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# **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 is expected to 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 capital and operating costs related to materials will help enable a wider and faster roll-out of carbon capture systems. It is apparent that there is a need to investigate the potential materials degradation and corrosion risks in the carbon capture processes and the related material selection issues.

The International Energy Agency Greenhouse Gas (IEA GHG) Research and Development Programme has sponsored a study of corrosion issues and materials selection in carbon capture, transport and storage. This paper summarises some of the outcomes of that study relating to the carbon capture systems. The focus is on materials degradation risks from the process streams and materials issues specific to the carbon capture processes. An overview is provided of corrosion and materials issues related to the three main carbon capture processes (Post-combustion, Precombustion (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.

Keywords: Carbon Capture; Corrosion; Materials; CO<sub>2</sub>

### 1. Introduction

In general, the carbon capture processes have so far only been operated on sub-commercial pilotscale 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 desulphurisation (FGD) plants and

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some gas processing applications. However, carbon capture processes do differ in some aspects which can be important for material performance and selection compared with equivalent gas processing systems in other industries.

The aim of the study was to cover corrosion and materials selection in the main alternative capture processes as fully as possible from capture plant to injection reservoir (materials for pipelines and wells are not covered in this paper). Generic process schemes were developed for carbon capture in Oxy-fuel, Post-combustion and Pre-combustion processes [<sup>1</sup>]. Some process variations and three different fuel types were included (natural gas and two coal types), so that a total of seven different process schemes were modelled in detail. The process stream data from this modelling was used as the basis of corrosion assessments and high-level materials selection. The materials selection for one of these process schemes, Post-Combustion with coal, is described in more detail in this paper, with shorter comments on the other processes. Issues generic to process plant, such as external corrosion, are not considered as standard industry practices exist to deal with these risks.

#### 2. 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 considered include general and localised  $CO_2$  corrosion; erosion –corrosion; various forms of stress-corrosion; low temperature hydrogen damage; microbially influenced corrosion; high temperature hydrogenation, sulphidation and metal dusting; and liquid metal embrittlement. 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, sulphur oxides, oxygen and hydrogen sulphide. The fuel type is significant here. 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.

#### **3. Related Experience**

The oil & gas industry has extensive experience with materials performance in environments containing CO<sub>2</sub>, including "sour" conditions with H<sub>2</sub>S present. Software packages are available to predict carbon steel corrosion rates in these conditions: "Electronic Corrosion Engineer"®, version 4, was used in the present study [<sup>2</sup>]. Service limits for stainless steels and CRAs are generally well established [<sup>3</sup>]. Corrosion in similar environments with low oxygen contents has also been studied to a limited extent [<sup>4</sup>, <sup>5</sup>]. The ISO15156 / NACE MR0175 and NACE MR0103 standards give detailed guidance on selection of metallic materials for H<sub>2</sub>S containing environments [<sup>6, 7</sup>]. There is also much experience on the effect of CO<sub>2</sub> on polymers [<sup>8, 9</sup>].

Materials performance in flue gas desulphurisation (FGD) plant is very relevant to similar acidoxidising conditions in carbon capture plant: the inlet for the capture plants in Post Combustion and Oxy-fuel scenarios when using coal firing would be 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 reducing conditions typically found in petrochemical processes or other CO<sub>2</sub>-handling industries. 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

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conditions drop below the dew point there is a risk of condensation of concentrated acids, and this is normally the 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 have conducted a useful survey of materials usage in FGD plant [<sup>10</sup>].

#### 4. Equipment common to the front end of capture processes

Low pressure, large volume flows are common at the front end of the capture plants and will be handled by ducting rather than piping. Typically, conditions are similar to the outlet end of FGD plant. A wide range of CRAs have been used for FGD outlet ducting from 316L, through higher alloy stainless steels, (317LMN, 904L and 6-Mo grades) to high nickel 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 [<sup>11</sup>].

The option of using carbon steel with non-metallic 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 vapour and other species including CO<sub>2</sub> and H<sub>2</sub>S, 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 vapour at service temperature should be considered [<sup>12</sup>]. Service experience with rubber lining has generally been poor. Flake-glass vinylester (FGV) coated steel is a standard coating option for moderate temperature use, with an expected service life of about 10 years to major maintenance. A less conventional approach is to use large diameter filament wound glass reinforced plastic (GRP) pipe, large diameter sections may be filament wound in-situ. GRP pipe also has initially larger capital outlay than FGV-lined ducting but is expected to last a 25 year design life without major maintenance.

