Corrosion and Materials Selection Issues in Carbon Capture Plants

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ABSTRACT

The construction of the process plant required for carbon capture in power generation and also other industrial processes will be among the most significant capital investments of the next 20-30 years. The correct choice of materials for piping, vessels and all types of equipment will be vital in ensuring the long-term performance, safety and high operational availability of the capture plants through their lifetime. Controlling materials related costs will help enable a wider and faster roll-out of carbon capture systems. In general, the carbon capture processes have so far only been operated on sub-commercial pilot-scale plants, and for a relatively short period, although there is much useful experience from other large-scale industrial processes with similar conditions, However, carbon capture processes do differ in some aspects which can be important for material performance and selection. This paper focuses on corrosion and materials degradation risks from the process streams and materials issues specific to the main proposed carbon capture processes (Post combustion, Pre combustion (IGCC) and Oxy-fuel). Some specific corrosion issues and problems are discussed. Areas where potential problems exist or where further studies are required are highlighted.

Key words: carbon capture, post-combustion, pre-combustion, oxy-fuel

INTRODUCTION

For most large CO_2 sources, including fossil fuel power plant, the cost of capturing and compressing the carbon dioxide is expected to be by far the largest component of the overall cost of carbon capture, transport and storage. This cost includes the capital costs of the capture plant, the direct operating costs of the plant and the loss of efficiency in the overall plant, i.e. lower usable power output in the case of electricity generation. Capture, including compression, may cost $ 20-45 / tonne CO_2 captured, while transport and storage combined may cost around $ 2-10 /tonne. [1] [2] The construction of these capture plants for power generation and also other industrial processes generating CO_2 will be among the most significant capital investments of the next 20-30 years: the European Commission anticipates total costs in the region of 1 billion Euro per full scale demonstration plant. [3] The correct choice of materials for piping, vessels and all types of equipment will be vital in ensuring the long-term performance, safety and high operational availability of the capture plants through their lifetime. Controlling materials related costs will help enable a wider and faster roll-out of carbon capture systems.

In general, the carbon capture processes have so far only been operated in sub-commercial scale pilot and demonstration plants, and for a relatively short period compared with the lifetime required for a typical power plant or industrial application. There is much useful experience from other large-scale industrial processes with similar conditions, for example flue gas desulphurization (FGD) plants and some gas processing applications. However, carbon capture processes do differ in some aspects which can be important for material performance and selection compared with comparable gas processing systems in other industries.

In some cases, there is an interaction between choices in the details of the process design and the corrosivity of the environment, and consequently the demands on materials. In particular cases, high-performance, expensive materials may have to be used if the environment is not controlled within suitable limits. The choice of materials also has to consider the functions of specific equipment, the options for construction for what is often very large scale plant, and the costs and practicality of maintenance or replacement. For some major items, there is a choice of potentially suitable alternatives, and the final selection would require finalising in the context of a specific plant design, considering factors such as plant availability and the balance between capital and operating costs.

This paper provides an overview of the corrosion and materials selection issues in the main alternative capture processes for power generation applications, including compression of the export gas. Typical process schemes for carbon capture in power generation using Oxy-fuel, Post-combustion and Pre-combustion processes are considered, including some process variations due to the effect of different fuel types.

OVERVIEW OF PROCESSES

The major alternative process anticipated for carbon capture in power generation are
- Post- combustion capture
- Oxy-fuel combustion capture
- Pre - combustion capture

Post-combustion Capture
Post-combustion capture refers to the processes in which CO_2 is separated from the flue gases downstream of the combustion. Post-combustion capture is suitable for retro-fitting to existing power plant, and also potentially to treat other industrial sources of CO_2. In outline, the typical processes

under development are amine scrubbing systems broadly similar to those used in gas treatment plants. In power plant applications the process takes the flue gas, if necessary after passing through a FGD unit. An extra cooler may be used to reduce the temperature of the saturated flue gas before it enters the absorber. For coal-fired combustion, an extra scrubber may be necessary at the front end to remove highly soluble components (such as SOx and HCl), particulates and liquid carryover from the flue gas.
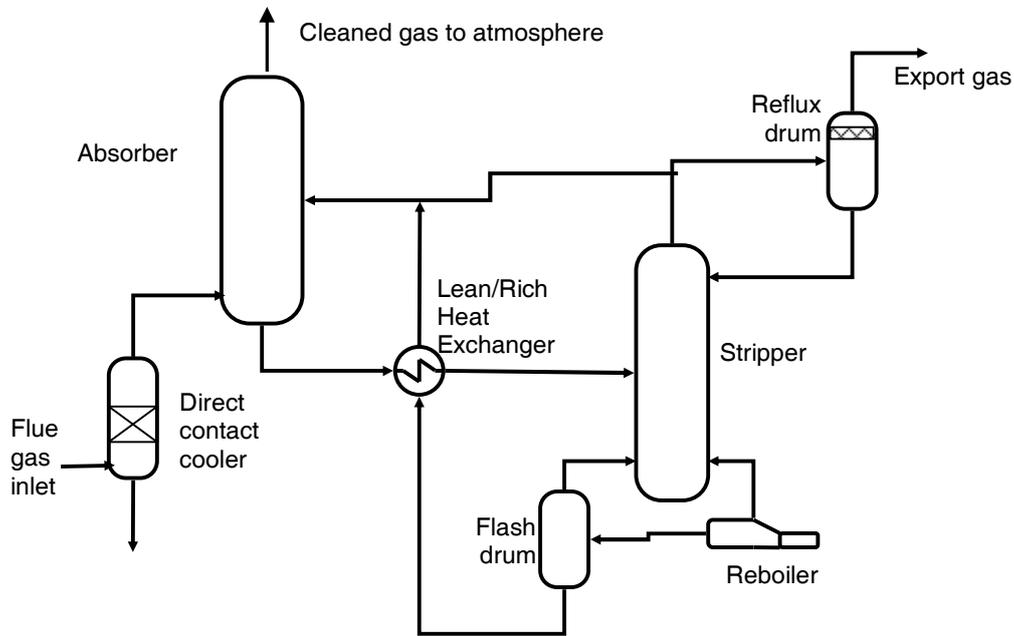
Figure 1 : Schematic diagram of carbon capture for the Post-combustion process

