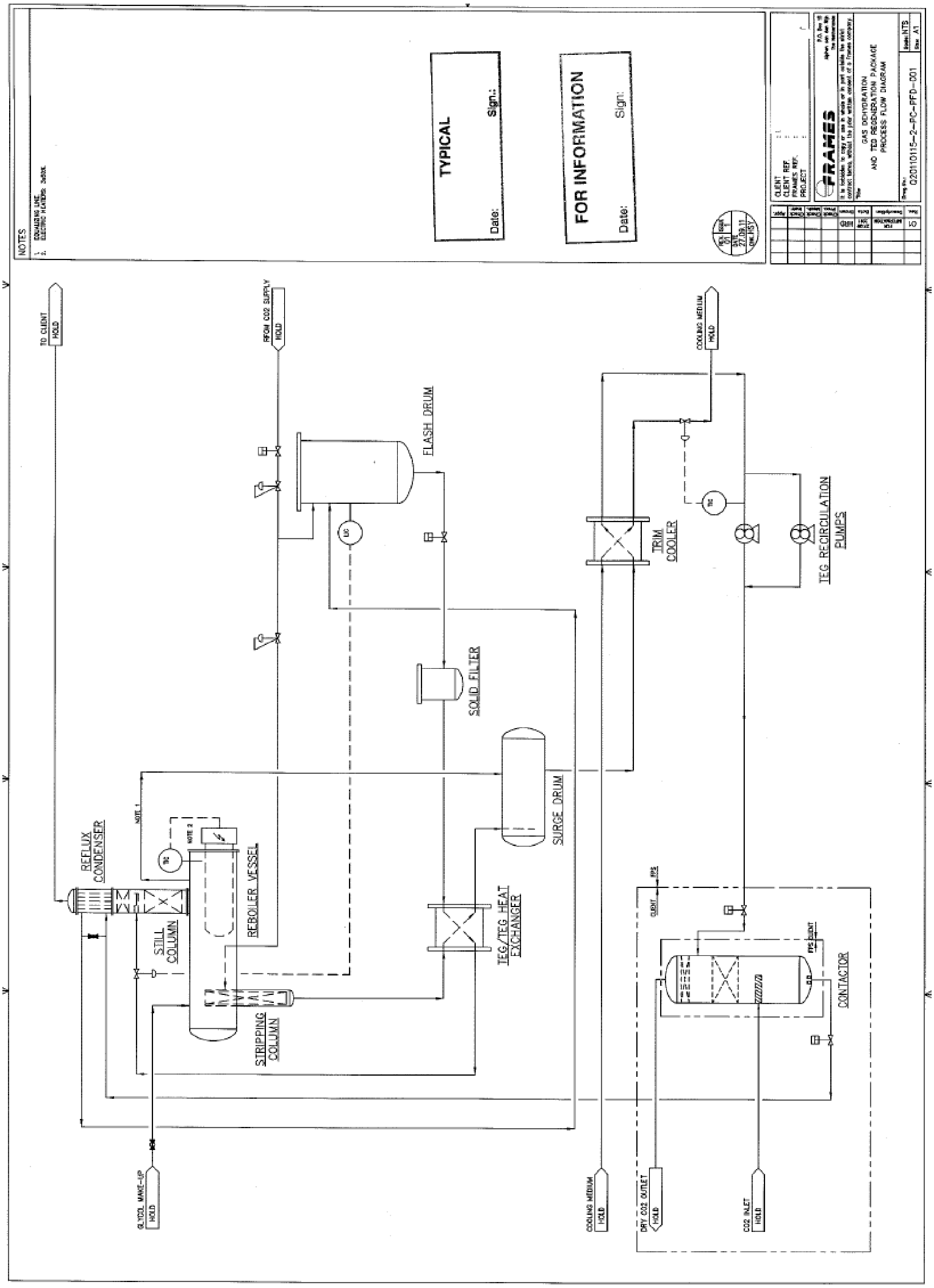
The provision of information from vendors for these systems was not sufficient for comparative discussion.

4.7.4 By-products Produced

Water is removed as a waste vent stream from the top of the still. Any CO_2 used as stripping gas, as well as any CO_2 absorbed into the circulating glycol stream, will be vented with the water. A very small amount of glycol will also be vented. A hot, wet gas stream is produced. This stream can be vented directly to atmosphere if it is contaminant free, or treated to remove undesirable contaminants. The stream can be cooled and the water removed from the waste gas prior to venting to atmosphere. The water can be sent to drain or recovered.

At the end of absorbent life the spent absorbent is removed from the process. It is normal to treat this material as contaminated waste, since impurities originally present in the raw gas stream will have been absorbed and concentrated.

Solids removed in the glycol circulation filter require to be disposed of as contaminated waste.



Reference: Frames BV, 2013

Figure 13 – A Typical PFD of a TEG Dehydration System Using Stripping Gas

4.7.5 Impurities

Impurities can have a detrimental effect on the dehydration process. Table 1 indicates the effects of different impurities on the TEG (and other) processing systems.

Impurity	Effect on the dehydration system	Notes
H_2O	Liquid droplets or mist (indicating water loading near saturation levels or higher) weaken the glycol solution, leading to high moisture in the product gas	Inlet separator or filter / coalescer will remove droplets. Droplets may form if there is a compression first step or should dehydration be the first stage, prior to compression, or if there is a problem with the knockout pot.
N_2, Ar, H_2, CH_4	Inert	No limit to the maximum tolerable concentration in feed gas
O_2	Degrades the glycol by oxidation to form organic acids	
H_2S		Glycerol plant had ~3000ppm H_2S in feed gas High H_2S content of the vent stream so it has to be vented at a height via a stack.
HCl, acids	Low glycol pH causes corrosion. Should be kept alkaline. Ranges quoted in literature vary[15], i.e. 7-9, 7.0-7.5, 6.5-8.5, 6-8.5, 7.5-8.0.	TEG process – Glycol solution can tolerate 200 ppm to < 600 ppm chlorides quoted, although typically 200 - 300ppm chloride range tolerated[15]. Glycerol process system - chloride specification is 70 ppm max.
Amines	Foaming	Inlet liquid filters/coalescers remove droplets
Aldehydes	Affects glycol pH and corrosion Foaming	Form carboxylic acids via Cannizzaro reactions. Can be formed from Glycol cracking or oxidation
NaCl	Corrosion of equipment	Carried forward in entrained water

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[15] 'Gas Dehydration Fundamentals – Part 4 – TEG Solution Monitoring and Maintenance', Ardeshir Azodi, Laurence Reid Gas Conditioning Conference, 2008

Impurity	**Effect on the dehydration system**	**Notes**
	If sodium chloride levels exceed the solubility level then reboiler fouling can occur Foaming	200 ppm chlorides maximum tolerable in feed gas
Caustic	High glycol pH (pH>9) can cause foaming and emulsification	
Methanol	High liquid methanol rates can cause flooding in the column	
Organic Acids	Affects glycol pH and corrosion Foaming	Carried forward or generated from oxidation of TEG or thermal decomposition products.
Oil carryover from compression	Collects in the glycol and reduces dehydration capacity.	An oil filter can be installed upstream of the dehydration unit.
CO, COS, NH_3, NOx, SO_2,		No information available

Table 1 – Effects of Impurities on TEG and Other Dehydration Processes

It is extremely important that the specific impurities and their associated normal and maximum concentrations are known, and adequately considered, during the design stage:

- An inlet filter/coalescer will remove liquids (such as amines, and water carrying sodium chloride in solution)
- Impurities can cause solids formation, resulting in fouling of equipment and foaming. Filtration / processing of the circulating stream will remove these and maintain low levels.

In the event that the levels of impurities cannot be tolerated it may be necessary to remove the impurities in a separate treatment system prior to the dehydration unit. This may require a catalytic reactor or use of an adsorbent (which may, or may not, be regenerable).

4.7.6 Issues with the TEG Process

TEG can degrade at temperatures in excess of 210°C. The reboiler temperature can be maintained at a margin below this temperature by minimisation of the regenerator operating pressure.

Foaming can cause problems with:

- Increased glycol losses into the CO2 and the still column vent,
- Reduced contact between gas and glycol solution thus reducing the drying efficiency

High removal efficiency internals ensure that if foaming occurs then solution entrainment is minimised.

Vendors advise that, provided the glycol regeneration unit is adequately sized for the full circulation capacity, then additional CO_2 contactors can be added to the system as required. The capital cost of expansion is thus reduced. If the regeneration unit has not been adequately sized at the start then a complete separate train incorporating contactor plus regeneration unit would have to be provided on up-rate. This option is obviously more expensive.

4.7.7 Advantages and Disadvantages of Liquid Desiccant Systems.

The main advantages of such liquid desiccant systems are:

- Relatively small CAPEX / OPEX
- Small pressure drop
- Ability to dehydrate gases containing impurities which are poisonous to solid sorbents
- Continuous process

The main disadvantages are:

- Smaller depression of dew-point (compared to solid desiccants)
- Foaming when gas contains light hydrocarbons

4.8 Solid Bed Desiccants

Dehydration takes place by adsorption. Gas is physically, rather than chemically, adsorbed to the surface of the adsorbent. Desirable properties for such dehydration adsorbents include:

- Good activity for water
- High mass transfer rate, to enable a high removal rate
- Large surface area – typically 500-800 m2/g
- High mechanical strength – minimizes dust formation and crushing. Strength when wet.
- Non-corrosive
- Non-toxic
- Chemically inert
- High bulk density

- Small volume changes upon adsorption and desorption of water
- Easy and economic regeneration
- Small resistance to gas flow, allowing a small pressure drop
- Easy regeneration
- Low cost

4.8.1 Types of Desiccant

There are three main types of solid adsorbent which are use for dehydration of acidic gases; silica gel, activated alumina and molecular sieve. All are regenerable.

Silica gel is synthetically produced and is essentially silicon dioxide, SiO_2. The end product is highly porous; it can dehydrate down to a typical dew-point of -50°C at atmospheric pressure and is relatively easy to regenerate. It has a large range of pore diameters, ranging from 10 to 1000 Angstroms, so adsorbs a large range of contaminants. Silica gel is acidic so can handle sour gases, but not alkaline materials, such as ammonia, or caustic. The sulphur from H_2S can deposit and block the surface. H_2S content should therefore be maintained at <5%.

Activated alumina, Al_2O_3, is a granular, porous adsorbent with similar properties to those of silica gel. It is a hydrated form of alumina oxide which can achieve dew-points of -70°C at atmospheric pressure It has a large pore size distribution range of between 10 to 10,000 Angstrom and the polar surface is not as strong as molecular sieves.

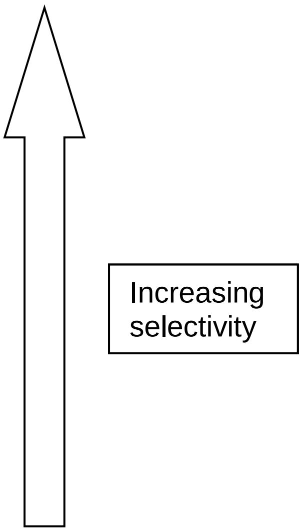
Molecular sieves are a class of synthetic zeolite aluminosilicates which can achieve dew-points of -100°C. They are crystalline, highly porous and have a very high surface area. They are effective for adsorption of polar compounds, such as water and H_2S, since they have localised polar charges on their surface. They have a narrow range of pore sizes so are selective towards smaller molecules. Several types of molecular sieve are available, based on pore size. The pore size is controlled by the specific cation in the makeup of the molecular sieve crystalline form. The molecular sieve crystals are held together by a binder (typically clay) which gives the product a shape, without interfering with flow of gas to the crystals. The binder particles are much smaller than the crystals. The binder is key to the particle mechanical strength.

Type	Cation	Pore size (Angstrom)
3A	Potassium	3
4A	Sodium	4
5A	Calcium	5
13X	Sodium	10

Table 2 - Details of Different Molecular Sieve Types

The predicted order of selectivity for Zeolite molecular sieves is:

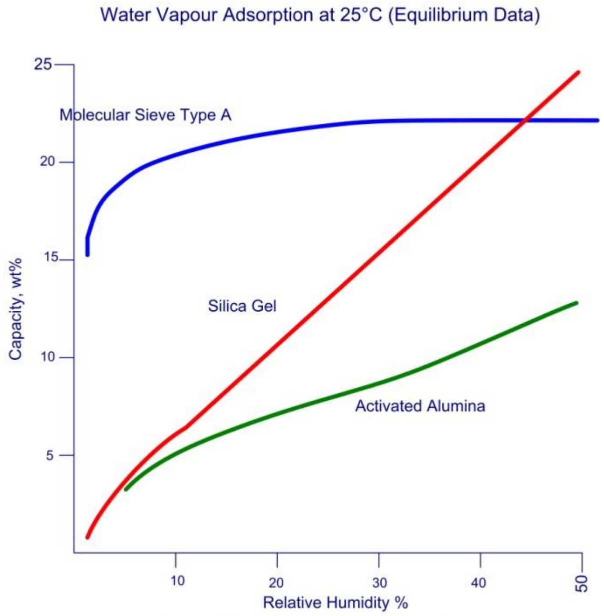
- Water
- Ammonia
- Iso-propanol
- Methanol
- Mercaptan
- Hydrogen Sulphide
- Aromatics
- Carbon Dioxide
- Olefins
- Sulphides



Polar molecules are adsorbed preferentially. Dehydration typically requires Type 3A or 4A molecular sieve. Type 3A will adsorb water and ammonia whilst Type 4A adsorbs water, ammonia, methanol, H_2S, CO_2, SO_2, C_2H_4, C_2H_8 and C_3H_6. They can produce gas of ~0.1 ppmv water content, but have a high regeneration temperature. Molecular sieve can operate at relatively high temperatures compared to other adsorbent types; typically up to 90°C. Acid resistant sieves are available for use with very sour gases.

4.8.2 Adsorption Capacity

The relative adsorption capacity of the different adsorbents is shown in Figure 14.



Adsorption on zeolite molecular sieves
produces a Langmuir-type isotherm

(Diagram for illustration only – do not scale)

Figure 14 – Relative Water Vapour Adsorption Capacity of Solid Desiccants at 25°C

4.8.3 Adsorption Process

Gas is passed through packed beds containing the solid desiccant. Adsorption is usually carried out from the top down, so as not to fluidise the bed at the higher flow rate. The behaviour within the vessel can be separated into several zones, as shown in Figure 15 and Figure 16:

- The equilibrium zone, at the top of the vessel, where there is equilibrium between the water partial pressure and the water adsorbed onto the bed. As time progresses and more water is adsorbed, the equilibrium zone expands. The quantity of water adsorbed is dependent upon the type of molecular sieve, the operating temperature and the water partial pressure in the gas stream.

- The Mass Transfer Zone (MTZ) is the zone in which mass transfer of water occurs from the CO2 to the adsorbent to achieve the product specification. It is not saturated with water. The length of the MTZ is effectively the length it takes the adsorbent to bring the impurities from their initial concentration to the final specification. It is dependent upon many factors, including the adsorbent type and size (which affects the diffusion kinetics), temperature and the flow velocity. Initially, just after a regeneration has been completed, the MTZ is located at the top of the bed. As water is adsorbed and the top section becomes saturated the MTZ moves down the bed. The bed should be regenerated either when, or before, the MTZ reaches the bottom of the bed, at which point water breakthrough will occur and the product water content will begin to rise.

- Below the MTZ is a volume of fresh adsorbent that has not yet been in contact with the impurities. Initially, after regeneration the whole bed will contain fresh adsorbent. As the process continues this zone becomes smaller as the MTZ and equilibrium zone move forward.

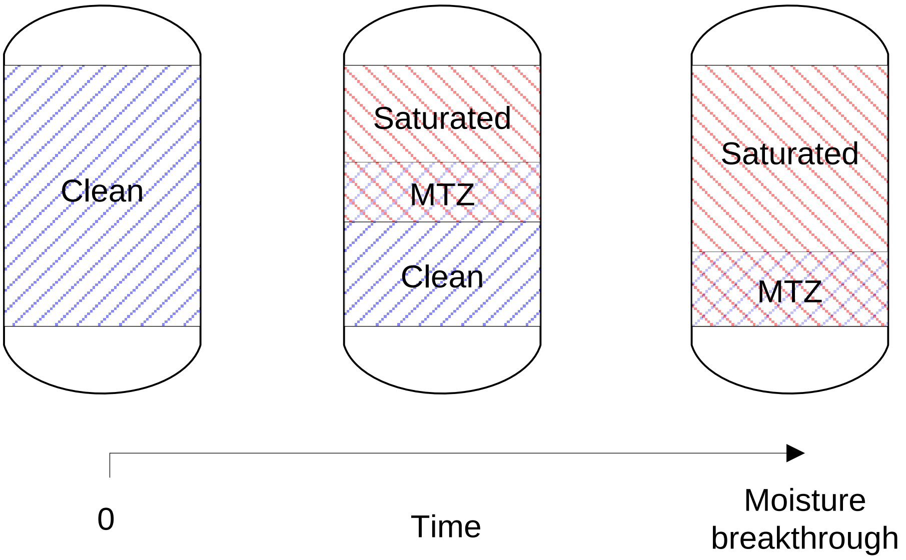


Figure 15 – Change in Adsorption Zones as Adsorption Progresses

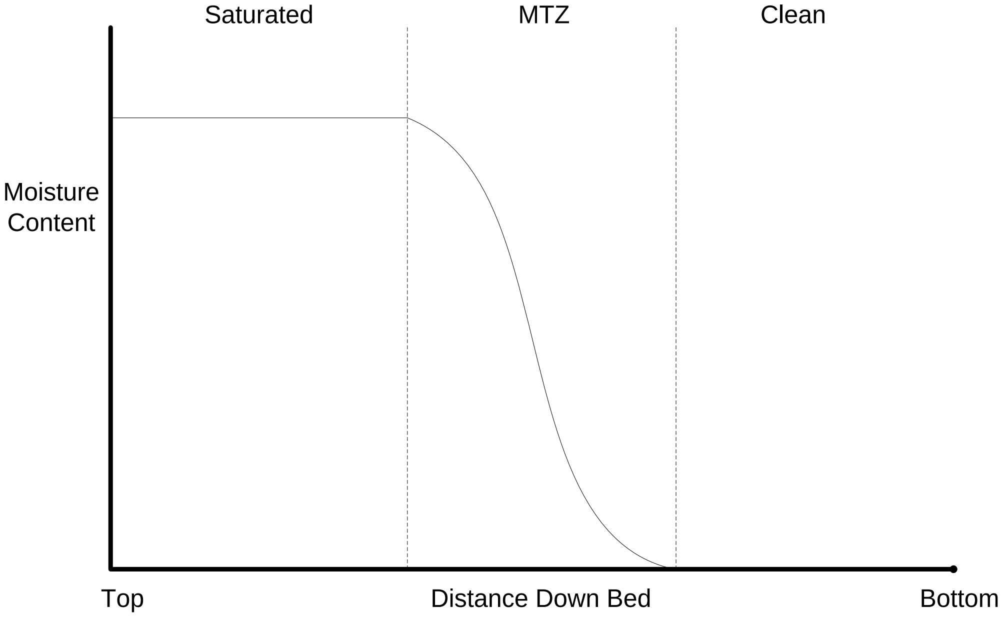


Figure 16 – Bed Concentration Profile in the Different Adsorption Zones

4.8.4 Regeneration

The beds become saturated over time so they must be regenerated to restore their functionality. A multi-bed system is therefore required to allow continuous operation; at least one bed is online, while at least one spent bed is being regenerated. Each type of desiccant has a different associated regeneration temperature:

Silica gel	120 - 230°C
Activated alumina	175 - 320°C
Molecular sieve	175 - 320°C

The regeneration temperature is dependent upon the type of adsorbent, contaminants which need to be removed, the pressure of the regeneration gas, feed gas composition, regeneration gas composition, etc, as well as the final moisture specification.

Regeneration pressure is dependent upon the regeneration technique selected by the vendor and the availability of streams which may be used to perform the regeneration. Oxyfuel processes in particular can have vent streams and/or excess nitrogen available to carry out the regeneration without requiring use of CO_2 product gas. In such cases regeneration pressure may be significantly lower than adsorption pressure.

The heat of adsorption is greater for molecular sieve than for activated alumina or silica gel. More regeneration energy is therefore required to remove the water from molecular sieves for the same amount of water adsorbed.

Several different types of regeneration are possible[16];

- Temperature or Thermal Swing
- Pressure Swing
- Thermal/Pressure Swing
- Purge gas stripping

Thermal Swing

Thermal swing regeneration is where the bed is heated to a high temperature (typically 200-320°C) and flushed with dry purge gas, as shown in Figure 19 and Figure 20. After a period of time at high temperature the bed is cooled with a portion of the clean, dry gas, as described in Section 4.8.9.Dry gas is returned to the inlet of the operating bed for dehydration. High water loadings can subsequently be obtained in the bed. Impurities (such as H_2S) stripped from the adsorption bed may require to be treated prior to the stream being recycled. Variations of the process exist and are outlined below.

The water-saturated gas from the regeneration cycle can be recycled to the front of the adsorbing bed(s) using a blower, or via the suction of the upstream compression stages. Product losses are thus minimised. Regeneration is carried out in the opposite direction so as not to push the adsorbed water through the whole bed. This keeps the end of the bed as dry as possible

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[16] Molecular Sieves Troubleshooting’, Peter Meyer, CECA SA, GPA Europe Annual Conference, September 2010.

Wet gas can be used for carrying out the regeneration, as shown in Figure 17 and Figure 18. However the cooling step must be carried out in the direction of dehydration to ensure that the wet gas does not saturate the normally dry end of the bed. Regenerated gas is returned to join the wet gas feed stream. The drive units for this can be as above or alternatively by installation of a pressure let-down valve in the wet feed gas supply, allowing the regeneration gas to re-enter the wet feed stream downstream of the PCV.

‘Heat of Compression’ drying, in which hot (wet) gas from the compressor discharge can be used to provide at least a part of the regeneration heat (thus providing recovery of some of the heat of compression) either by:

- Directing part of the hot gas stream to the inlet of the regenerating bed, as shown in Figure 21

- Passing at least a part of the hot gas through a gas/gas interchanger to heat the regeneration gas stream.

This process has been developed by SPX to improve the heat recovery from the process as a whole. Compressor delivery temperatures obviously affect the extent of heating which can be achieved. Ramgen compressors can have very high delivery temperatures of ~ 240°C. This is sufficient to enable adequate regeneration bed temperatures to be achieved without the requirement for additional heating. The regeneration bed temperatures achieved determine the final product dryness.

Options also exist for cooling. The regeneration stream can be taken from the cooled compressor discharge, upstream of a restriction. Wet gas is used on the cooling duty. Spent regeneration gas can be returned downstream of the restriction and combined with the main flow prior to passing to the drying bed. A warmer stream therefore has to be dried

The side stream of hot gas can be taken from the compressor discharge, as above, but spent gas can be cooled local to the drying unit, as shown in Figure 22.

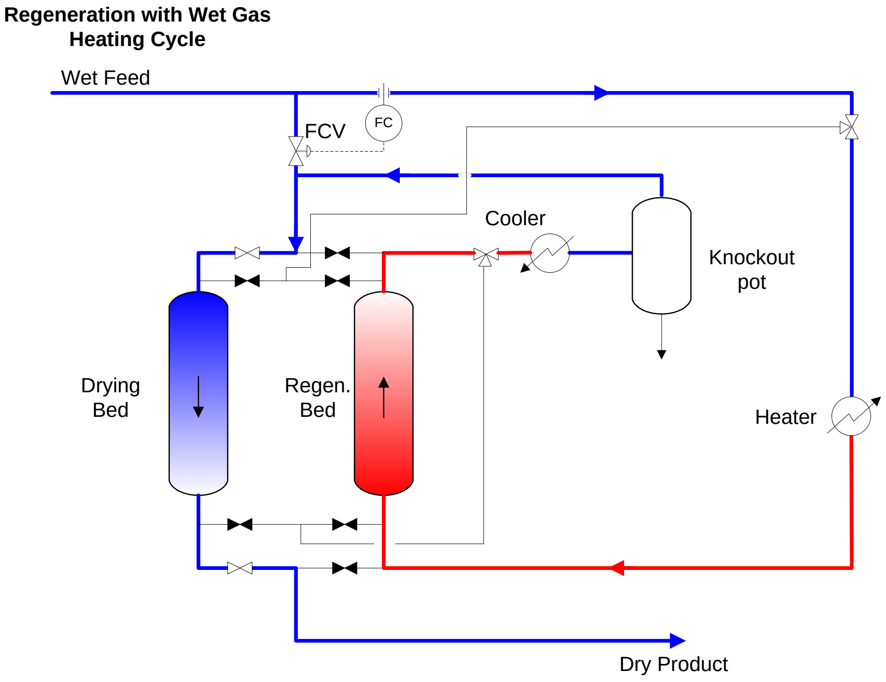

Figure 17 – Regeneration with Wet gas – Heating Cycle

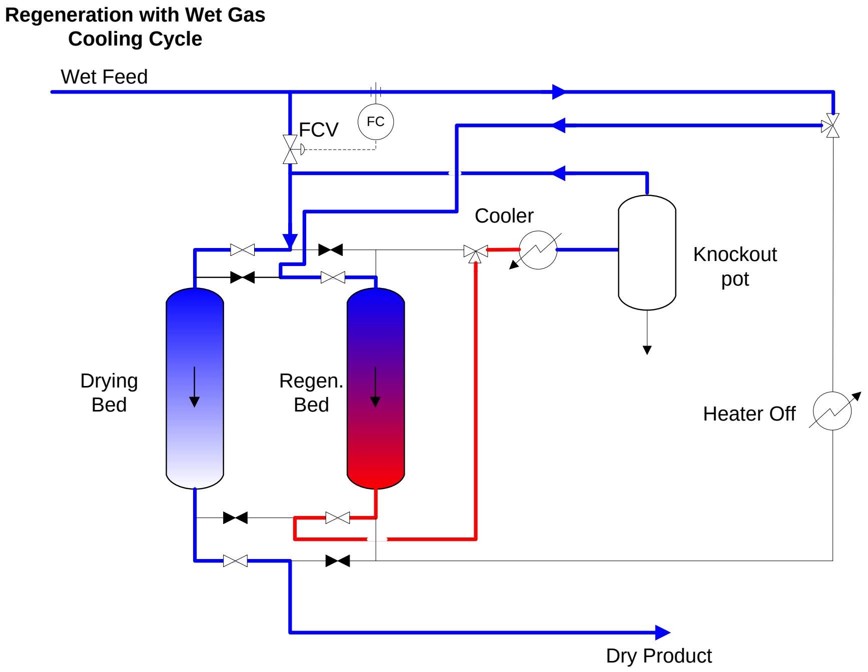

Figure 18 - Regeneration with Wet gas – Cooling Cycle

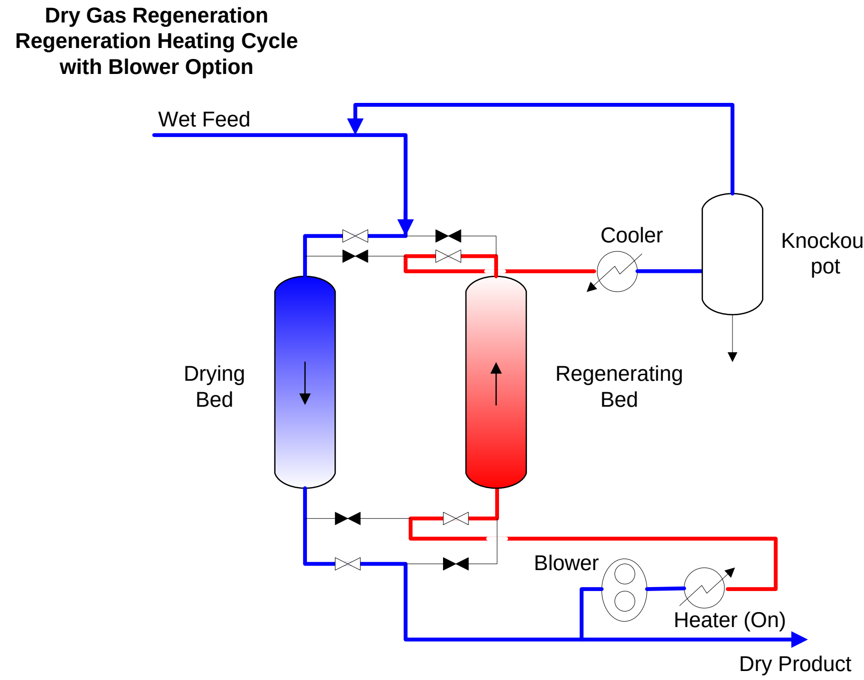

Figure 19 – Dry Gas Regeneration with Blower – Heating Cycle

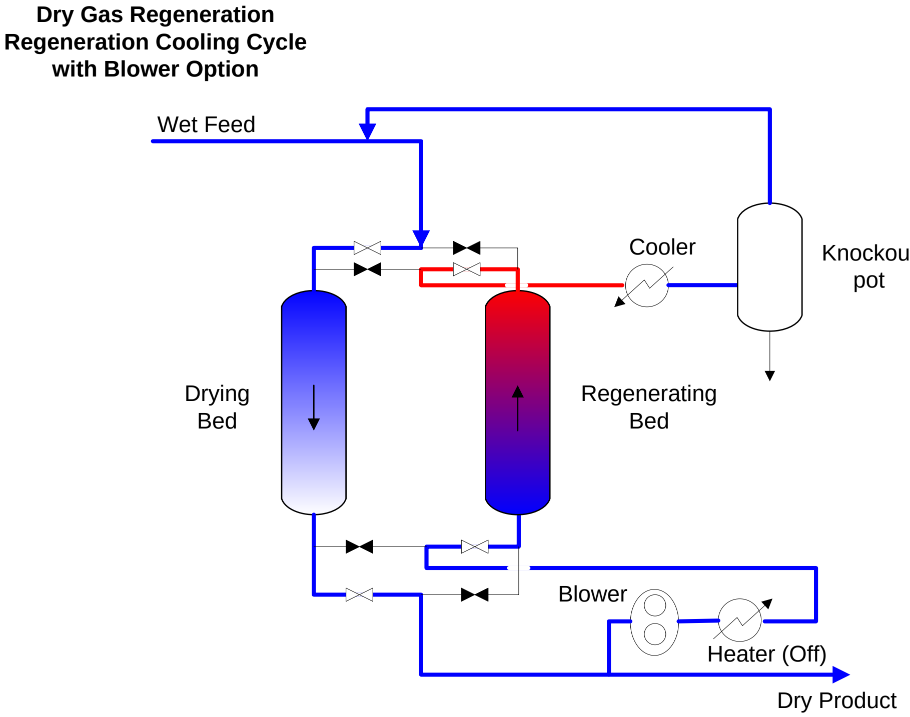

Figure 20 - Dry Gas Regeneration with Blower – Cooling Cycle

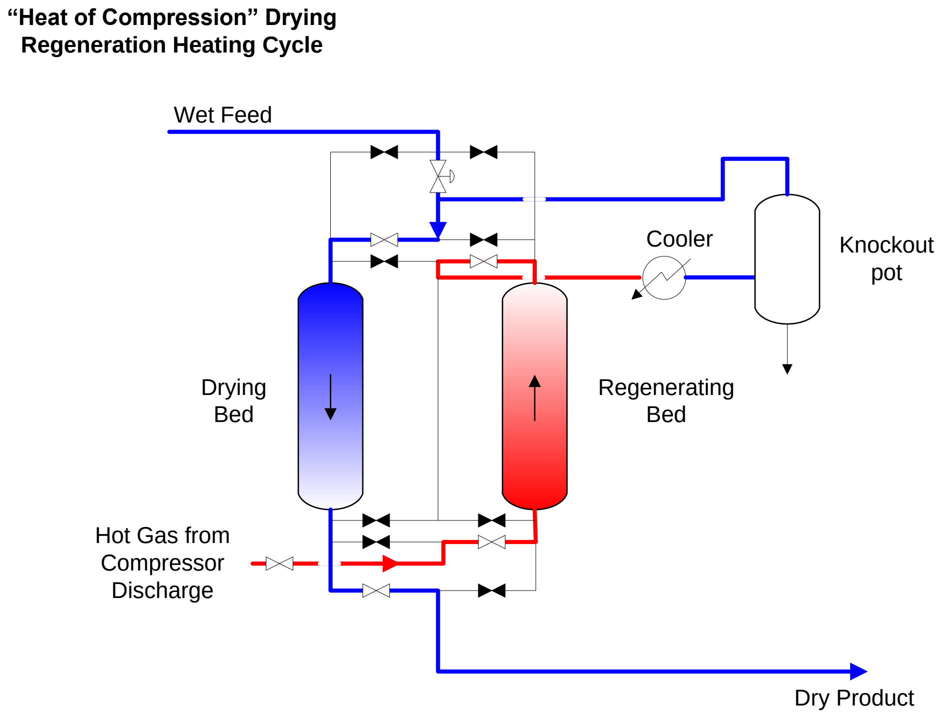

Figure 21 – ‘Heat of Compression’ Drying – Regeneration Heating Cycle

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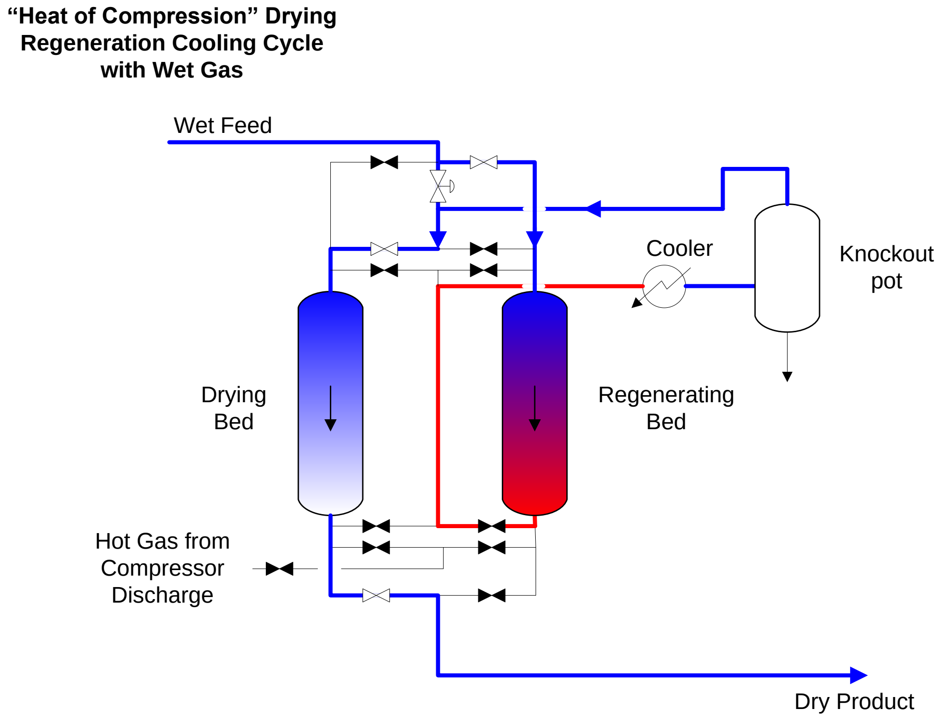


Figure 22 – Heat of Compression Drying – Regeneration Cooling Cycle with Wet Gas

Pressure Swing

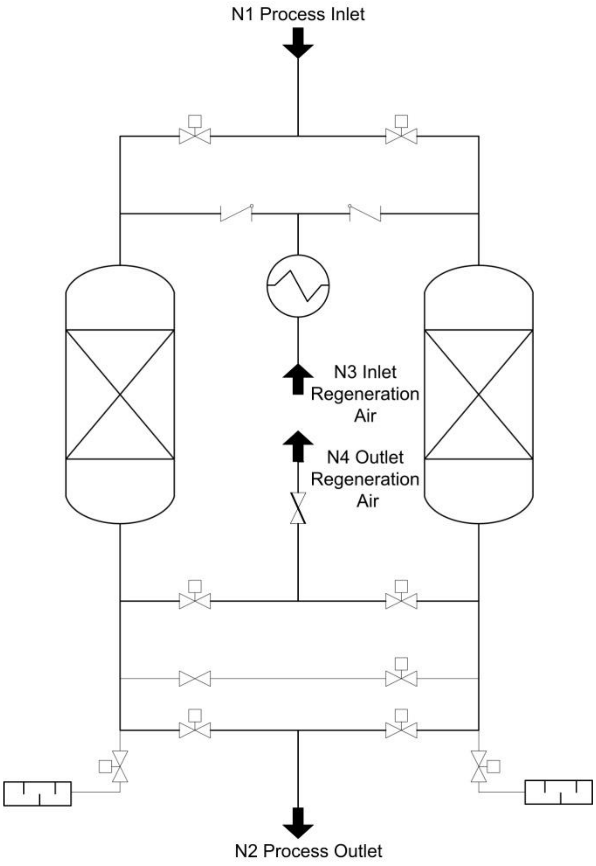
Pressure swing, at isothermal conditions, uses lower pressure, or vacuum, to desorb the bed. This enables fast cycling and less regeneration equipment. Gas is typically vented. It is not usually used alone for dehydration since moisture is held strongly and heat is required to provide the energy necessary to overcome the heat of adsorption. Regeneration is carried out in the downward direction to avoid fluidisation of the regenerating bed on relatively rapid depressurisation.