#### 5. Equipment common to the exit of capture processes

In all three processes the export  $CO_2$  gas stream is compressed after the capture plant and before transport. There is extensive experience in compression of  $CO_2$  in fertiliser plants, in oil and gas service, and also in various  $CO_2$  injection projects, including the Weyburn and Statoil operations  $[^{13}, ^{4}, ^{15}]$ . Gas compression depends on small clearances between critical parts (eg impeller and casing diaphragm) and so demands minimal wear or corrosion. Compressor operating conditions are usually dry as the presence of droplets risks serious erosion damage to the high-velocity moving parts, but CRA materials are necessary, for example to cover downtime conditions when condensation may occur. Martensitic stainless steels are often the materials of choice for impellers and shafts due to their combination of moderate cost, some corrosion resistance and the ability to achieve high strengths by heat-treatment. The  $CO_2$  export streams are expected to be relatively clean. 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. Low alloy steels can be used for the stages of compression after dehydration.

#### 6. Post -combustion Capture Process

The capture plant takes flue gases after combustion and, in the case of coal-firing, after an FGD unit.  $CO_2$  is removed by a solvent process: a generic monoethanolamine (MEA) solvent process was used as the basis for process modelling. Fig. 1 provides a schematic of the process and outline of materials selection. 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. This is a low pressure, large volume flow and will be handled by ducting rather than piping.

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 [<sup>16</sup>].



Figure 2 Legend for Materials Selection Diagrams (stripes indicate lined / clad materials)

In petrochemical service, carbon steel is generally the main material of construction. Austenitic stainless steels are typically used for higher temperature equipment and locations where erosion – corrosion may be an issue [<sup>17</sup>]. Refinery amine systems normally aim to operate in oxygen-free conditions, and stringent measures are taken to minimise oxygen ingress. In contrast, the Post-combustion Capture system contains high levels of oxygen as well as trace SO<sub>2</sub>, which would create severe problems in conventional amine systems. Oxygen degrades amines, forming a variety of products including organic acids and heat-stable salts which increases the corrosivity of the environment and reduces the efficiency of operation. As well as being corrosive to carbon steel, these acids can cause damage to stainless steels at the temperatures in the reboiler [<sup>18</sup>]. Other undesirable contaminants include sulphur-containing species (SO<sub>2</sub>, sulphates etc), chlorides, ammonia and cyanides. The development of particular amine blends and of proprietary additives for CCS applications should alleviate the problem of oxidation [<sup>19</sup>, <sup>20</sup>]. Because reducing oxidation losses is in any case necessary for effective and economic operation, it is assumed for the purpose of materials selection that the formation of organic acids and heat stable salts will be controlled in any future CCS amine system.

The Absorber Vessel in the amine system requires special consideration because of its size, estimated at 15 -20 m diameter and 50 m height. As it runs at just over atmospheric pressure it is not a pressure vessel under normal design codes. Construction techniques used for similar units in FGD include steel panel-towers with external stiffening, ring-stiffened circular steel towers or a

circular reinforced concrete structure. Selection of appropriate stainless steels and CRAs as linings or for solid-wall construction will depend critically on the chemistry of the amine system, including oxygen and chloride levels. Both carbon steel and concrete must be lined for protection against the environment. FGV coating has generally proved more reliable than rubber lining of steel in similar applications, as it also has in ducting applications. Only specialist organic coatings are suitable for use with amines, which are strong solvents for many coatings. Tiling is more suitable for use on concrete. The leading candidates for absorber columns are therefore: concrete with acid resistant tiling; and sheet steel with FGV or epoxy–phenolic coatings. It should be noted that post-weld heat treatment is necessary for coated or lined carbon steel constructions [<sup>21</sup>], a significant issue on this scale of construction, and which therefore favours the concrete construction approach.

Unlike the Absorber vessel, the  $CO_2$  Strippers are pressure-vessels. At this stage there should be no halides present in the vapour or liquids, so a lower-cost CRA such as 316L stainless steel can be used where carbon steel is not adequate. Otherwise, where chloride ions are carried over, more expensive CRA cladding materials with higher Mo content would be necessary.

#### 7. Oxy-fuel Capture Processes

Two CO<sub>2</sub> output qualities were considered, namely a high CO<sub>2</sub> (99.99%) case and a low CO<sub>2</sub> (97%) case. The two configurations have a different layout only in the cryogenic CO<sub>2</sub> purification process, which does not affect significantly the corrosion risks and material selection in the capture plant.