Oxy-fuel Combustion capture

Oxy-fuel combustion uses a high oxygen gas stream instead of air to burn the fuel. For CCS applications this has the benefit of producing a flue gas with a much higher CO_2 content than conventional combustion, typically about 60 - 70% CO_2. The carbon capture unit is located downstream of the oxy-fuel combustion process and the FGD unit (when present). SOx and NOx are removed as acids with water in successive vessels. The stream is then dried and, if necessary, mercury may be captured at this point. The other major components of the gas stream, N_2, Ar and O_2 are then removed from the CO_2 stream by cryogenic separation.
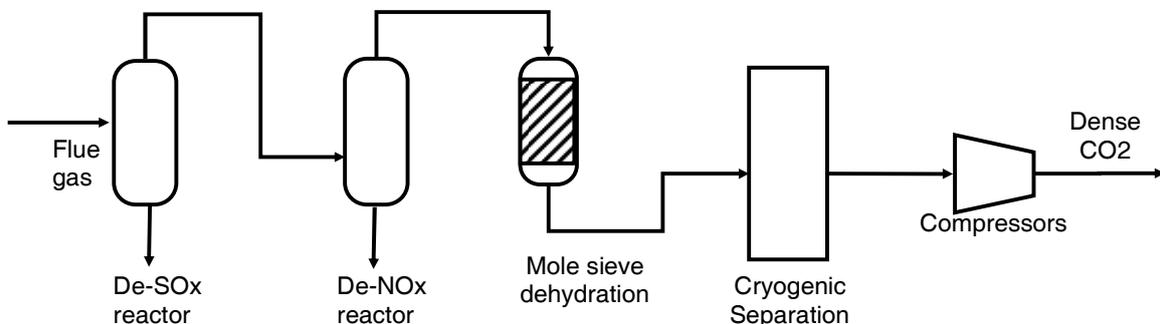
Figure 2 : Schematic diagram of carbon capture for Oxy-fuel combustion

Precombustion Capture

Also known as integrated gasification combined cycle (IGCC); this process involves production of synthetic gas (syngas), which is essentially a mixture of hydrogen, CO_2 and CO generated from natural gas or coal. The gasification reaction in the IGCC process is an established technology and not included in the scope of this study. [4] In the carbon capture version of the IGCC process, however, syngas shift reactors are added downstream of the gasification, in order to convert CO to CO_2 as shown below:

$$CO + H_2O \Leftrightarrow CO_2 + H_2 \tag{1}$$

The CO_2 generated by the shift reactors can be extracted further downstream in the CO_2 absorber; any unconverted CO will eventually be converted to CO_2 in the gas turbine and will be emitted to atmosphere.