Pressure swing combined with heat. This process typically uses low pressure gas or ambient air as the regenerant, as shown in Figure 23. Losses of CO_2 occur on depressurisation. A blower passes the ambient air over an electric heater and through the desiccant. The hot air stream (containing desorbed impurities) is vented. If significant quantities of H_2S are present in the CO_2 then the regeneration sequence will commence with a low temperature gas purge to remove the H_2S. The stream will require treatment prior to being vented to atmosphere. Once the moisture has been removed from the bed the heater is switched off and cold ambient air is passed through the bed. At the end of the cycle the regenerated drier is purged with CO_2, prior to re-pressurisation and bed changeover. The bed should be reloaded with dry CO_2 to reduce the potential for high temperatures of adsorption. Care needs to be taken to ensure the design adequately considers the chilling of the gas, both in the vessel due to expansion and in the downstream equipment after pressure let-down. Impurities (such as H_2S) stripped from the adsorption bed may require to be treated prior to the stream being vented to atmosphere. CO_2 losses are higher with this regeneration process due to the depressurisation and purging cycles.

This regeneration process has the advantages of being a simple regeneration process with a small footprint requirement. However, it also has the disadvantages of having a regeneration vent gas stream, vessel depressurisation (and associated cooling), loss of CO_2 gas to vent, issues with vent contaminant handling, the risk of introducing air into the CO_2 product, additional vessel wall thickness due to pressure and thermal cycling and additional regeneration heat as a result of thicker vessels..

Purge Gas Stripping

Purge gas stripping, Figure 23, uses non-adsorbing purge gas to desorb the bed by reducing the partial pressure of the water. High operating temperatures and low operating pressures give more efficient stripping. This process is typically used in processes where downstream cryogenic processing is carried out to remove inert gases. These inert gasses can be used to carry out the purge, prior to power recovery in an expander. Gases are typically sent to vent. This process may be required in cases where the CO_2 gas has a high impurity content of species such as NOx, which can be adsorbed onto the bed. On regeneration a high concentration slug of impurity passes into the purge gas, rather than being recycled to the process. Occasionally processes such as oxyfuel combustion have excess inert gas, such as waste nitrogen, which could be used on this duty.



Reference: AMEC illustration of process information provided by SPX 14/12/12

Figure 23 - Schematic of Molecular Sieve Process with Purge Gas Regeneration Process

4.8.5 Operation

Some units are operated on a fixed cycle time, in which the cycles always have the same duration, irrespective of the gas flow rate through the bed. Other units are operated until moisture breakthrough occurs, when moisture is observed to rise at the bed exit. The molecular sieve capacity gradually decreases with time. This ageing is taken into account in the fixed cycle time arrangement but for the moisture breakthrough case the bed adsorption time will gradually decrease. If run on a fixed time basis then;

- The adsorbent is not fully water saturated
- The bed has to be regenerated on a higher frequency than would be required for the analysis based case
- The actual regeneration is shorter than for the analysis based changeover since less water has been adsorbed
- The adsorption time is set based on the end of life performance of the adsorbent

- Operating costs are higher since the bed is regenerated and heated more frequently and the heat involved is not only that required for water removal but the heat to warm the equipment and adsorbent as well.

- Typically the amount of heat required to regenerate a bed is significantly more than that required to remove the water.

For the analysis method, as the bed ages, the time between regenerations reduces and ultimately, at the end of life, will be similar to that of the fixed time adsorption. There is an operational and design balance to reach between the rate of ageing against material selection, volume of water absorbed, pressure and temperature.

The process pressure also plays a part in the selection of regeneration method and time. Higher pressures effectively require thick wall material to be used. This affects mechanical costs and also regeneration cost as the higher mass of metal will require additional heat to bring the bed to the required temperature.

The fixed time regeneration has the advantage of being more forgiving to a single inadequate regeneration, since a portion of the bed is not water-saturated. The product gas is maintained continuously at a very low level, does not have peaks at raised (albeit within specification) moisture values and is not reliant on the moisture analyser.

Ultimately, after a few years operation, the adsorption media will require replacement to prevent water breakthrough.

Multiple bed systems typically use 2 beds – one online and one being regenerated. Design is normally based on an adsorption time of 6 to 12 hours per bed. With a two bed system the regeneration of the spent vessel (heating, desorption, cooling and bed switchover) will have to be done within that time. With very small systems (or low water content) the cycle can be longer. When cycle time becomes critical (<6 hours) then more adsorption beds can be added to permit continuous processing of the feed. Generally for the same gas processing rate, a larger number of beds can result in the requirement for a smaller regeneration heater due to the smaller gas flows required for regeneration of the smaller diameter vessel.

The number of beds can be extended to enable different operational patterns, flexibility or reliability. In natural gas systems, at high pressure and flow, up to 5 beds and beyond are common. In the case of higher bed numbers the operability changes slightly; one bed can be regenerating, another cooling and multiple beds in operational mode.

Turndown varies from 10 to 30%, depending on the minimum flow requirements of the beds. Excessive low flow can cause channelling and bypassing of part of the adsorbent bed which can result in premature breakthrough of moisture. Adsorption beds can typically handle faster ramp rates than a liquid based process.

It should be noted that different capture technology options may have knock on effects on dehydration design that are yet to be fully understood. The general discussions herein are based on the premise of single media solutions, where dehydration occurs in vessels packed with a single type of media. Technologies such as Oxyfuel may require multiple media selection to ensure that the dehydration process is suitably acid resistant. This is generally unknown at this time, but the nature of a more acidic gas can be expected from Oxyfuel so a variation of media may be required.

4.8.6 By-products Produced

For a conventional regeneration scheme, in which the water is condensed out of the circulating CO_2 gas, a waste water stream is produced, containing dissolved CO_2. This is typically sent to drain if clean, or collected in a contaminated water tank and sent for offsite disposal or reprocessed for re-use, as appropriate.

For a system which uses low pressure waste gas, or air, as the regenerant:

- CO2 depressurisation occurs to atmosphere
- A hot, wet gas stream is produced. This stream can be vented directly to atmosphere if it is contaminant free, or treated to remove undesirable contaminants. The stream can be cooled and the water removed from the waste gas prior to venting to atmosphere. The water can be sent to drain or recovered, as above.
- The regenerated bed is purged with CO2 to remove the air/waste gas from the adsorption beds, prior to bringing the bed back online. CO2 purge gas is vented to atmosphere.

Dust collected in the fines filters downstream of the adsorbent beds is treated as contaminated waste.

At the end of adsorbent life the adsorbent, associated guard layer (if present) and support balls are removed from the vessels. It is normal to treat these solids as contaminated waste, since they will have adsorbed and concentrated impurities originally present in the raw gas stream. It is normal to regenerate the adsorbent prior to removal from the bed to minimise the contaminants present.

4.8.7 Contamination of the CO_2

Typically there are no impurities introduced into the CO_2 from the adsorbent, other than the dust which may be present. The dust levels are typically worse after an adsorbent change since dust can be generated during the loading procedure. The downstream fines filters collect the dust.

For a system which uses low pressure waste gas, or air, as the regenerant then there is a risk of introduction of these gases into the CO_2 if an adequate dry CO_2 purge has not taken place.

4.8.8 Effects of Impurities

Impurities content in the feed gas must be kept under control[17]:

- Impurities can be adsorbed in preference to water and they can be difficult to displace or remove during regeneration. In regards to molecular sieve, selection of the correct type should minimise/avoid such co-adsorption

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[17] 'Molecular Sieves Contaminants: Effects, Consequences and Mitigation', A Terrigeol, CECA SA, GPA Europe Annual Conference, May 2012.

- Impurities may chemically attack the adsorbent, destroying the binder and possibly the structure. The adsorbent can turn to powder. Such impurities may further react during the regeneration cycle due to the high temperatures experienced

- Liquid can agglomerate the particles, leading to uneven flow distribution

- Permanent fouling of the pores can occur due to the formation of coke

- Oxygen can react with other species present in the regeneration heater where temperatures in the range 230 to 300°C are present or in the adsorbent bed where the adsorbent can act as a catalyst. This is particularly of concern in cases where H2S is present; elemental sulphur can be formed which can block the adsorbent pores or form solid sulphur clumps which can affect the flow through the bed

- Corrosion and/or attack of the equipment materials of construction may occur.

These effectively reduce the adsorption capacity of the bed, either temporarily or permanently, resulting in premature gas breakthrough. High pressure drop and channelling may also occur. Gross contamination may require a complete replacement charge. Typical effects of specific impurities[18] on molecular sieve are given in Table 3 along with estimated maximum impurity levels[19,20] which can be tolerated by molecular sieve.

It is therefore extremely important that the specific impurities and their associated normal and maximum concentrations are known, and adequately considered, during the design stage:

- A guard layer at the top of the adsorption beds can protect the adsorbent from some of the above impurities, especially liquid carryover. For example, a 500 mm deep silica gel layer can be installed above a molecular sieve bed.

- Acid resistant grades of adsorbent can also be used.

- Extra volume of media can be added, giving a margin to allow for adsorbent deterioration.

- Metalwork (vessels and pipe work) should be insulated to prevent / minimise condensation at cold surfaces.

- In the event that the levels of impurities cannot be tolerated, either because of their damaging effects or the increase in dehydration adsorbent volume required to deal with them, then it may be more appropriate to remove the impurities in a separate treatment system upstream of the dehydration unit. This may require a catalytic reactor or use of an adsorbent (which may, or may not, be regenerable). The dehydration media vendor should be able to advise on the most appropriate approach to be taken. The vendor may be able to provide another media which is suitable for removal of the impurity, without adversely affecting the dehydration media.

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[18] 'Molecular Sieves Contaminants: Effects, Consequences and Mitigation', A Terrigeol, CECA, SA, Gas Processors Association, Annual Conference, May 2012.

[19] Verbal communication from media vendor, 20/11/12

[20] 'Effects of Contaminants o Molecular Sieves' Tony Purcell, Grace Davison, Hydrocarbon Engineering, march/April 1997.

Effects of Impurities on Molecular Sieve Dehydration Process

Impurity	Maximum tolerable concentration in FEED gas	Effect on molecular sieve	Notes
H_2O	-	Liquid droplets or mist - exhaust the molecular sieve more quickly, leading to moisture breakthrough - react with the molecular sieve damaging the clay binder. The sieve may break down and form dust	Adequately sized knockout pots and Silica gel guard bed may be appropriate
N_2, Ar, H_2, CH_4	No limit	Inert.	
O_2	If CH_4 or other hydrocarbons present then problems can start at ~ 15-50 ppmv, possibly higher If CH_4, hydrocarbons, and sulphur species are not present then there is no limit on the O_2 levels	In the regeneration heater - iron oxides present catalyse the reaction with carbonaceous materials, such as methane, to form CO_2 +H_2O. Coke formation can result from higher hydrocarbons and can block pores. C8-C10 are of concern since they are non-volatile and build up in the molecular sieve. In the presence of sulphur products at ambient temperature (e.g. H_2S) SO_2, H_2O and possibly elemental sulphur form. The sulphur can block pores and form clumps	
CO	No limit	CO is less polar than CO_2, so is inert	
NOx		In the humid conditions these acidic species adsorb on the binder and attack the zeolite structure. Molecular sieve life is reduced. They desorb during regeneration and form acids in the regeneration cooler and separator where liquid water is formed.	A combined system – with an alumina bed above the molecular sieve will help
SO_2			
H_2S	1000 ppmv / nil	Important to know how much is present, even at low levels, due to	Would form sulphide + other species with

Effects of Impurities on Molecular Sieve Dehydration Process			
Impurity	**Maximum tolerable concentration in FEED gas**	**Effect on molecular sieve**	**Notes**
	(Note 1)	the generation of COS (see below) Values > 1000ppmv are too acidic and damage the mol sieve. Nil quoted by one vendor due to concerns about SO_2 and free sulphur generation when O_2 present.	Activated alumina
COS		$H_2S + CO_2 \Leftrightarrow COS + H_2O$ Water saturated gas present at inlet, with little/no COS present. COS is not very polar so not strongly adsorbed. Equilibrium constant is small at low temperature, so equilibrium is to the left. As water is removed in the adsorption process the equilibrium moves to the right, generating COS The mol sieve can also catalyse the formation of COS. At higher temperatures the equilibrium constant increases significantly. On regeneration the reaction equilibrium is much further towards the right, forming more COS. As moisture is desorbed from the bed the water concentration increases. When the gas is cooled the equilibrium moves to the left, forming H_2S and CO_2 in the regeneration cooler/separator, potentially resulting in corrosion issues.	Type 3A molecular sieve do not adsorb significant CO_2 or H_2S, so form low levels of COS Type 4A sieve is much more active and leads to high conversion levels of COS. Specific products have been developed to minimise COS conversion.
HCl, acids	Nil, intolerable, 1 ppmv	All acids are able to destroy the zeolite framework by a de-alumination process, causing dust. Occurs at high temperatures during regeneration.	Use of acid resistant molecular sieve will assist. Preferable to remove these prior to adsorption. A sacrificial layer of activated alumina will remove the Cl^- (promoted types). Layer will have a

Effects of Impurities on Molecular Sieve Dehydration Process			
Impurity	**Maximum tolerable concentration in FEED gas**	**Effect on molecular sieve**	**Notes**
			limited life.
Amines		Adsorb on the media causing permanent damage. On regeneration heating they decompose and form - coke - ammonia, which forms NH_4^+ with water and reacts with the sieve, replacing the cation in the structure, weakening it and forming dust. Released cations can hinder normal adsorption kinetics.	From upstream CO_2 capture process Silica gel or activated alumina guard bed may be appropriate Use of resistant molecular sieve will reduce extent of dust formation
NH_3		Adsorbed on type 3A and 4A sieves. Less strongly adsorbed than water and displaced by water as front moves through the bed. May be peaks of NH_3 in product gas. High bed temperatures may occur on co-adsorption. On regeneration ammonia is desorbed before water. Ammonia in the presence of liquid water can carry out ion exchange with the cations in the molecular sieve; the water can leach the cations out of the structure, significantly weakening it. Eventually will collapse to an amorphous clay. Ammonia & H_2S can react in the presence of water to form ammonium sulphide	Add extra capacity to the bed to cater for the ammonia adsorption. (Assume another 5-10ppmv of water present at the levels of ammonia present in the quoted case analyses.)
Aldehydes	< 200 ppmv	C=O can dimerise and trimerise to give non-volatile components. A slow build-up of coking components results. Molecular sieves act as catalyst for aldol condensation of aldehydes and	Some of the impurities and by-products are highly toxic

Effects of Impurities on Molecular Sieve Dehydration Process			
Impurity	**Maximum tolerable concentration in FEED gas**	**Effect on molecular sieve**	**Notes**
		ketones. Polymerisation may occur at low temperatures. Impurities and by-products are highly toxic.	
NaCl		Collect in the pores and damage the structure of the binder and crystals. The top of the bed breaks down forming dust and agglomerates	Carried forward in entrained water
Caustic		Chemically attacks the binder and zeolite structure, forming dust.	From upstream acid gas removal process Silica gel guard bed may be appropriate Use of resistant molecular sieve will reduce extent of dust formation
Methanol		Competes with water for adsorption. Increases the MTZ length, resulting in premature breakthrough. Methanol will decompose on molecular sieve at temperatures above ~240°C on the active sieve surface to produce H_2 and CO. It could also give H_2, CO_2 and carbon, but this is much less likely.	Add extra capacity to the bed Maintain regeneration temperatures below 240°C.
Oil carryover from compression		Adsorbed by the binder, or in the macropores. It is not completely removed during regeneration and eventually cracks, polymerises or reacts to form coke. Premature desiccant aging results	Macroporous buffer gel protective layer can adsorb heavy impurities which may be removed on regeneration. Alternatively an oil filter can be installed upstream of the dehydration unit.
Glycols, di-glycolamine (DGA), diiso-propylene (DIPA)		Adsorbed by the binder, or in the macropores. It is not completely removed during regeneration and eventually cracks, polymerises or reacts to form coke. Premature desiccant aging results In severe	

Effects of Impurities on Molecular Sieve Dehydration Process			
Impurity	**Maximum tolerable concentration in FEED gas**	**Effect on molecular sieve**	**Notes**
		cases molecular sieve can cement together resulting in channelling. At low gas flows during regeneration channelling is worse and the regeneration is inadequate, resulting in very premature breakthrough.	
Heavy Metals		Not absorbed in A and X-type sieves. Considered as not harmful to molecular sieve performance.	Toxicity rating on disposal needs to consider the toxics present.

Notes:

1. Responses from different vendors
2. Formation of dust can cause problems with increased pressure drop and reduction of the molecular sieve area available for adsorption. Premature water breakthrough may occur.
3. Clumps and agglomerates reduce the area available for flow, leading to channelling, high pressure drop and premature breakthrough.

Table 3 - Effects of Impurities on Molecular Sieve Dehydration Process

Modified grades of molecular sieve are available which are more resistant to damage:

- The binder can be modified to be more robust, such that the particles are able to withstand impact from liquids or acid attack. The particles maintain their integrity and dehydration capacity

- The molecular sieve can be modified to minimise H2S co-adsorption and the subsequent formation of COS.

4.8.9 Process Description

This description is based on a typical pressurised regeneration system using molecular sieve as desiccant; molecular sieve can typically achieve < 1ppmv moisture content in the product gas. The arrangement for higher product moisture requirements with different desiccants is similar. Figure 24 and Figure 25 illustrate the process.

Water-saturated CO_2 enters the gas dehydration unit. The unit typically consists of two adsorber vessels, with one adsorber in service whilst the other is being regenerated. (It should be noted that the number of adsorber vessels is dependent upon the total flow of CO_2 to be treated and the duration of the adsorption cycle.)

CO_2 enters the top of the online adsorption bed. In this example adsorption takes place in the downwards direction through the bed. The adsorber vessel is provided with (from top to bottom): flow distributors, ceramic balls, a silica gel guard layer, molecular sieve material, ceramic supporting balls and a support grid. The silica gel guard layer protects the sensitive molecular sieve from any droplet carryover which might occur. The droplet carryover could be highly acidic and has the potential to damage the main bed. In some circumstances the use of a guard layer is not sufficient and a sacrificial bed of lower cost media, or a guard bed of acid resistant media can be employed as the first stage in the process. Dry CO_2 product gas leaves the bottom of the online adsorber and passes through a dry gas after-filter to ensure that entrained molecular sieve particles are removed.

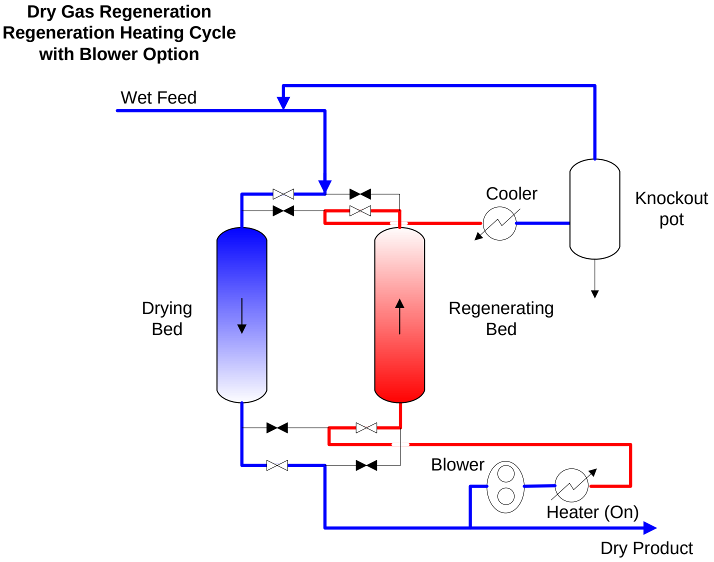

Figure 24 – Dry Gas Regeneration with Blower – Heating Cycle

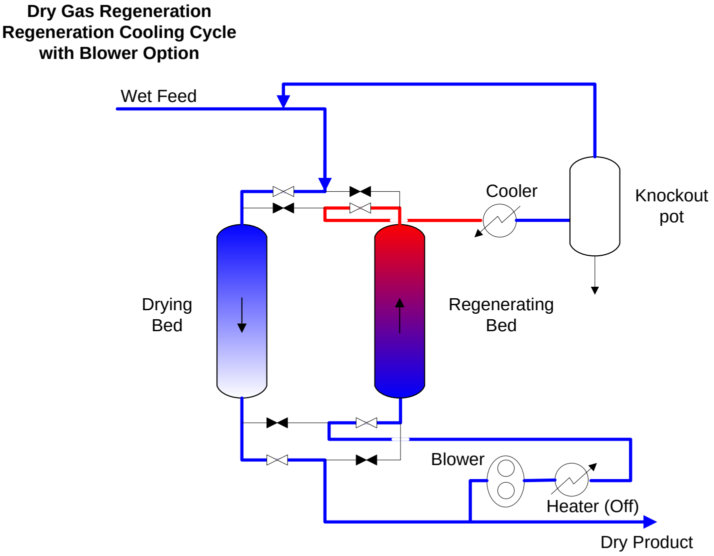

Figure 25 - Dry Gas Regeneration with Blower – Cooling Cycle

The adsorbers are designed to remain in adsorption mode for a certain cycle time – in this case 8 hours. A typical sequence for a two-bed adsorption unit on an 8 hour adsorption time is shown in Figure 26.

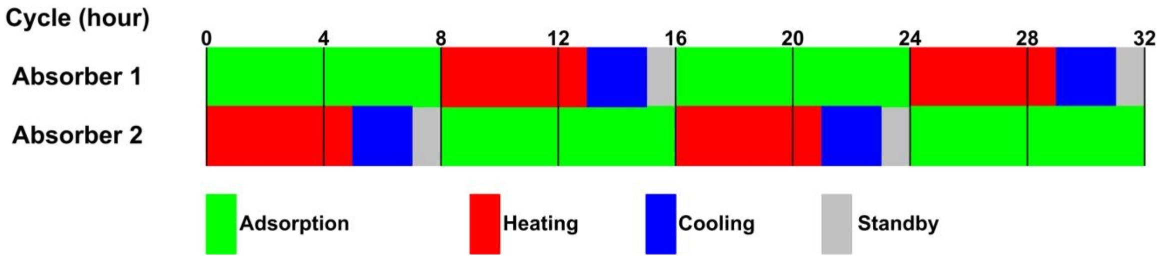

Figure 26 – Sequence for Two-Bed Adsorption Unit

Switching valves automatically move the beds through the sequence of adsorption and regeneration modes by automatically diverting the gas flows. Equipment, such as heaters, are automatically turned on / off, as required, by the sequence control system

After 8 hours, the online bed is near saturation and requires regeneration. The regeneration process is carried out in the opposite direction to the adsorption process; in this case flow is upwards through the regenerating vessel for both the heating and cooling cycle. A slipstream of dry CO_2 product gas is used to regenerate the spent bed. Regeneration is carried out by heating the spent bed to approximately 230 °C for 5 hrs, to ensure that all water components are removed from the bed. The heat required to achieve the high temperatures is supplied by an electrical regeneration gas heater. The regeneration gas temperature is monitored at the exit from the heater. The quantity of gas used for regeneration is dependent upon the total flow and the cycle time. Duty/standby blower/compressors are installed to compensate for pressure losses during the regeneration process. Water released from the molecular sieve during the heating cycle is conveyed by the regeneration gas flow into the regeneration gas cooler and the gas is cooled to a maximum temperature of 35°C. Condensed water is removed in the regeneration gas separator vessel. Saturated CO_2 gas is returned to the inlet of the online adsorber and combined with the main flow of saturated gas. After the 5 hour heating cycle the heater is switched off. Dry CO_2 product gas, at ambient temperature, passes to the hot bed. The cooling of the bed is monitored with the downstream temperature transmitter. Cooling will be stopped when the bed temperature is at or below 35 °C. The cooled, regenerated bed can be safely brought back online in adsorption duty. During changeover the two vessels will operate in parallel, to reduce flow surges in the product stream. The spent adsorber will then be taken offline for regeneration.

During the regeneration process, as the bed is heated a large volume of water vapour is released from the molecular sieve. Initially the front section of the bed heats up while the downstream part remains cold. The water contacts the cooler vessel walls and condenses on the top and sides of the vessel. This is known as ‘adsorption reflux’. The liquid water generated can form agglomerated clumps of material. Over time and successive regeneration operations this agglomerated mass builds up. Gas cannot pass through the agglomerated mass at the walls and the effective diameter is substantially reduced, increasing pressure drop and reducing the effective volume of available molecular sieve for dehydration duty. In the above process, the bed undergoing regeneration is therefore held at ~120°C for a period of time to ensure that the downstream sections of molecular sieve and the vessel walls have warmed sufficiently to prevent / minimise the condensation of water. Once the holding period is completed the bed is heated to regeneration temperature.

4.8.10 Bed Configurations

Bed configurations vary depending on flow rate, available pressure drop, the extent of water removal required, and other factors, such as location issues. The illustrations provided in this study are typically simple two bed systems. In general, as bed numbers increase then the initial inclination is to operate beds in parallel. For multi-bed systems each bed will be at a different point in the adsorption/regeneration cycle, thus there will be beds that are adsorbing, cooling or regenerating in one train. Multiple beds can exist on adsorption duty, although they will have been online for different times. This has the advantage of more continuous heat usage, particularly from heat of compression processes, but is dependent on saturation and regeneration time of the bed.

An example of a three bed system is shown in Figure 27.

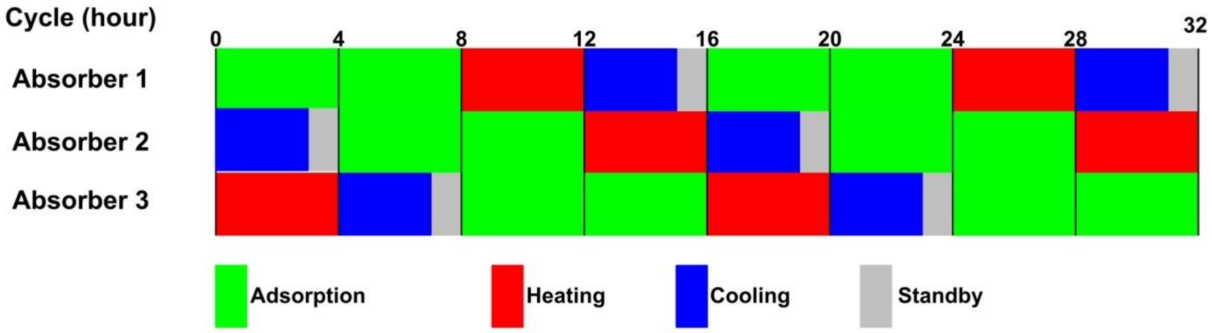

Figure 27 Three bed regeneration process (example)

As the duty increases parallel trains are typically employed. These also allow broader turn down ranges, since an operational bed or train can be removed from service. Operating in series is generally not provided. However, it may become relevant where:

- A guard or sacrificial bed is required to remove impurities from the gas stream if these may damage the media,
- The required adsorbent is of different grades to meet the quality requirements,
- The required mass transfer zone is too deep to be contained in one bed.

This has not been indicated as the case by the vendors who contributed to this study. Studies for the UK CCS competition both indicated single trains with parallel beds for the design flow rate. As it becomes necessary to treat larger flows multi-bed process trains can be expected as well as the use of parallel trains.

4.8.11 Equipment Configurations

So far the illustrations and descriptions consider a simple two bed system, as proposed by most vendors. The final configuration of the dehydration system is dependent on a number of factors. These typically include:

- Removal requirement
- Pressure drop
- Available streams to use in regeneration, rather than the CO_2 stream
- Regeneration conditions required to enable use of the above stream
- Flow rate
- Energy requirements
- Adsorbent type and performance
    - Pressure drop
    - Efficiency
    - Optimal bed height

The pressure drop that is tolerable in the system, imposed by the bed, associated valvery and filtration, is linked to the flow rate through the system and the medium being used. Systems with low tolerance of pressure drop would normally require additional parallel units to reduce the flow and pressure drop consideration. For high flow rates an optimal vessel size is sought balanced against the cost of fewer larger vs. more smaller vessels. This balance is also influenced by the heat requirements of such systems, where smaller vessels can generally be heated and regenerated more rapidly than larger vessels. The above issues are interlinked and influence the complex design of such systems. This overall design also has to be balanced against CAPEX changes and OPEX impacts of regeneration. There is no clear correlation over the CAPEX impact of bed configurations or numbers given the dependencies on many factors. It can be expected that for larger flows, nearer full commercial scale parallel trains or parallel beds will become the norm and that there will be marginal CAPEX saving, typically around the use of common utility provisions.

Outline calculations to provide initial sizing are well reported for natural gas processes and need validation for CO_2. These calculations provide some initial basis, but this would generally require either vendor engagement or/and cost benefit analysis to reach an optimal solution.

In terms of regeneration technology options the route to selection is less clear. The use of heat of compression regeneration has some distinct benefits in that it allows for heat recovery from a process which overall has a high energy penalty. Wet gas regeneration is more established, but requires external heating sources, typically fired or electric heaters, whilst dry gas requires the same plus additional pressure support to overcome the pressure drop of the working bed. The selection of a regeneration method is therefore typically left to the vendors and will mature as deployment increases. However any integration of the regeneration heat supply with the parent process is beneficial and needs to be considered further.

4.8.12 Further Considerations

Consideration should also be given in design and equipment selection to the configuration options available.

Regeneration can be carried out in the upflow or downflow direction. With pressurized regeneration using thermal regeneration the regeneration volume flow is less than that of adsorption so to avoid bed fluidization the adsorption is carried out in the downwards direction with regeneration in the upwards direction. When regeneration involves rapid depressurisation then bed fluidization may be more likely during depressurization so adsorption is carried out in the upward direction allowing regeneration in the downward direction. For low pressure regeneration using vent gases or inert gases, the regeneration may be carried out downwards if the regeneration gas volumes are larger than that involved during adsorption.

Regeneration in the downflow flow/counter current direction in a bed avoids the regeneration reflux issue.

It is noted that whilst information on the impact of impurities on molecular sieves is detailed further work is required for silica gel, alumina and other media.

The impact of impurities from vendor information and research on the issue is not clear. In theory those impurities with an affinity to water or the desiccant material will adsorb on the material. They could then be released into the regeneration gas stream or remain on the desiccant, eventually leading to reduced efficiency or poisoning of the material. This is common in natural gas processes. However, there is little research available for CO_2 that would indicate how performance is affected or if any retention takes place.

4.9 Membranes

Molecules can permeate membranes using a variety of different mechanisms, which are largely dictated by the size of the membrane pores. With pores larger than 20 Angstrom there is very little selectivity and separation is generally based on molecular weight differences; with pores of 5-10 Angstrom surface flow occurs. Those of relevance to dehydration are typically of < 5 Angstrom:

- <5 Å are molecular sieves which are based on size since the smaller molecules have higher diffusion coefficients and higher permeability coefficients. These typically have high selectivity.
- Dense membranes (no pores) are:
  - Solution-diffusion based where permeability is a function of both the gas solubility and the diffusion coefficient of the gas in the membrane
  - Ion transport ceramic or metal membranes

Membranes have either high selectivity or high permeability while it is desirable for them to be high in both. High mechanical stability is also important.

Membranes in use tend to be multi-layers of different materials. Membranes in industrial use have been used on low flow rate natural gas duties to separate out water and other impurities (including CO_2) from the main gas stream. Membrane processes have been used on natural gas duty; they require several processing stages to avoid high hydrocarbon losses and pressure drop is therefore large. The process has been proven on low capacity units.

Membranes have the advantage of not using solvents, are smaller and lighter than traditional TEG plants and at low rates the capital cost is less than that of a TEG plant. Membranes have not been used to date on either CO_2 separation or CO_2 dehydration duties[21].

The driving force for separation of gases is the partial pressure difference across the membrane. The permeate is collected at lower pressure than the feed.

The influence of water on membrane performance is not well understood. Water has a very high permeability in polymers but high humidity can influence membrane performance; the CO_2 permeability can be significantly reduced or increased, or not affected at all. The extent of these effects is dependent upon the type of membrane being used. Particulates need to be totally removed; they can have a devastating effect on membrane performance.

The effect of impurities (in the raw CO_2 gas stream) on membrane performance has not been investigated; further research is required.

Membrane technology does not currently exist for dehydration of CO_2. A patent[22] for general gas dehydration exists. Ongoing research[23,24] indicates that this is an active area of development. As of yet however, there is no process listed which can achieve this duty.

If a membrane dehydration process is developed for gaseous phase dehydration of CO_2 their application will likely be limited. The large number of parallel units required to carry out the dehydration occupy a large footprint. Their application would be limited to small flow rates, as currently happens with natural gas applications.

4.10 Other

Gas Liquids Engineering claim to have a thermodynamic based dehydration process[25], which is patent pending. They claim to have operating units already installed. Literature indicates that a moisture content of 30 lb/MMscf (632 ppmv) is achievable for an increase in compression power.

4.11 Future Novel Dehydration Technology / Process Improvements or Enhancements

There is no indication of any novel technology on the near horizon which is applicable to dehydration of CO_2 for CCS.

Improvements and enhancements of individual processes are described in the relevant sections above.

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[21] 'Membrane processes and postcombustion carbon dioxide capture: challenges and prospects', Eric Favre, Chemical Engineering Journal, 171, 2011, 782-793.

[22] 'Process for the dehydration of a gas' RJ Arrowsmith, K Jones, United States Patent number 5,641,337, dated 24th June, 1997.

[23] 'Membrane dehydration of supercritical carbon dioxide', University of Twente, http://www.utwente.nl/tnw/mtg/people/phd/Koziara/info/Koziara%20Research.docx/

[24] 'Mixed water vapour/gas transport through the rubbery polymer PEBAX 1074', J Potreck, K Nijmeijer, T Kosinski, M Wessling, Journal of Membrane Science, 338, 2009, 11-16

[25] ' CO2 dehydration for pipeline safety', Carbon Capture Journal Sept-Oct 2011

The main area of development appears to be in acid resistant desiccant; however media vendors are not prepared to discuss ongoing research work in this area. There have been recent improvements in acidic resistant molecular sieves, where improved binders enable the molecular sieve to better withstand acidic impurities contained in the raw CO_2 gas.

5.0 Comparison of Different Dehydration Methods

The relative applicability ranges of the various different dehydration technologies are shown in Figure 28.

5.1 Combinations of Dehydration Techniques

It is usually most appropriate to consider combinations of different dehydration techniques to achieve the required target moisture content. A few examples are given below.

It is invariably cheaper to offload the final dehydration system by use of more basic techniques, if they can be applied. For example, if saturated low pressure gas is supplied it is beneficial to use the compression/cooling equipment (which have to be provided anyway to reach the export conditions) to raise the pressure, knockout the condensed water and reduce the gas equilibrium moisture content as part of the normal compression process. This has the effects of:

- Minimising the moisture fed to the final dehydration package
- Reducing the actual volume of raw gas which has to be processed in the final dehydration plant, which results in smaller equipment

The presence of certain impurities/contaminants may physically damage solid molecular sieve desiccant. It may be considered prudent to install a short section of guard layer (containing silica gel or activated alumina) immediately above the molecular sieve. The guard layer is better able to deal with the impurities. The guard layer, however, will have a design life and once the guard layer has aged then protection is no longer afforded to the molecular sieve, which will quickly deteriorate.