Figure 3 Schematic Materials Selection Diagram for Carbon Capture on an Oxy-Fuel Power Plant

The inlet gas stream is acid-oxidising, similar to the Post-Combustion case, although temperatures and pressures are generally higher, favouring the use of CRA lined 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 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.



Figure 4 Schematic Materials Selection Diagram for Separate Capture on a Pre-combustion Power Plant

Conditions after the  $De-SO_x$  reactors are more benign and lower alloy CRAs such as 316/316L can be used for wet areas. All streams downstream of the molecular sieve dehydration are dry. Materials selection in the cryogenic separation unit is based on minimum temperature. There may be a need to fit mercury removal to protect the aluminium components.

## 8. Precombustion (IGCC) Capture Processes

In the CCS version of IGCC, shift reactors are added downstream of the gasification, in order to convert CO to CO<sub>2</sub>. The CO<sub>2</sub> generated from the shift reactors is then extracted in the CO<sub>2</sub> capture plant. A physical solvent process using a mixture of dimethyl ethers of polyethylene glycol was used as the basis of the study, as opposed to a chemical solvent process (e.g. using amines). Conventional IGCC plants generally have an acid gas removal system optimised for the H<sub>2</sub>S removal to minimise levels of SO<sub>2</sub> emissions [<sup>22</sup>]. In the CCS situation, it is desired to remove the maximum percentage of CO<sub>2</sub>, while in the coal-fired cases, also removing H<sub>2</sub>S. Two schemes were studied: Co-Capture removes CO<sub>2</sub> and H<sub>2</sub>S as a single export stream for storage; Separate Capture produces a higher purity CO<sub>2</sub> stream, with separate removal of H<sub>2</sub>S via a Claus-process sulphur recovery unit. This second option may be preferred if high levels of H<sub>2</sub>S are not acceptable in the gas export stream.

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<sub>2</sub>S present from coal-firing will require sour service materials 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 sulphidation. Refinery experience provides a good guide to materials selection, for example API RP 941[<sup>23</sup>], although the hydrogen partial pressures are relatively low compared with some refinery environments. In the coal-fired cases, sulphidation attack demands stainless steels and stabilised grades such as AISI 321 or 347 are necessary for extended service at higher temperatures, and where lower 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<sub>2</sub>S has a generally beneficial effect in reducing the corrosion rate and allows wider use of carbon steel than than in the gas-firing case. Where CRAs are necessary (eg for turbulent areas, wet syngas or rich solvent), the reducing conditions and absence of chlorides means that 316L is adequate.

A significant feature in the Separate Capture process is that an external gas stream is used to strip  $CO_2$  from the solvent in the H<sub>2</sub>S concentrator vessel, in order to increase the H<sub>2</sub>S to  $CO_2$  ratio in the solvent. The quality of this gas stream is critical: introducing significant concentrations of air (oxygen) into the system with the stripping gas creates a risk of producing extremely corrosive conditions for both carbon steel and CRAs due to reaction of oxygen with H<sub>2</sub>S. Only the very highest alloy CRAs would be resistant to these conditions, which would have substantial cost impact. There are two obvious sources of stripping gas for the H2S concentrator, namely nitrogen from the air separation unit, or a side stream from the clean fuel gas. A limited oxygen content will allow the use of carbon steel and low-alloy CRAs in the solvent system. 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 essential.

#### 9. Summary

The corrosion risks involved in three different CCS technologies and seven different process schemes have been assessed.

From a corrosion point of view, there is a wide range of environments in the different CCS processes. In general, the high  $CO_2$  levels mean that wet process environments tend to be acidic and unprotected carbon steel cannot be used. There are acid-oxidising conditions in many streams which present particular risks to stainless steels and corrosion resistant alloys. In some situations, highperformance, expensive, materials may have to be used if impurities and trace components in the environment are not controlled within suitable limits. Optionally non-metallic linings may be applied in parts of the plant but associated with a higher level of routine maintenance.

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

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 solvent gas treatment systems with oxygen present, and the in high pressure, supercritical / liquid CO<sub>2</sub> conditions during and after compression. However, in general, the materials and corrosion knowledge exists to select cost-effective and reliable materials of construction for carbon capture plants, whilst the associated costs and difficulty of fabrication may make some carbon capture plant options more practical or cost-effective than competing process approaches.

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<sup>1</sup> 

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