The high temperature syngas streams exiting from the shift reactors are cooled and the condensed water is removed before the dried syngas enters the capture plant proper. Typical process schemes use a physical solvent process for CO2 capture: solvent processes are more suited to the higher total pressure and CO_2 fraction in the pre-combustion situation in contrast to post-combustion, where chemical (amine) processes are the dominant technology. When using coal-firing, the syngas may contain amounts of hydrogen sulfide. Hydrogen sulfide may be captured separately from CO_2 (for example if H_2S is not desired in transport and sequestration stages), or may be captured along with the CO_2 stream. This results in two process configurations, namely "separate-capture" and "co-capture". The H_2S content in natural-gas-based syngas is minimal, so the co-capture configuration applies.
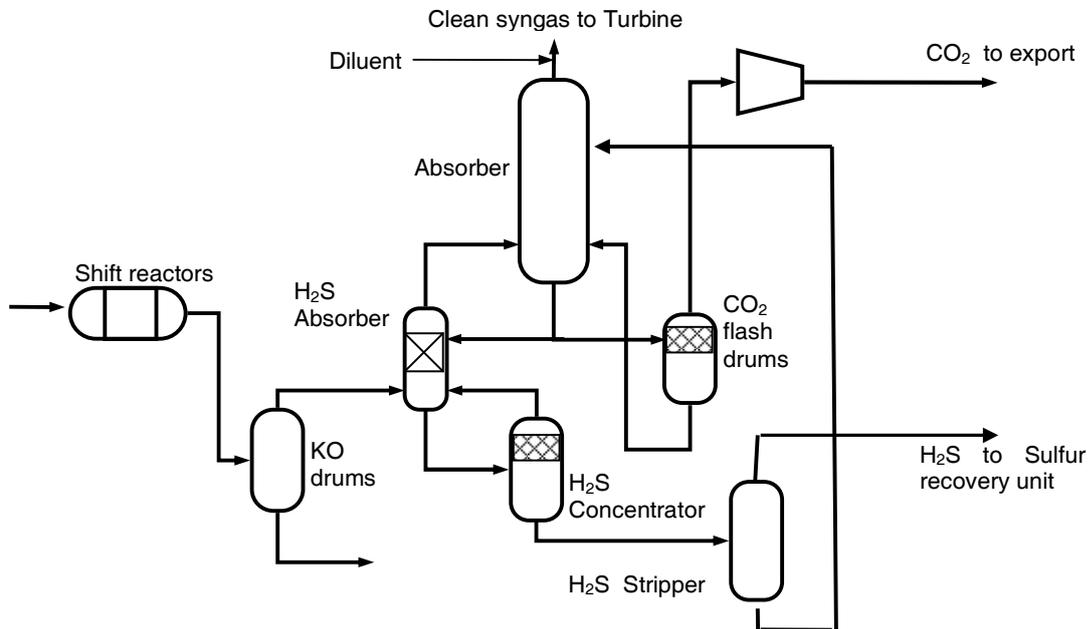

Figure 3(a) : Schematic Diagram of separate capture process for Pre-combustion
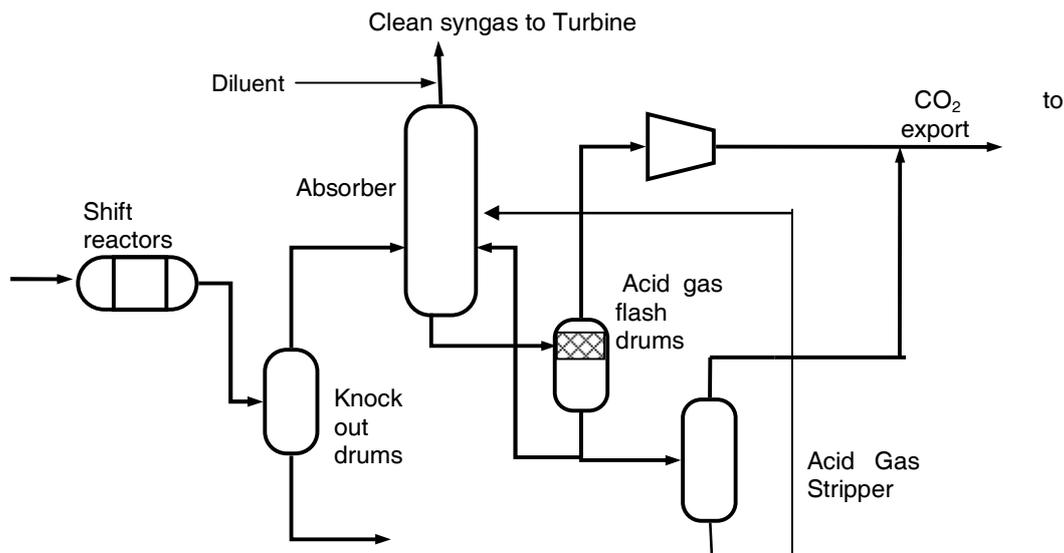
Figure 3 (b) : Schematic Diagram of the co-capture process for Pre-combustion

Environmental Conditions and Corrosion Risks

From a materials degradation and corrosion point of view, there is a wide range of environments amongst the different carbon-capture processes. In general, the high CO_2 levels mean that wet process environments tend to be acidic, resulting in high corrosion rates for unprotected carbon steel. There are acid-oxidising conditions in some process streams which present particular risks to carbon steel and also many stainless steels and corrosion resistant alloys (CRAs). Corrosion risks for metals include general and localised CO_2 corrosion; erosion–corrosion; various forms of stress-corrosion; low temperature hydrogen damage; high temperature hydrogenation, sulphidation and metal dusting; and liquid metal embrittlement.