Multiple dehydration techniques in series can be used. For example compression/cooling, followed by a TEG system, followed by molecular sieve polishing. The benefits of such systems are dependent upon the individual process requirements. They can provide a higher level of product moisture integrity, in the event of a malfunction. The extent of capital cost penalty is process specific.

In the event that a second molecular sieve dehydration chain is required to achieve lower moisture levels, it may be prudent to consider offloading the molecular sieve system by installing a TEG system upstream. Smaller adsorber bed volumes and / or increased bed adsorption time will result.

A cost benefit analysis should be carried out for each application to determine the most cost effective option.

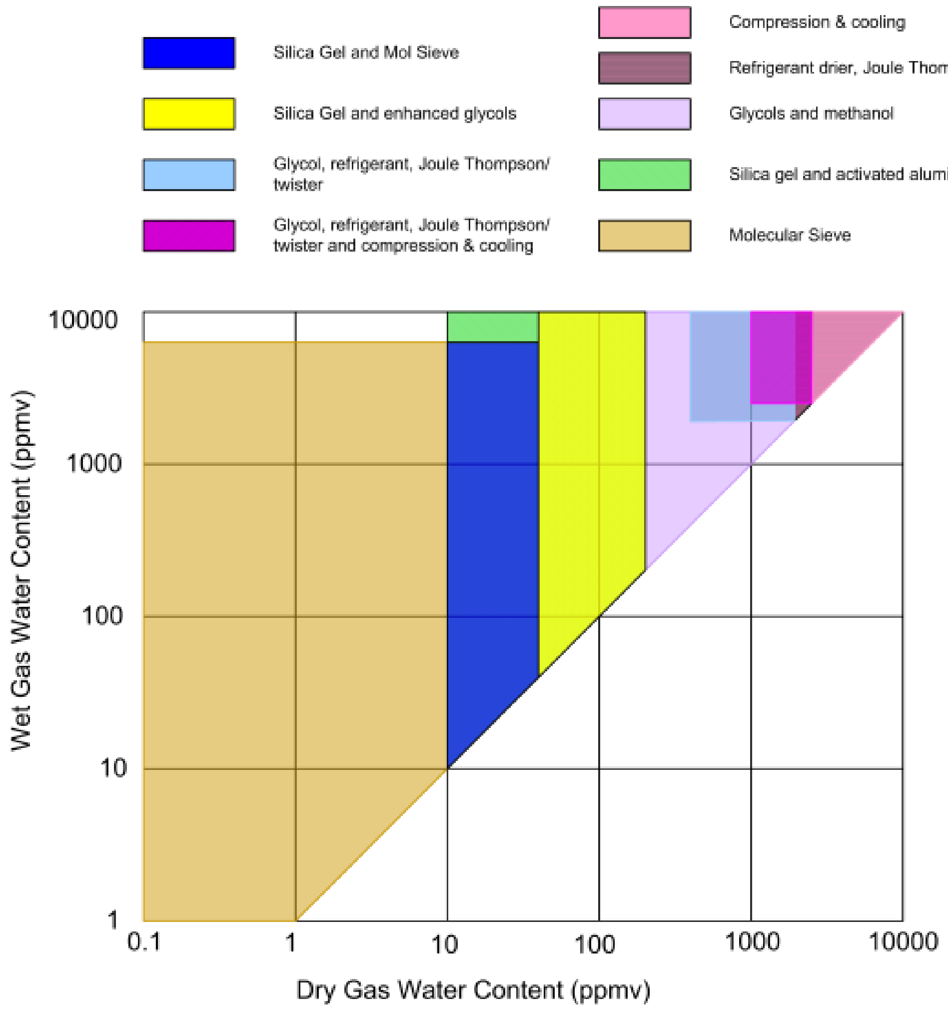

Figure 28 – Ranges of Applicability of Different Dehydration Technologies

6.0 Basis of Design

The basic information for use in the dehydration package design and order of magnitude costing for this study is summarised in the following sections.

6.1 Location

The plant is assumed to be at a Coastal location in the North East of the Netherlands.

6.1.1 Ambient Conditions

Ambient conditions at the given location are:

Temperature, ºC:

- Dry bulb, average 9ºC
- Maximum 30ºC
- Minimum -10ºC

Humidity (average) % 60

Pressure (average) kPa 101.3

6.2 Utilities / Services

Cooling Water

- Once through Seawater
- Water available at 15 ºC. Maximum temperature rise is 10ºC

Electricity: 50 Hz, 380kV grid connection voltage

6.3 Dehydration Package Design Basis

Plant life: 25 years

Turndown: ≥50%

Allowable pressure drop across the dehydration package: 1.5 bar

Minimum equipment design temperature shall include for depressurisation of the CO_2.

The dehydration package will be normally unmanned and monitored from the control room.

Typical order of magnitude costs would include consideration of, but are not limited to, the following items:

Inclusions

- Regeneration of the drying medium to be provided. Both online and offline regeneration should be provided to enable regeneration when the main gas compressor is not in use.
- Located in a non-hazardous zone
- Vendor to supply a full system package including all inter-connecting pipe work, valves, instrumentation, control, junction boxes (at skid edge), insulation, skid structure, platforms and ladders necessary.
- Spare parts for commissioning and 2 years operation to be included
- Control panel for unit control to be provided

- Testing
- Full documentation

Exclusions

- Foundation drawings
- Inter-connecting pipe work between skid boundary and existing equipment
- Lighting
- Lifting equipment
- Fire and gas detection equipment
- MCC equipment, switchgear, transformers

6.4 CO_2 capture and delivery details

90% capture assumed

Delivery conditions to transport pipeline: 110 bar, ≤30ºC

CO_2 product specification (volume basis):

N2/Ar	4%
O2	100 ppm
CO	0.2%
CH4 + hydrocarbons	4%
H2S	200 ppm
SO2	100 ppm
NO2	100 ppm
Total non-condensables	4%

7.0 Capture Processes

Several different types of CO_2 capture processes exist. The type selected for use is dependent upon the basic type of combustion process in operation, e.g. coal or natural gas. The CO_2 produced by the various combustion and associated capture processes are of different quality, containing different inerts and impurities, with varying compositions and conditions. The dehydration process can be significantly affected by these differences; it is therefore necessary to consider the different types of capture process separately within this study. The different types of combustion process are considered to be covered by the range of impurity and inerts cases; the base case gives the lower impurity levels and the test cases allow for higher impurities. Vendors were also requested to indicate the maximum inerts / impurity values that can be tolerated by their processes and to identify the resulting effects on their process design.

There are many different processes within each type of capture plant; they are not all covered, however the results are expected to be generally applicable for all types, although adjustments to either upstream conditioning equipment, or the dehydration process itself, may be required if significant levels of impurity are present.

7.1 Post-combustion Capture

Post-combustion capture is used to separate low concentrations (3% – 15%) of CO_2 from low pressure flue gases generated by combustion of fuels in air. This process is typically retrofitted to existing power plants.

The chemical solvents used are alkaline solutions used to absorb the acidic gases. They have historically been amine based, such as monoethanolamine (MEA), but advanced solvents, based on primary amines, diamines, sterically hindered amines and ammonia have been developed for the CCS market. These modern solvents have generally been selected to require a lower amount of heat for solvent regeneration / CO_2 recovery. The various absorption / regeneration processes are all essentially similar, irrespective of the chemical solvent used.

SOx, NOx and HCl, impurities in the flue gas react with the chemical solvents to form ‘heat stable’, non-reclaimable salts; these impurities are therefore essentially removed prior to entering the capture plant. Upstream flue gas desulphurisation and DeNOx units are thus essential.

7.1.1 Process Description

Generally the processes require that the flue gases be cooled to <50°C and acidic impurities be removed to low levels, typically ~10ppm v/v, otherwise amine losses increase proportionately with the impurities remaining in the flue gases. The CO_2 produced from amine systems typically has excellent purity but is saturated with water.

Process flow diagrams (PFDs) for the process are shown in Figure 29 and Figure 30

Flue gas to be purified is passed through the direct contact cooler (DCC), which contains a circulating weak caustic solution. This cools the gas stream, condenses out some of the water and removes acidic impurities and particulates. Gas from the top of the DCC is blown into the base of the absorber and passes upward through the absorber, counter current to a stream of the CO_2-lean chemical solution. Purified flue gas is washed, leaves the top of the absorber and passes to the stack. The CO_2 absorbs into the lean solution with liberation of the heat of reaction. Heat is removed from various points in the absorber via external coolers. The CO_2-rich solution from the bottom of the absorber is heated by heat interchange against CO_2-lean solution from the bottom of the stripping column. The CO_2-rich solution is fed to the stripping column at some point near the top. A considerable amount of heat is supplied via a stripper reboiler to desorb the CO_2 from the rich amine solution. The CO_2-lean solution from the stripper bottoms, after partial cooling in the lean-to-rich solution heat exchanger, is further cooled by heat exchange with water or air, and fed into the top of the absorber to complete the solution cycle. The raw CO_2 from the top of the stripping column is washed and cooled to condense a major portion of the water vapour. The resulting stream is at close to atmospheric pressure and just above ambient temperature. The collected condensate is continually fed back to the top of the stripping column, at a point above the rich-solution feed, and serves to prevent the amine solution from becoming progressively more concentrated and returns amine vapours, carried by the CO_2 gas stream, back to the process.

Enhancements to the basic capture process exist. For example, an additional stripping / flashing stage can be added to the rich amine stream between the CO_2 absorber and regenerator to reduce oxygen levels in the raw CO_2 gas to around 20 – 30 ppmv.

The water-saturated raw CO_2 gas is passed forward to the compression and conditioning section; conditioning typically comprises of dehydration and other conditioning processes required achieve the CO_2 product specification. Multi-stage compression is used. Knockout pots on the compressor suction lines prevent droplet carryover into the compressor. The stream is compressed and cooled; condensed water is removed in the knockout pots and the gas stream passes to the dehydration system.

The CO_2 dehydration system is sized to reduce the water content to a level sufficiently below the CO_2 specification. The dry CO_2 gas is further compressed and cooled. The knockout pots ensure that any liquid CO_2 formed is removed prior to entering the next compression stage. A sufficient number of additional compressor stages are provided to raise the CO_2 pressure to that required for export.

The dehydration process can be located at several different positions along the compression train. The actual location is usually determined for each individual project based on both technical and economic considerations. The range of temperature and pressure conditions, which may be experienced under different scenarios, along with conditions required for hydrate formation, ice formation and liquid CO_2 formation, need to be considered in selecting the location of the dehydration plant. The pressure for dehydration will therefore be determined to some extent by the available compressor inter-stage pressures, although the pressure ratio can be adjusted, if required, to achieve an acceptable solution. This dictates the number of overall compression stages required to achieve the export line pressure.

A previous study[26] identified the potential for application of Ramgen compressor technology on a post combustion plant. Ramgen compressors have very high pressure ratios per stage and as such the potential location for the dehydration package is limited. The study indicated that the compression duty could be carried out using two compression stages. The available pressures for dehydration were therefore 11 Bara and 111 Bara. It is preferred to carry out the dehydration duty in the gas phase, therefore dehydration would be done at 11 Bara. However, processes exist to carry out the dehydration at 111 Bara, if necessary.

The base case raw CO_2 composition data inlet the dehydration system, as shown in Table 8, is based on a typical modern amine capture plant. Higher inert and impurity levels are catered for via the inert and impurity test cases listed in the same Table.

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[26] ‘Rotating Equipment for Carbon Dioxide Capture and Storage’, IEAGHG Report: 2010/07, September 2011

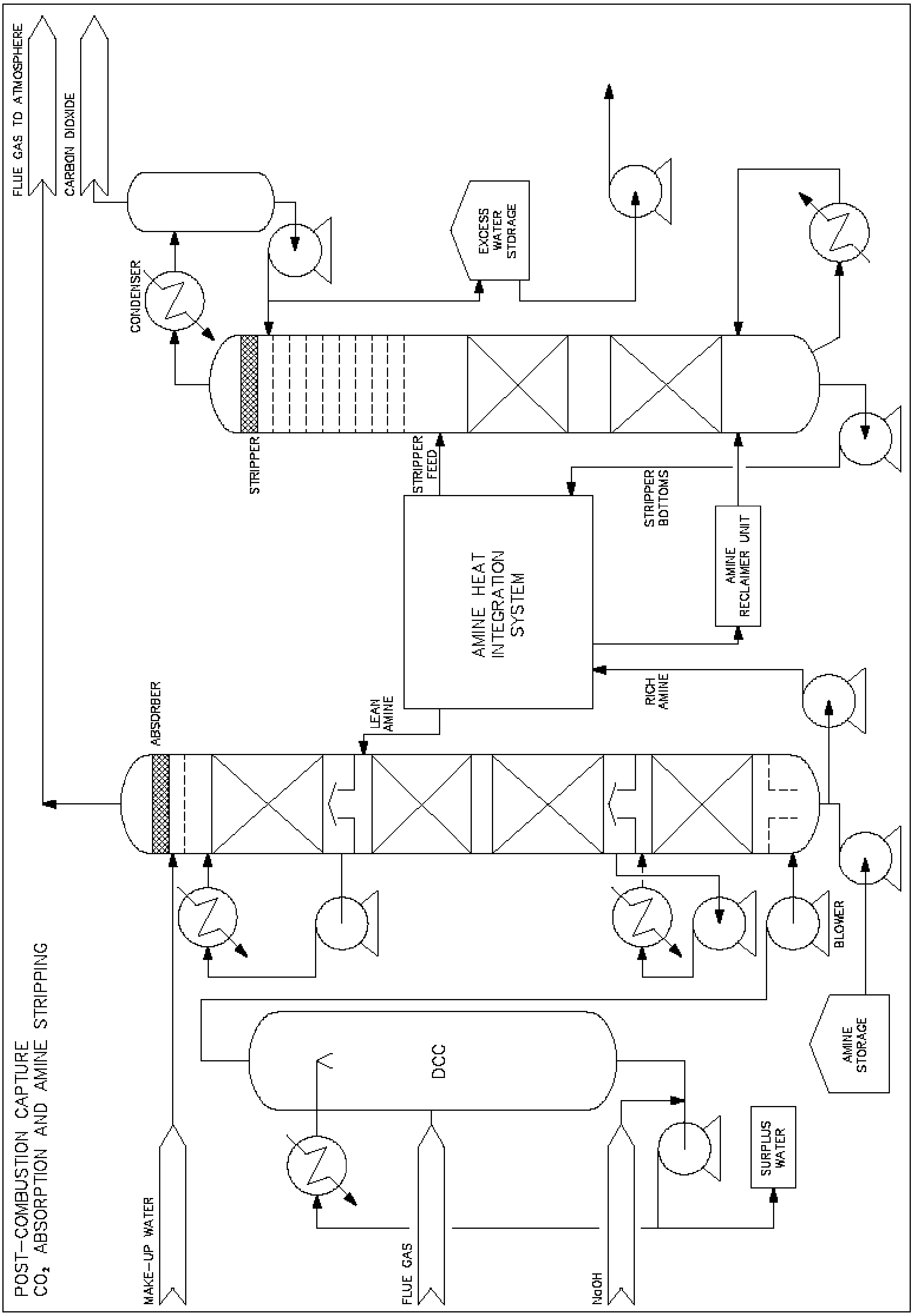

Figure 29 – Post-Combustion Capture Process PFD

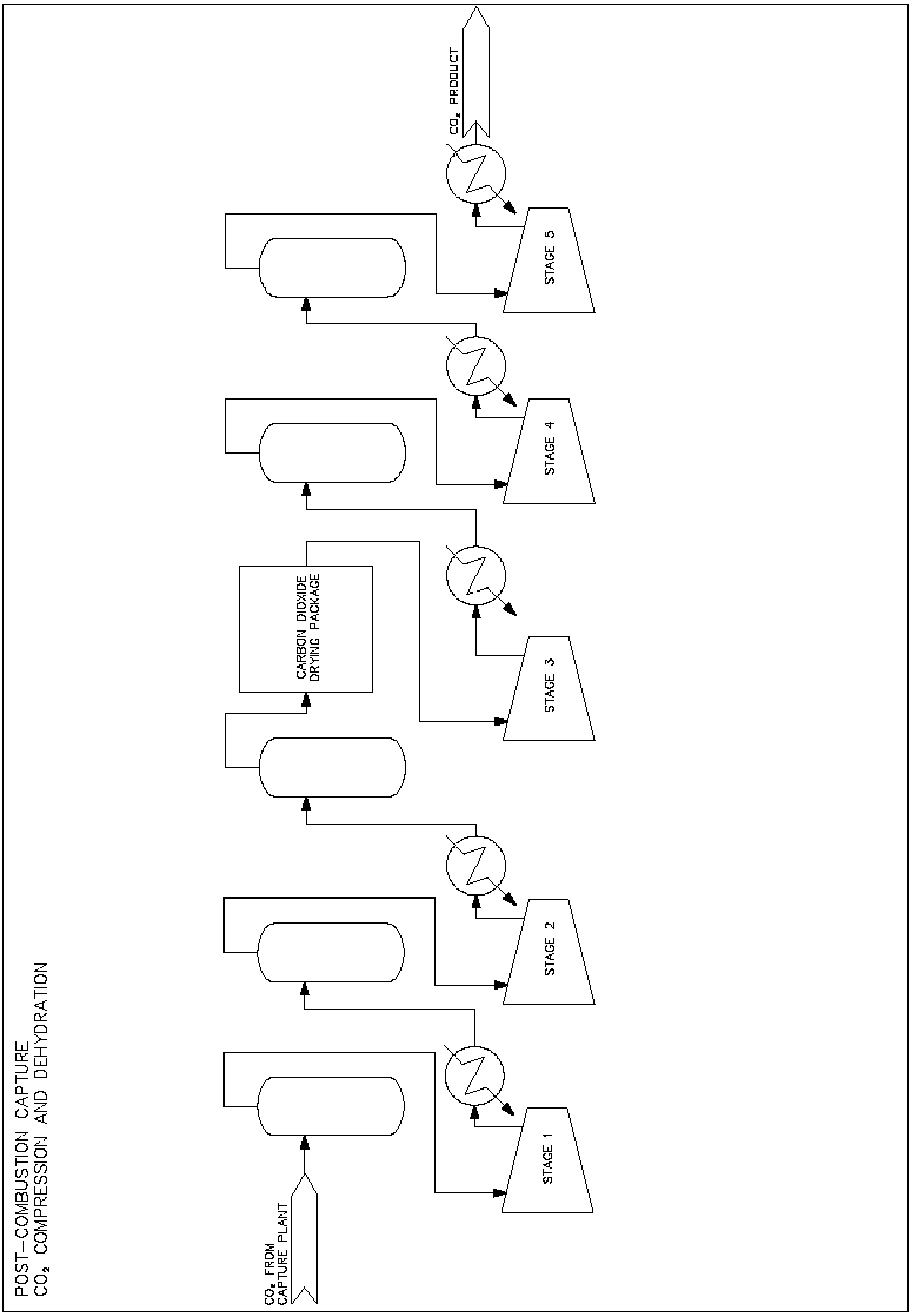

Figure 30 – Compression and Dehydration PFD for Post-Combustion Capture

7.2 Pre-combustion Capture

Pre-combustion capture is used to remove acid gases (CO_2, H_2S, COS, HCN) from synthesis gas, downstream of a gasifier, to the specification required for further processing. The fuel to the gasifier may be biomass, coal or petcoke and additional equipment may be provided. Here we consider coal gasification, but generally the issues relating to water content and dehydration remain the same.

Coal is converted to hydrogen and carbon monoxide, to form synthesis gas, at relatively high pressures. The carbon monoxide undergoes a water-shift to form CO_2 and hydrogen. The CO_2 is at a high concentration of ~ 40% and is removed by use of physical solvents. The remaining hydrogen rich stream is then combusted in a clean process.

Physical solvents include Rectisol (licensed by Linde and Lurgi) and Selexol (licensed by UOP). These processes are well proven and can remove the sulphur content and CO_2 content separately, producing different product streams of H_2S rich gas (which is usually sent to a sulphur removal unit for production of sulphur) and multiple CO_2 streams of different compositions and at different conditions.

Vendors of the physical solvent processes were approached and requested to provide details of expected CO_2 compositions which would be produced by their process.

7.2.1 Acid Gas Removal (AGR) Basis of Design

Details of feed gas to the AGR section were selected from consideration of cases used in previous IEA GHG studies[27,28] combined with other information available to AMEC. Raw syngas composition and conditions used are given in Table 4.

Composition	Units	Inlet AGR
H_2	%	54.97
CO	%	2.84
CO_2	%	40.17
N_2	%	0.68
O_2	ppmv	0
CH_4	ppmv	200
H_2S	ppmv	2200
COS	ppmv	20
Ar	ppmv	7900
H_2O	ppmv	3100
HCN	ppmv	0
NH_3	ppmv	0
Temperature	ºC	38
Pressure	Bara	28

Table 4 – Conditions at the Inlet to the Pre-combustion Capture Plant

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[27] 'Potential for Improvement in gasification Combined Cycle Power Generation with CO2 Capture', Report Number PH 4/19, May 2003, IEA Greenhouse Gas R&D Programme

[28] Co-production of Hydrogen and Electricity by Coal Gasification with CO2 Capture, Technical Study, Report Number 2007/13, September 2007, IEA Greenhouse Gas R&D Programme, Attachment B

The pressures used are lower than those used in previous studies since:

- There is higher moisture content in the feed gas compared to post combustion feed gas.
- The conditions are more reflective of pressures experienced in recent projects

Relevant basis of design data provided to pre-combustion capture vendors:

- ≥ 90% CO2 capture required
- Turndown ≥ 50%
- Ambient Conditions
- Temperature

Average dry-bulb	ºC	9
Maximum	ºC	30
Minimum	ºC	-10

Humidity average	%	60
Pressure average	kPa	101.3

- Cooling water - seawater. Temperature 15ºC. Max temperature rise 10ºC.
- CO2 in product gas is expected to be > 98%
- Target H2S in CO2 product 100ppm max, preferably lower.

This data was provided to the AGR vendors who were asked to determine the CO_2 specification, advise on the resulting moisture content and impurities, and whether there were process modifications which could be made to achieve lower moisture content.

7.2.2 Rectisol Process

The Rectisol process uses chilled methanol as the solvent. Methanol has the advantages of high stability, good solubility for CO_2 and H_2S / COS and is readily available. It can remove a large number of impurities to low levels and provide sulphur-rich and CO_2-rich streams for further processing. Methanol is a chemically and thermally stable solvent and, as such, has no associated degradation or disposal problems.

At low temperatures methanol has significantly higher solubility for other components than other physical wash processes do at their operating conditions. This allows methanol to achieve sharp separations; CO_2 product streams are essentially free of sulphur products and sulphur streams produced are suitable for passing to a Claus process for sulphur recovery.

High solubility of CO_2 and H_2S in methanol occur at a relatively low solvent recirculation rate compared to other possible wash systems. This results in lower utility figures.

Various configurations of the Rectisol system exist, depending upon whether the CO_2 and sulphur impurities are captured separately or together; separate CO_2 streams are required for this study.

7.2.3 Process Description

The basic process and equipment is similar for all the different vendors, with various modifications and complexities available. Typical simplified process PFDs are shown in Figure 31 and Figure 32.

The shifted gas stream, at 38°C and 28 Bara, is cooled against the Rectisol product streams, chilled and washed in the absorber with cold methanol to remove unwanted impurities. Lean methanol is fed to the top of the column and the heat of acid gas absorption is removed by refrigeration. The temperature in the Rectisol wash unit depends on the feed gas composition / temperature / pressure and the required products; in this case the acid gas removal within the Rectisol wash unit is carried out at approx -20°C. Purified, hydrogen rich gas leaves the top of the absorber, is warmed against the feed stream and sent for further processing.

A side stream of CO_2 rich solution is removed from the middle of the absorber, the flow is split and the streams let down in pressure into the top of the medium pressure (MP) and low pressure (LP) regeneration units, chilling in the process as the CO_2 gas is desorbed as part of the flash. CO_2 / sulphur rich methanol, from the bottom of the absorber, is let-down in pressure and sent to the bottom of the MP regenerator. Desorbed MP CO_2, at ~3.5 Bara is warmed to 30°C against the feed gas, to improve heat integration, and sent for compression and conditioning.

Sulphur-rich methanol from the bottom of the MP regenerator is let down into the middle of the LP regenerator. Cold, flashed gas is contacted with the CO_2-rich methanol. Desorbed LP CO_2 gas from the top of the column, at ~1.5 Bara is warmed to 30 C against the feed gas, to improve heat integration, and sent for compression and conditioning.

CO_2 desorption takes place at around -60°C in the MP / LP cold regeneration towers.

Sulphur rich methanol from the base of the LP regenerator is heated and sent to the top of the hot regenerator. A steam heated reboiler assists to overcome the heat of absorption of the sulphur components. The H_2S / COS rich stream from the top of the tower is cooled and is available for use in a Claus plant for sulphur recovery. Lean methanol from the bottom of the hot regenerator is split; part of the stream is cooled and returned to the top of the absorber unit and the other part is heated and fed to a stripper unit with stream heated reboiler. Waste water is removed from the base of the stripper and the stripper overheads are sent to the bottom of the hot regenerator.

Linde was approached to provide CO_2 quality data based on the data provided in Section 7.2.1. In addition they assumed that:

- Sulphur is removed from the syngas to a level of H2S + COS of < 1 ppmv
- H2S + COS content in the acid gas > 40 mol%

Vendors were asked to aim for an H_2S+COS content of < 100 ppmv in the raw CO_2 product with the aim of reducing the levels further. Linde advised that they can achieve levels down to

20 ppmv relatively easily. To achieve lower levels of ~10 ppmv and lower will require a higher investment cost. Their results are contained in Figure 33 and Table 5.

The CO_2 product streams are almost dry, containing < 1 ppmv moisture, so subsequent dehydration is not required. The product CO_2 contains methanol as an additional impurity; the actual methanol content is dependent upon the temperature and pressure at which the CO_2 is produced. In this case the temperature is ~ -50 to -60°C; levels of around 220 ppmv methanol have been quoted. This is within the CO_2 product specification. Methanol is not expected to condense out in the compressor inter-stages.

The CO_2 product streams pass forward to the compression and conditioning plant. The LP stream passes through a knockout pot to remove liquid droplets and enters the first stage compressor. The MP CO_2 is combined with the hot compressor discharge gas, is cooled, passes through the 2nd stage inlet knockout pot and enters the second stage compressor. An appropriate number of compressor stages are provided to meet the required export conditions. In this case further conditioning is not required.

7.2.4 Selexol Process

The Selexol process uses a solution mixture of dimethyl ethers of polyethylene glycol as the solvent. These have a very low vapour pressure and there is thus no resulting contamination of the CO_2 product with the solvent; impurity levels of Selexol are <1ppmv. The material is biodegradable and non-toxic. The solvent has a high capacity for impurities, including H_2S, CO_2 and COS. It allows selective removal of H_2S and CO_2. Various configurations of the process exist; the configuration used here allows for separate sulphur-rich and CO_2-rich streams to be produced.

7.2.5 Process Description

Typical simplified PFDs are shown in Figure 34 and Figure 35.

The shifted gas stream, at 38°C and 28 Bara, is fed to the sulphur absorber where it is contacted against CO_2-rich solution which enters the top of the column. Sulphur-rich solution leaves the bottom of the sulphur absorber, is heated and enters the concentrator. CO_2-contaning gas from the top of the concentrator is fed back to the sulphur absorber. Liquid from the base of the concentrator is sent to the regenerator where the H_2S is thermally stripped from the solution and sent for further processing. Lean solution from the base of the regenerator is cooled, flow is split and sent to the top of the sulphur absorber and the CO_2 absorber.

Sulphur-lean gas from the top of the sulphur absorber enters the bottom of the CO_2 absorber. Purified, hydrogen rich gas leaves the top of the CO_2 absorber and sent for further processing.

CO_2 rich solution from the base of the CO_2 absorber is split. One part is pumped to the top of the sulphur absorber while the other is sent to a series of flash vessel in which the pressure is dropped stage wise. Offgas from the first vessel is returned to the base of the CO_2 absorber. Medium pressure CO_2, at 4.3 Bara, 9C is released from the second flash vessel. LP CO_2 gas at 1.3 Bara, 6C is released from the third flash vessel. Both the streams are sent to compression and condition section for further processing. Lean solution from the bottom of the 3rd stage flash is pumped to the CO_2 absorber as a side stream.

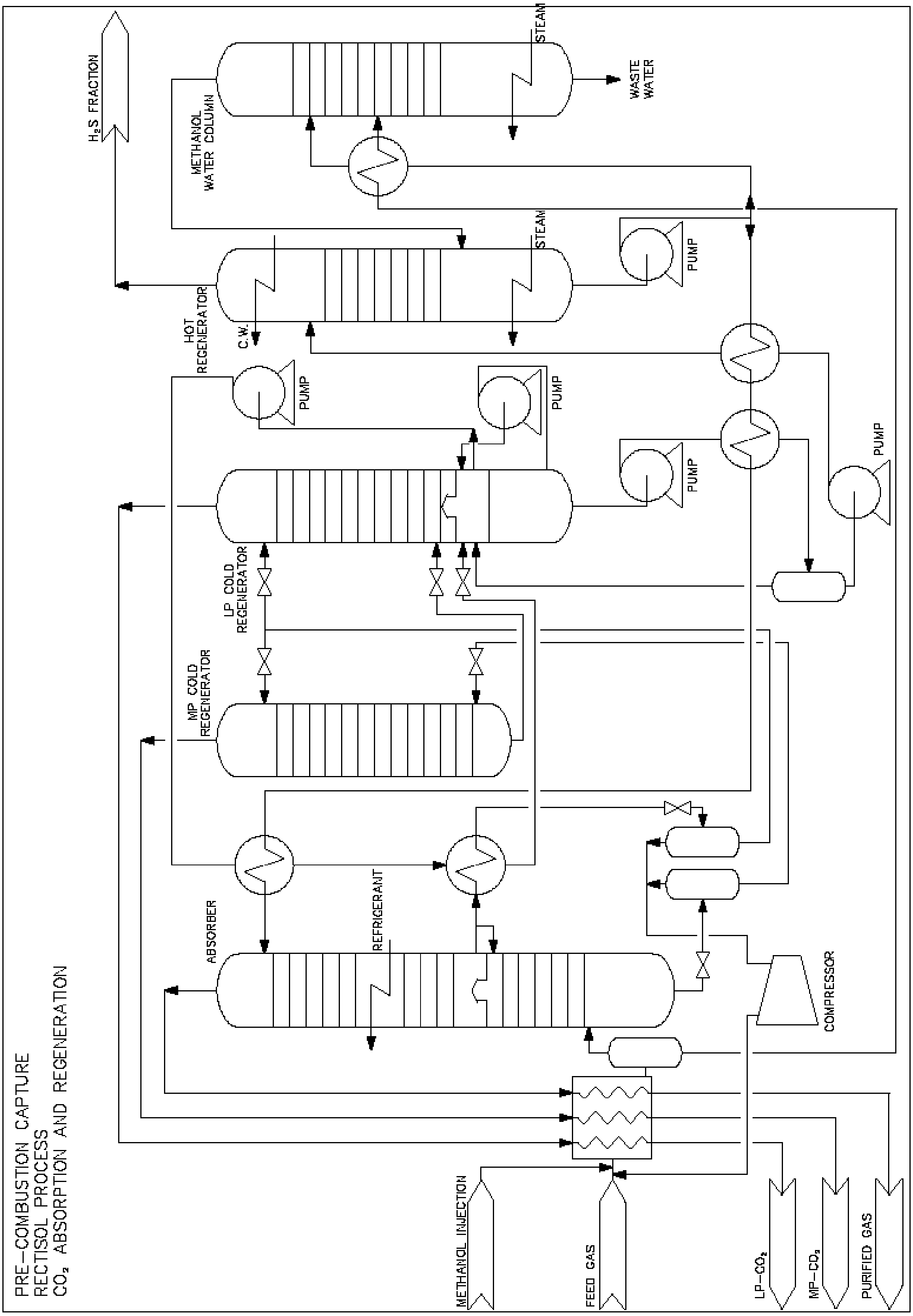


Figure 31 – Rectisol Process PFD

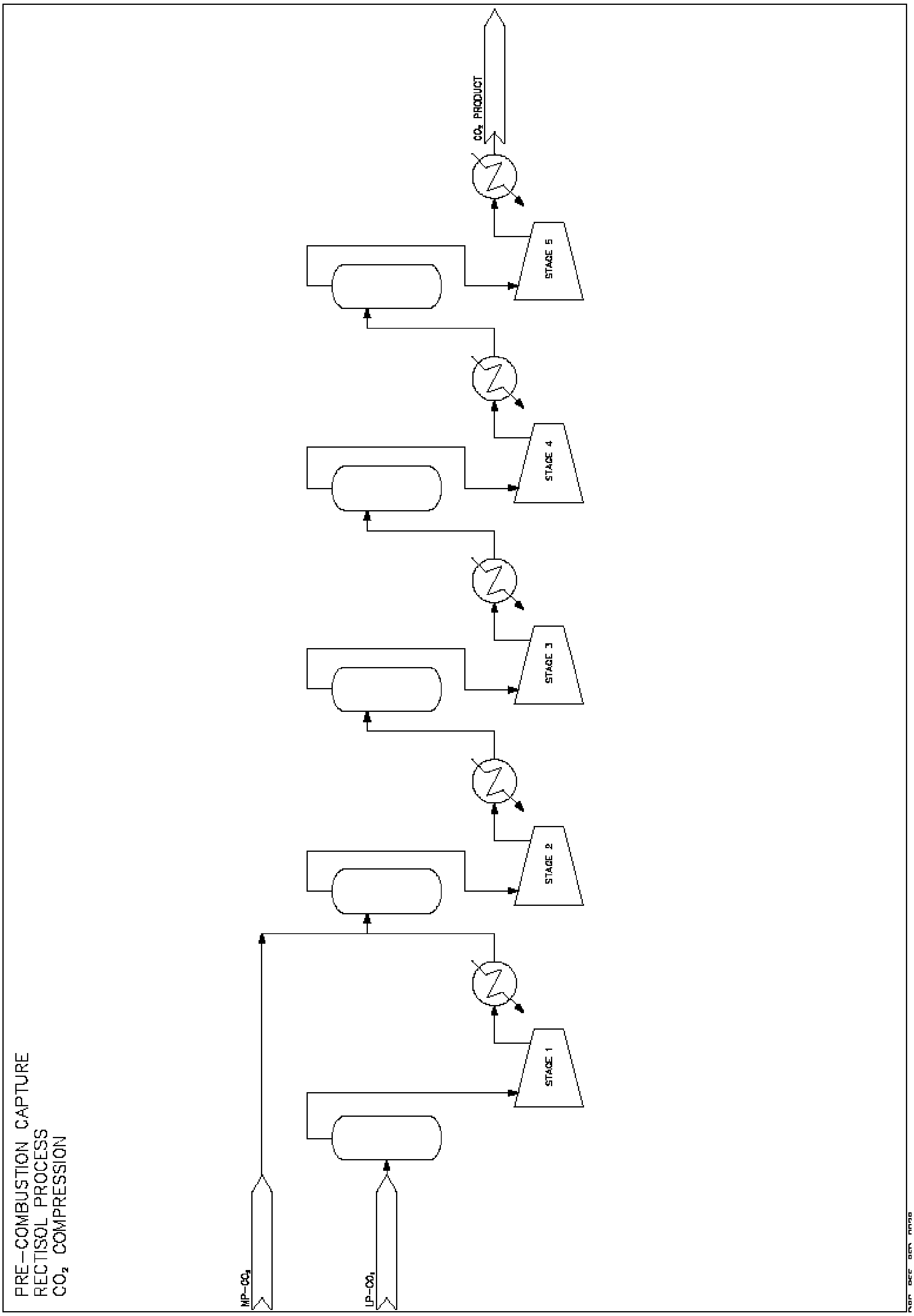
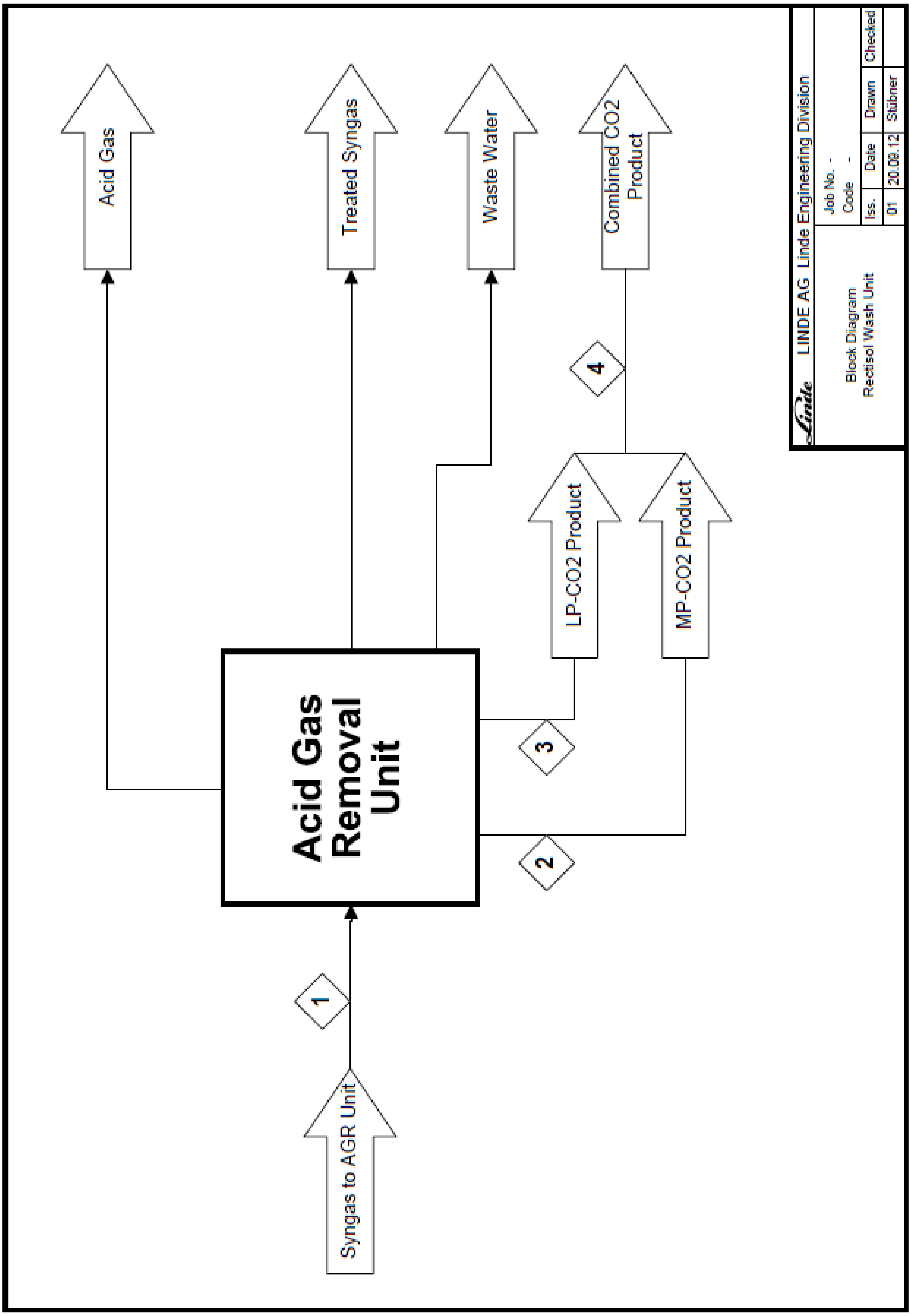
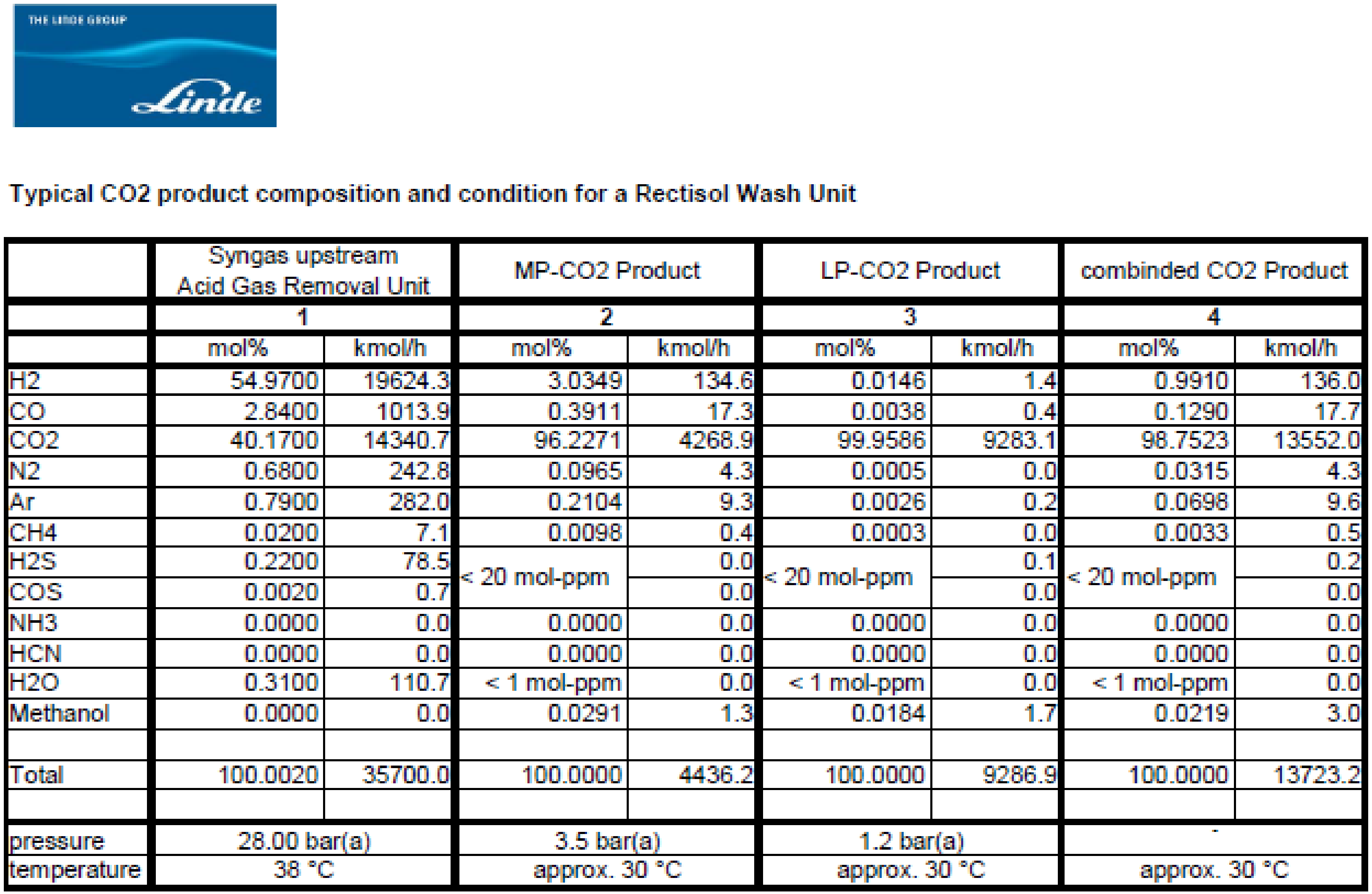


Figure 32 - Compression and Dehydration PFD for Rectisol Process



Reference: Linde, 2012, supplied via e-mail 26/9/12

Figure 33 – Overview of Rectisol Process



Typical CO2 product composition and condition for a Rectisol Wash Unit

	Syngas upstream Acid Gas Removal Unit		MP-CO2 Product		LP-CO2 Product		combinded CO2 Product	
	1		2		3		4	
	mol%	kmol/h	mol%	kmol/h	mol%	kmol/h	mol%	kmol/h
H2	54.9700	19624.3	3.0349	134.6	0.0146	1.4	0.9910	136.0
CO	2.8400	1013.9	0.3911	17.3	0.0038	0.4	0.1290	17.7
CO2	40.1700	14340.7	96.2271	4268.9	99.9586	9283.1	98.7523	13552.0
N2	0.6800	242.8	0.0965	4.3	0.0005	0.0	0.0315	4.3
Ar	0.7900	282.0	0.2104	9.3	0.0026	0.2	0.0698	9.6
CH4	0.0200	7.1	0.0098	0.4	0.0003	0.0	0.0033	0.5
H2S	0.2200	78.5	< 20 mol-ppm	0.0	< 20 mol-ppm	0.1	< 20 mol-ppm	0.2
COS	0.0020	0.7		0.0		0.0		0.0
NH3	0.0000	0.0	0.0000	0.0	0.0000	0.0	0.0000	0.0
HCN	0.0000	0.0	0.0000	0.0	0.0000	0.0	0.0000	0.0
H2O	0.3100	110.7	< 1 mol-ppm	0.0	< 1 mol-ppm	0.0	< 1 mol-ppm	0.0
Methanol	0.0000	0.0	0.0291	1.3	0.0184	1.7	0.0219	3.0
Total	100.0020	35700.0	100.0000	4436.2	100.0000	9286.9	100.0000	13723.2
pressure	28.00 bar(a)		3.5 bar(a)		1.2 bar(a)		-	
temperature	38 °C		approx. 30 °C		approx. 30 °C		approx. 30 °C	

Reference: Linde, 2012, supplied via e-mail 26/9/12

Table 5 – CO_2 Product Specifications from a Rectisol Unit

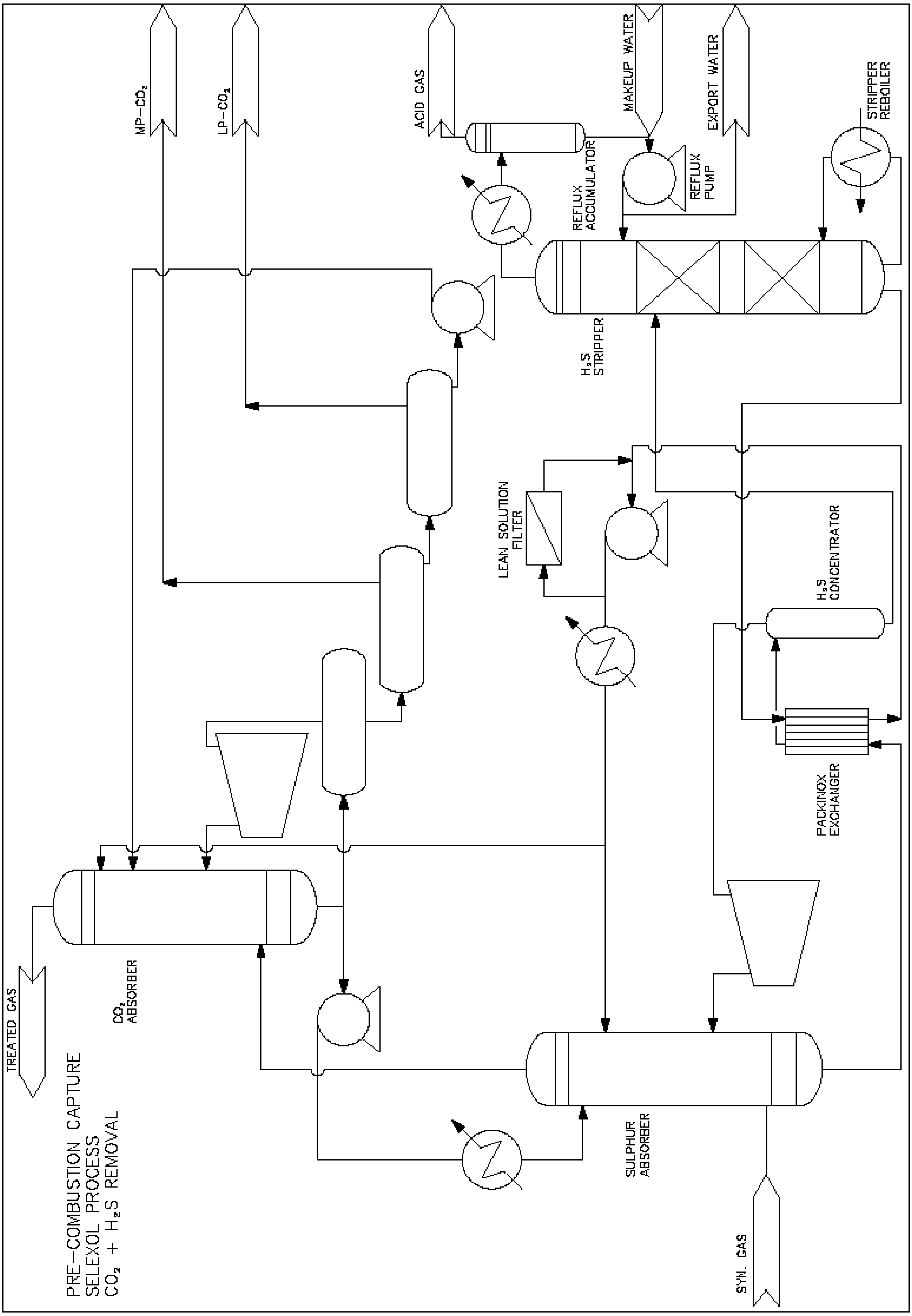


Figure 34 – Selexol Process PFD

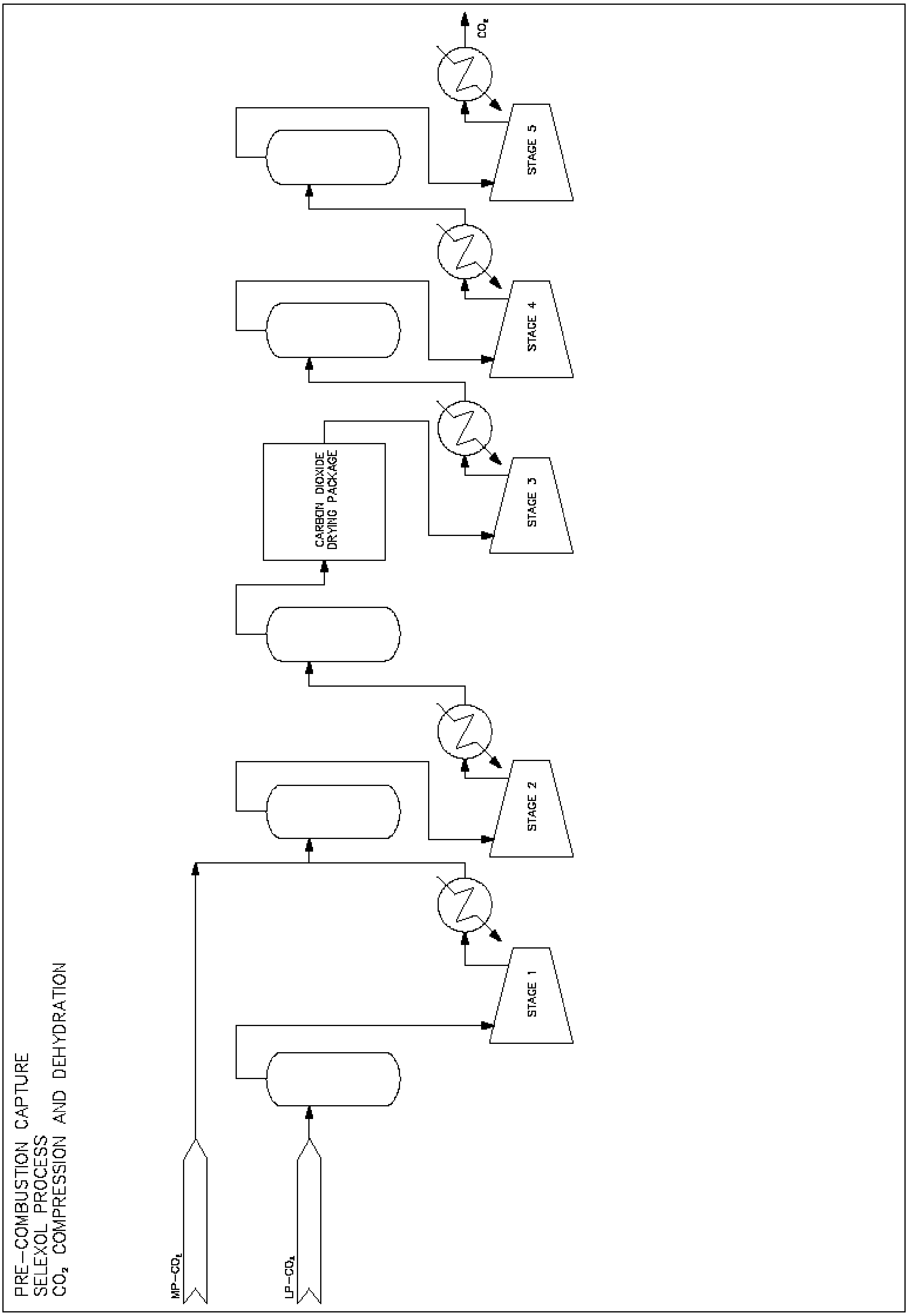


Figure 35 - Compression and Dehydration PFD for Selexol Process

UOP were asked to provide CO_2 quality data, based on the data provide in Section 7.2.1. Vendors were asked to aim for an H_2S+COS content of < 100 ppmv in the raw CO_2 product with the aim of reducing the levels further. UOP advise that they can achieve levels down to 20 ppmv relatively easily. To achieve lower levels of ~10 ppmv and lower will require larger solvent recirculation rate. UOP results are contained in Table 6.

Selexol has a low vapour pressure so there is minimal contamination of the CO_2 by the Selexol process. The Selexol solution contains water so the CO_2 gas is effectively saturated with water. UOP advise that lower water levels of around 500-1000ppmv are achievable, but only at pressures in excess of 10 Barg; at these conditions the CO_2 content of this HP stream would be significantly less than 98%.

If sulphur removal is not required, then the process can use pure Selexol and solvent regeneration can be carried out by flashing alone. In this case significantly lower water content will be present in the CO_2 product.

UOP also advised that they have alternative plant arrangements, in which the Selexol process can be applied in combination with the Ortloff DRCF process, in which two major product streams are generated: a high purity liquid CO_2 stream and a sweet gas stream. Significant savings in power consumption are achievable. The process can be applied to syngas treating for the combined removal of sulphur and CO_2.

The CO_2 product streams pass forward to the compression and conditioning plant. The LP stream passes through a knockout pot to remove liquid droplets and enters the first stage compressor. The MP CO_2 is combined with the cooled compressor discharge gas, passes through the 2nd stage inlet knockout pot and enters the second stage compressor. An appropriate number of compressor stages are provided to meet the required export conditions. Water is removed from the knockout pots at each compression stage. The dehydration unit is located at an appropriate compressor inter-stage condition and is fed with water-saturated CO_2 gas.

7.3 Oxy-fuel combustion

In oxy-fuel combustion the fuel is combusted in oxygen, rather than air, giving a more complete combustion. The exhaust stream is high in CO_2. Inert gases are removed from the CO_2 stream by condensation.

As far as dehydration is concerned there are essentially two different types of oxyfuel combustion process – high pressure dehydration and low pressure dehydration.

7.3.1 High pressure dehydration

Figure 36 and Figure 37 illustrate the process.

A previous IEA GHG Study report[29] has been used as the reference for this case, which incorporates the Air Products process scheme reported in their patent[30,31] for CO_2 purification.

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[29] 'Water Usage and Loss Analysis of Bituminous Coal Fired Power Plants with Capture', IEA GHG Study Report 2010/05, March 2011

[30] 'Purification of CO_2' United States Patent US 7,416,716 B2, August 26, 2008

[31] 'Purification of oxyfuel-derived CO2', Vince White, Laura Torrente-Murciano, David Sturgeon, David Chadwick, International Journal of Greenhouse Gas Control, 4, 2010

The Air Products patented process, tested at the Vattenfall Schwarze Pumpe facility, indicates that SO_2 is removed from CO_2 gas by maintaining the feed gas at elevated pressure (in excess of 3 Bara) in the presence of oxygen, water and NOx for a period of time sufficient to convert the SO_2 to sulphuric acid. Once the SO_2 has been substantially removed then the NOx converts to nitric acid. NO behaves as a catalyst for the SO_2 oxidation. Aqueous sulphuric and nitric acid are removed from the separators. Resultant flue gas is essentially SO_2-free and NOx-lean. Although the patent indicates pressure in excess of 3 Bara other information suggests that the pressure is in excess of 10 Bara.

The original IEA GHG study assumed that all the SO_2 and 90% of the NOx contained in the flue gas was removed. Other publications[32,33,34] imply that the system is not so efficient. Thus the original stream data[35] has been modified for SOx removal of 95% and NOx removal of 85%. The gas composition inlet the dehydration package is given in Table 8.

7.3.2 Process Description

CO_2-rich flue gas at approximately 110°C is quenched with water in a venturi scrubber and passes to the indirect contact cooler for further cooling to around 35°C. Around half of the resultant flue gas is returned to the boiler system. The remainder of the flue gas is sent to the compression section. The pressure exit the first compressor stage is ~15 Bara. Flue gas is cooled to ~30°C and passed to the first contacting column. Gas is contacted against a counter current flow of weak acid. The column provides sufficient holding time to convert all of the SO_2 to sulphuric acid and part of the NOx to nitric acid. A mix of aqueous sulphuric acid containing some nitric acid, is removed from the bottom of the column. Part of this stream is re-circulated to the top of the first contacting column and the residual is removed as waste.

The SO_2-lean raw CO_2 gas leaving the top of the first contacting column is compressed to 30 Bara, cooled to ~30°C to remove the heat of compression, and passed to the second contacting column. Gas passing up the column is contacted against a counter current flow of aqueous nitric acid solution. Contact time is sufficient to convert most of the remaining NOx contaminant to produce nitric acid. Fresh water is added to the top of the column to assist with NOx conversion and to ensure that acid droplets are not entrained with the gas. Part of the aqueous nitric acid stream from the bottom of the column is recycled to the top of the second contacting column and the excess is removed as waste. The SO_2-lean, NOx-lean gas from the top of the contacting column is passed to the dehydration unit for drying. The stream is high in inerts content, is water saturated and has a relatively low CO_2 content of around 76% (dry basis).

The raw CO_2 feed stream is dried to << 10 ppmv water content to prevent ice formation in the downstream cryogenic unit. The feed stream is cooled to ~ -25°C. Liquid CO_2 formed is separated from the nitrogen, argon, oxygen and residual CO_2 gas in the first separator. The gas stream is further cooled to -54°C to further condense the CO_2, which is removed in the second separator. The inert gases, containing residual, gaseous CO_2 are warmed, let-down in

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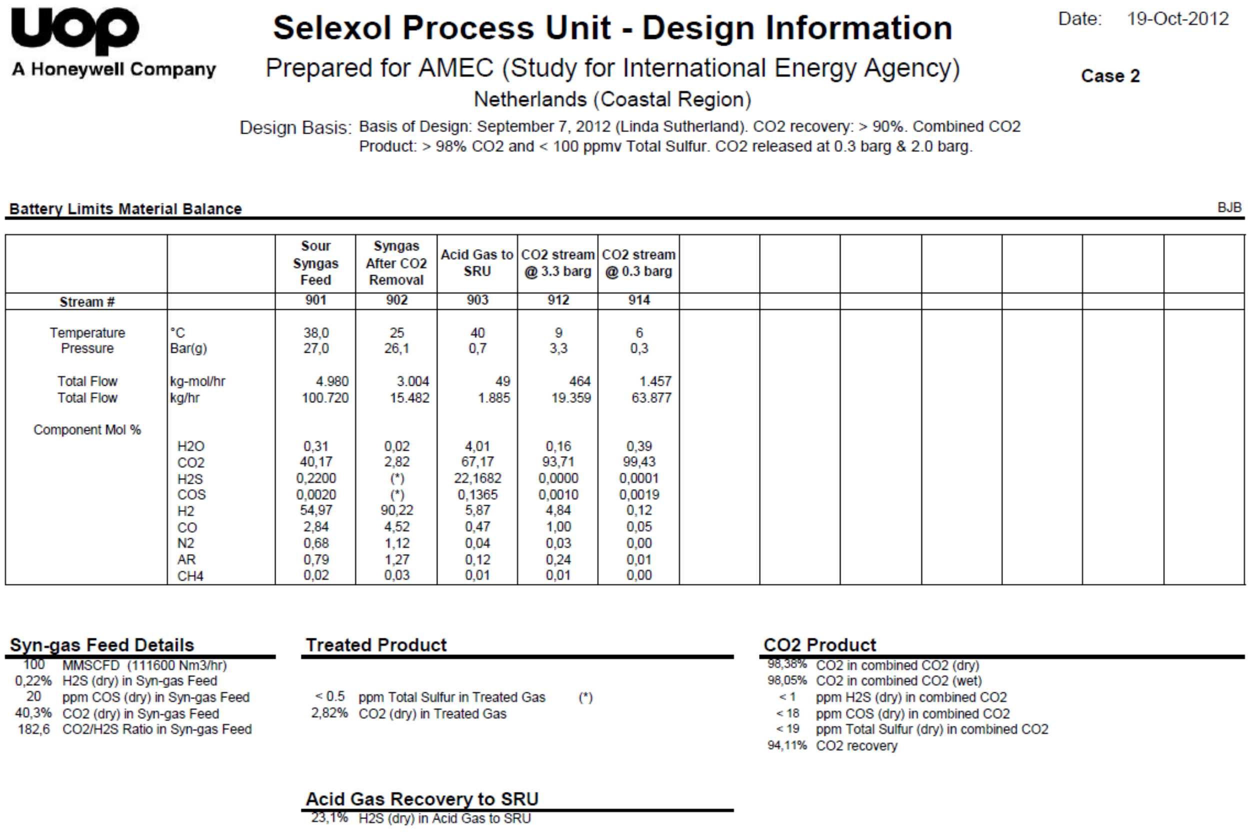
[32] ‘Removal of SOx from compressed oxyfuel-derived CO2’, European Patent Application, EP 2 404 655 A2, filing date 07.07.2011.

[33] ‘ASU and CO2 processing units for oxyfuel CO_2 capture plants’, Vince White, Presentation to 3rd Asia Pacific Partnership Oxy-fuel Working Group, September 2011

[34] ‘Air Products oxyfuel CO_2 compression and purification developments’, Vince White, Frank Petrocelli, 2nd Oxyfuel Combustion Conference, September 2011

[35] ‘Purification of oxyfuel-derived CO2’, Vince White, Laura Torrente-Murciano, David Sturgeon, David Chadwick, International Journal of Greenhouse Gas Control, 4, 2010

pressure through an expander (for power recovery) and vented to atmosphere along with small quantities of CO_2. CO_2 liquid from the first separator is expanded through a Joule Thompson valve to 18.8 Bara and is used to cool the feed gas. Liquid from the second separator is heated, expanded through a valve to 9.7 Barg, -55°C and is used to refrigerate the gas from the first separator. The CO_2 stream is warmed to 8°C, compressed to 18.7 Bara, combined with the CO_2 from the first separator and compressed to meet the required export pressure. A CO_2 content of >96% is achieved in the product gas.



UOP
A Honeywell Company

Selexol Process Unit - Design Information

Prepared for AMEC (Study for International Energy Agency)
Netherlands (Coastal Region)

Date: 19-Oct-2012

Case 2

Design Basis: Basis of Design: September 7, 2012 (Linda Sutherland). CO2 recovery: > 90%. Combined CO2 Product: > 98% CO2 and < 100 ppmv Total Sulfur. CO2 released at 0.3 barg & 2.0 barg.

Battery Limits Material Balance BJB

		Sour Syngas Feed	Syngas After CO2 Removal	Acid Gas to SRU	CO2 stream @ 3.3 barg	CO2 stream @ 0.3 barg
Stream #		**901**	**902**	**903**	**912**	**914**
Temperature	°C	38,0	25	40	9	6
Pressure	Bar(g)	27,0	26,1	0,7	3,3	0,3
Total Flow	kg-mol/hr	4.980	3.004	49	464	1.457
Total Flow	kg/hr	100.720	15.482	1.885	19.359	63.877
Component Mol %						
	H2O	0,31	0,02	4,01	0,16	0,39
	CO2	40,17	2,82	67,17	93,71	99,43
	H2S	0,2200	(*)	22,1682	0,0000	0,0001
	COS	0,0020	(*)	0,1365	0,0010	0,0019
	H2	54,97	90,22	5,87	4,84	0,12
	CO	2,84	4,52	0,47	1,00	0,05
	N2	0,68	1,12	0,04	0,03	0,00
	AR	0,79	1,27	0,12	0,24	0,01
	CH4	0,02	0,03	0,01	0,01	0,00

Syn-gas Feed Details

100	MMSCFD (111600 Nm3/hr)
0,22%	H2S (dry) in Syn-gas Feed
20	ppm COS (dry) in Syn-gas Feed
40,3%	CO2 (dry) in Syn-gas Feed
182,6	CO2/H2S Ratio in Syn-gas Feed

Treated Product

< 0.5	ppm Total Sulfur in Treated Gas (*)
2,82%	CO2 (dry) in Treated Gas

Acid Gas Recovery to SRU

23,1%	H2S (dry) in Acid Gas to SRU

CO2 Product

98,38%	CO2 in combined CO2 (dry)
98,05%	CO2 in combined CO2 (wet)
< 1	ppm H2S (dry) in combined CO2
< 18	ppm COS (dry) in combined CO2
< 19	ppm Total Sulfur (dry) in combined CO2
94,11%	CO2 recovery

Reference: UOP, 2012, supplied by e-mail 19/10/12

Table 6 – CO_2 Product Specifications from a Selexol Unit

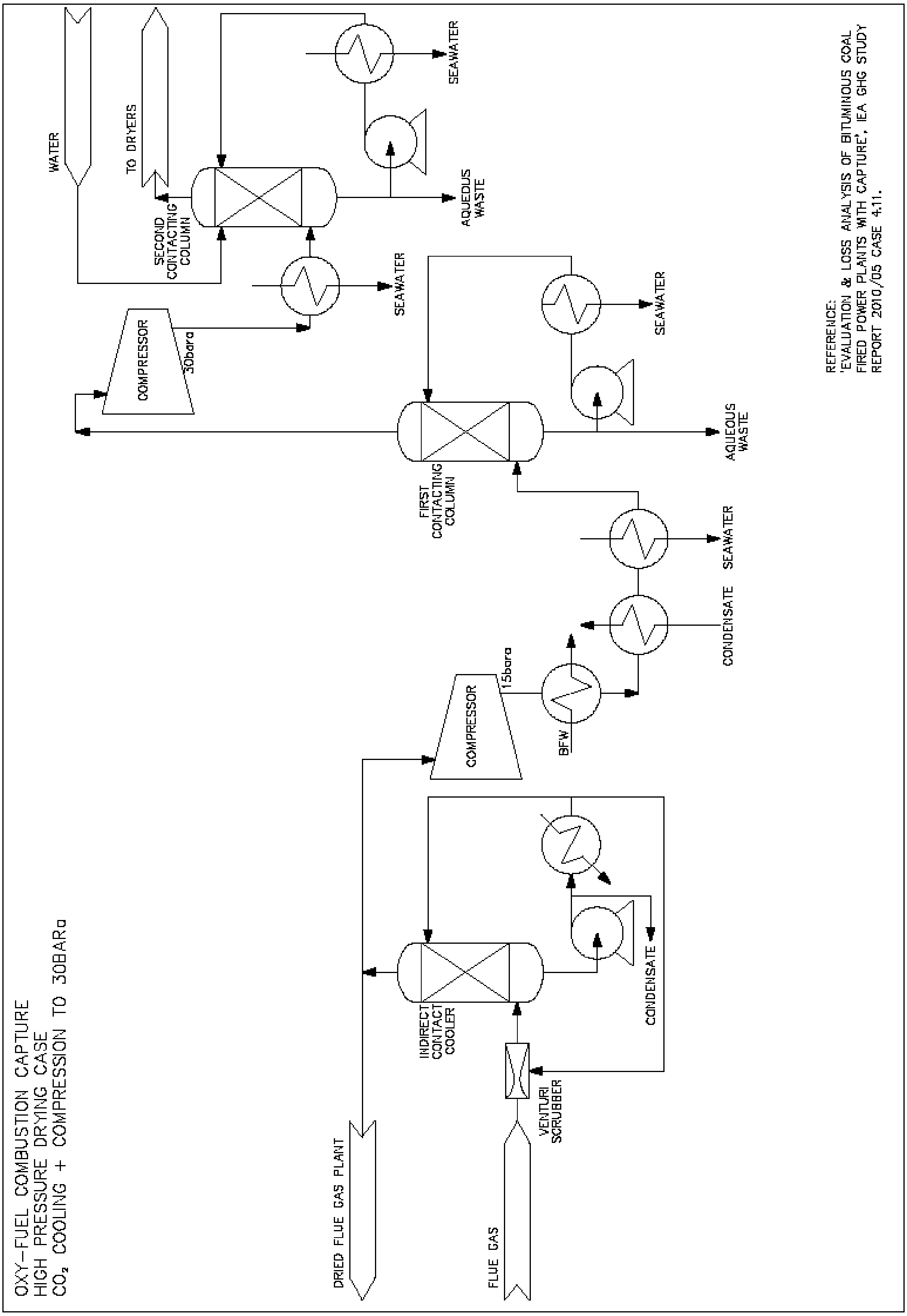
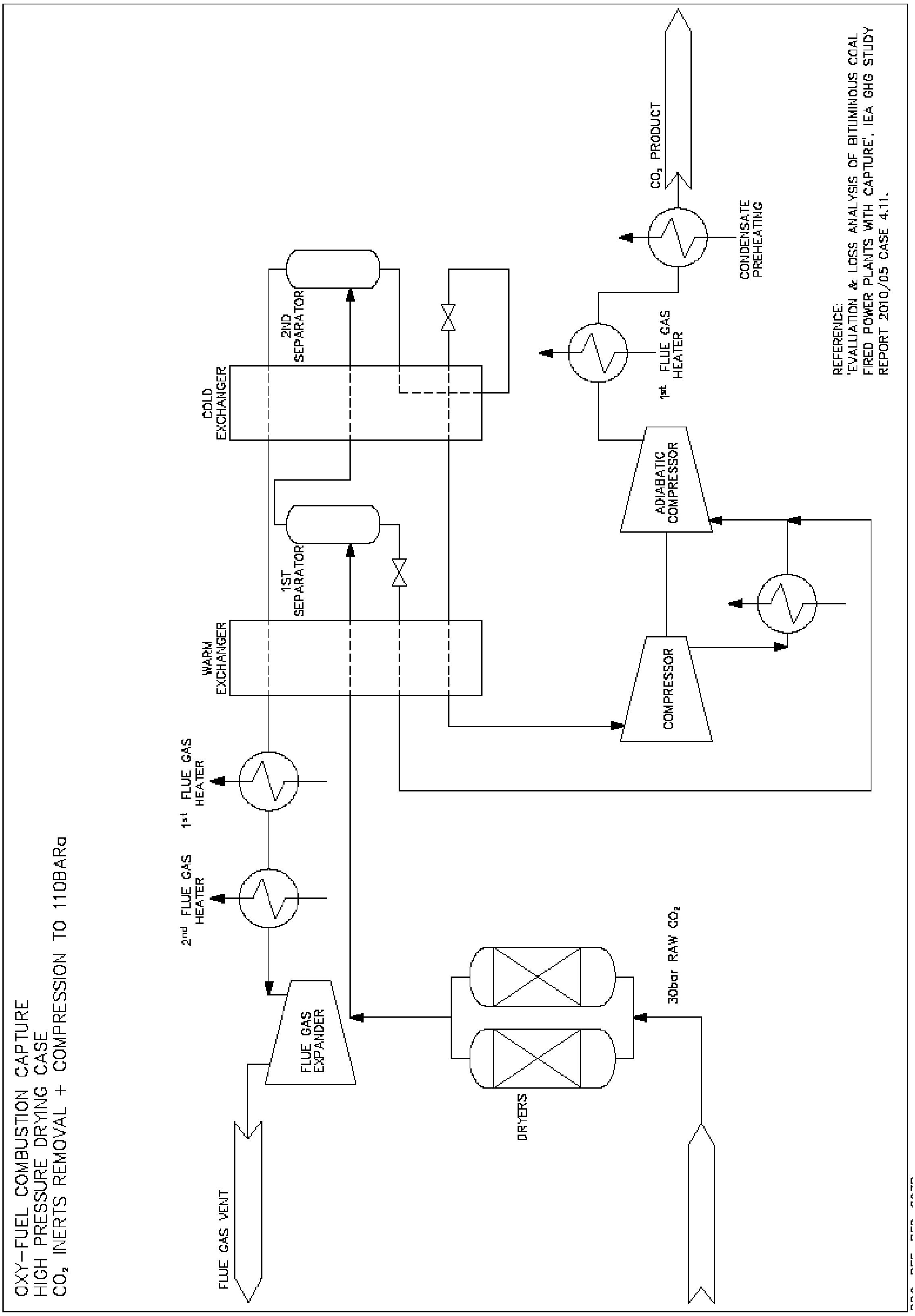


Figure 36 – Oxyfuel Combustion – High Pressure Drying Process – PFD for Cooling and Compression to 30 Bara



REFERENCE:
'EVALUATION & LOSS ANALYSIS OF BITUMINOUS COAL FIRED POWER PLANTS WITH CAPTURE', IEA GHG STUDY REPORT 2010/05 CASE 4.11.