Table 1: Example Stream Conditions at the Front End of Carbon Capture Units [5]

Component, mol%	Precombustion		Post combustion		Oxy-fuel
	Coal-fired, after shift reactors	Gas-fired after shift reactors	Coal Fired, after FGD	Gas Fired	Coal Fired, after FGD
Carbon Dioxide	25-35	16	14	13	70-80
Water	20-30	21	10	7	3-5
Oxygen	-	-	4	4	3-5
Nitrogen	0 - 6	-	72	75	15-20
Argon	0 -1	-	0.9	0.9	2-5
Carbon Monoxide	1 - 3	0.5	-	-	-
Sulfur Dioxide	-	-	0.004	-	0.01 - 0.5
Nitrogen Oxide	-	-	-	-	0.01- 0.07
Hydrogen	35-45	63	-	-	-
Hydrogen Sulfide	0.02-0.4	-	-	-	-
Others	Hg		SOx, NOx, Hg	NOx	SOx, NOx, Hg
Temperature (°C)	330	240	45	45	30
Pressure (MPa)	3-4	3-4	circa 0.1	circa 0.1	circa 0.1

Polymers are potentially susceptible to swelling and changes in physical properties due to absorption of CO_2. The moderate operating pressures typical of capture plant are not high risk in regard to rapid gas

decompression, but after compression pressures are high enough to present a risk to susceptible materials.

The minor components in the process streams can have dramatic effects on the severity of the environments, including species such as chlorides, sulfur and nitrogen oxides, oxygen, cyanides and hydrogen sulfide. The fuel type is significant here, with coal-firing producing higher levels of potentially harmful species than natural gas-firing. Although FGD plant will remove a large proportion of water soluble species, some carry-over of SOx, NOx and halides is expected.

Related Experience

Materials performance in flue gas desulphurisation (FGD) plant is very relevant to the similar acid-oxidising conditions in carbon capture plant: the inlet for the capture plants in Post Combustion and Oxy-fuel scenarios when using coal firing would be directly from an FGD unit. The distinguishing feature of the flue gas environment is the presence of the oxidising acid species NO_x and SO_x. These are absent in the oxygen-free or reducing conditions typically found in petrochemical processes. Although SO_2 is mostly removed from the flue gas in the FGD plant before reaching the CCS plant, there is still sufficient SO_2 to contribute significantly to the acidity. Where the conditions drop below the dew point there is a risk of condensation of concentrated acids, and this is the major cause of corrosion encountered in FGD systems. Dew point, acidity (pH), temperature, halide concentration (chlorides and fluorides), crevice conditions, and gas velocity all must be considered in defining the corrosivity of the environment. EPRI [1] have conducted a useful survey of materials usage in FGD plant. [6]

The oil & gas industry has extensive experience with materials performance in oxygen-free environments containing CO_2, including "sour" conditions with H_2S present. Service limits for stainless steels and CRAs are generally well established. [7] The ISO15156 / NACE MR0175 and NACE MR0103 standards give detailed guidance on selection of metallic materials for H_2S containing environments. [8, 9]. There is also much experience on the effect of CO_2 on polymers. [10, 11]

CORROSION AND MATERIALS SELECTION ISSUES

Post -combustion Capture Process

The capture plant takes flue gases after combustion and, in the case of coal-firing, after an FGD unit. The incoming flue gas contains CO_2 with water, oxygen, some SO_x and NO_x and other contaminants and is extremely corrosive to carbon steel wherever free water is present.

Ducting

Incoming flue gas is a low pressure, large volume stream and will be handled by ducting rather than piping. Conditions are similar to the outlet end of FGD plant. The outlet stream from CO2 strippers or desorbers before compression in Post-Combustion and Precombustion processes is also a low pressure and high volume stream, but with higher purity CO2 and higher temperature than the flue gases.

A wide range of CRAs have been used for FGD outlet ducting from AISI[2] 316L (S31603), through higher alloy stainless steels, such as 317LMN (S31726) , 904L (N08904) and 6-Mo grades, to nickel-based alloys. Ducting is typically lined (wall-papered), while nozzles and connections are solid, and often in a higher grade alloy than the ducting linings. Properly applied (with a large number of slot welds to mitigate fatigue), CRA wall-papering is a low maintenance, lifetime solution; however some installations have suffered early damage and required substantial repairs and downtime. [12]

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[1] Electric Power Research Institute, 3420 Hillview Avenue, Palo Alto, California, USA
[2] American Iron and Steel Institute, 1140 Connecticut Ave., NW Suite 705, Washington DC, USA

The option of using carbon steel with non-metallic coatings or linings has frequently been considered for reduced capital outlay in FGD plants where maintenance can be tolerated. All polymer linings and coatings allow some permeation of water vapor and other species including CO_2 and H_2S, and eventually this will lead to disbondment of the lining and corrosion of the steel substrate. For coating, only resins which are resistant to water vapor at service temperature should be considered. [13] Service experience with rubber lining has generally been poor. Flake-glass vinylester (FGV) coated steel is a standard coating option for moderate temperature use, but only has an expected service life of around 10 years to major maintenance.