Figure 37 - Oxyfuel Combustion – High Pressure Drying Process – PFD for Dehydration, Inerts Removal and Final Compression

7.3.3 Low pressure dehydration

Low pressure dehydration is carried out in the Air Liquide cryogenic low oxygen CO_2 purification process[36] and also by Linde.

Information on the Air Liquide process is not freely available. Air Liquide have proposed dehydration at pressures down to ~ 3 Bara in the past, however they are progressing various strategies[37] as regards impurities management. These include:

- Removal of SOx in a caustic scrubbing section, followed by compression and dehydration at the pressure required for the cryogenic process. The NOx impurities pass through the dehydration unit and are removed in the downstream cryogenic unit in a separate steam to the inerts content. Regeneration of the spent molecular sieve is carried out using non-condensible gases which have been removed from the CO2 stream in the cryogenic section and are subsequently vented. On initial heating the regeneration gas will contain high NOx levels as adsorbed material is desorbed. The purified CO2 stream is compressed to the required export conditions.
- Low pressure drying (<10 bar) to avoid formation of acid streams, followed by compression and cryogenic separation. An inerts stream, an SO2/NO2 stream and a CO2 stream are produced The CO2 stream is compressed to the required export conditions.
- Figure 38 provides an outline PFD.
- Variations of the high pressure dehydration scheme involve using the separated NO2 as a reagent for SO2/NOx removal at low pressure in a combination of a low and high pressure scrubbers and also at compressor inter-stages as condensed aqueous acid streams.

These concepts have been tested at the Lacq pilot plant and in testing at the Callide pilot plant. Acid resistant adsorbents are also being evaluated on a high pressure dehydration unit at the Total Lacq plant to assess performance and ageing phenomenon. Further testing will be carried out at the CIUDEN pilot plant.

Linde have presented a process[38] which they have been testing at the Schwarze Pumpe Oxyfuel pilot plant since 2008 and which is to be incorporated into the Oxyfuel demonstration plant at Janschwalde Power plant. The process involves dehydration over the range 5 – 18 Bara.

The Linde process details have been used to develop the flowsheet for the low pressure dehydration case. The dehydration operating pressure has been assumed to be 5 Bara, which is at the lower end of the operating pressure range, and thus covers the entire range of

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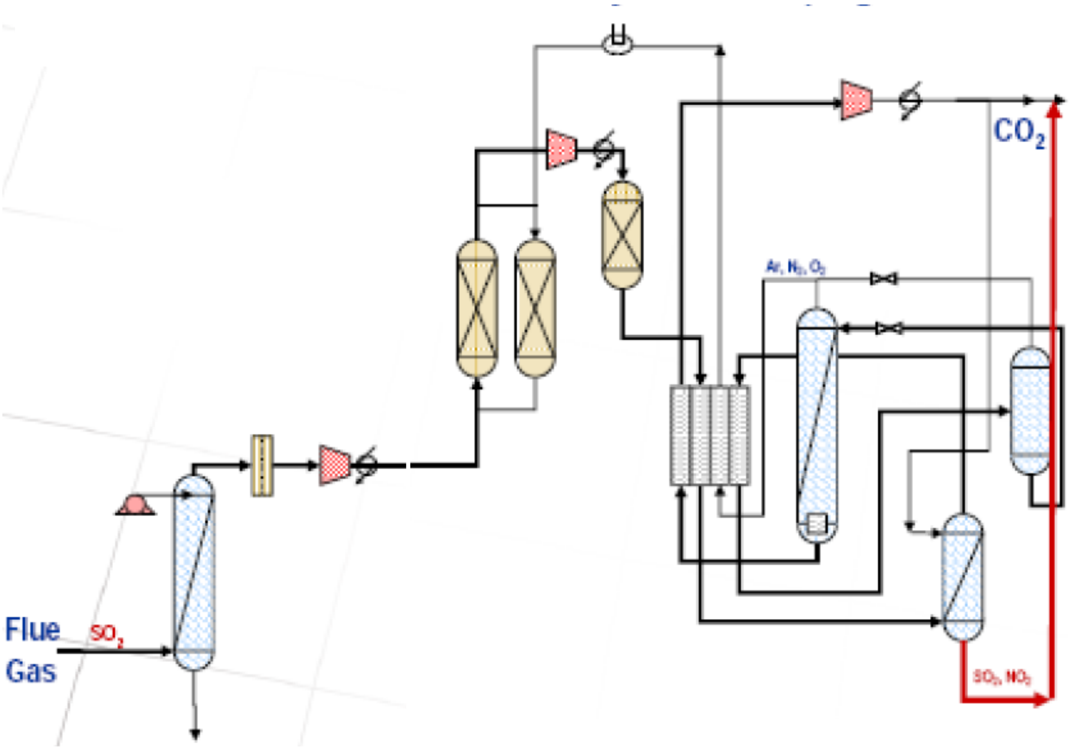
[36] 'Process for recycling of top Gas during CO2 separation', United States Patent number US 2008/0196583, Aug. 21, 2008

[37] 'CO2 purification unit for oxy-coal combustion systems', John-Pierre Tranier, Philippe Court, Arthur Darde, Nicholas Perrin, Air Liquide presentation at 1st International Oxyfuel Combustion Conference, Cottbus, September 2009.

[38] 'Development of the CO2 demonstration plant from the Experience of the CO2 pilot plant Schwarze Pumpe', Roland Ritter, Linde presentation at 2nd Oxyfuel Combustion Conference, Yeppoon, September 2011

potential dehydration pressures. (Note: Subsequent data has indicated that 12 Barg has been selected as the most appropriate pressure. The effects of this are discussed later).



Reference: "Co2 Purification Unit for Oxy-Coal Combustion Systems, Jean-Pierre Tranier, Air Liquide, 1st International Oxyfuel Combustion Conference, Cottbus, September 9, 2009

Figure 38 – Air Liquide Outline PFD

7.3.4 Process Description

Figure 39 and Figure 40 give outline PFDs of the process. It is assumed that basic flue gas desulphurisation has been carried out in the main process prior to entering the conditioning section. Raw gas enters the bottom of the combined direct contact cooler and deep desulphuriser. Gas is contacted with caustic solution to remove the residual sulphur content. Caustic solution from the base of the column is pumped and re-circulated around the lower packed section. A purge of solution is removed as contaminated process water and disposed of.

Sulphur-free gas from the lower section of the column passes to the upper section where the gas is washed against circulating water to remove any caustic droplets. The gas is compressed to above 5 Bara and enters the pre-cooling and DeNOx column (LICONOX process). The NOx-loaded gas is washed against a circulating alkaline solution of either:

- Ammonia solution in which NOx is reacted to form ammonium nitrate / nitrite solution. The ammonium nitrite rich solution is regenerated by thermal decomposition to provide the washing media. Spent salt is removed as a purge

- Caustic solution in which NOx is reacted to form sodium nitrate / nitrite. The spent salt solution is removed from the circulating stream.

A water scrubbing section at the top of the column minimises loss of alkaline solution.

NOx conversion is a function of the operating pressure. Preliminary results indicate that a NOx conversion of ~80 - 85% may be achieved at 5 Bara, whereas >95% conversion is achieved at 15 Bara. (Subsequent to this analysis a further paper from Linde[39] was identified in which more recent analysis was available. Linde now suggest that an operating pressure of 12 Barg, with NOx conversion of 93%, is more appropriate since the NO/NOx ratio is >0.7 at pH>6.4. This is more favourable towards the nitrite selective process, giving around 90% selectivity. The process appears to be based upon the aqueous ammonia wash option. The equipment has to be located at a compressor inter-stage and these pressure requirements need to be fed into the compressor design.) The feed composition to the dehydration package is based upon the 5 Bara conditions, with 80% NOx conversion. Composition is given in Table 8.

Water saturated, purified gas, containing residual NOx, passes to the CO_2 drying package. The downstream cryogenic process requires that a high water specification of <10 ppmv be achieved. An adsorption-type drier unit will therefore be required. Dried gas, at around 1 ppmv, passes through the mercury removal unit, is compressed to the pressure required for purification and passed to the cryogenic purification and separation plant. Inert vent gases from the purification plant are vented to atmosphere. During times of regeneration these vent gases are used to regenerate the spent adsorption bed. At the start of regeneration high NOx concentrations can be experienced in the gas leaving the regenerated bed as the NOx gas desorbs from the adsorption bed. These vent and regeneration gases are sent to an atmospheric vent, via an expander for power recovery. Further vent gas treatment may therefore be required.

CO_2 product from the cryogenic purification section is in both liquid and vapour form. Liquid CO_2 is pumped to export conditions.

Low and medium pressure gaseous CO_2 streams are produced. The low pressure stream is compressed in the first stage compressor, cooled and combined with the high pressure stream. The combined stream passes though the knockout pot prior to entering the 2nd stage compressor. The appropriate number of compressor stages are provided for the CO_2 to reach the export pressure.

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[39] ‘ Cold DeNOx development for oxyfuel power plants’, F Winkler, N Schoedel, H_J Zander, R Ritter, International Journal of Greenhouse Gas Control, 5, 2011, S231-S237

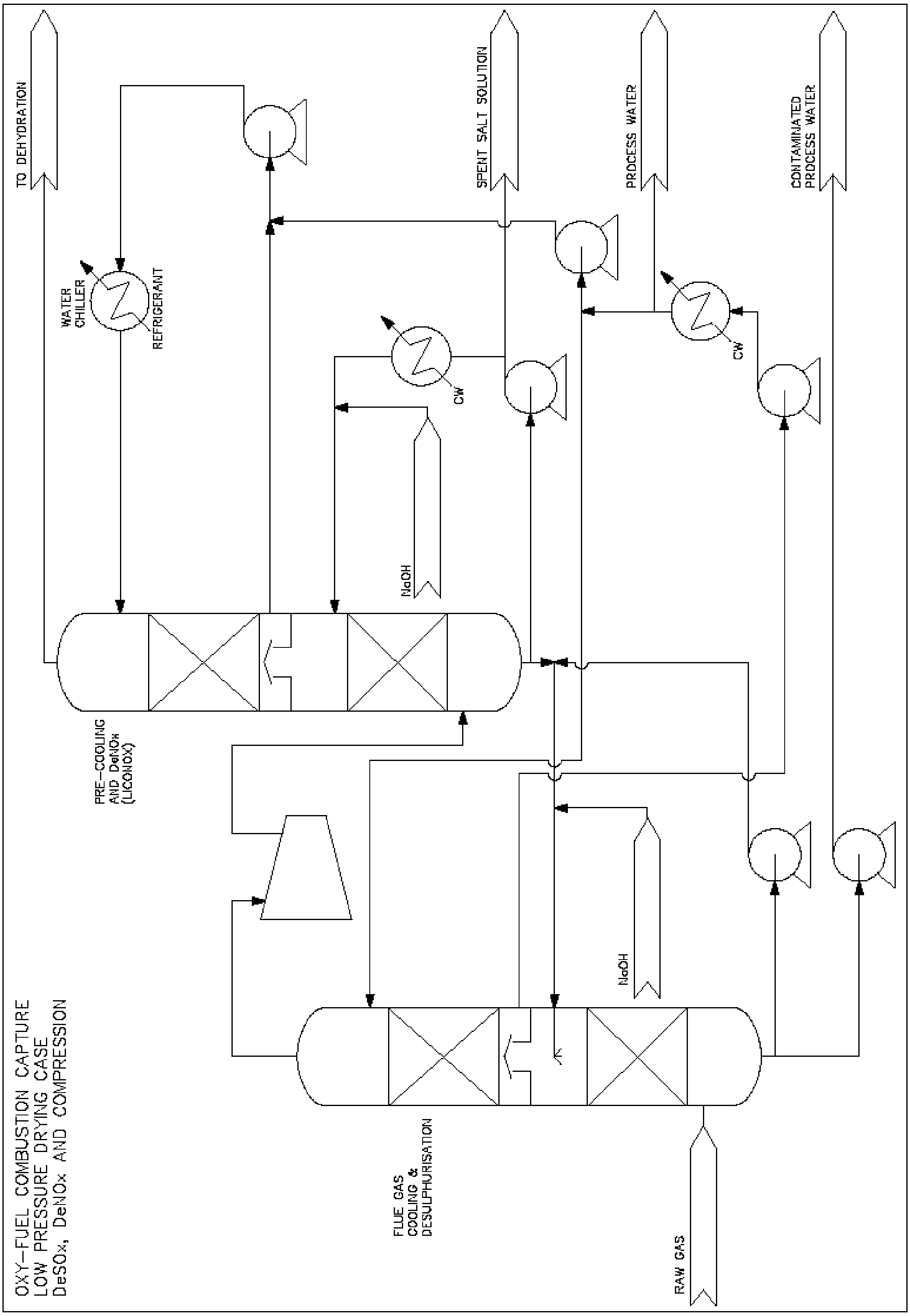

Figure 39 - Oxyfuel Combustion – Low Pressure Drying Process – PFD for DeSOx, DeNOx and Compression

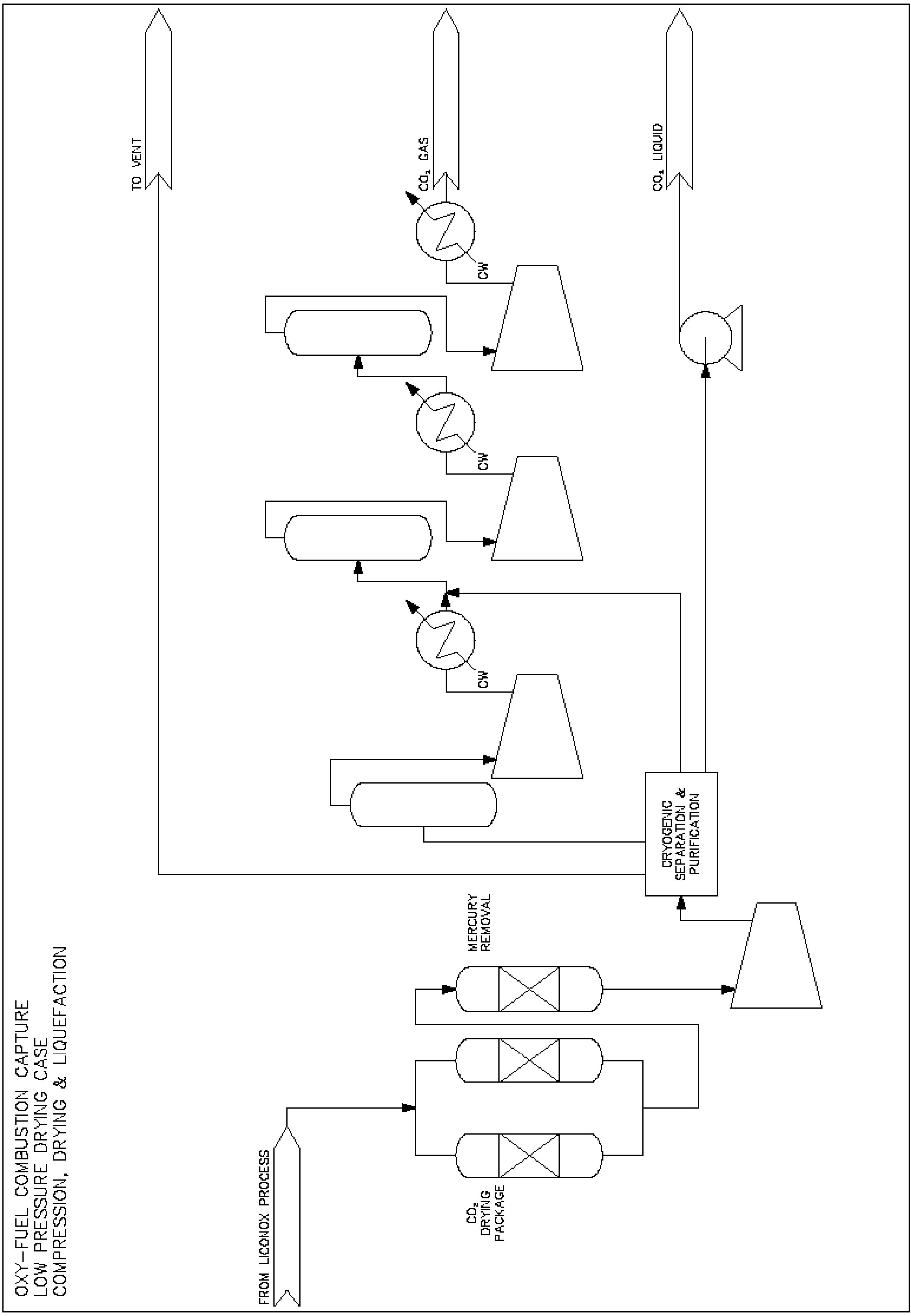

Figure 40 **- Oxyfuel Combustion – Low Pressure Drying Process – PFD for Dehydration, Inerts Removal and Final Compression**

8.0 Cases for Consideration by Dehydration Vendors

Many cases have been identified for consideration by dehydration vendors. These have been selected to give coverage of the range of variables considered important in sizing / selecting the dehydration process.

8.1 Variables for Investigation

This section describes / explains the variables which need to be considered as part of the cases for consideration. It is not required that all variables should be considered in all cases. Several different cases need to be evaluated. These are detailed in the case matrix in Section 8.2

8.1.1 Types of Capture Process

There are three main types of CO_2 processes, as described in Section 7.0 above:

- Pre-combustion capture, in which CO2 is removed from synthetic gas at high pressure. Typical capture processes are Selexol and Rectisol.
- Post combustion capture, where CO2 is captured from flue gas at low pressure using typically amine-based solvents
- Oxy-fuel combustion in which the product stream is high in CO2 and inerts. No actual capture is required and a range of different pressures is possible.

The different types of process need to be considered when sizing / selecting the dehydration system since levels of inerts and impurities are different and the streams are at very different conditions.

8.1.2 Moisture Levels

The target CO_2 moisture levels selected for evaluation are based on several considerations:

- Prevent free water. This is to avoid / minimise corrosion.
- Avoid formation of hydrates.

The actual acceptable moisture value is dependent on several factors: the local minimum ambient temperature, local seawater minimum temperatures (for subsea pipelines), the minimum temperature to be expected during processing of the CO_2, the corresponding operating pressures as well as the requirements of downstream equipment. Required moisture values for pipelines quoted in literature vary considerably between 10 and 600 ppmv. This study investigates three different moisture levels:

- 500 - 600ppmv, 550ppmv average to be used – this value is used in pipeline systems where high ambient temperatures are experienced.

- ~50 ppmv – indications from research on hydrate formations indicates that this level may be required to avoid hydrate regions in subsea pipelines.
- <10 ppmv – these low values are a requirement where downstream processing involves cryogenic conditions

8.1.3 Flow rates

Different ranges of power plant size exist, generating different amounts of CO_2 gas. Values quoted include for an availability of ~85%. The ranges considered are:

- 1 - 3 million tonnes / year CO2 – an average rate of 265 te/hr - typical for gas-fired power plant
- 3 - 6 million te/yr – an average rate of 600 te/hr – typical for coal-fired power plant
- > 6 million te/year – typical for power plant networks.

Table 7 shows a basic comparison of emission values to generation rating for gas or coal conventional power technology. This study looks at the lower two ranges of CO_2 capacities. Vendors have been requested to advise the maximum rate achievable for a single dehydration train.

Emissions, tonnes/year	t/h	Gas, MW	Coal, MW
1,000,000	114	380	170
2,000,000	228	760	340
3,000,000	342	1141	510
4,000,000	457	1521	680
5,000,000	571	1901	850
6,000,000	685	2281	1020
7,000,000	799	2662	1190
8,000,000	913	3042	1361
9,000,000	1027	3422	1531
10,000,000	1142	3802	1701
15,000,000	1712	5703	2551
20,000,000	2283	7605	3401
25,000,000	2854	9506	4252

Table 7 Emissions to power rating equivalents

8.1.4 Pressure

Export Conditions

Liquid CO_2 is supplied over the range 6 to 20 Bara, at around -53C to -20ºC respectively (i.e. at near boiling point). The CO_2 is processed as a gas, chilled and condensed and the liquid is let-down to the required pressure. Gas is generated on let-down and is recycled and reprocessed through the gas plant or used elsewhere. Liquid CO_2 will have been dehydrated in the gas phase. Pre-liquefaction gas pressures will be within the same range as those considered for gas drying. A separate CO_2 liquid drying case is not therefore considered as appropriate.

Gas / supercritical CO_2 can be transported in pipelines over the range of 10 bar to 200 bar. Lower pressures may be used for transporting small quantities of CO_2 locally to an aggregation point for onward compression. Larger quantities of CO_2 may be transported over moderate distances in the gas phase at pressures up to 60 Bara (depending on the minimum temperature). The region from 60 Bara to 80 Bara is unlikely to be used because two-phases may form. Supercritical CO_2 will be transported at pressures from 80-200 Bara.

Dehydration Operating Pressure

The water solubility in high purity CO_2 gas passes through a minimum and increases. Actual pressure and temperature influence this minimum solubility. At near ambient conditions (of +4 to +25 ºC) this minimum occurs at ~25 to 65 Bara respectively for pure CO_2. While it is desirable to use the compressor inter-stage cooling and knockout to remove as much of the water as possible, thus offloading the dehydration unit, it is necessary to consider CO_2 liquefaction conditions and conditions for hydrate formation in determining the optimum point for location of a dehydration unit.

Supercritical CO_2 has a high level of water solubility. Supercritical CO_2 would likely be dehydrated at a compressor inter-stage pressure, with CO_2 in the gas phase, unless the CO2 occurs naturally at supercritical conditions.

The pressure at which CO_2 drying is required can therefore be dependent upon several considerations:

- Hydrate formation conditions
- Undesired liquid CO2 formation conditions
- Water solubility in CO2
- Compressor inter-stage conditions available. These conditions can be limited in some cases, such as occur with the use of Ramgen high pressure ratio compressors.
- Inter-stage cooling temperatures available
- Minimum temperatures experienced at the point of dehydration and also downstream
- CO2 export pressure
- CO2 supply pressure

- Downstream processing requirements, for example liquefaction / cryogenic processes
- Capital / operating cost of dehydration equipment

Dehydration of post-combustion and pre-combustion capture cases can be carried out at a variety of different pressures, depending upon the supply pressure and the compressor inter-stage conditions available. Post combustion gas is typically provided at 1-3 Bara, while pre-combustion gas (multi-stream) can be supplied over a wider range of conditions, typically 1-15 Bara. Oxyfuel cases span a range of pressures from ~5 to 30 Bara, dependent upon the supply pressure and downstream processing requirements. For CCS, drying pressures are likely to be in the range of LP compression.

30 Bara has been selected as the base case from which sensitivity variations are made. Sensitivity to pressure is considered, where operating pressures are varied over the range 30, 20 and 10 Bara for the post combustion case. The sensitivity effect of pressure on other capture cases is expected to be similar. The low pressure oxyfuel cases are carried out at 5 Bara.

Vendors were requested to advise of any CO_2 drying experience at pressures in excess of 30 Bara, and at supercritical conditions in particular. The range of pressures for the different combustion / capture types provides a reasonable variation to indicate the effects of pressure on the dehydration process capital cost.

8.1.5 Design Pressure

The design pressure is process specific. The process may be inherently safe (designed to cater for the highest pressure which may be achieved) or rely on excess gas being released. The design pressure may be based on:

- The maximum operating pressure + 10%
- The maximum pressure that the equipment will experience on a plant shutdown, or trip, when a downstream compressor stops and gas passes back to the low pressure side via the anti-surge system. Plants are often designed for this “settle-out” pressure to avoid undesirable environmental release of gas. That does not mean to say, however, that pressure protection is not required.

For the purposes of this study the former philosophy has been adopted.

8.1.6 Composition

The various types of combustion process, combined with the capture process used, and the purification processes, whether they be upstream or downstream of the dehydration unit, essentially determine the conditions and composition inlet the dehydration system.

For the purposes of this study it was essential to consider the ranges of components in each case and consider the effects that these components might have on the dehydration process. Consider post-combustion capture: The raw gas from the combustion plant is preconditioned, passes through the capture plant and is provided at low pressure to the compression plant. Gas is compressed, condensable gases are removed and the gas is passed to the dehydration plant. It was decided to select the best composition specification as the base case

(Composition 1 in Table 8) and to evaluate the effects of higher inerts and impurities by having a different composition for impurity levels (Compositions 5 – 7)

The various compositions are listed in Table 8. Compositions 1 to 4 cover the normal lower end of the inerts and impurity ranges for the various capture processes. Compositions 5 to 7 cover the normal upper inerts and impurity composition ranges.

8.1.7 Inerts

The different CO_2 production / capture processes contain various inerts and each can be at very different concentrations in different cases. Typical inerts include nitrogen, hydrogen, argon, methane. The levels of inerts are often capture process specific.

Each case has specified inerts content. A single high inerts sensitivity case is included to investigate the effect of inerts concentration on sizing, capital and operational cost of equipment.

8.1.8 Impurities

The presence of impurities needs to be considered when evaluating desiccants since they may cause degradation of the drying medium. Raw CO_2 streams can contain multiple impurities. These are often fuel (coal, gas, etc) and capture process specific. Impurities include NOx, SOx, H_2S, COS, HCl, O_2, methanol, polyethylene glycol, ethers, amines, ammonia, aldehydes, and traces of alcohols, acetones/acetates, formamides/amides, organic acids, etc.

Each case has specified impurities content. Impurities sensitivity cases are included to investigate the effect of the main impurities on sizing, capital and operational cost of equipment.

Vendors have been asked if there are any impurities, in addition to those given above, which would cause problems and at what levels. The vendors have also been asked to provide details of cut-off levels for the impurities listed above and additional impurities provided by vendor.

Process Type / Sensitivity Analysis		**Post-combustion capture**	**Pre-combustion capture**	**Oxy-fuel combustion**		**High Inerts**	**High Impurities**	
			Selexol	**High pressure**	**Low pressure**			
Composition No		**1**	**2**	**3**	**4**	**5**	**6**	**7**
Components	Units							
CO_2	Mol% dry	99.94	98.38	75.86	75.86	95.94	99.94	99.94
H_2O	Mol%	Sat	sat	sat	sat	sat	sat	Sat
N_2	Mol% dry	0.05	0.0072	15.22	15.22	4	0.05	0.05
Ar	Mol% dry	0	0.065	2.45	2.45	0	0	0
H_2	Mol% dry	0	1.26			0	0	0
CH_4	Mol% dry	0	0.0024	0	0	0	0	0
O_2	-	30 ppmv	0	6.24 %	6.24 %	30 ppmv	300 ppmv	30 ppmv
CO	-	10 ppmv	0.279%	50 ppmv	50 ppmv	10 ppmv	10 ppmv	10 ppmv

Process Type / Sensitivity Analysis		**Post-combustion capture**	**Pre-combustion capture**	**Oxy-fuel combustion**		**High Inerts**	**High Impurities**	
			Selexol	**High pressure**	**Low pressure**			
Composition No		**1**	**2**	**3**	**4**	**5**	**6**	**7**
Components	Units							
NOx	Ppmv	30	0	60 ppmv	82 ppmv	30	30	100
SO_2	Ppmv	15	0	170	0	15	15	100
H_2S	Ppmv	1	1	0	0	1	1	100
COS	Ppmv	0	16	0	0	0	0	0
HCl	Ppmv	1	0	0	0	1	1	1
Amines	Ppmv	1	0			1	1	20
NH_3	Ppmv	5	0	0	0	5	5	5
Aldehydes	Ppmv	20	0	0	0	20	20	20
Conditions								
Temperature	ºC	30	30	30	30	30	30	30

Process Type / Sensitivity Analysis		**Post-combustion capture**	**Pre-combustion capture**	**Oxy-fuel combustion**		**High Inerts**	**High Impurities**	
			Selexol	**High pressure**	**Low pressure**			
Composition No		**1**	**2**	**3**	**4**	**5**	**6**	**7**
Components	Units							
Pressure	Bara	30	30	30	5	30	30	30

Table 8 – Dehydration Inlet Compositions for the Different Cases

8.2 Summary of Cases for Consideration

The cases for consideration by vendors is summarised in Table 9. These cases effectively summarise the range of conditions at which dehydration plants will normally be expected to operate for CCS projects. It should be noted that the Rectisol process has been eliminated from this study since the product CO_2 has very low moisture and does not require downstream dehydration.

Each combustion / capture process has a set of 'base cases' which cover the composition and operating conditions experienced by a typical process. These base cases are case numbers 3, 13, 15 and 17. These are based on a CO_2 flow rate of 265 te/hr. Actual rates in the individual cases may be higher to account for the lower CO_2 composition in the gas stream inlet dehydration.

Cases 1, 2, 3 and 9, 10, 11 consider the effect of target moisture, over the range <10, 50 and 550 ppmv at two different flow rates of 265 te/hr and 600 te/hr.

Operating pressure sensitivity is evaluated at 265 te/hr in cases 3, 4 and 5. Vendors were requested to advise of any CO_2 drying experience at pressures in excess of 30 Bara, and at supercritical conditions in particular.

Effects of high levels of non-condensable and impurities are considered in cases 3, 6, 7 and 8.

The effects of higher rates are evaluated on each of the base cases by comparing cases 3 and 11, 13 and 14, 15 and 16, 17 and 18.

Vendors were asked to consider the maximum rate for which a single train of equipment could be used, via cases 12 and 19, which cover the extremes of operating pressure ranges.

Case No	**Process Type**	**Carbon Dioxide Flow rate from capture plant, te/hr**	**Operating Pressure, Bara**	**Lowest acceptable Design Pressure for CO_2 contact equipment Barg**	**Temperature ºC**	**Composition No**	**Target Moisture ppmv**
1	Post-C	265	30	37	30	1	550
2		265	30	37	30	1	50
3		265	30	37	30	1	<10
4		265	20	25	30	1	<10
5		265	10	13	30	1	<10
6		265	30	37	30	5	<10
7		265	30	37	30	6	<10
8		265	30	37	30	7	<10
9		600	30	37	30	1	550
10		600	30	37	30	1	50
11		600	30	37	30	1	<10
12		Max for single	30	37	30	1	<10

Case No	**Process Type**	**Carbon Dioxide Flow rate from capture plant, te/hr**	**Operating Pressure, Bara**	**Lowest acceptable Design Pressure for CO_2 contact equipment Barg**	**Temperature ºC**	**Composition No**	**Target Moisture ppmv**
		train					
13	Pre-C (Selexol)	270	30	37	30	2	<10
14		610	30	37	30	2	<10
15	Oxyfuel (High Pressure)	350	30	37	30	3	<10
16		800	30	37	30	3	<10
17	Oxyfuel (Low Pressure)	350	5	7	30	4	<10
18		800	5	7	30	4	<10
19		Max for single train	5	7	30	4	<10

Table 9 – Dehydration Cases to be Considered by Vendors

9.0 Evaluation of Data Received from Dehydration Vendors

Technical information from vendors has been added to the main body of the report, where appropriate. Most vendors supply adsorption packages only. A smaller number provide liquid desiccant systems.

9.1 Engagement of Dehydration Package Vendors

Engagement by dehydration vendors was generally poor. Several of the vendors approached refused to contribute; others wanted an involvement but failed to produce any data.

SPX Flow Technology produced a complete set of sizing, capital cost and utility usages data for solid desiccant for all of the cases requested. Frames Process Systems provided equivalent data for solid adsorbent and TEG dehydration for one case. Exterran were unable to help with provision of data but provided contact details for media vendors.

Other vendors either declined at the start or said they would provide data but subsequently refused to respond to multiple communication attempts.

The lack of vendor involvement was disappointing. During discussions, both with those who took part as well as those who declined to assist, there were several comments of note:

- Vendors complained about the large number of CCS projects for which they have quoted, but which have never been funded
- The failure of the UK government to select a suitable project after the first round of DECC competitions, the lack of agreement between the EU and UK governments on allocation of the NER300 budget and issues surrounding the current DECC competition have led vendors to believe that there is little political commitment towards funding of CCS projects.

As a result, there appears to have been a recent step change in the attitude of vendors towards CCS activities. Although several vendors originally had CCS activities as a target market, believing that this was an area of growth, several are now of the opinion that this is no longer an area of significant interest.

Re-engagement of vendors is therefore an area which should be addressed by industry bodies as a priority.

9.2 Dehydration Media Vendors

Solid desiccant vendors were helpful with information such as the number and size of beds to be used, the online time / regeneration frequency, and the effects of impurities on the dehydration media. Zeochem, Grace Materials Technologies and UOP Products provided data.

9.3 Technology Assessment Sheets

Technology assessment sheets were completed for each of the main technology types using data provided by vendors and / or from literature searches. These are contained in Appendix 2. The technology assessment forms were used to compare the different process and identify those which are able to be used on CO_2 dehydration duty. They also highlight areas where information is not in the public domain or areas which require further research.

The first sections effectively consist of very general, initial summary assessment criteria:

- Process Viability – an evaluation of the science underlying each proposed technology to ensure that it is based on sound scientific knowledge and not dependent upon unproven approaches that would themselves require to be proven and/or developed prior to making the technology viable

- Process Maturity – an evaluation of the stage of development of each proposed technology to ensure that it is sufficiently developed to allow detailed engineering to commence. Since process technologies tend toward optimisation as they are successfully implemented in multiple and ever-larger installations, the judgement on the maturity of a given process could be easily answered by identifying whether or not a plant of a representative size already exists.

These effectively determine whether the process is in a state such that it could be used in current day CCS processes.

In order to get a better qualitative assessment of the various processes further detailed criteria were investigated, where possible. These comprised of information pertaining to efficiency, footprint, chemical requirements and by-products produced, effects of impurities, process control and HSE issues. Relevant data from the Technology Assessment sheets has been written into the main body of this report.

9.4 Plant Performance Data – Solid Bed Desiccants

9.4.1 Dehydration Media

Although most vendors do supply a mix of different media (i.e. activated alumina, silica gel, and molecular sieve) they all provided data for molecular sieve systems. This is believed to be the most performance and cost efficient option for CO_2 service.

Vendors have selected either Type 3A or Type 4A molecular sieve. In cases where high impurities are present, such as in the high impurities and the oxyfuel cases (compositions 7, 3 and 4 respectively) in Section 8.1.6, acid resistant versions of the above grades have been selected.

Type 4A sieve retains the best performance in cases where carbonic acid forms due to the presence of liquid water (carryover from upstream or through reflux condensation during regeneration).

9.4.2 Quantity of Desiccant

The quantity of desiccant required is a function of the adsorption time selected the number of beds in parallel and any margin added due to the presence of impurities. Lower pressure operation will require larger diameter beds and larger bed volumes to cater for the larger volume of gas and the increase in moisture present.

Typical media life of between 2 and 4 years is expected, typically 3 years. Maloperation can lead to a considerable reduction in the expected life. However, good operating practices and control of impurities may extend the life beyond that which vendors are prepared to guarantee.

Vendors have quoted between 48 te and 102 te of total adsorbent required for a rate of 265 te/hr of CO_2. The difference is due to the range in adsorption times which vary from 8 to 24 hours per bed.

9.4.3 Package Pressure Drop.

Different vendors quote quite different values. Desiccant vendors quote very low values since they are interested in the pressure drop across the bed alone. Dehydration package vendors quote different values, since they need to incorporate the additional effects of the routing values, pre-filters, product gas filters etc.

Generally pressure drops are as given in Table 10.

Unit	**Pressure Drop (Bara)**	
	Start of life	**End of life**
Adsorption bed	0.012 to 0.25	-
Dehydration package (no filtration)	0.08	0.15
Dehydration Package (with pre and post filtration)	1.0	2 .0

Table 10 - Pressure Drops for Dehydration by Adsorption

9.4.4 Maximum Size of a Single Train

Vendors typically limit the maximum vessel diameter due to a limitation in equipment manufacturing facilities[40]. (A maximum diameter of 5m was quoted by one vendor.) Larger equipment is available but the capital cost would be expected to increase significantly; equipment generally becomes very expensive well before the diameter limit is reached. At high rates the number of parallel beds can be increased to keep the vessel diameters down, but the regeneration rates required increase since:

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[40] SPX vendor questionnaire

- The number of beds to be regenerated within the bed adsorption time has increased above one. More regenerations have to be carried out within the bed adsorption time.

- It is desirable to keep the bed size small, to avoid the requirement for large volumes of desiccant and associated vessels. Available adsorption time is thus minimised. A fast turnaround of regenerating beds is therefore required.

There becomes a point when it is more practical to split the feed across an additional number of trains.

Data received from vendors for the 30 Bara operating pressure is summarised in Table 11. One set of data suggests that a single train can handle around 300 – 350 te/hr of CO_2 raw gas with a 2 bed system before an additional train is required. Other data suggests that a single train is possible for 600 te/hr capacity with large bed diameters and varying adsorption times and numbers of beds in parallel.

Vendor	**CO_2 rate (te/hr)**	**Regeneration gas through beds on adsorption duty** Note 2	**No of trains**	**Total no of beds**	**Bed diameter (m)**	**Adsorption time (hrs)**	**Regeneration cycle time (hrs)**
Vendor 1	350	No	2	2 beds per train	-	6	5.5
	600	No	2		-	6	5.5
Vendor 2	600	No Note 1	1	3	3.5	-	-
Vendor 3	600	Yes	1	2	6	24	12
	600	Yes	1	3	4.2	12	5.75
Vendor 4	600	Yes	1	2	5.3	12	11.1

Table 11 – Size of Dehydration Trains

Notes

1. If regeneration gas is recycled through the adsorption beds then bed sizing would be larger, in which case 2 parallel trains of 3 beds each would be recommended.

2. The fate of the regeneration gas varies according to vendor process. Vendor 1 & 2 discharges the regeneration gas to atmosphere Vendors 3 & 4 route the gas back to the working regeneration bed to remove the water and route the gas into the process.

Limited data for the saturated gas at 30°C, 5 Bara cases indicates that the maximum train capacity is around 100-120 te/hr.

9.4.5 Future Expansion

If future expansion capacity is built into a dehydration package (i.e. allowance is made for future adsorption beds at the outset) then they can be added at a later date. However if no allowance is made during design then an additional dehydration train would be required, since the bed adsorption time, regeneration loop and associated regeneration equipment would not be large enough to regenerate the spent bed before the next bed in sequence required regeneration.

9.4.6 Lead Times

Typical lead times quoted for an adsorbent dehydration package varies; 36 – 52 weeks for one vendor and 58 – 64 weeks for the other. The variance in lead times could be the result of a number of factors. For example on smaller flows vendors can have modular or standards designs built and available or the operating model of the vendor may include pre-built strategies. This is not uncommon in the provision of acid gas units or water treatment industries where modular units can operate over a wide range of flows and the market supports the investment. Some systems particularly larger units will require long lead times for delivery to allow vessels and equipment to be purchased and manufactured. In this case the range is wide and the author was surprised by the short turnaround for one vendor, atypical experience would lead you to expect 30-60 weeks depending on the technology type and capacity.

9.4.7 Footprint

Footprints vary considerably. For Case 3 at 265 te/hr CO_2 the options are:

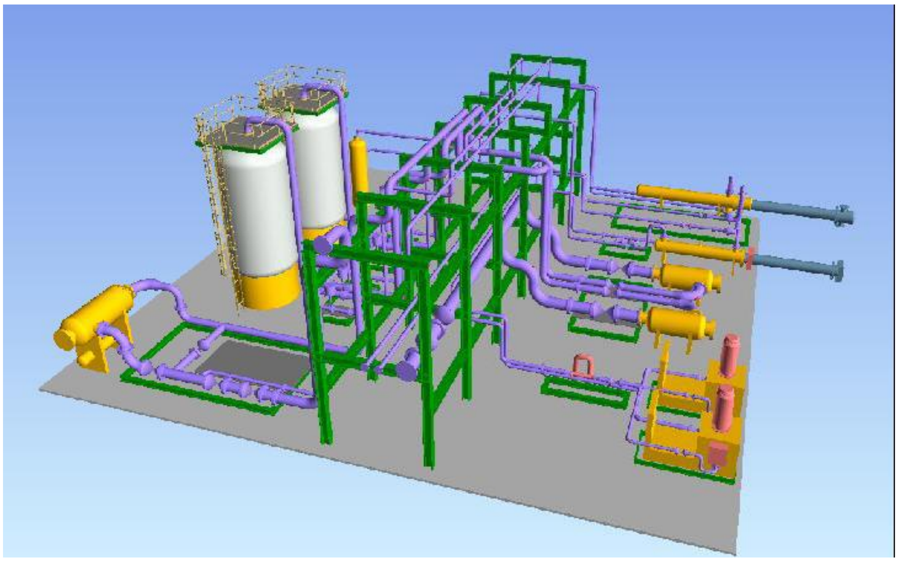
- For the package using low pressure regeneration:

  10000 mm length x 6000 mm width x 3400 mm height

- For the package using pressurised regeneration with CO_2 the vendor advises that they can attempt to fit the equipment into available space by installing equipment on multi platform levels. Options presented for the same package size are:

  Option 1 - 27,000mm length x 25,000 mm width x 9,500 mm height.

  The associated layout for Option 1 is:

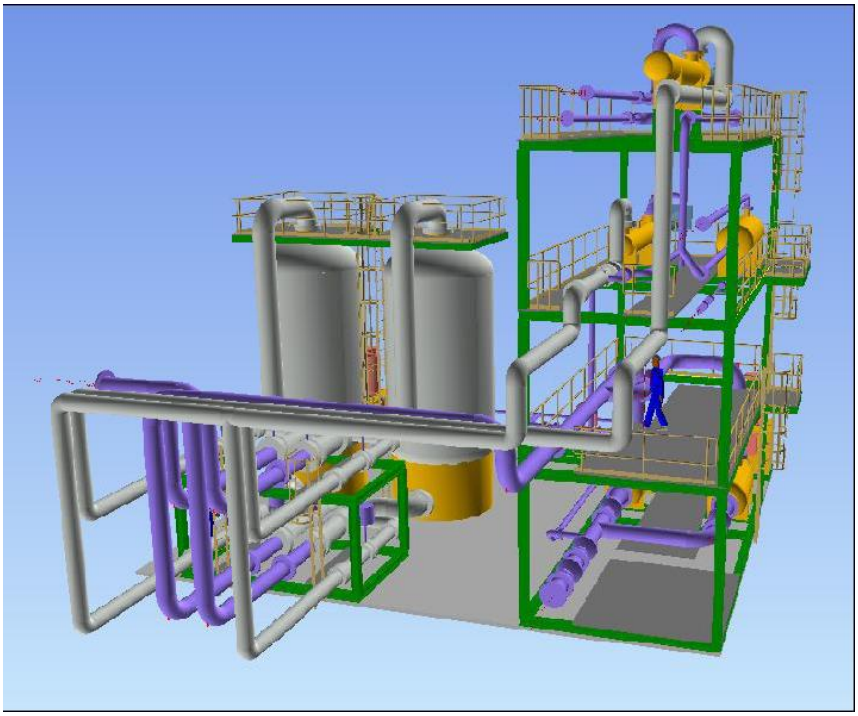


Reference: Supplied by Frames 29/10/12

Figure 41 – Typical Layout for Option 1

Option 2 - 15,000mm length x 14,000 width x 14,000 height

The associated layout for option 2 is:



Reference: Supplied by Frames 29/10/12

Figure 42 - Typical Layout for Option 2

9.4.8 Heat and Mass Balance

A heat and mass balance and associated PFD are provided in Figure 43 and Table 12 for a molecular sieve package which uses pressurised CO_2 for regeneration. The case is a snapshot of a 2 bed system with the spent bed part way through regeneration, i.e. the bed is partially heated. Spent regeneration gas is returned to the inlet of the adsorption bed.

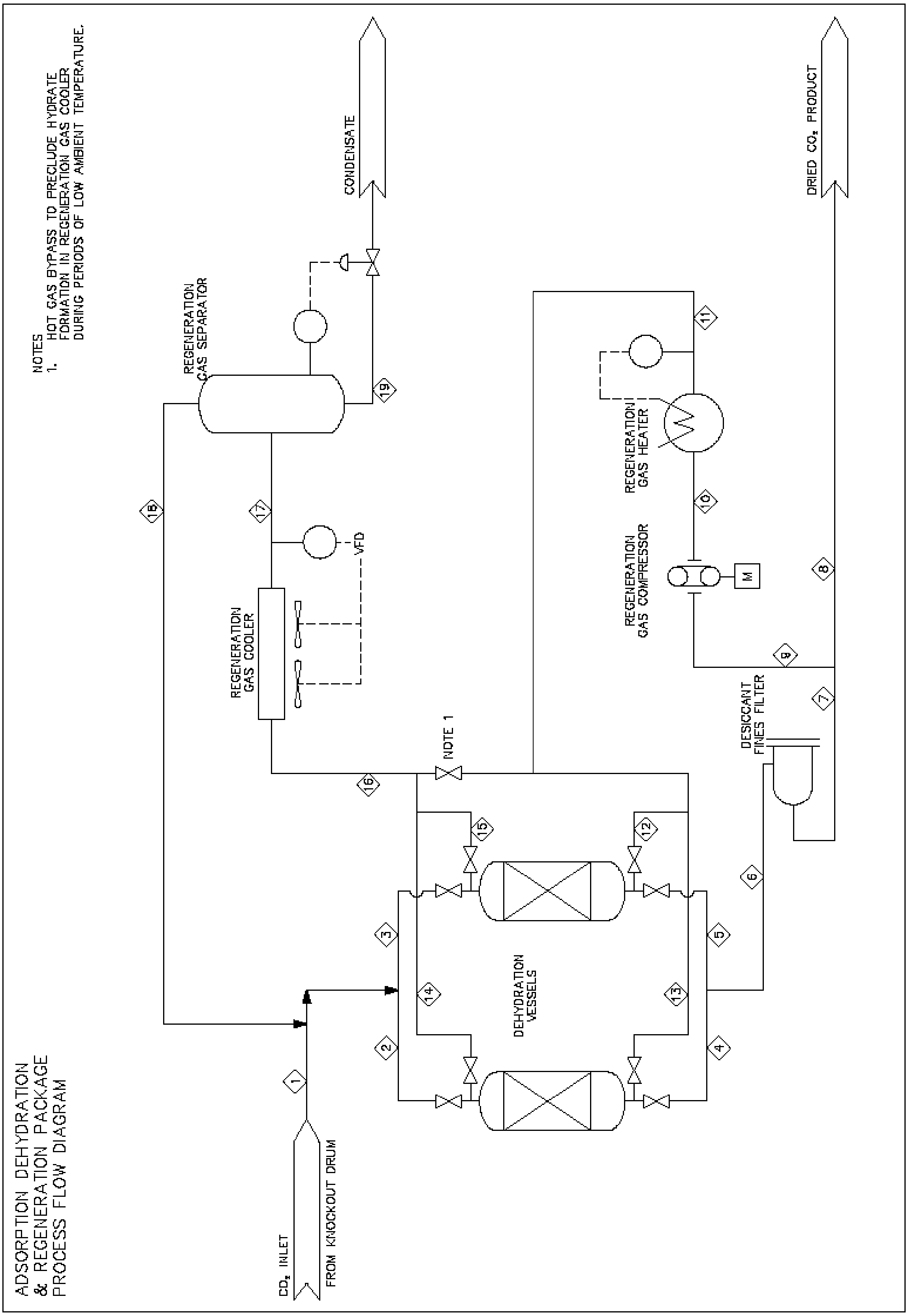


Figure 43 **– PFD for Molecular Sieve Dehydration Unit**

Heat and Material Balance
Adsorption Dehydration
Post-combustion case at 265 te/hr

Stream	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
Temperature (°C)	30	30	30	29.2	29.2	29.2	28.9	28.9	28.9	34.5	230	230	230	120	120	120	30	30	30
Pressure (Bara)	30	30	30	29.3	29.3	29.3	29	29	29	30.6	30.4	30.4	30.4	30.4	30.4	30.4	30.2	30	30
TOTAL FLOW																			
Mass Flow (kg/hr)	265,000	302,940	0	302,655	0	302,655	302,655	264,822	37,832	37,832	37,832	37,832	0	0	38,318	38,318	38,318	37,854	464
Molar Flow (kg-mol/hr)	6,031	6,894		6,878	0	6,878	6,878	6,018	860	860	860	860	0	0	887	887	887	861	26
GASEOUS PHASE																			
Mass Flow (kg/hr)	265,000	302,940	0	302,655	0	302,655	302,655	264,822	37,832	37,832	37,832	37,832	0	0	38,318	38,318	37,854	37,854	0
Molar Flow (kg-mol/hr)	6,031	6,894		6,878	0	6,878	6,878	6,018	860	860	860	860	0	0	887	887	862	862	0
Molecular Weight	43.9	43.9	43.9	44.0	44.0	44	44	44.0	44.0	44.0	44.0	44.0	44.0	43.2	43.2	43.2	43.9	43.9	
Composition (mol %)																			
CO_2	99.72	99.72	99.72	99.95	99.95	99.95	99.95	99.95	99.95	99.95	99.95	99.95	99.95	96.91	96.91	96.91	99.72	99.72	
H_2O	0.23	0.23	0.23	0	0	0	0	0	0	0	0	0	0	3.04	3.04	3.04	0.23	0.23	
N_2	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	
LIQUID PHASE																			
Mass Flow (kg/hr)																	463.7		463.7

Table 12 – Heat and Mass Balance For a Molecular Sieve Dehydration Unit

9.4.9 Power Consumption

Power consumption is a function of operating pressure, for the same gas rate. For the limited data available it suggests that minimum power consumption occurs at around 30 Bara, as shown in Figure 44. The relationship between power and pressure is complex. Main compression power is ignored here and power consumption is from the provision of circulation compression and heating/cooling. Generally as the equipment specification changes from high volume to high pressure costs decrease as the volumetric flow decreases, increases with pressure and an optimal point occurs around 30 bar.

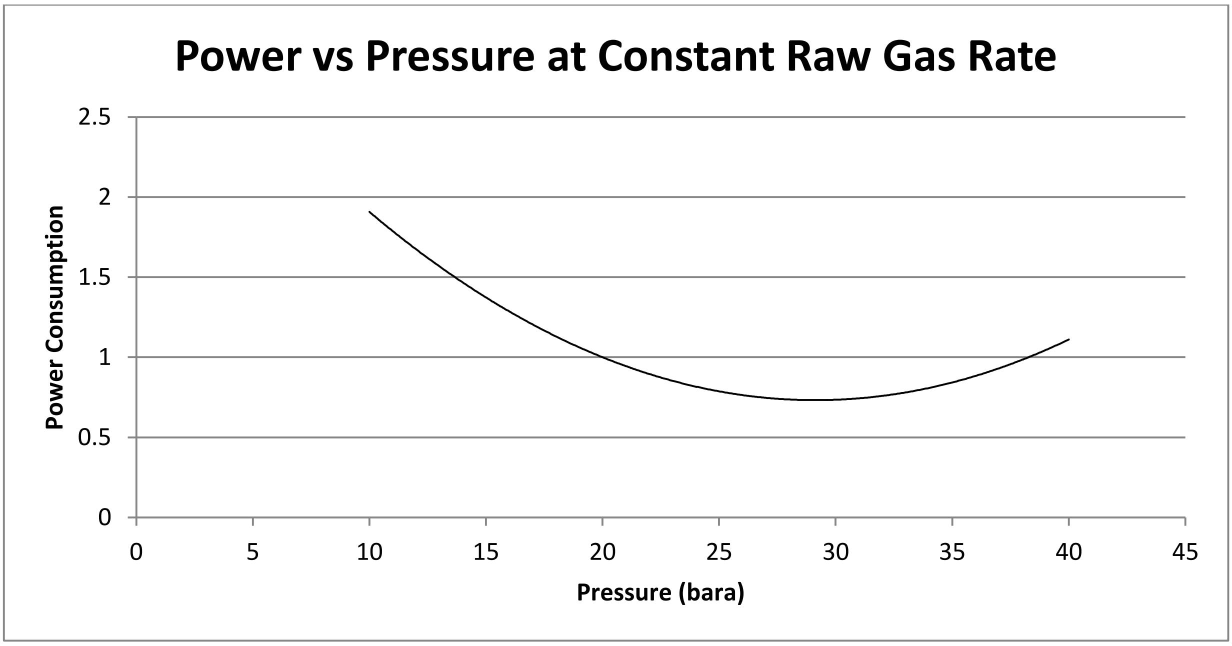


Figure 44 – The Effect of Power Consumption versus Operating Pressure

9.5 Plant Performance Data – Liquid Desiccants

9.5.1 Dehydration Media

Although several glycol systems are available Frames have selected TEG as the most appropriate desiccant for processing of the CO_2 stream. All subsequent costing is based on TEG.

9.5.2 Quantity of Desiccant

Frames information suggests that around 30 te of TEG is required for a system to process 265 te/hr of water saturated raw CO_2 gas at 30Bara, 30°C.

9.5.3 Package Pressure Drop.

The TEG package pressure drop is effectively the pressure drop across the contactor. This is stated as 0.7 bar.

9.5.4 Maximum Size of a Single Train

Literature advises that glycol flowrates of up to 1000 m^3/day with TEG purity of 99.99% are achievable. A 265 te/hr CO_2 plant requires a TEG circulation rate of ~ 3.1 m^3/hr, or 75 m^3/day. Thus a TEG regeneration unit could potentially handle the moisture from 3,500 te/hr of CO_2 gas, although multiple contactors may be required to be able to process the quantity of gas.

9.5.5 Future Expansion

If future expansion capacity is built into a TEG dehydration package (i.e. adequate allowance is made for the future glycol processing requirements) then additional contactors can be added at a later date. However if no allowance is made during design then an additional dehydration train would be required.

9.5.6 Contamination of the CO_2

Glycol is introduced into the CO_2 at a rate which is dependent upon the operating pressure, temperature and gas flow rate. Losses from the system have to be made up.

9.5.7 Lead Times

Typical lead times quoted by the vendor for a TEG package is 54 – 60 weeks.

9.5.8 Footprint

Approximate dimensions of the package are:

- Width - 4,500 mm
- Length - 12,000 mm
- Height - 6,000 (reboiler top), 9,000 (reflux condenser top nozzle)

Approximate weight of the package:

- Weight - 50,000kg

The proposed outline arrangement and associated layout are shown in Figure 45 and Figure 46.

9.5.9 Heat and Mass Balance

A heat and mass balance and associated outline PFD for a generic TEG dehydration system are provided in Figure 45 and Table 13. In modelling the process it is apparent that the impurities in the system and the water-CO_2-Glycol interactions are not well defined and require further work. The information provided by this model is simple, it does not consider the potential to recover flash gas or CO_2 in the wet gas from the regeneration still. Further more detailed analysis should be sought from the appropriate vendor. The energy demand of the regeneration column reboiler is provided for information, energy requirements of pumps in the system are dependent on configuration and are therefore not quoted.

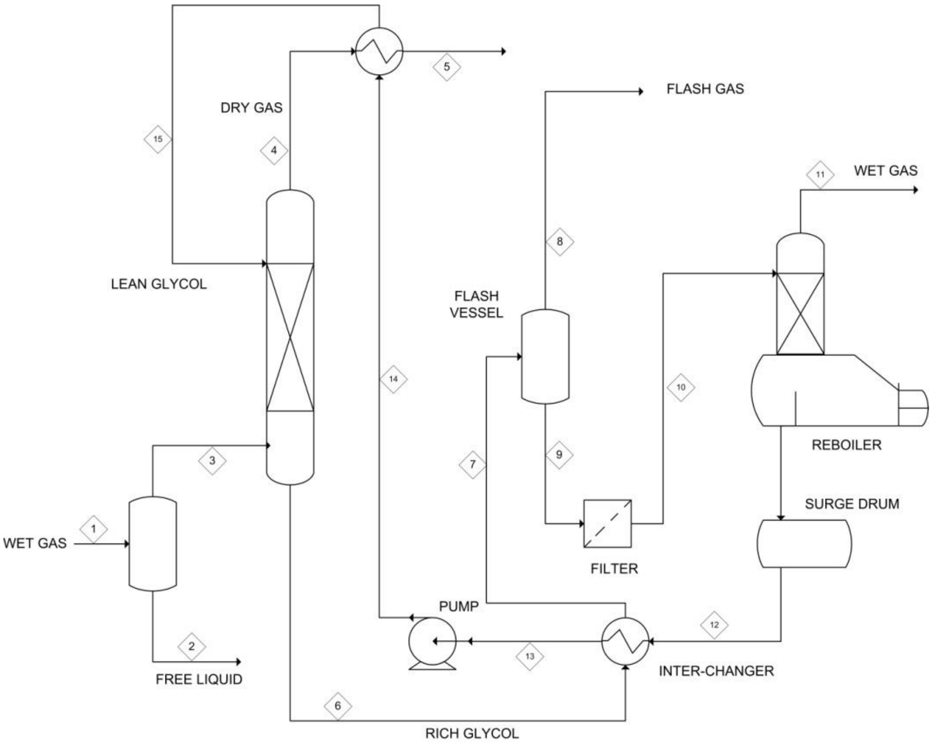
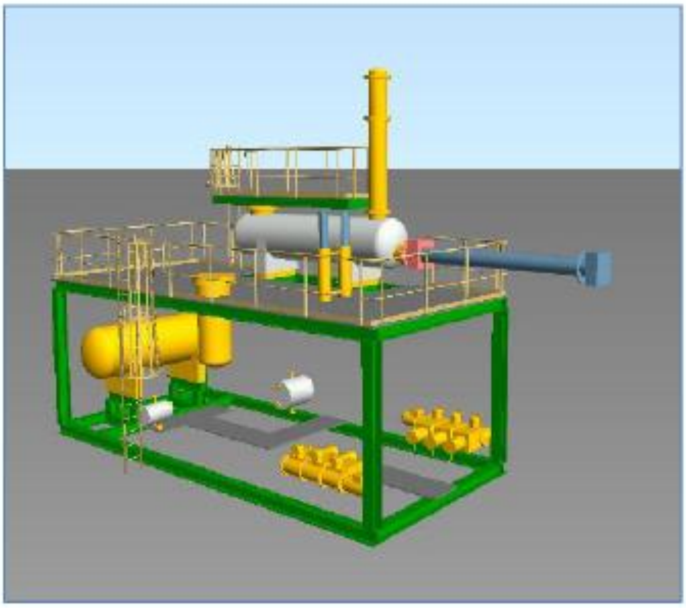


Figure 45 - Schematic of a TEG Regeneration Process



Reference: Supplied by Frames 29/10/12

Figure 46 - Typical Layout for a TEG System

Heat and Material Balance
Glycol Dehydration
Post-combustion case at 265 te/hr

Stream	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Temperature (°C)	30	30	30	30	31	31	110	98	98	98	102	204	121	120	60
Pressure (Bara)	30.00	30.00	30.00	28.00	27.66	30.00	29.31	1.10	1.10	1.10	1.01	1.03	1.03	28.00	28.00
TOTAL FLOW															
Mass Flow (te/hr)	265	0	265	264	264	3.5	3.5	0.3	3.2	3.2	0.2	2.99	2.99	2.99	2.99
Molar Flow (kg-mol/hr)	6,021	0	6,021	6,003	6,003	40.3	40.3	9	31.5	31.5	11.2	21.4	21.4	21.4	21.4
GASEOUS PHASE															
Vapour Fraction	1	0	1	1	1	0	0	1	0	0	1	0	0	0	0
Composition (mol%)															
CO2	99.72	1.20	99.72	99.93	99.93	15.11	15.11	68.22	0.30	0.30	10.95	0.00	0.00	0.00	0.00
H20	0.22	98.80	0.22	0.01	0.01	35.70	35.70	31.60	36.84	36.84	88.96	7.51	7.51	7.49	7.46
N2	0.05	0.00	0.05	0.05	0.05	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TEG	0.00	0.00	0.00	0.00	0.00	49.14	49.14	0.06	62.82	62.82	0.04	92.47	92.47	92.49	92.52
Key Energy															
Regeneration Reboiler	368	kW													

Table 13 - Heat and Mass Balance for Generic TEG Dehydration System

10.0 Economics of Vendor Proposals

10.1 Capital Cost

The capital costs of the dehydration equipment are a minor part of the overall costs for a CCS plant. The equipment uninstalled costs are therefore presented.

Data presented is a combination of data received from different vendors (as part of this study), data from previous AMEC projects and AMEC modelling and cost estimating. Costs are presented as an equipment cost index where each option is indexed against a single case. This allows correction for currency and country variations.

10.1.1 Solid Desiccants:

Data presented is for a relatively pure CO_2 stream containing > 99% CO_2 with low levels of impurities. A wide spread in the data is present from different vendors – this is due to differences in several factors:

- The regeneration techniques proposed by the different vendors.
- Lower pressure regeneration systems will be less costly. The SPX proposed system assumes the vessel is fully depressured and atmospheric air is heated and blown through the vessel to atmosphere. The amount of equipment required is thus significantly lower than for a high pressure regeneration using CO2. The volume of CO2 gas passing through the online bed is also lower since there is no regeneration gas to be processed. Smaller bed size results.
- Use of the CO2 compression facility to provide the driving force for the regeneration gas results in provision of less equipment within the dehydration package, but larger compression & cooling equipment and more costly compression variable costs.
- Materials of construction proposed
- The number and size of the individual adsorption beds proposed
- The number of parallel dehydration trains proposed.

Operating pressure has an effect on the capital costs. Limited available data indicates that capital cost is minimised for an operating pressure of between 25-30 Bara. Figure 47 indicates the trend for a fixed feedrate of 265 te/hr based on:

- The design pressure is set to be 10% above the maximum operating pressure.
- The data is based on a depressured regeneration with air

The minimum point may be at a different location for a specific case since:

- In cases where regeneration at pressure is carried out there is significantly more high pressure equipment present.

- Selection of the design pressure will influence the vessel thickness and subsequent cost. Dehydration equipment is typically located at a compressor inter-stage pressure; on compressor shutdown, or trip, the plant settle out pressure must be considered in selection of the design pressure.

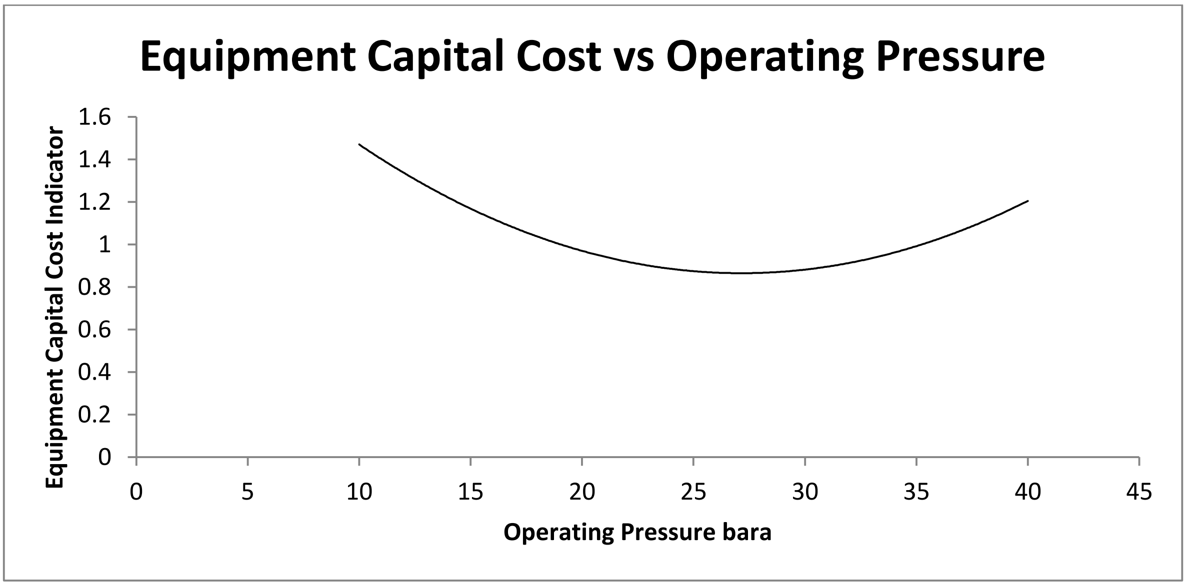


Figure 47 – Equipment Capital Cost Indication for an Adsorption System Versus Operating Pressure

There is a wide spread in the capital cost data received from vendors. The maximum and minimum trends versus rate for a fixed operating pressure are shown in Figure 48. Pressure has an effect on several variables:

- There is a significantly higher water content present in low operating pressure systems compared to high operating pressure systems. The dehydration equipment therefore has to remove significantly more water at low pressure.
- Gas volumes are higher at low operating pressure for the same mass rate. Larger equipment is therefore required.
- Equipment with lower design pressure has less metal thickness than high pressure equipment.

The effect of contaminants on capital cost is not assessed at this time. The impact is not quantifiable by the vendors providing data to this study.

This combination of factors results in Figure 47 showing an optimum pressure in terms of capital cost. Effectively at this point the three criteria are optimal, the water content is reduced by compression without excessive pressure leading to high pressure equipment, and the equipment size has also reduced.

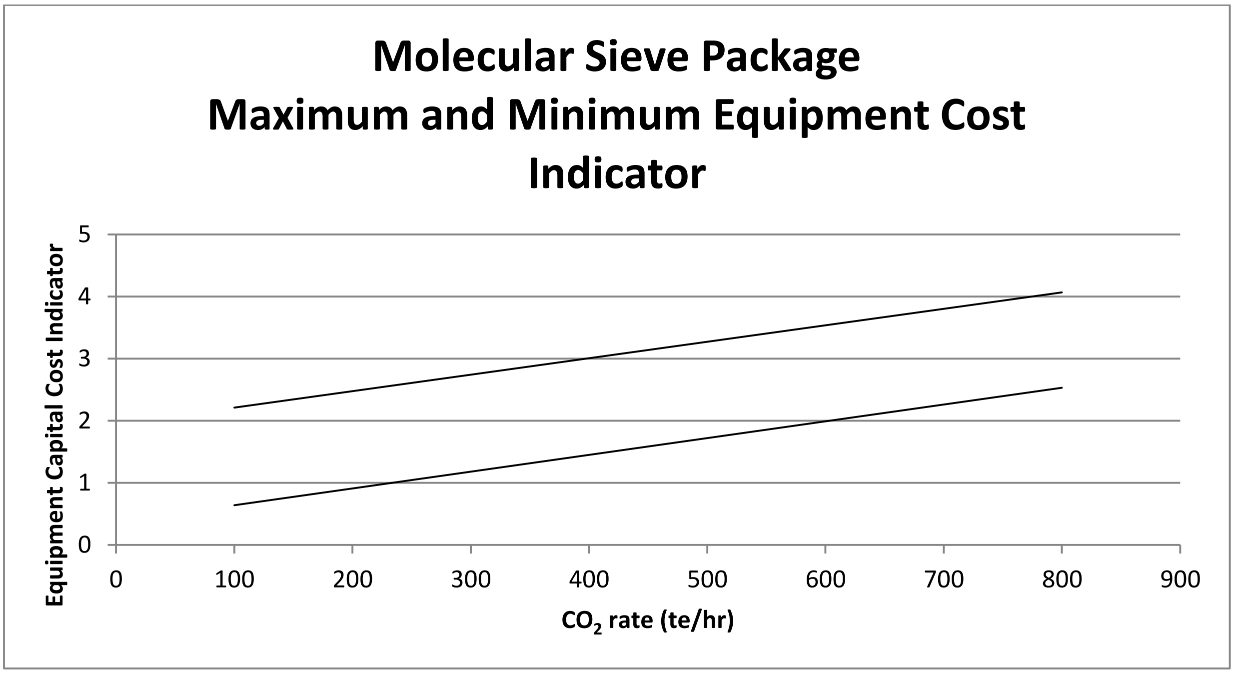


Figure 48 – Maximum and Minimum Equipment Capital Cost Indication for a Molecular Sieve Adsorption System

There is no difference between the costs of the molecular sieve equipment for target moistures of 550ppmv, 50pmv and <10ppmv. Media suppliers and package vendors all advised that it is normal to design for removal of the water stream to <1ppmv, irrespective of the target moisture required.

In the case of high inerts content the cost of the equipment is higher per tonne of CO_2 present than for a low inerts gas. This is due to:

- The increased volume of raw gas per te of CO2 present, which requires larger diameter desiccant beds
- The higher amount of water present in the increased volume of gas. This extra amount of water has to be removed. A larger volume of desiccant is therefore required to dry the gas.

For a high inerts gas it is recommended that the 'CO_2 rate' value in the graph above be increased in proportion to the fractional increase in total volume of the gas due to the inerts content, prior to reading the cost indicator values.

In the case of high impurities:

- Increased oxygen levels to 300 ppmv have no effect on the equipment cost or on dehydration media selected.
- The case with 100ppmv NOx, 100ppmv SO2 and 100ppmv H2S results in the requirement of:

- The use of an acid resistant media with an increase in media volume of ~ 5% and an increase in media cost of ~15%.
- An increase in equipment capital cost of ~7%

10.1.2 Liquid Desiccants

Data on liquid desiccants is lacking. Many vendors declined to provide data. The data presented is for water saturated raw gas at 30 Bara, 30°C. The raw gas stream is relatively pure containing > 99% CO_2 with low levels of impurities. Product moisture is 50 ppmv. The TEG process includes the use of stripping gas to increase the TEG concentration and thus provide lower moisture levels.

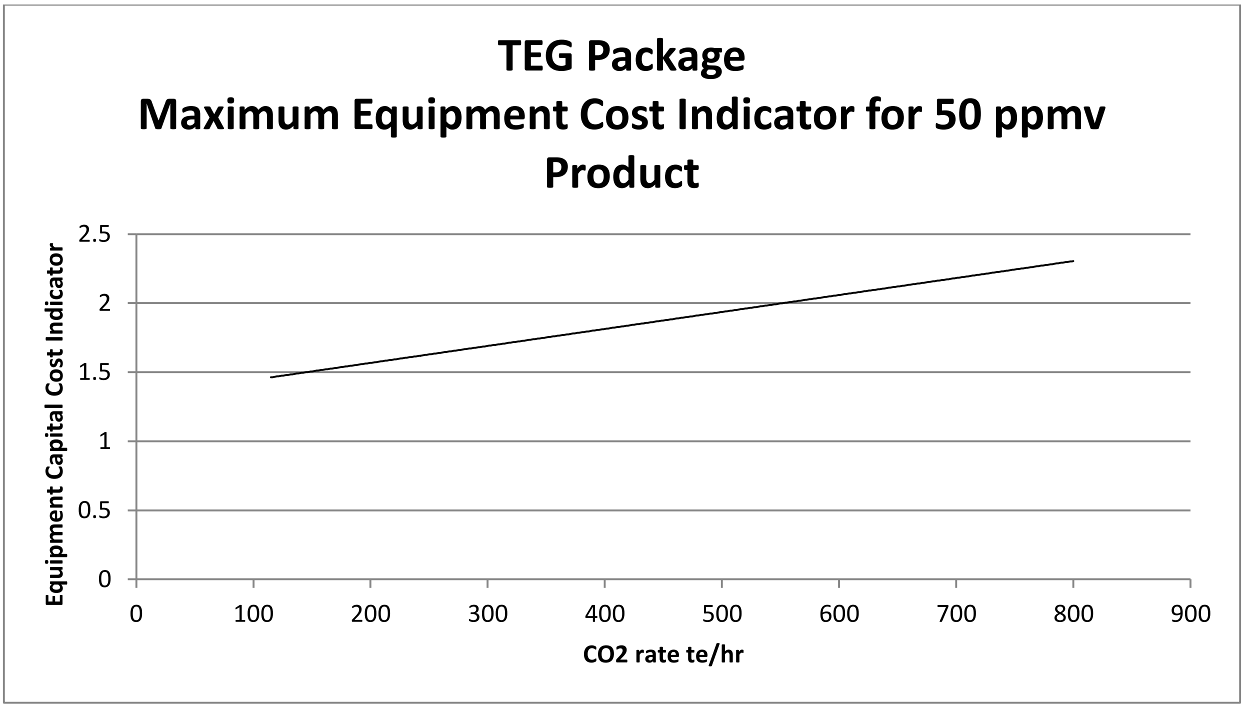


Figure 49 - Maximum Equipment Capital Cost Indication for a TEG System

Higher levels of target product moisture (in excess of ~ 150 ppmv) will require more basic equipment; the stripper will not be required. The cost for such a system will therefore be lower.