An alternative approach is to use large diameter filament wound glass reinforced plastic (GRP) pipe, large diameter sections may be filament wound in-situ. It is tolerant of wide variations in flue gas composition and levels of trace contaminants. GRP pipe typically has larger capital outlay than FGV-lined ducting but is expected to last a 25 year design life without major maintenance. [14]

Amine Unit

Amine gas treatment units are widely used in upstream oil and gas applications and in refineries for removing CO_2, H_2S and related species such as mercaptans, from hydrocarbon gas streams. In petrochemical service, carbon steel is generally the main material of construction. Austenitic stainless steels are typically used where there are high CO_2 loadings, for higher temperature areas and locations where erosion–corrosion may be an issue. [15, 16] Refinery amine systems normally aim to operate in oxygen-free conditions, and stringent measures are taken to minimise oxygen ingress. In contrast, the flue gas contains high levels of oxygen. Oxygen degrades conventional amines, forming a variety of products including organic acids and heat-stable salts, thus reducing the efficiency of operation, but also potentially increasing the corrosivity of the environment. As well as being corrosive to carbon steel, these acids can cause damage to stainless steels at the temperatures in the reboiler and stripper. Other undesirable contaminants in flue gases include sulfur-containing species (SO_2, sulfates etc), chlorides, ammonia and cyanides. Amine systems in carbon capture may also operate with higher CO_2 loadings in the lean amine than is usual for gas treatment applications, hence making the lean amine relatively more corrosive. [17] A great deal of effort has been made in developing amines suitable for carbon capture conditions. Corrosion behavior has been studied in laboratory conditions, and also in pilot and demonstration plant. So far, the indications are that conventional materials selections can be used: carbon steel for cold lean amine and 300-series stainless steels for rich amine, high temperature sections and high velocity areas.[18] Nevertheless, some caution is prudent and testing of materials with the specific amine chemistries is strongly recommended.

The Absorber Vessel in the amine system requires special consideration because of its size. For example, the absorber in the Mongstad demonstration plant (Norway) is 3.5 x 2m cross-section by 62 m height, [19] while absorbers for full-scale power plants are expected to be as much as 15 -20 m diameter. As the absorber runs at just over atmospheric pressure it is not a pressure vessel under normal design codes. Construction techniques used for similar units in FGD service include steel panel-towers with external stiffening, ring-stiffened circular steel towers or a slip-cast, reinforced concrete structure – the option used at Mongstad. It should be noted that post-weld heat treatment is necessary for coated or lined carbon steel constructions,[20] a significant issue on this scale of construction, and which therefore favors the concrete construction approach. Concrete does need protection from the acid gases. Tiling has been used in some FGD applications, while polymer lining is used at Mongstad. Polypropylene lining has shown good performance in field testing. [18]

Unlike the Absorber vessel, the CO_2 Strippers are pressure-vessels. At this stage there should be only be low levels of halides present as there are several washes and knock-out vessels before this point, so lower-cost CRAs such as S31600 stainless steel can be considered where carbon steel is not adequate. Depending on design requirements, duplex or lean duplex stainless steel may be more economic due to their higher strength. Otherwise, where chloride ions are carried over, more expensive CRA cladding materials with higher Mo content would be necessary. Stripper overheads are particularly

aggressive (high CO_2 partial pressure) and higher alloy stainless steels may be necessary, especially if the stripper is run at higher temperature and pressure than usual in order to improve the efficiency of the compression stages (see below).
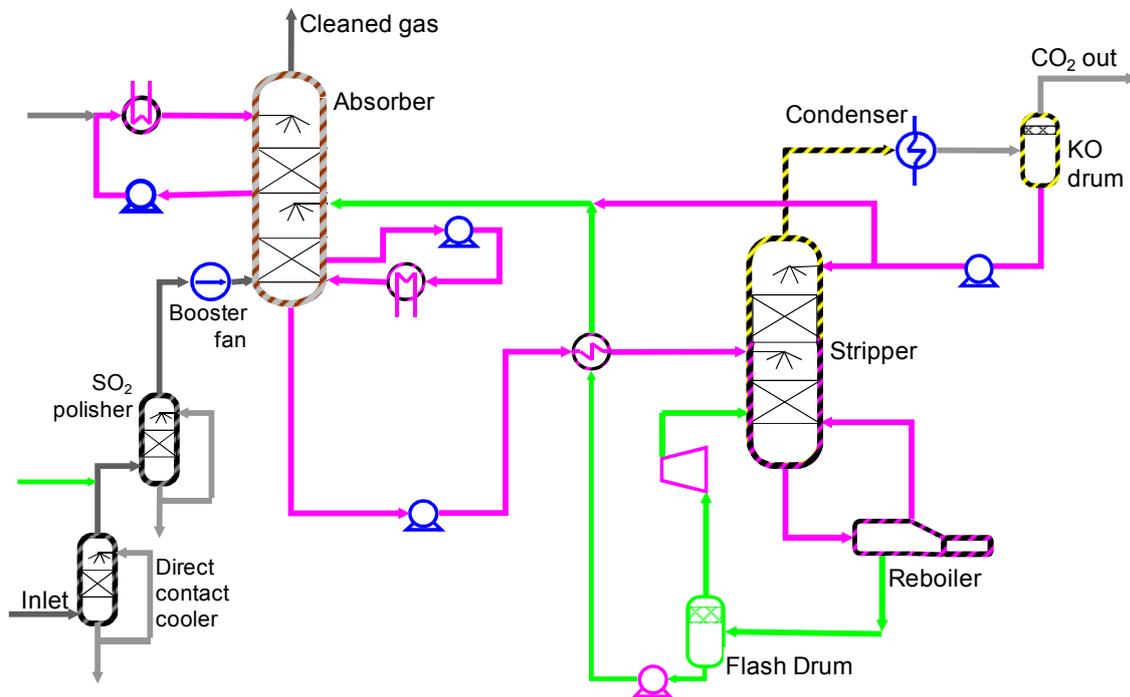

Figure 4   Schematic Materials Selection Diagram for Post Combustion Capture on a Coal-fired Power Plant

▬	Carbon / low alloy steels	▬	Martensitic stainless steel
▬	Carbon / low alloy steels + corrosion allowance	▬	Non metallic (flake glass/GRP/FRP/PP)
▬	Duplex stainless steel	▬	Nickel alloys
▬	Austenitic stainless steel	▬	Concrete
▬	Special stainless steel	▬	Aluminium, other specified materials
		═	Low temperature carbon steel

Oxy-fuel Capture Processes

Many projects have studied high temperature corrosion upstream of the capture plant in the oxy-fuel combustion unit. Much useful information on this topic is available through the IEAGHG [3] Oxyfuel Combustion Research Network.

The inlet to the capture plant is low pressure and acid-oxidising, similar to the Post-Combustion case and similar considerations apply for the inlet ducting. The inlet gas has to be raised to around 15-30 bar (1.5-3.0 MPa) pressure for the de-SOx / deNOx reactors in the CO_2 clean-up process. The higher pressure and temperature after compression will tend to favour use of CRA-lined ducting or piping for wet gas compared with GRP ducting. Although the average content of SO_2 is low, it is very soluble in water and there is a risk of dew-point corrosion from small volumes of acid mist or condensation in the

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inlet ducting and pipework. The reactions involving NO_x and SO_x are complex and so is prediction of which species are present at which points in the process, including possible upset conditions and start-up / shut-down states. A conservative materials selection is therefore advisable. Compressors in the inlet gas stream similarly require higher alloy materials than those on the export gas streams after the capture plant.

Conditions after the De-SO_x reactors are more benign and lower alloy CRAs such as AISI 300-series stainless steels can be used for wet areas. The gas is then dried to allow cryogenic separation, and carbon steel can be widely used from that point onwards. Minimum temperatures rather than the corrosion risks require stainless steel or aluminium for some items in the cryogenic separation unit, and a mercury removal unit is necessary to protect the aluminium components.[21]
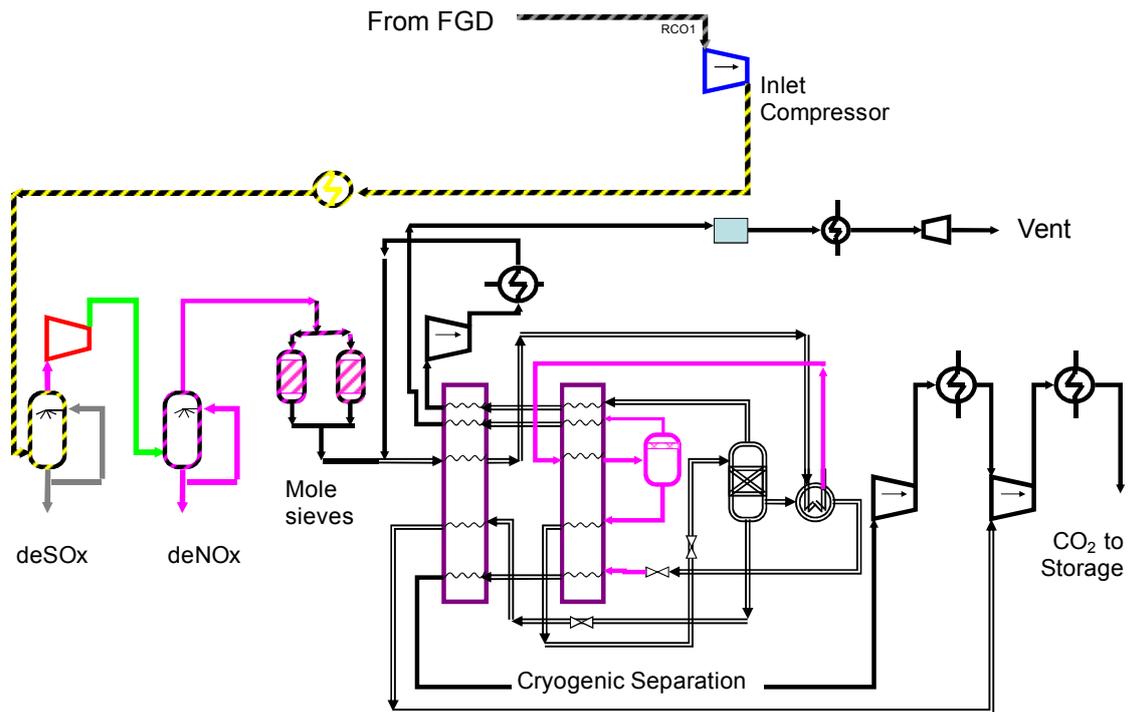

Figure 5: Schematic Materials Selection Diagram for Carbon Capture on an Oxy-Fuel Power Plant

Precombustion (IGCC) Capture Processes

Unlike the other two processes discussed, the inlet gas stream is essentially an oxygen-free, reducing environment and as such presents different corrosion and materials issues. H_2S present from coal-firing will require materials suitable for sour-service in many parts of the plant where wet conditions are possible either in normal operation or process upsets.