In the case of high inerts content the cost of the equipment is higher per tonne of CO_2 present than for a low inerts gas. This is due to:

- The increased volume of raw gas per te of CO2 present, which requires a larger diameter contactor

- The higher amount of water present in the increased volume of gas. This extra amount of water has to be removed. A larger circulation rate of TEG is therefore required; equipment in the TEG circulation will loop will be larger.

For a high inerts gas it is recommended that the 'CO_2 rate' value in the graph above be increased in proportion to the fractional increase in total volume of the gas due to the inerts content, prior to reading the cost indicator values.

It is recommended that impurity issues be discussed with the vendor at an early stage, since they may recommend removal of these upstream of the dehydration equipment.

10.2 Operating Costs

The basic criteria for the techno-economic comparison have been extracted from IEA GHG guidelines[41] and a previous IEA GHG study report[42], and are listed below. Use of consistent data enables work to be combined with data from other IEA GHG reports.

The dehydration processes from different vendors have different utility requirements. Different utility consumptions have different associated power demands, which affect the overall net electrical efficiency of the power plant. The conceptual criteria used to determine these equivalent values are described in Reference 42. Once-through seawater is assumed to provide the cooling water duty.

For each utility the figures in Table 14 are available to convert each utility requirement into an equivalent power demand. With the limited data provided by vendors only the cooling water is used.

Utility	Case Involved	Specific equivalent electrical consumption
LP steam – 7.5 Bara	Pre-combustion	191 kWe/te/h
LP steam – 3.3 Bara	Post combustion	172 kWe/te/h
LP steam – 2.5 Bara	Oxy-combustion	145 kWe/te/h
Cooling Water	All	0.102 kW/m^3/h

Table 14 – Equivalent Electrical Consumption of Different Utilities

Other minor utilities, such as the instrument air requirement for valve operation, etc have been ignored as they have a negligible effect on this analysis.

The main factors applied to this analysis are defined as follows:

- The cost of consumed electricity is assumed to be 3.8 € cents /kWh (to cover lost export electricity revenue rather than generation costs).

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[41] IEA GHG R&D Programme, 'Criteria for Technical and Economic Assessment of Plants with Low CO_2 Emissions, Version V-1, May 2009

[42] 'Rotating Equipment for Carbon Dioxide Capture and Storage', IEAGHG Report: 2010/07, September 2011

- Maintenance costs of 3.4% of investment cost
- Insurance and taxes costs of 2% of investment cost

Costs have been estimated, and are presented in Table 15, for the following cases:

- Solid desiccant at 265 te/hr – Case 3 has been estimated for 2 different vendors, one using low pressure regeneration with atmospheric air (minimum case) and another using CO2 at pressure for regeneration (maximum case). These cases form the minimum and maximum capital cost packages. A 3 year desiccant life has been used, as per vendor advice.
- Liquid desiccant at 265 te/hr – Case 2 has been used. Only a single vendor has provided data. This case is expected to be at the higher end of the package capital cost. TEG desiccant life has been quoted as 3-10 years, depending upon the extent of impurities present. A value of 3 years has been assumed for this analysis.

Electricity values quoted include the additional compression power required to overcome the dehydration plant pressure drop, assuming a compressor polytropic efficiency of 85%.

Thus, comparing data from the same vendor indicates that the TEG system operating cost is approximately 50% of the molecular sieve package, based on the assumptions given above. However, the more basic molecular sieve package operating costs are around 50% of the TEG values quoted. Estimated minimum operating costs for molecular sieve packages over a range of rates are shown in Figure 50.

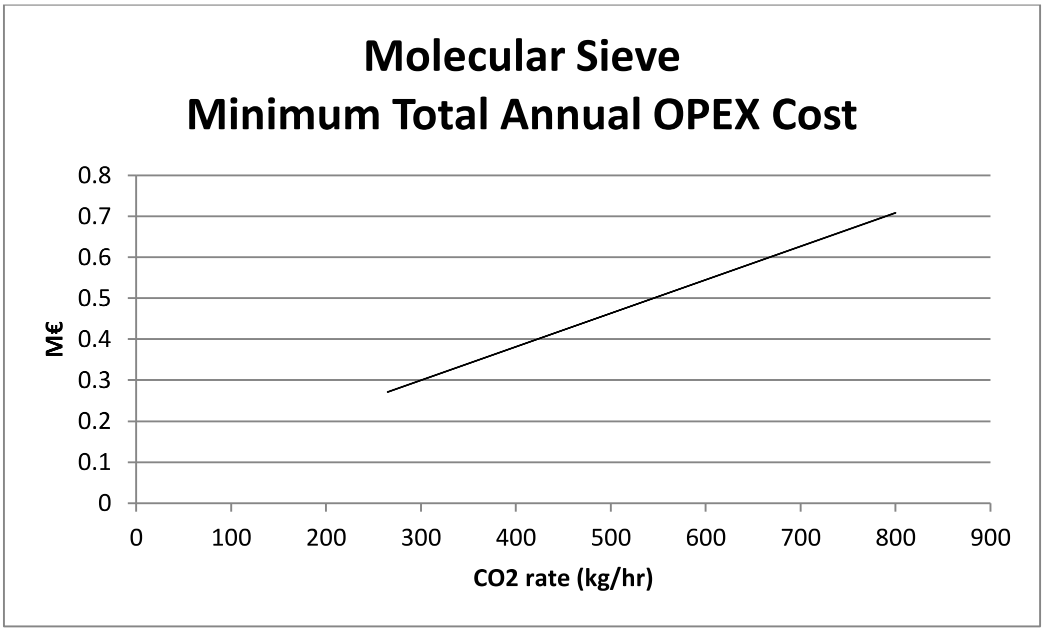

Figure 50 - Minimum Total Annual Operating Costs for Molecular Sieve Versus Rate

	Molecular Sieve		TEG
Capital Max / Min limit	Min	Max	Max
Case No	3	3	2
Power			
Dehydration package pressure drop (bar)	0.15	1.5	0.7
Additional power consumed by compressor (kW)	20	215	106
Power consumed by dehydration package (kW) (averaged)	433	1456	350
Cooling water rate (m3/hr)	0	9	10
Equivalent power associated with cooling water (kW)	0.0	0.9	1.0
Total Power consumed (kW) (average)	**453.3**	**1672.2**	**457.0**
Desiccant			
Quantity in plant (te)	29.2	60	30
Life of desiccant (years)	3	3	3
Quantity per year, equivalent (tepa)	9.7	20	10
Desiccant top up requirement (tepa)	0.000	0.000	15.000
Total annual consumption of desiccant (tepa)	**9.73**	**20.00**	**25.00**
Operating Costs (MM Euro/year) (based on 7446 operating hours/year)			
Electricity production cost (Euro/kWh)	0.038	0.038	0.038
Power cost (MM Euro/year)	0.128	0.473	0.129
Desiccant cost (Euro/te)	3500	3500	3500
Desiccant cost (MM Euro/year)	0.034	0.070	0.088
Other chemicals (Euro/te)	0.000	0.000	0.000
Disposal of waste desiccant (Euro/te)	0.000	0.000	0.000
Labour Costs (MM Euro/year)			
No of operators	0.100	0.100	0.100
Salary	0.065	0.065	0.065
Direct Labour Cost	0.007	0.007	0.007
Administration (30% of labour cost)	0.020	0.057	0.036
Total Labour Cost	0.027	0.064	0.043
Maintenance Costs (MM Euro/year)	0.153	0.459	0.286
Insurance and Taxes (MM Euro/year)	0.090	0.270	0.168
Total Annual Cost (MM Euro/year)	**0.432**	**1.336**	**0.713**

Table 15 – Operating Cost Estimates for Different Types of Dehydration

Limited data indicates that the effect of impurities on operating cost is effectively negligible. The increased bed volume results in an increased capital cost, which impacts onto maintenance costs and taxes / insurance. Desiccant cost increases but regeneration power consumption is significantly reduced.

11.0 Process Selection Guidance

This guidance gives an overview of the process involved in:

- Determination of the required target moisture content, post dehydration
- Selection of the most appropriate combination of dehydration technologies
- Determination of appropriate dehydration operating conditions, and hence the location of the dehydration unit within the plant.

11.1 Basis of Selection

The selection criteria are based on dehydration of gaseous phase, near pure CO_2.

The physical property data is estimated for pure CO_2. Other bodies may have their own, more accurate data which can be used.

It is essential that consideration is given to the effects of inerts and impurities on the phase envelope, since these can have a considerable impact on the phase change conditions, and thus on the allowable operating conditions.

The method can be used for the evaluation of other gases but:

- Some criteria may not apply
- It may be essential to consider additional criteria, specific to the gas and the process being considered.

In evaluating whether liquid CO_2 / hydrates / water ice are present it is important to ensure that there is sufficient margin between the conditions for occurrence and the actual operating conditions.

Process selection is a balance between initial capital cost and operating costs. Cost minimisation techniques can be used to select the best option overall, however Clients frequently have an opinion on whether they wish to minimise capital or operating costs, in which case a weighting can be applied.

11.2 Selection Criteria

Step	Method	Notes
1.	Identify product moisture specification	This should have been selected giving due consideration to the full range of operating and ambient conditions which might be experienced in the downstream equipment and considering hydrate formation, corrosion, etc
2.	Consider if in-plant downstream processing conditions require a lower moisture specification than that required by the product specification	For example, cryogenic processing, or other low temperature or high pressure conditions. Consider the list given in Section 0
3.	Determine target moisture specification for the dehydration package	Use the lower of the values from steps 1 and 2 above and apply an adequate design margin
4.	Identify raw feed conditions and phase	This guidance is based on gas phase only
5.	Determine raw gas moisture content	
6.	Identify applicable dehydration technologies	Based on inlet and exit moisture contents. Refer to Figure 28. Plot the reference point. All technologies to the left and below the reference point on the graph can be used if a single dehydration item is required, although those further away from the reference point are likely to be more complex and more expensive in both capital and operating costs. Technologies above and to the right of the reference point can be used in combination, provided that the selected processes meet/overlap, thus ensuring that the full range of conditions are covered.
7.	Select preferred method of cooling, e.g. air coolers, cooling water	

Step	Method	Notes
8.	Identify/estimate minimum temperatures for cooling medium	
9.	Select pressure for dehydration	If using compression/cooling consider moisture minima – refer to Figure 7 and Figure 8
10.	Determine range of operating conditions of wet gas	
11.	Can liquid CO_2 form in wet gas, or on cold tube surfaces	Refer to Figure 5 for pure CO_2 or refer to phase envelope. If liquid CO_2 forms, then reject the set of conditions and return to step 9
12.	Can hydrates form in wet gas, or on cold tube surfaces	Refer to Figure 2, Figure 3, and Figure 4 for pure CO_2. Consider formation of other hydrates if high levels of impurities present, for example H_2S. The CCS specification allows the presence of low levels of H_2S. If hydrates form, then reject the set of conditions and return to step 9
13.	Can water ice form in wet gas, or on cold tube surfaces	If water ice forms, then reject the set of conditions and return to step 9
14.	Generate datasheet(s)	If evaluating the best location for dehydration, then consider several different conditions
15.	Obtain quotations from vendors	Emphasis should be given that guaranteed figures, in conjunction with a liability scheme, should be obtained in the quotation from vendors References should be sought from vendors
16.	Evaluate quotations and vendors' proposed	

Step	**Method**	**Notes**
	dehydration method(s) versus requirements	
17.	Consider footprint required versus that available	
18.	Evaluate each proposed dehydration method	Consider the extent of process contamination, effluents generated, product losses, desiccant and additive make-up, guaranteed desiccant life, effects of impurities, equipment design conditions, etc. Has the vendor considered the possibility of corrosion, hydrate formation, liquid CO_2 formation, water ice formation, etc, (especially during regeneration) and designed accordingly Is the proposal acceptable? If not, reject this proposal.
19.	Evaluate CAPEX/OPEX over a range of available conditions	For each proposed dehydration method determine the best set of conditions based on preferred CAPEX/OPEX weighting. Consider the dehydration package utility/services requirements and convert these to power equivalent data, as per Table 14. Consider evaluating data in the forms of Figure 47 and Table 15.
20.	Select preferred option/method and associated operating conditions.	
21.	Incorporate the dehydration package into the design	

Table 16 – Selection Criteria

12.0 Water Monitoring Instrumentation

The drying unit is a critical piece of equipment for both safety and operational reasons. The drier performance should be monitored to ensure that water breakthrough does not occur, thus preventing dewing which could cause excessive corrosion or the formation of hydrates or ice. It is important that a continuous monitoring system is used; manual sampling and analysis will not be sufficient.

12.1 Data provided to Vendors

Moisture analysis is fundamental to maintaining the integrity of the downstream pipelines and equipment. Data provided to vendors are listed below:

12.1.1 Moisture Specification

Three different moisture specifications were investigated, as summarised in Table 17 below.

Moisture Specification (ppmv)	Actual (ppmv)	Moisture level on excursion	Notes
550	100 - 300	saturated	
50	30 (TEG) <1 (Mol sieve)	saturated	In the case of molecular sieve the actual moisture level achievable may be effectively nil. Analyser must therefore be capable of operation in dry conditions.
<10	<1	saturated	

Table 17 – Moisture Specifications for Water Monitoring

12.1.2 Non- CO_2 Components

Vendors have been provided with a list of components, as listed in Table 8, and expected ranges of composition, and asked to consider the effects of these components on the proposed analysis techniques.

12.1.3 Operating Conditions in the Line Exit Dehydration

Normal operating temperature is 30°C.

Normal operating conditions can vary, depending upon the actual process being considered. Pressures were stated to be over the range 3 Bara to 50 Bara. Vendors were informed that downstream conditions of up to 200 Bara may occur.

12.2 Data Requested from Vendors

Vendors were asked to provide the information on the following items for each of the techniques proposed:

- Measuring principle
- Accuracy
- Available ranges and limits of detection
- Repeatability
- Reliability
- Maintenance requirements
- Interference on the analyser performance, if any, from other impurities present in the process stream
- Indication of Cost
- Outline sampling requirements
- Calibration requirements, including gas bottles recommended
- Response time - ’wet to dry’ and ‘dry to wet’
- Preferred position of the meter

12.3 Analysis Vendor Responses

Several companies, who provide industrial moisture measuring instrumentation, were approached. Many declined to assist or did not reply at all; responses from those who replied are summarised below.

Moisture Control and Measurement Ltd, Systech Instruments, AMCS and Process Analyser Systems Ltd proposed a range of different techniques and provided relevant data. The proposed techniques cover a range of different physico-chemical measuring principles, specifically:

- Laser absorption spectroscopy
- Phosphorous pentoxide (P2O5) coated cell
- Quartz crystal cell
- Silicon sensor

All techniques can measure down to very low ppm levels, with some capable of achieving down to ppb levels. The number of available techniques is limited due to:

- The CO2 background gas
- The gas contaminants
- Vendors require:

- The gas composition
- Combinations of different impurities which may occur
- Target accuracies
- Intervention periods

before they can define the most appropriate methodology to apply. Several vendors have therefore provided maximum concentrations for various components; they have concerns re corrosion especially if water breakthrough occurs.

The upper analysis limit is generally used to determine whether an auto-zeroing or more sophisticated approach is required. However, the potential for corrosion may result in more frequent zero/span/linearity checks.

Table 18 summarises the responses from the vendors who provided data.

Budget costs for the instrument vary for a single instrument. The relative cost indicator values given exclude the sampling system and analyser housing/building, as these requirements are project specific.

12.4 Discussion

There appears to be equipment available to do the continuous moisture monitoring. However impurities must be considered in detail. Their normal concentration and their concentration ranges during both normal operation and also on excursion needs to be quantified and comprehensively discussed with vendors.

It is important that the actual application is fully discussed with the vendors to enable the most appropriate device to be selected.

Values quoted in the Table 18 are for the analyser only. The sampling system can significantly influence the overall performance and recovery time from upset. A properly designed sample system is essential. Sampling usually involves pressure let-down and sample heating will be required to ensure that Joule Thomson chilling does not result in condensation of any of the components present, which can affect both the analyser itself and the analysis result.

A reasonable response time is essential to ensure that off-spec product is quickly detected and remedial actions taken promptly. The sampling system can have a significant effect on the overall response time.

Consideration of the conditions which the sensor may experience under upset conditions must be included to ensure that damage or prolonged erroneous readings do not occur.

Maintenance frequency can be dependent on the gas quality. Means should be provided to enable periodic cleaning of the sensor and associated lines in the event that a contamination incident occurs. Particulates are a particular issue for some types of device, such as the phosphorous pentoxide device; particulates can block the capillary.

Company	**AMCS**	**AMCS**	**MCM**	**Systech**	**MEECO**	**Tiger Optics**
Model No.	**3050 OLV**	**5100**	**MicroView**	**MM500**	**Aquavolt / Aquavolt+**	**HALO-500-H_2O**
Measuring principle	Quartz Crystal Cell.	Tuneable diode laser absorption spectroscopy (TDLAS)	Heated Silicon sensor operating at a fixed temperature which responds to partial water vapour pressure expressed in ppmv terms. This is sampled at atmospheric pressure and low flow (less than 500ml/min)	Phosphorous Pentoxide Sensor (P_2O_5) Two platinum wires wound on a cylindrical silica former. The electrodes are coated with a film of P_2O_5 which is hygroscopic and absorbs all the moisture present. A voltage applied to the cell dissociates the water into hydrogen and oxygen the current in the cell represents the number of molecules dissociated. Catalytic effect possible with some gases which may increase the moisture content. Rhodium electrodes will give improved results.	Phosphorous Pentoxide Sensor (P_2O_5) – principle as for Systech	Cavity Ring Down Spectroscopy (CRDS) Laser Technology
Accuracy	± 10% of reading	Application dependent – typically ±2% of full scale range.	Without zero or span correction ±3 ppm or ±3°C dew point, whichever is the greater. With zero and span correction reduced to less than ±1°C dew point. Claims subject to a detailed analysis of gas composition and agreement on required response times and intervention periods.	±5% of reading or ±0.4 ppm(v)	±5% or 0.4ppm, whichever is greater (Aquavolt) ±2% or 20ppb, whichever is greater (Aquavolt+)	±4% of reading or 10ppb
Static Repeatability	± 5% of reading	Better than 2% of full scale range.	Hysteresis is virtually eliminated by using a heated sensor in combination with a ‘push purge’ sensor drying feature.	± 2% of reading		
Range	0.1 to 2500 ppmv SLR version has a range of 0-5ppm.	0 to 100ppm	0.1-100 ppm or 1-1000 ppm Custom ranges possible.	0.01 to 1000 ppm (Auto ranging)	0 - 1000 ppm v(Aquavolt) 0 - 20ppmv (Aquavolt+)	20ppb to 500ppm (higher range possible if required)
Limit of detection	0.1 ppmv	4 ppm	0.1 ppm on the highest sensitivity range available	0.01ppm	1ppm (Aquavolt) 35ppb (Aquavolt+)	
Response time	Near real time	< 1 second photometric response. Total system response dependent on sample flowrate.	Wet to dry is less than 2 minutes using push purge sensor drying feature and is the fastest available commercially. Dry to wet is less than 30 seconds	90% within 60 seconds. Dry to wet response considerably faster.		
Pressure limits	1.3 to 3.3 Barg. Pressure reducer required at pressures above 3 Barg. Max input pressure is 200 Bara	0.7 to 1.7 Bara	Sensor and its housing is pressure tested to withstand 230 bar g, but operates at atmospheric pressure to minimise absorption/desorption effects in the sample system, reduce retention times and risk of contamination	0.25 to 7 Barg sample Pressure tested to 75 Barg	10-3000 psig	10 - 125 psig

Company	**AMCS**	**AMCS**	**MCM**	**Systech**	**MEECO**	**Tiger Optics**
Model No.	**3050 OLV**	**5100**	**MicroView**	**MM500**	**Aquavolt / Aquavolt+**	**HALO-500-H_2O**
Temperature limits	0 to 100 deg C		The temperature of the sensor is held at 45 C for stability during operation. Gas sample temperature must be kept below that. The lower temperature limit is -25 C	0 to 40˚C	0 - 60°C	0 - 60°C
Reliability			Excellent track record of fault free operation claimed on UK Nuclear and industrial installations.		MTBF > 93 years	800 units working worldwide with no reported failures to date.
Maintenance	Cell, Drier and Moisture Generator will need to be replaced every 2 years	Non-contact measurement. No spares required over lifetime of analyser	Zero correction is automatic. Span adjustment done annually.	Performance can be maintained by re-coating. Frequency of recoating can vary between few months to several years	Sensor change annually	Annual zero check
Interference of other substances	Ammonia and mercury, where present, .are problems at the levels quoted (50 ppmv and 16 ppm respectively).	No issues with components and compositions specified.	Any polar molecules or heavy hydrocarbons above C6 would interfere with the measurement H_2S levels below 100 ppm can be handled by the auto-zeroing routines.	Methanol will be electrolysed in sensor, giving increased moisture reading HNO_3 and H_2SO_4 will be OK if maintained at low ppm levels Amines will deactivate the P_2O_5 film after ~ 1 week of exposure to 10 ppm amine vapour. Mercury will have to be removed with a trap.	Stated as "none expected"	Stated as "none expected"
Relative Cost Indicator (where 5 indicates that the item price is 5 times as costly as the base price of 1)	6	5	5 8 for a dual sensor version	1	3	6
Sampling requirements / Enclosure	Approx. 150 sccm sample flow required		Sample system Heated sample line (possibly) Enclosure	Included with the instrument	Removal of particulates and normal gas conditioning good practice.	
Calibration requirements	No gasses required (Analyser creates its own-NIST traceable calibration using an internal moisture generator)	No calibration gasses required - internal reference cell used.	Site calibration not recommended. Spare transmitter substituted.	Via calibration gasses	No calibration gasses required	No calibration gasses required
Other	Version available for use in Zone 1 hazardous area.	Measures a variety of gases, including moisture ATEX Zone 1 and Zone 2 versions available.			Aquavolt provided to existing CCS plants	

Table 18 – Summary of Moisture Metering Vendor Responses

Care needs to be taken to ensure that any of the components present are not capable of reaction at the cell surface, where reactions may be catalysed, such as may occur in the presence of platinum electrodes held at temperature. Reactions may cause contamination of the cell or form water and result in erroneous readings.

The moisture meter should not be affected by flow fluctuations in the main line since they take a sample from the line and drop the pressure to that required for analysis. Fluctuating compositions should be acceptable, provided that high impurity levels are not present. The moisture systems can cater for fluctuation in moisture content, as indicated in Table 18 via the information provided on ‘Response Times’.

13.0 Operational Management of Dehydration in CCS Systems

13.1 Recommended Systems

13.1.1 Moisture Analysis

The target moisture content of the dry CO_2 gas should have been set with a sufficiently large margin of safety so that minor operational problems with the plant, or dehydration equipment in particular, should not present any problems.

Moisture in the gas can cause corrosion and hydrate formation. At least two moisture analysis points are recommended; if a fault develops at one location then the second location will act as a backup. The analysis points should be located at different points in the plant: one immediately after dehydration and another further downstream, possibly located after compression, adjacent to the compression and conditioning plant boundary, as shown in Figure 51. This second point will confirm the quality of the CO_2 prior to export from the plant.

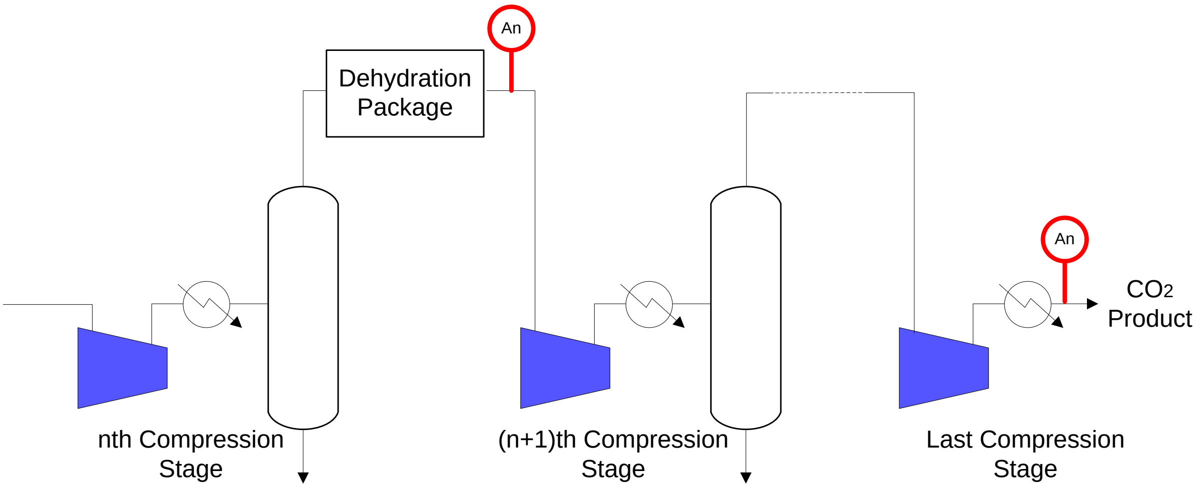

Figure 51 – Location of Analysis Points

Each location should have two analytical devices, so that if one fails / has problems the other can be brought online. A typical reason for failure of a device can be moisture breakthrough causing saturation of the cell, which may require a considerable length of time to recover, or contamination of the analyser which may subsequently require cleaning and reactivation.

13.1.2 Process Monitoring and Operation

Written procedures should cover normal, abnormal and emergency operation as well as start-up, shutdown and maintenance. These should be based on an appropriate assessment of the consequences. Operators and maintenance personnel should be trained in the operating systems, procedures and safety policies.

A computerised data collection, monitoring and control system should be installed to oversee flows, pressures, temperatures and online analysis. Alarms should be highlighted to the operator to indicate the approach of, or exceedance of, allowable moisture conditions. Data and analytical tools, such as historical trending and live trending, should be available to enable manual monitoring and problem diagnosis, enabling appropriate actions to be taken.

Action plans should be developed so that operators know what actions to carry out in the event of an excursion. Typical problems and issues associated with the type of dehydration unit installed should be tabled and troubleshooting actions which should be undertaken to confirm the problem and restore conditions should be listed and itemised.

13.2 Prevention

Water monitoring instrumentation should be routinely checked and calibrated.

It is important that the lines & equipment are maintained clean and dry during maintenance activities. Pigging may be used for dewatering and line cleaning post commissioning or maintenance activities. Intelligent pigs can be can be used to monitor the status of the pipeline with respect to internal corrosion, formation and propagation of cracks and damage by external processes.

It may be considered prudent to install corrosion coupons and / or corrosion probes at vulnerable locations. These can be monitored to observe any gross effects which may result from moisture breakthrough. Wall thickness measurements can also be taken on flow lines and vessels.

Care should be taken during pressurisation / depressurisation to avoid desiccant breakup and damage to vessel internals. The maximum allowable rate of pressure change for solid desiccant systems is typically:

- < 50 psi / min for pressurisation
- < 30 psi / min for depressurisation

Long-term performance of the dehydration process itself should be routinely monitored and used to identify potential premature end of life: These include:

- Monitoring of key incoming impurities and action should be taken to minimise these
- Upstream knockout pots should be monitored to ensure that liquid / mist carryover does not occur.

Solid desiccant

- It may be useful to occasionally determine the maximum capacity of the adsorption beds43 so as to predict the time to replacement. This should be carried out in advance of a planned overhaul and involves allowing the beds to continue in adsorption mode longer than would be normal with the cycle time. Monitoring the gas dew point/moisture content will indicate when breakthrough occurs and also when the maximum tolerable moisture level occurs. The beds will subsequently require a longer regeneration cycle to ensure that the additional adsorbed moisture is removed. It should be noted that if a protective guard layer has been provided to cater for the presence of impurities or liquid carryover then this may have a different residual life to the desiccant, depending upon the original guard bed design life and the operating history of the dehydration package feed. The guard bed may require to be changed before the desiccant. Operating with a ‘saturated’ guard bed may dramatically affect the integrity of the solid desiccant.

- The solid adsorption regeneration cycle can be monitored to indicate when the regeneration ability is tailing off.

- Pressure drop of the individual desiccant beds versus flow can be used to indicate potential bed problems.

Liquid desiccant

- Liquid dehydration solution should be routinely analysed for water, pH, hydrocarbons, foaming tendency and inorganic salts, especially chlorides.

13.3 Possible Excursions and Remedial Actions

In the event that excessive moisture ends up in the downstream process then consideration should be given to the following potential actions:

- Stop passing CO2 gas forward and maintain the upstream plant and the CO2 compression and conditioning plant running at low rates. Flow to the downstream plant will cease. Vent the gas downstream of the dehydration unit (via a properly designed vent point which takes into account the low temperatures which may occur, the risk of solid and liquid CO2 formation, dispersion of the CO2 to avoid toxic levels at ground level or impacting on nearby plant, CO2 slumping due to the presence of cold gas, etc) Continue until the moisture is back within specification. Confirm the following prior to restoring gas forward flow:
    - The dehydration unit is stable and operating as designed
    - The analysers are reading correctly and have recovered from any ill effects suffered as result of the excursion
    - The CO2 stream is back onspec and results are stable.

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[43] ‘Gas Purification’, A Kohl, R Nielsen, Gulf Publishing Company, 5th Edition, 1007

- If a plant circulation loop exists it may be prudent to recirculate the CO2 gas around the compression and conditioning at low rates unit until good product quality has been restored, operation is stable and the source of the original problem has been determined and rectified. This, however, will require that both upstream and downstream plants are taken offline and put onto hot standby, ready to start within a short time.

- If moisture levels are set based on corrosion limits, the moisture is offspec for cold conditions (but is acceptable for warm conditions) and warm conditions are prevalent at the time, then it may be appropriate to continue running at minimum rates passing gas forward while the conditions around the dehydration unit are restored. If moisture levels are shown to continue to rise and approach unacceptable levels then forward flow should be ceased.

- If hydrate formation is a concern then hydrate inhibitor may be added to prevent build-up.

- Development of a plan re what to do if off-spec gas has reached downstream equipment. The decision may be taken to pass the slug of gas forward on restart, or to bring it back and vent it. Care needs to be taken to ensure that the downstream line / equipment pressure is maintained at acceptable values. The actual course of action may be dependent upon the extent of the moisture excursion and the conditions prevalent in the line / equipment at the time. For example, when corrosion is the limiting concern then under warm ambient conditions it may be possible to accept higher moisture content than would be the case under cold ambient conditions. The dense phase pipeline may be able to handle higher moisture content than the main plant due to the inflexion in the water saturation conditions in CO2 which occurs. The pipelines typically operate at pressures in excess of 100 Bara.

- In the event hydrates form and cause a restriction in a line or equipment then it is possible to depressurise upstream and/or downstream of the restriction and allow the system to warm by the action of ambient surroundings or external heat tracing. The combination of temperature rise and pressure decay will eventually lead to melting of the solid hydrate. Care needs to be taken to ensure that a significant pressure differential does not exist across the restriction. Chemical injection points may be used to add inhibitor, such as methanol.

Typical issues with molecular sieves[44] include:

- If the regeneration gas rate is too low, or the regeneration gas temperature is inadequate, or there is insufficient regeneration time allowed then the bed undergoing regeneration will not heat up throughout to a temperature sufficient to overcome the heat of adsorption to drive off the required amount of the adsorbed products. As a result the top part of the bed will remain high in water. When brought back online the bed will saturate more quickly and premature water breakthrough will occur.

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[44] 'Molecular Sieves Troubleshooting', Peter Meyer, CECA SA, GPA Europe Annual Conference, September 2010.

- Channelling can occur at low regeneration gas rates, resulting in a situation in which the gas does not pass evenly through the entire bed but has a preferred ‘channel’. As a result significant parts of the bed will not be adequately regenerated or adequately cooled prior to being put back into adsorption mode. A hot bed may not adsorb sufficient water to enable product gas to meet the target moisture values. Hot product gas may result for a period of time.

- If the impurity content is higher than expected then the impurities may adsorb onto the bed in preference to water, effectively shortening the adsorption life of the bed. The online bed therefore requires regeneration before the regenerating bed has finished its sequence. In addition impurities may cause coking of the beds due to the high temperatures experienced during regeneration. Coking can lead to loss of adsorption capacity.

- Unequal flow distribution between beds (assuming that there is more than one bed online during adsorption mode) can occur if the beds have not been evenly loaded. This can result in premature moisture breakthrough from the ‘high flowing’ bed.

- If the bed is heated too quickly during regeneration the first layer of adsorbent becomes very hot, desorbing moisture, which moves forward onto the cold parts of the bed. The gas stream cools and water condenses out onto the adsorbent and vessel walls. When that part of the bed heats up the water boils off. The binder can be leached from the adsorbent which disintegrates and can subsequently form agglomerates, resulting in flow channelling and high pressure drop. The heating procedure should include a slow heating ramp rate and a preliminary heating step to a lower temperature, which is held for a period of time to allow the bed to heat through, prior to heating to the required regeneration temperature.

Typical issues with liquid desiccant systems include:

- Foaming due to the presence of impurities and glycol aging products. This can result in an increase in product moisture and carryover of glycol out of the contactor. A de-foamer can be used to combat the situation. A filter can remove solid contaminants.

- Excessive regenerator temperatures, and a hot still temperature, can result in the loss of a large amount of glycol out the top of the column. Glycol decomposes at temperatures of ~210°C to form corrosive materials.

- Low pH of the circulating system indicates the presence of corrosive materials. The pH should be maintained within an appropriate range by dosing.

- Build-up of solids (formed as a result of corrosion or particulate build-up) should be removed by the solids filter.

14.0 Future Developments

14.1 Near Horizon Technology

Work on membranes for use in dehydration of supercritical CO_2 is ongoing. Whilst information is not abundant work in the field is being considered, but is at early stages of research and development.

Media vendors are continually developing acid resistant grades of solid desiccant to cater for the challenging impurities present in feed gas. Vendors, however, are not prepared to discuss these sensitive areas of work.

14.2 Further Work

There are several areas in which additional work is required to enable a full and adequate consideration of dehydration processes and issues.

The effects of inerts and impurities on the CO_2 stream physical properties needs to be determined. Impurities and inerts can cause:

- Significant changes in the phase envelope appear to occur.
- The saturated water content of CO2 can be significantly increased or reduced.

This has a direct impact on the dehydration equipment, and Joule Thomson cooling in particular. It is therefore important that the effects of inerts / impurities are fully understood; to date this has not been done and this may involve a large amount of work to obtain accurate physical properties.

Thereafter further work is required to generate accurate physical property estimation methods to enable these physical properties to be adequately modelled.

Hydrates may form prior to water dewing. It has been recommended that the water content selected be < 60% of saturation to avoid hydrate formation. Other references suggest that the maximum amount of hydrates that can be formed with dissolved water in the CCS stream will be too small to cause operational problems[45]. This should be further investigated and the issue quantified.

A considerable amount of work needs to be carried out with vendors. Vendor engagement was lacking during this study; many vendors' opinions have recently changed as a result of:

- The cancellation of most major CCS projects; much work had gone into provision of quotations
- Failure of the various DECC and NER300 competitions to assign the considerable amounts of money originally stated as available for CCS development and establishment

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[45] 'DYNAMIS: Towards Hydrogen and Electricity Production with Carbon Dioxide Capture and Storage, D 3.1.3, DYNAMIS CO_2 Quality Recommendations', E de Visser, C Hendriks, July 2007.

15.0 Conclusions and Recommendations

15.1 Background Issues

Whilst several vendors (SPX Flow Technology, Frames Process Systems, Exterran (UK) Ltd, Zeochem AG, UOP Products Ltd, and Grace Materials Technologies) have assisted in this study, most others have been unable, or unwilling, to do so. This may be for several reasons, not least of which is a booming oil and gas market. Engagement in CCS as a market is very low. Several comments were received regarding the fact that vendors have provided many quotations for CCS projects but without any orders being placed. Within the timeframe of this study one of the vendors changed from stating at the beginning that they regard CCS as a core target area for their business and would be very happy to assist in providing data to suddenly changing tack and providing minimal data of a generic form.