Materials selection for the shift reactors area has to consider high temperature corrosion issues including hydrogen attack, metal dusting and, in the case of coal-firing, sulfidation. Refinery experience provides an initial guide to materials selection, for example API RP 941,[22] although the hydrogen partial pressures are relatively low compared with some refinery environments. With gas–firing, carbon steels and Cr-Mo steels are adequate for many items. In the coal-fired case, sulfidation attack demands stainless steels, and stabilised grades such as AISI 321 (S32100) or 347 (S34700) are necessary for extended service at higher temperatures. Where minimal corrosion rates are desirable for specific components, then higher chromium stainless steels or specialised Cr-Ni-Co alloys may be needed.

Carbon steel can be used for some of the streams in the solvent system. In fact with coal-firing the presence of H_2S has a generally beneficial effect in reducing the corrosion rate and allows wider use of carbon steel than in gas-firing cases. Where CRAs are necessary (eg for turbulent areas, wet syngas or rich solvent), the oxygen-free conditions and absence of chlorides mean that 300-series stainless steels are generally adequate.

With coal-firing, ingress of oxygen into the capture process creates a risk of extremely corrosive conditions for both carbon steel and CRAs due to reaction of oxygen with H_2S, producing sulfur and sulfur acids. In the separate capture scheme, one possible source of oxygen ingress is the external gas stream used to strip CO_2 from the solvent in the H_2S concentrator vessel. Only a strictly limited oxygen content will allow the use of carbon steel and low-alloy CRAs in the solvent system. There are two obvious sources of low-oxygen stripping gas for the H_2S concentrator, namely high-purity nitrogen from the air separation unit, or a side stream from the cleaned syngas. It is critical that the oxygen content is strictly controlled in operations, and continuous monitoring of the oxygen content in the stripping gas stream is suggested. Other possible sources of oxygen ingress, including make-up chemicals for example, must also be controlled.
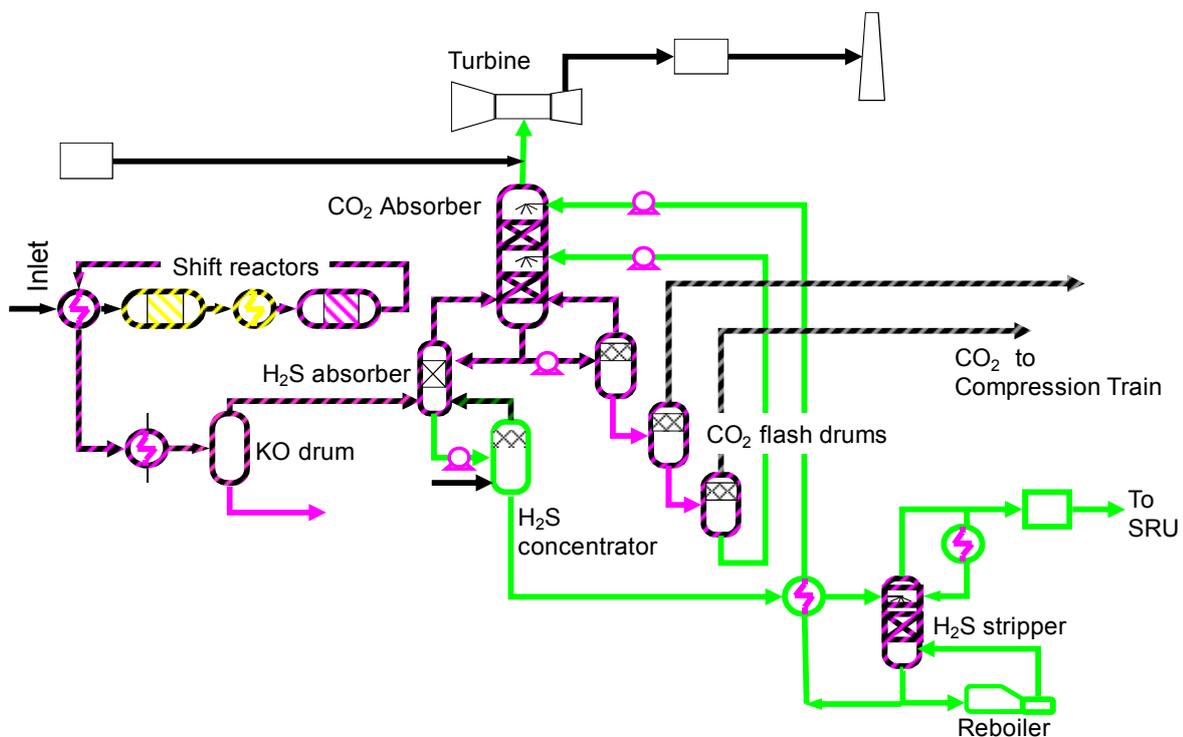

Figure 6: Schematic Materials Selection Diagram for Separate Capture on a Pre-combustion Power Plant .

COMPRESSION AND PROCESS INTEGRATION

Compression

Carbon dioxide capture plants need to have CO_2 compression facilities since the typical processes capture CO_2 at pressures well below those needed for transport and underground injection. Reciprocating compressors are used in some existing operations, but based on present studies, centrifugal compressors (either gear or in-line) are expected to be the base-line option for future power plant applications.[23][24]

In the oxy-fuel process, the CO_2 export stream is fully dried before entering the main compressor train, so carbon and low alloy steels can be used throughout.

In the other two processes, the CO_2 streams entering the compression trains are at or near dew-point and potentially corrosive. The gas streams by this point are expected to be relatively clean, with minimal levels of salts, solids or sulfur oxides. In particular, the low chloride conditions greatly reduce the risk of pitting or stress-corrosion in martensitic stainless steels. Despite the high CO_2 contents, the conditions are therefore not particularly aggressive. Operating conditions within compressors and on outlets side are normally dry due to the temperature increase on compression, but CRA materials are necessary for example to cover downtime conditions when condensation may occur. Martensitic stainless steels are often the materials of choice due to their combination of moderate cost, some corrosion resistance and the ability to achieve high strengths by heat-treatment.

At an intermediate point in the compression train, the stream is dehydrated. Usually this is at a point slightly below the critical pressure so that drying occurs in the gas phase, while the maximum amount of water has been removed by successive suction drums at the earlier compression stages. This minimises the capital and operating costs of the dehydration unit, although this is offset to some extent by the need to have corrosion resistant materials in all compression stages upstream of dehydration. Low alloy steels can be used for the final stages after the dehydrators.

Process Integration

The power required for compression represents a significant part of the parasitic energy consumption of the capture processes, perhaps as much as 50-80 MW for a full-size power plant or around 10% or more of the net power output. Optimising compression and its integration into the energy balance of the whole plant is therefore an important contribution to overall efficiency. Some of the possible strategies have implications for corrosion and materials selection.

Integration of compressor inter- and after-coolers with power generation can potentially recover some energy, e.g. by heating boiler feed water. This requires heat-exchangers at several positions along the compression train. One corrosion hazard identified here is that any leaks within the exchangers, either of CO_2 into feed water or of water into a high pressure, dry CO_2 stream have the potential for causing rapid corrosion damage. So, although the materials requirements for the exchangers may not be demanding, a high integrity construction is vital.

The overall compression range in post-combustion and pre-combustion processes is from near-atmospheric pressure to the pipeline inlet pressure of 100-150 bar (10-15 MPa). Depending on the power plant size, using a single axial compressor for the lowest pressure part of the compression could avoid the need for multiple compressor trains and achieve a small reduction in the overall power consumption. However, the axial compressor would have to be fully in corrosion resistant materials, which is relatively more expensive for that design than for centrifugal designs, making this an expensive option in CAPEX terms.

Raising the inlet pressure to the compressor train would of course reduce the energy requirement for compression. For amine gas treatment, this translates to a higher pressure and hence higher temperature in the CO_2 stripper. Increased temperature in the stripper will risk faster degradation of amine (depending on the particular chemical), but also more severe conditions as regards corrosion. Corrosion of 300-series stainless steels in existing amine units is known associated with both unusually high levels of thermal degradation products and with temperature excursions above the usual operating maximum of about 110-120°C in the stripper (reboiler temperature is slightly greater). The first corrosion mitigation measure is usually to control the temperature. Deliberate use of higher operating temperatures may demand more corrosion resistant grades of stainless steel. So far, most studies of amine performance and corrosion for carbon capture have focused on normal operating temperature ranges; the implications of increased temperature operation is an area for possible future study.

SUMMARY

There is a range of environments in the different CO_2 capture processes. In general, the high CO_2 levels mean that wet process environments tend to be aggressive and unprotected carbon steel cannot be used. Post combustion and oxy-fuel processes have predominately acid-oxidising conditions which present particular risks to stainless steels and corrosion resistant alloys, while reducing conditions are characteristic of the pre-combustion process.

The minor components in the process streams have a great influence on the corrosivity. In some situations, high-performance, expensive, materials may have to be used if trace components cannot be controlled within suitable limits.

For the moderate pressures and temperatures in the majority of capture plant process streams there is much useful materials performance experience from other industries. There is a relative lack of data (especially long-term data) on a few specific issues, such as corrosion risks in amine and other gas treatment systems with oxygen present or at operating temperatures beyond conventional limits. However, in general, the materials and corrosion knowledge exists to select cost-effective and reliable materials of construction for carbon capture plants.

There are several competing technical solutions and materials selections for some major capital items such as ducting, the compression trains and large, low-pressure vessels. Each solution has a different balance of initial cost, service life, expected down-time and maintenance intervals. Detailed studies are required to determine the optimum solution for each specific project.

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