Re-engagement of vendors is therefore an area which should be addressed by industry bodies as a priority.

Due to the lack of vendor engagement many of the conclusions presented are of a preliminary quality.

Dehydration media vendors were generally more helpful, assisting with estimates of the number of beds and bed size. They were also able to assist with information on the effects of impurities on the molecular sieve adsorbent as well as side reactions which could occur under the processing conditions and during regeneration in particular.

Background issues, relevant to CO_2, were summarised in Section 3. These indicate that:

- The presence of inerts and impurities can lead to significant changes in the CO2 physical properties and rates of corrosion. These changes are not well understood and further work is required to adequately quantify the effects

- Equations of state need to be developed which adequately reflect the physical properties of CO2 containing inerts and impurities

- There are limits to the extent of cooling that can be applied to the wet CO2 gas before water ice, hydrates or liquid CO2 form. This must be considered in the selection of cooling medium and wet gas conditions.

- There is a wide range in dry CO2 moisture specifications used for pipelines in the literature. Although it is not the intention of this study to specify what the target moisture should be guidance is given on the types of issues which should be considered when setting the dry CO2 moisture specification. It should be noted that this value is not merely determined by downstream pipeline conditions but also by coincident conditions which may occur within the processing plant, which may be very different to those experienced by the pipeline.

Dehydration technology options were discussed. Some of the techniques do not achieve low moisture levels, however they are straightforward, low cost processes, often required in a process anyway (such as compressor inter-stage cooling and knockout) so are important in offloading the dehydration unit, resulting in smaller, less costly dehydration systems.

The benefits of some of these options, which involve low temperature chilling, are limited due to the risk of formation of water ice / liquid CO_2 or hydrates. Large pressure drops are required to provide the Joule Thomson chilling so low pressure options are less viable.

Several liquid and solid desiccant systems were investigated; most are applicable for use with gaseous CO_2; glycerol is valid for supercritical / high pressure CO_2. The different processes and desiccants can achieve orders of magnitude different product moisture contents. Basic liquid desiccant systems can achieve ~150 ppmv moisture, enhanced liquid desiccant systems can achieve down to 30 ppmv moisture. Solid desiccant systems can achieve lower levels; activated alumina and silica gel can attain down to 10 ppmv while molecular sieve can achieve down to 0.1 ppmv moisture.

A chart, summarising the range of applicability of the different dehydration technologies has been produced; dehydration process applicability is dependent upon both the wet gas and target dry gas moisture contents.

The main dehydration processes examined in the study are:

- TEG liquid absorbent
- Molecular sieve adsorbent

These were selected based on the vendor recommendations.

15.2 Technologies

Several different types of CO_2 capture processes exist. The type selected for use is dependent upon the basic type of combustion process in operation, e.g. coal or natural gas. The CO_2 streams produced by the various combustion and capture processes are of different quality, containing different types of inerts and impurities, with varying compositions and conditions. The dehydration process can be significantly affected by these differences:

- Post combustion capture gas is delivered water-saturated at pressures just above atmospheric
- Pre-combustion capture provides multi-stream gases at low pressure and medium pressure conditions.
    - The Rectisol capture process delivers dry CO2 gas at < 1 ppmv moisture containing small levels of methanol. Further dehydration is not required. The methanol content is not expected to be condensed out in the subsequent compression / cooling process.
    - The Selexol solution contains water so the CO2 gas is effectively saturated with water. Selexol has a low vapour pressure so there is minimal contamination of the CO2 by the process. UOP advise that lower water levels of around 500-1000ppmv are achievable, but only at pressures in excess of 10 Barg; at these conditions the CO2 content of this HP stream would be significantly less than 98%. If sulphur removal is not required, then the process can use pure Selexol and solvent regeneration can be carried out by flashing alone. In this case significantly lower water content will be present in the CO2 product.

- Oxyfuel combustion gas compositions (dry basis) for the different processes are effectively similar, with the exception of water content and NOx / SO2 impurities. The streams are water saturated.

The information from the different process capture types have been used to produce a set of dehydration feed gas compositions. Base case data represent the minimum / normal impurity levels. Water content of saturated gas is dependent upon the temperature / pressure of the gas stream. Test cases have been used to consider the higher impurities and inerts.

Dehydration of post-combustion and pre-combustion capture cases can be carried out at a variety of different pressures, depending upon the supply pressure and the compressor inter-stage conditions available. Oxyfuel cases span a range of pressures from ~5 to 30 Bara, dependent upon the supply pressure and downstream processing requirements. Drying pressures are likely to be in the range of LP compression.

Information from both package vendors and media vendors centred around two basic process mediums; TEG and molecular sieves. The following data is therefore based upon these media.

Type 3A or 4A molecular sieve have been proposed with acid resistant grades proposed in cases containing high levels of undesirable impurities, typically NOx, SOx and H_2S. The quantity of desiccant required is a function of the adsorption time selected, the number of beds in parallel and any margin added due to the presence of impurities. Lower pressure operation will require larger diameter beds and larger bed volumes to cater for the larger volume of gas and the increase in moisture present.

Typical media life of both molecular sieve and TEG is expected to vary between 2 and 4 years, typically 3 years.

The maximum train size appears to vary considerably. For molecular sieve cases with feed gas at 30 Bara, 30°C the range (from different vendors) varied between 300 and 600 te/hr. The limitations appear to be based on several factors including the maximum vessel diameter which can be manufactured, the capital cost of the vessel (which begins to increase dramatically before the maximum diameter is reached), the maximum number of beds of a certain size in parallel, the adsorption time (and thus size) of each bed and the regeneration rate (which sets the time before a bed can be back in commission). It is desirable to keep the bed size small, to avoid the requirement for large volumes of desiccant and associated vessels; available adsorption time is minimised and a fast turnaround of regenerating beds is therefore required. There becomes a point when it is more practical to split the feed across an additional number of trains. It is undesirable to have bed adsorption times of less than 6 hours.

Preliminary estimates indicate that a TEG regeneration unit could potentially handle the moisture from 3,500 te/hr of CO_2 gas, although multiple contactors may be required to be able to process the quantity of gas.

If future expansion capacity is built into a dehydration package then capacity can be added at a later date.

- For molecular sieve, if an allowance is made for future adsorption beds at the outset then they can be added at a later date. The bed adsorption time, regeneration loop and associated regeneration equipment need to be large enough to regenerate an increased number of beds within the available adsorption time of the beds.

- For a TEG system adequate allowance needs to be made for the future glycol processing requirements. Additional contactors can be added. Dehydrating to <10ppm is achievable but not easy.

CO_2 contamination from the dehydration process / media and waste by-products have been discussed and quantified, where information is available. CO_2 losses from the process have also been considered.

15.3 Impurities

The effects of impurities and inerts on the dehydration systems were investigated and summarised. Where available, the maximum allowable concentrations have been advised. In the case of solid desiccant several approaches can be taken to deal with impurities:

- Additional amounts of desiccant can be added to cater for the effects
- Acid resistant desiccant can be used, which can better withstand the impurities
- Protective layers of activated alumina or silica gel, better able to withstand the impurity, can be added as guard layers to the top of molecular sieve beds. In some cases regeneration of the bed has the effect of regenerating the guard layer, but in some cases the bed is sacrificial, in which case the whole bed has to be replaced when the guard layer has been exhausted.

In the case of liquid desiccant impurities can:

- Form solids, which are removed by in-line filtration
- Cause foaming, resulting in losses of desiccant due to entrainment, and reduced moisture removal from the gas stream. High efficiency internals minimise the carryover of desiccant. Anti-foam can be added to limit the foaming and enable control of the process.
- React with the desiccant to form corrosive products. Oxygen can react with TEG to form organic acids.

It is extremely important that the specific impurities, and their normal and maximum concentrations are known and adequately considered during design. In the event that the levels of impurities cannot be tolerated, either because of their damaging effects or the increase in dehydration adsorbent volume required to deal with them, then it may be more appropriate to remove the impurities in a separate treatment system, located upstream of the dehydration unit. This may require a catalytic reactor or use of an adsorbent (which may, or may not, be regenerable). The dehydration vendor may be able to advise on the most appropriate approach to be taken.

The specification for dehydration plant in all three technologies is driven by two elements, the required transport entry specification and the configuration of the process unit. There is no common specification and care should be taken in considering the composition of the stream specified for dehydration.

15.4 Costs

There is a wide spread in molecular sieve capital cost data from different vendors for fixed operating pressure. The data has been used to set the maximum and minimum cost lines and has the cost indicator plotted against rate. The differences are due to several factors:

- Different regeneration techniques are proposed by the different vendors. Atmospheric pressure regeneration with air will be less costly. The amount of equipment required is significantly lower than for a high pressure regeneration using CO2. The volume of CO2 gas passing through the online bed is also lower since there is no regeneration gas to be processed. Smaller bed size results. The regeneration options are project and vendor specific not technology specific.
- Use of the CO2 compression facility to provide the driving force for the regeneration gas results in provision of less equipment within the dehydration package, but larger compression & cooling equipment and more costly compression costs.
- The materials of construction proposed
- The number and size of the individual adsorption beds proposed
- The number of parallel dehydration trains proposed.

Operating pressure has an effect on the molecular sieve equipment capital costs. Limited available data indicates that equipment capital cost passes through a minima. The actual minima location is expected to be application specific depending upon:

- The reasons given above for differences in capital cost
- The equipment design pressure - whether it is set to be 10% above the maximum operating pressure or designed for compressor settle out pressure on compressor trip.
- The type of regeneration and the extent of regeneration equipment supplied.

There is no difference between the capital costs of the molecular sieve equipment for target moistures of 550ppmv, 50pmv and <10ppmv. Media suppliers and package vendors all advised that it is normal to design for removal of the water stream to <1ppmv, irrespective of the target moisture required.

Data on liquid desiccants is lacking. The data presented is for water saturated raw gas at 30 Bara, 30°C. The raw gas stream is relatively pure containing > 99% CO_2 with low levels of impurities. Product moisture is 50 ppmv; the TEG process includes the use of stripping gas to increase the TEG concentration. The available data is understood to form the maximum cost line; the cost indicator is plotted against rate.

Higher levels of target product moisture (in excess of ~ 150 ppmv) will require more basic equipment; the stripper will not be required. The cost for such a system will therefore be lower.

In the case of high impurities:

- Increased oxygen levels of 300 ppmv have no effect on the molecular sieve equipment cost or on the solid desiccant selected. Oxygen is, however, known to degrade TEG; acceptable limits are not known so the effect on TEG equipment capital cost cannot be evaluated

- The case with 100ppmv NOx, 100ppmv SO2 and 100ppmv H2S results in the requirement of:

  - The use of an acid resistant molecular sieve with an increase in media volume of ~ 5% and an increase in media cost of ~15%.

  - An increase in molecular sieve equipment capital cost of ~7%

- The effects on TEG equipment capital cost cannot be evaluated

It is recommended that impurity issues be discussed with the vendor at an early stage, since they may recommend removal of these upstream of the dehydration equipment. For cases where high acid gas levels exist, solid media may require guard or sacrificial beds to defend the dehydration media. This potentially adds costs to the solid media systems.

In the case of high inerts content the cost of the equipment is higher per tonne of CO_2 present than for a low inerts gas. This is due to:

- The increased volume of raw gas per te of CO2 present, which requires a larger diameter TEG contactor and larger diameter solid desiccant beds

- The higher amount of water present in the increased volume of gas. This extra amount of water has to be removed. A larger circulation rate of TEG is therefore required; equipment in the TEG circulation loop will be larger. Larger volumes of solid desiccant are required to remove the larger amount of water; larger bed sizes result.

For a high inerts gas it is recommended that the 'CO_2 rate' value in the capital cost indicator versus rate graphs be increased in proportion to the fractional increase in total volume of the gas due to the inerts content, prior to reading the cost indicator values.

Operating costs estimates have been estimated for 3 different cases:

- Solid desiccant at 265 te/hr – Options from two different vendors, one using low pressure regeneration with atmospheric air and another using CO2 at pressure for regeneration. These cases form the minimum and maximum capital cost packages. A 3 year molecular sieve life has been used, as per vendor advice.

- Liquid desiccant at 265 te/hr – Only a single vendor has provided data. TEG desiccant life has been quoted as 3 -10 years, depending upon the extent of impurities present. A value of 3 years has been assumed for this analysis.

Comparing data from the same vendor indicates that the TEG system annual operating cost is significantly lower than that for the molecular sieve package. However, the more basic molecular sieve package, from a different vendor, but for the same raw gas conditions, indicates that the annual operating costs are significantly lower than those for the TEG system. Estimated minimum operating costs for molecular sieve packages are presented versus rate.

Operating pressures of 10, 20 and 30 Bara were investigated for the same set of post-combustion conditions for molecular sieve packages. Information from vendors is limited; however it suggests that operating pressure has an effect on operating costs; the regeneration power consumption passes through a minima. The actual minima pressure is expected to vary for individual applications.

Limited data indicates that the effect of impurities on molecular sieve operating cost is effectively negligible. The increased bed volume results in an increased capital cost, which impacts onto maintenance costs and taxes / insurance. Desiccant cost increases but regeneration power consumption is reduced.

15.5 Selection

Basic advice on selection of the most appropriate dehydration technology is provided for dehydration of gaseous CO_2. The pressure at which CO_2 drying is required is dependent upon many considerations, including:

- Hydrate formation conditions
- Undesired liquid CO2 formation conditions
- Water solubility in CO2
- Compressor inter-stage conditions available. These conditions can be limited in some cases, such as occur with the use of Ramgen high pressure ratio compressors.
- Inter-stage cooling temperatures available
- Minimum temperatures experienced at the point of dehydration and also downstream
- CO2 export pressure
- CO2 supply pressure
- Downstream processing requirements, for example liquefaction / cryogenic processes
- Capital / operating cost of dehydration equipment

15.6 Operational

Operational issues were considered. The drier performance should be monitored to ensure that water breakthrough does not occur. It is important that a continuous monitoring system is used; manual sampling and analysis will not be sufficient. The number of available analysis techniques is limited due to the presence of CO_2 itself and the potential contaminants.

There appears to be equipment available to do the continuous moisture monitoring. However impurities must be considered in detail. Their normal concentration and their concentration ranges during both normal operation and also on excursion needs to be quantified and comprehensively discussed with vendors. It is important that the actual application is fully discussed with the vendors to enable the most appropriate device to be selected.

The sampling system can significantly influence the overall performance and recovery time from upset. A properly designed sample system is essential. Sampling usually involves pressure let-down and sample heating will be required to ensure that Joule Thomson chilling does not result in condensation of any of the components present, which can affect both the analyser and the analysis result.

A reasonable response time is essential to ensure that offspec product is quickly detected and remedial actions taken promptly. The sampling system can have a significant effect on the overall response time.

Consideration of the conditions which the sensor may experience under upset conditions must be included to ensure that damage or prolonged erroneous readings do not occur.

Maintenance frequency can be dependent on the gas quality. Means should be provided to enable periodic cleaning of the sensor and associated lines in the event that a contamination incident occurs. Particulates are a particular issue for some types of device, such as the phosphorous pentoxide device; particulates can block the capillary.

Care needs to be taken to ensure that any of the components present are not capable of reaction at the cell surface, where reactions may be catalysed, such as may occur in the presence of platinum electrodes held at temperature. Reactions may cause contamination of the cell or form water and result in erroneous readings.

At least two moisture analysis points are recommended; if a fault develops at one location then the second location will act as a backup. The analysis points should be located at different points in the plant: one immediately after dehydration and another further downstream, possibly located after compression, adjacent to the compression and conditioning plant boundary

Each location should have two analytical devices, so that if one fails / has problems the other can be brought online.

Suggested remedial actions have been described in the event that excessive moisture ends up in the downstream process. Operating Plants should develop plans regarding what to do if off-spec gas has reached downstream equipment. The actual course of action may be dependent upon the extent of the moisture excursion and the conditions prevalent in the line / equipment at the time.

15.7 Further Work

Areas requiring further work have been proposed to enable a full and adequate consideration of dehydration processes and issues. These include the effect of inerts and impurities on physical properties and generation of equations of state which adequately model the physical properties.

Re-engagement of vendors should be addressed by industry bodies as a priority.

16.0 Appendices

Appendix 1 – Vendor Details

Dehydration Package Vendors

Frames Process Systems B.V.

PO Box 15

2400 AA Alphen aan den Rijn

The Netherlands

Tel: +31 172 50 48 00

fps@frames-group.com

www.frames-group.com

Frames supply the following types of dehydration system and equipment

- Absorption with TEG
- Adsorption with silica gel, molecular sieve or activated alumina

Their designs are tailor made for the specific process parameters.

SPX Flow Technology Etten Leur B.V.

Munnikenheiweg 41

4879 NE Etten Leur

The Netherlands

www.spxft.com

SPX supply the following types of dehydration system and equipment

- Adsorption with silica gel, molecular sieve or activated alumina
- Refrigeration.

They can provide either bespoke or standard sized equipment

Exterran (UK) Ltd

Westgate

Aldridge

Walsall

West Midlands

WS9 8EX

UK

Tel: +44(0)1922 450200

Fax: +44 (0)1922 450230

www.exterran.com

Exterran supply the following types of dehydration system and equipment

- Adsorption with molecular sieve

Prosernat

Tour Franklin

100/101 Terrasse Boieldieu

92042 Paris La Défense - France

Tel +33 (0)1 47 67 20 00

Fax: +33 (0)1 47 67 20 07

www.prosernat.com

Prosernat supply the following types of dehydration system and equipment

- Adsorption with silica gel, molecular sieve or activated alumina
- Absorption with TEG and chilled methanol

GL Noble Denton

Holywell Park

Ashby Road

Loughborough

Leicestershire

LE11 3GR

UK

Phone +44 1509 282183

Fax +44 1509 283080

Mobile: 07854 169968

Business Area E-mail: Adapt@gl-group.com

www.gl-group.com

www.gl-nobledenton.com

GL Noble Denton supply the following types of dehydration system and equipment

- Silica gel, glycol, low temperature separation

Cameron Limited

Cameron House

61-73 Staines Road West

Sunbury-on-Thames

Middlesex,

TW16 7AH

UK

TEL +44.1932.732000

Cameron supply the following types of dehydration system and equipment

- Absorption with TEG
- Adsorption with silica gel, molecular sieve or activated alumina

Dehydration Media Vendors

Zeochem AG

CH-8707 Uetikon

Switzerland

+41 44 922 93 83

www.zeochem.com

Member of CHP Group

Zeochem supply the following dehydration media:

- Molecular sieve, silica gel and activated alumina

UOP Products UK Limited

“Liongate”

Ladymead

Guildford,

Surrey

GU1 1AT

UK

Tel: +44 (0) 1483 304848

www.uop.com

UOP supply the following dehydration media:

- Molecular sieve and activated alumina

Grace Materials Technologies

Grace Davison

Oak Park Business Centre

Alington Road

Little Barford

St Neots

PE19 6WL

UK

Tel: +44 (0) 1480 219115

Fax: +44 (0) 1480 324 433

Grace supply the following dehydration media:

- Molecular sieve

BASF Catalysts Germany GmbH

CCP/E-B –

30173 Hannover

Deutschland

Tel: +31 306669437

BASF supply the following dehydration media:

- Molecular sieve, silica gel and activated alumina

Analyser Vendors

Moisture Control & Measurement Ltd

Rudgate,

Thorp Arch Estate,

Wetherby,

West Yorkshire,

LS23 7AT,

UK

Tel +44 (0)1937 843927

Fax: +44 (0)1937 842524

Systech Instruments Ltd

17 Thame Park Business Centre

Wenman Road

Thame

Oxfordshire

OX9 3XA

UK

Tel: +44 (0)1844 216838

Fax: +44 (0)1844 217220

www.systechillinois.com

AMCS

14 Woodside

South Marsdon Park

Swindon

Wiltshire

SN3 4WA

UK

Tel: +44 (0) 1793 824111

Fax: +44 (0) 1793 824222

sales@amcs.co.uk

www.amcs.co.uk

Process Analyser Systems Ltd.

Boston House

Grove Technology Park

WANTAGE

Oxon,

OX12 9FF

UK

Tel: +44 (0) 1235 769841

www.pasuk.com

Appendix 2 – Technology Assessment Forms

Technology Assessment Form

Client	IEA GHG	Contract No.	1853		
Project	Dehydration Study	Made by	LMS	Date	
Technology	Triethylene glycol (TEG)				

Viability		
Is the process proven in the field, FOAK, NOAK or research yet to be proven but may be suitable in the future? Is FOAK or research likely to deliver solution in the required timeframe?	Well proven on natural gas.and proven on CO2 (Frames) CCS duty - Shell Quest CCS, Canada - Engineering Study carried out in 2012	
	Capacity	Shell Quest Study for > 1 million tepa
	Limits	
	Availability at scale?	Yes, definitely on nat gas and studies on CO2
References	Frames - Shell Quest Engineering Study	

					x	
0	1	2	3	4	5	6
<Poor		**Assessment**				Best>

Maturity		
Is the technology deployed at scale? Where, how many, what range of sizes exist? Could it be scaled if required?	Yes - many plants on natural gas (+ other gases)	
	Largest sized units provided 2.3MMNm3/day CO2, 8 MMNm3/day Natural gas	
References	Frames Questionnaire	

					x	
0	1	2	3	4	5	6
<Poor			**Assessment**			Best>

Flexibility/operation

Is the process steady state only- what levels of turn down can be achieved? What flexibility can the process reach? Is it a stable or unstable process?	Can be turned down to 10%. Stable, but has known issues relating to foaming, reaction with impurities, loss of TEG to the gas stream, loss of CO2 gas into the TEG which subsequently goes to vent
References	Frames Questionnaire

				x		
0	1	2	3	4	5	6
<Poor			**Assessment**			Best>

Retrofit Capability

Can the technology be retrofitted? What modifications would be required? How easy would the integration be?	Yes, as part of a capture and conditioning unit fitted to existiing flue gas system. Major project at power plant, with breakins to flue gas system. Major modifications, as far as the power plant is concerned, are on utility and services supplies and modification of these systems will have a major impact on the power plant
References	

				x		
0	1	2	3	4	5	6
<Poor			**Assessment**			Best>

Potential for the process to be by-passed?

Can the process be bypassed or is it integral to a critical unit? What impact would bypassing have on the units performance? Does it have standby condition requirements?	Do not want to bypass the unit as a whole due to moisture carryover. Could bypass a unit if several units are installed and run the plant on reduced rate (provided it is above SEL for the remainder of the plant) If capture system bypassed on a post combustion plat then the power station could continue to run. The TEG unit could be kept on hot standby by continuous circulation of the TEG.. System can be ramped up in 15 mins from hot standby or 3-5 hours from cold start-up.
References	Frames Questionnaire

			x			
0	1	2	3	4	5	6
<Poor			**Assessment**			Best>

Efficiency/performance

What are the typical efficiency and performance expectations?	Glycol losses to entrainment and dissolution in CO2 10-20 kg/MMNm3
References	

			x			
0	1	2	3	4	5	6
<Poor			**Assessment**			Best>

Host/Parent Plant Efficiency/Performance Impact

What impact does the process have on the parent/host plant in terms of efficiency perfomance?	
References	

				x		
0	1	2	3	4	5	6
<Poor			**Assessment**			Best>

Footprint

Indication of plant physical size, plot and height. Will the plant represent significant planning issues compared to host plant?	265 te/hr CO2 takes up 4.5m x 12m x 6m (reboiler top) 9m high (reflux condenser top nozzle) + contactor 2m diam x 10.to 13m height Approx 50 te weight Minor footprint in comparison the capture plant
References	Frames Questionnaire

					x	
0	1	2	3	4	5	6
<Poor			**Assessment**			Best>

Parasitic Load	
What is the utility, power and thermal load likely to be? Does if cause significant efficiency loss? Are new facilities required?	350 kW electrical reqt for 265 te/hr CO2. Inst air required for valve operation 1 N m3/hr Cooling water 15 te/hr
References	Frames Questionnaire

				x		
0	1	2	3	4	5	6
<Poor			**Assessment**			Best>

Chemical requirements	
What chemicals are required? What delivery and storage arrangements are required?	TEG - typically 20-30 te initial charge + regular top ups to replace losses & degraded material. Typical glycol loss due to entrainment and dissolution in CO2 gas are 10-20kg/MMNm3 Charge typically lasts 3-10 years, depending on the operation. Additives? Dried CO2 required for TEG regeneration in cases where low moisture (<150ppmv) required. This CO2 is vented.
References	Frames Questionnaire

				x		
0	1	2	3	4	5	6
<Poor			**Assessment**			Best>

Additional fuel requirements	
Does the process require fuel for process or support units? What types and volumes?	No
References	

						x
0	1	2	3	4	5	6
<Poor			**Assessment**			Best>

By-products/treatment requirements	
What by-products are produced by the process? Waste products and volumes and disposal routes? Additional waste stream treatment needs?	Waste solids from filter Overhead vapours from the reboiler, containing water, CO2 (~1% lost) and possible impurities. Waste TEG at end of life
References	Frames Questionnaire

			x			
0	1	2	3	4	5	6
<Poor			**Assessment**			Best>

Effects of Impurities & Inerts	
Can the process handle the presence of impurities and inerts? What are the acceptable limits?	O2 causes degradation of the TEG Inert gases do not cause any problem - will pass through. Foaming, corrosion and emulsification are the main concerns from impurities. Minor quantities of TEG are introduced into the CO2 product gas.
References	Frames Questionnaire Gas Dehydration Fundamentals – Part 4 – TEG Solution Monitoring and Maintenance', Ardeshir Azodi, Laurence Reid Gas Conditioning Conference, 2008

			x			
0	1	2	3	4	5	6
<Poor			**Assessment**			Best>

Control	
Will the facility integrate to existing control systems? Is it highly automated or needs manual operation? Is the system difficult to control - narrow operating bands, runaway potential etc?	Package has its own control panel which can be controlled from either the UCP HMI or the DCS. System is designed for fully automated operation and is not difficult to control. Foaming may cause problems if significant quantities of impurities present
References	Frames Questionnaire

			x			
0	1	2	3	4	5	6
<Poor			**Assessment**			Best>

HSE Assessment

Is the process dangerous? Reactive, oxidizing, high temperature or pressure, explosion potential, toxic or harmful material in use and on release, flammable?	Flashpoint 165C Flammable limits 0.9% - 9.2% Vapour heavier than air Inhalation and contact with skin and eyes to be avoided.
References	

			x			
0	1	2	3	4	5	6
<Poor			**Assessment**			Best>

HSE Dangerous Chemicals

Identify hazardous materials. Outline handling, hazard and storage requirements? Would specialist emergency response be required?	Triethylene glycol is stable and non-corrosive at normal storage conditions. Above ground, outside storage - winter conditions may require heating of tanks and lines due to high viscosity and high freezing point. Continuous exposure to high temperatures causes degradation. Disposal of filter waste and spent TEG at end of life.
References	Dow brochure ' Triethylene glycol'

			x			
0	1	2	3	4	5	6
<Poor			**Assessment**			Best>

HSE Training

Specific training and competency requirements?	Around 2-5 days operator training required, depending on their previous experience.
References	Frames Questionnaire

				x		
0	1	2	3	4	5	6
<Poor			**Assessment**			Best>

Expertise Requirements	
Identify any expertise that will be required on site? Specialist training/experience requirements?	No specialist experience necessary, other than above training requirements.
References	

				x		
0	1	2	3	4	5	6
<Poor			**Assessment**			Best>

0	Total Score = 70	108
<Poor	**Assessment**	Best>

Technology Assessment Form

Client	IEA GHG	Contract No.	1853		
Project	Dehydration Study	Made by	LMS	Date	
Technology	Twister Separation				

Combines condensation and separation at supersonic velocity. Can be used to separate hydrates from the gas stream. Available

information is based on natural gas. Venturi device. Liquid removed from low pressure point, prior to pressure recovery on expansion.

Better dehydration can thus be achieved. Introduction of 'swirl' valves can improve moisture separation.

Can be combined with hydrate removal

Concern re CO2 liquefaction at the process conditions

Viability		
Is the process proven in the field, FOAK, NOAK or research yet to be proven but may be suitable in the future? Is FOAK or research likely to deliver solution in the required timeframe?	Recently proven on natural gas processes, particularly offshore. No information on CO2. May be used to offload the dehydration package.	
	Capacity	
	Limits	
	Availability at scale?	
References		

			x			
0	1	2	3	4	5	6
<Poor			**Assessment**			Best>

Maturity	
Is the technology deployed at scale? Where, how many, what range of sizes exist? Could it be scaled if required?	Multiple tubes installed in parallel.
References	

			x			
0	1	2	3	4	5	6
<Poor			**Assessment**			Best>

Flexibility/operation	
Is the process steady state only- what levels of turn down can be achieved? What flexibility can the process reach? Is it a stable or unstable process?	Fixed actual flow device. Sonic flow required in the tube. Turndown will require tubes to be taken offline or an adjustment made to operating pressure. Care needs to be taken to ensure that liquid CO2 does not form.
References	

			x			
0	1	2	3	4	5	6
<Poor			**Assessment**			Best>

Retrofit Capability	
Can the technology be retrofitted? What modifications would be required? How easy would the integration be?	Yes, as part of a capture and conditioning unit fitted to existing flue gas system. Major project at power plant, with break-ins to flue gas system.
References	

			x			
0	1	2	3	4	5	6
<Poor			**Assessment**			Best>

Potential for the process to be by-passed?	
Can the process be bypassed or is it integral to a critical unit? What impact would bypassing have on the units performance? Does it have standby condition requirements?	Each tube is a fixed actual flow device. Conditions quickly achieved on start-up. Not advisable to bypass the unit while online unless rate reduction requires it.
References	

		x				
0	1	2	3	4	5	6
<Poor			**Assessment**			Best>

Efficiency/performance	
What are the typical efficiency and performance expectations?	Better knockout performance than knockout pots. Pressure drop expected to be 25-35% of feed pressure, i.e. considerable, compared to other moisture elimination systems. Heat required for hydrate removal
References	

		x				
0	1	2	3	4	5	6
<Poor			**Assessment**			Best>

Host/Parent Plant Efficiency/Performance Impact	
What impact does the process have on the parent/host plant in terms of efficiency performance?	Increased pressure drop required. Increased compression costs.
References	

		x				
0	1	2	3	4	5	6
<Poor			**Assessment**			Best>

Footprint	
Indication of plant physical size, plot and height. Will the plant represent significant planning issues compared to host plant?	Smaller footprint than a knockout drum Compact and low weight Multiple units required. Still require a dehydration polisher.
References	

		x				
0	1	2	3	4	5	6
<Poor			**Assessment**			Best>

Parasitic Load

What is the utility, power and thermal load likely to be? Does if cause significant efficiency loss? Are new facilities required?	Additional pressure required to overcome large PD. Polisher unit still required.
References	

			x			
0	1	2	3	4	5	6
<Poor			**Assessment**			Best>

Chemical requirements

What chemicals are required? What delivery and storage arrangements are required?	None
References	

						x
0	1	2	3	4	5	6
<Poor			**Assessment**			Best>

Additional fuel requirements

Does the process require fuel for process or support units? What types and volumes?	N/A
References	

						x
0	1	2	3	4	5	6
<Poor			**Assessment**			Best>

By-products/treatment requirements	
What by-products are produced by the process? Waste products and volumes and disposal routes? Additional waste stream treatment needs?	Aqueous streams containing dissolved CO2 and impurities.
References	

			x			
0	1	2	3	4	5	6
<Poor			**Assessment**			Best>

Effects of Impurities & Inerts	
Can the process handle the presence of impurities and inerts? What are the acceptable limits?	
References	

			x			
0	1	2	3	4	5	6
<Poor			**Assessment**			Best>

Control	
Will the facility integrate to existing control systems? Is it highly automated or needs manual operation? Is the system difficult to control - narrow operating bands, runaway potential etc?	
References	

				x		
0	1	2	3	4	5	6
<Poor			**Assessment**			Best>

HSE Assessment	
Is the process dangerous? Reactive, oxidizing, high temperature or pressure, explosion potential, toxic or harmful material in use and on release, flammable?	N/A
References	

			x			
0	1	2	3	4	5	6
<Poor			**Assessment**			Best>

HSE Dangerous Chemicals	
Identify hazardous materials. Outline handling, hazard and storage requirements? Would specialist emergency response be required?	N/A
References	

					x	
0	1	2	3	4	5	6
<Poor			**Assessment**			Best>

HSE Training	
Specific training and competency requirements?	N/A
References	

				x		
0	1	2	3	4	5	6
<Poor			**Assessment**			Best>

Expertise Requirements	
Identify any expertise that will be required on site? Specialist training/experience requirements?	N/A
References	

				x		
0	1	2	3	4	5	6
<Poor			**Assessment**			Best>

0	Total Score = 61	108
<Poor	**Assessment**	Best>

Technology Assessment Form

Client	IEA GHG	Contract No.	1853		
Project	Dehydration Study	Made by	LMS	Date	
Technology	Methanol				

Viability		
Is the process proven in the field, FOAK, NOAK or research yet to be proven but may be suitable in the future? Is FOAK or research likely to deliver solution in the required timeframe?	Main constituent in Rectisol process. Prosernat have a methanol based process, but have not replied to queries. Methanol has a relatively high vapour pressure at normal process conditions so either chilled methanol or methanol recovery would be required to prevent high methanol losses into the product gas. Methanol has a high selectivity for CO2, especially at low temperatures so an alternative process may be more appropriate.	
	Capacity	
	Limits	
	Availability at scale?	Rectisol processes exist at required scale
References		

		x				
0	1	2	3	4	5	6
<Poor		**Assessment**				Best>

Maturity	
Is the technology deployed at scale? Where, how many, what range of sizes exist? Could it be scaled if required?	Rectisol units available at CCS capacity No details from vendor
References	

		x				
0	1	2	3	4	5	6
<Poor		**Assessment**				Best>

Technology Assessment Form

Client	IEA GHG	Contract No.	1853	
Project	Dehydration Study	Made by		Date
Technology	Membranes			

Viability		
Is the process proven in the field, FOAK, NOAK or research yet to be proven but may be suitable in the future? Is FOAK or research likely to deliver solution in the required timeframe?	Research - yet to be proven. Research is underway on dehydration of supercritical CO2 (100-200 bar) at the University of Twente. Aim is to develop suitable membranes. Patents exist for dehydration of natural gas from saturation (at ~ 10 Bara) down to <150ppmv moisture. CO2 dehydration is a more difficult duty. CO2 permeability is reduced by the presence of water, the extent of which is dependent on the particular polymer type.	
	Capacity	
	Limits	
	Availability at scale?	
References	US Patent 5,641,337 "Process for the dehydration of a gas" "Membrane processes and post combustion carbon dioxide capture: Challenges and prospects", Eric Favre, Chemical Engineering Journal, 171 (2011) 782 - 793 http://www.academictransfer.com/employer/UT/vacancy/4462/lang/en/ http://www.utwente.nl/tnw/mtg/people/phd/Koziara/info/Koziara%20Research.docx/	

	x					
0	1	2	3	4	5	6
<Poor		**Assessment**			Best >	

Maturity	
Is the technology deployed at scale? Where, how many, what range of sizes exist? Could it be scaled if required?	No
References	

x						
0	1	2	3	4	5	6
<Poor		**Assessment**			Best >	

Technology Assessment Form

Client	IEA GHG	Contract No.	1853	
Project	Dehydration Study	Made by	LMS	Date
Technology	Shell Oil Co Glycerol Process			

Viability		
Is the process proven in the field, FOAK, NOAK or research yet to be proven but may be suitable in the future? Is FOAK or research likely to deliver solution in the required timeframe?	Proven on supercritical CO2 where high pressure would result in considerable losses of alternative liquid desiccants, e.g. TEG	
	Capacity	35 MMscfd supercritical CO2 at 140 bar
	Limits	
	Availability at scale?	
References	"Use glycerol to dehydrate supercritical CO2", Beitler, Hydrocarbon Processing, July.2011 'CO2 dehydration scheme aids Hungarian EOR Project'. G Udvardi, Y Ouchi, E A Thoes, C B Wallace, Oil & Gas Journal, October, 1990	

				x		
0	1	2	3	4	5	6
<Poor			**Assessment**			

Maturity	
Is the technology deployed at scale? Where, how many, what range of sizes exist? Could it be scaled if required?	Yes - at supercritical conditions
References	

			x			
0	1	2	3	4	5	6
<Poor			**Assessment**			Best >