



## Assessing the risk of corrosion in amine-based CO<sub>2</sub> capture process



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### ABSTRACT

This paper presents a study on the risk of corrosion within a post-combustion and amine-based carbon capture installation with the use of selected risk assessment methods like the HAZard and OPerability study (HAZOP), Delphi technique and Fault Tree Analysis (FTA). As in alkanolamine plants, due to economic reasons most of the equipment and piping is constructed of carbon steel, these parts of the installations may suffer from corrosion by several agents like wet acid gases, oxygen and products of the degradation of amines. The study presented within this paper shows this does not only occur in the case of carbon steel, but also other types of materials used within the installation may suffer from corrosion. The correct choice of materials is vital in ensuring the long-term performance, safety and operational availability of CO<sub>2</sub> capture plants. A lack of information about previous operational problems or accidents within one-to-one size installations presents a great challenge when conducting risk assessment. This is why a methodology of risk identification and evaluation for CO<sub>2</sub> capture installations is proposed, along with its practical application. This method is based on the experience gained from worldwide pilot plants and from a Polish research project on the CO<sub>2</sub> capture process. All new technologies need to be investigated with special care, especially when having little knowledge about their behaviour while connected to the existing equipment of any power plant.

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### 1. Introduction

The combustion of fossil fuels to generate electricity and cement production is the largest source of CO<sub>2</sub> emissions. Fossil fuel combustion accounts for about 92% of total global CO<sub>2</sub> emissions (Oliwier et al., 2014). Global CO<sub>2</sub> emissions from fossil-fuel use and cement production reached 35.3 Pg CO<sub>2</sub> in 2013 and coal consumption was responsible for about 40% of total CO<sub>2</sub> emissions (Oliwier et al., 2014). Fossil fuels continue to dominate global energy structure and the problems of the CO<sub>2</sub> emissions from its combustion is a major global issue. As a result, in the need for the accelerated development of technologies for cleaner and more efficiently use of fossil fuels, Carbon Capture and Utilization (CCU) and Carbon Capture and Storage (CCS) are considered to have the

potential to reduce CO<sub>2</sub> emissions.

Nowadays, carbon capture technology readiness levels allow around 90% of the carbon dioxide (CO<sub>2</sub>) from power plants, production of steel, cement and other industrial processes to be captured.

Within the most commercially available technologies for chemical absorption of CO<sub>2</sub> the following five should be mentioned: Fluor's Econamine FG Plus, Mitsubishi Heavy Industries KS solvent, Cansolv Technologies, Aker Clean Carbon, and Alstom's Chilled Ammonia Process (Global CCS Institute, 2013; IPCC, 2005). All of these use either aqueous pure amines or blends of amines.

Chemical absorption processes based on organic solvents such as amines are currently the preferred option for post-combustion CO<sub>2</sub> capture. The most widely-studied solvent for post-combustion CO<sub>2</sub> capture is an aqueous solution of monoethanolamine (MEA). Amines have been used for many years for the removal of acid gases in gas treatment or in refineries. At least a dozen commercial CO<sub>2</sub> capture plants were commissioned globally, ranging in size from 90 to 1200 Mg/day CO<sub>2</sub> during 1978–2000

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**Table 1**  
Large-scale CCS projects in operation stage using amine-based capture method (Global CCS Institute, 2014).

Project name	Location	Operation date	Industry	Capture type	Capture capacity (Tg per annum)	Capture method
Boundary Dam Integrated Carbon Capture and Sequestration Demonstration Project	Canada	2014	Power Generation	Post-combustion capture	1.0	Absorption chemical solvent-based process (Amine), Shell Global Cansolv technology
In Salah CO <sub>2</sub> Storage	Algeria	2004	Natural Gas Processing	Pre-combustion capture (natural gas processing)	CO <sub>2</sub> cont. of 1–10%, is removed from the gas stream (injection suspended)	Absorption chemical solvent-based process (Amine)
Sleipner CO <sub>2</sub> Storage Project	Norway	1996	Natural Gas Processing	Pre-combustion capture (natural gas processing)	0.9	Absorption chemical solvent-based process (Amine)
Snøhvit CO <sub>2</sub> Storage Project	Norway	2008	Natural Gas Processing	Pre-combustion capture (natural gas processing)	0.7	Absorption chemical solvent-based process (Amine)

(Rameshni, 2009). The first commercial process plant with a capacity of 90% recovery of CO<sub>2</sub> from flue gas containing 8%<sub>vol</sub> CO<sub>2</sub> was built in Malaysia in 1999, by Kansai Mitsubishi Carbon Dioxide Recovery, (Rameshni, 2009). Currently, Fluor Company is actively trying to commercialize CO<sub>2</sub> capture technologies based on MEA (30%w/w solution) with inhibitors to prevent degradation and equipment corrosion (Global CCS Report, 2012). Fluor's technology (Econamine FG Plus) offers a post-combustion CO<sub>2</sub> capture option to remove CO<sub>2</sub> from low-pressure, oxygen-containing, flue gas streams. The solvent formulation is designed to recover CO<sub>2</sub> from streams containing low amounts of oxygen that are at near-atmospheric pressure. The use of aqueous MEA for the removal of CO<sub>2</sub> from flue gases is described elsewhere (Global CCS Report, 2012; Johnson et al., 2009; Reddy and Gilmartin, 2008; Tenaska, 2012).

There are 22 large-scale integrated CCS projects (LSIPs)<sup>1</sup> in operation and construction (execute stage) around the world. Total CO<sub>2</sub> capture capacity of the world's large-scale CCS projects is around 40 Tg per annum (Global CCS Institute, 2014). It should be emphasized that only one of them, the Boundary Dam Integrated Carbon Capture and Storage Project in Canada, is a commercial-scale project – the world's first full scale project. The list of CCS projects in the operational stage, using amine-based capture method, is presented in Table 1.

Corrosion has always been considered as one of the major operational problems in alkanolamine power plants (Mesgarian, 2014). The results of Worldwide research (Kittel et al., 2009; Wang et al., 2011; Kwak et al., 2012; Cousins et al., 2013; Radgen et al., 2014; Gao et al., 2011) show that the rate of corrosion strongly depends on the temperature and purity of the flue gas, as well as on the type of materials selected for the installation's construction.

The main goal of this study was to analyse the mechanisms affecting the amine-based carbon capture process and to identify possible deviations from the regular workings of the full scale installation in order to limit, or even avoid the risk of corrosion. To achieve this goal, firstly, a HAZOP analysis of the system was conducted, supported by the Delphi technique, in order to assess the criticality of possible deviations from the expected performance of the system. The knowledge of the researchers and the practitioners, who were dealing with the post-combustion capture process, was crucial when identifying parts of the installation which were

possibly most affected by the process itself. Secondly all the available information concerning worldwide operational incidents was analysed, not only within the CCS projects using an amine-based capture method, but also from laboratory-scale research on the influence of amines on different materials. Finally a new approach to risk evaluation for CO<sub>2</sub> capture installations was proposed, with the establishment of criteria for likelihood and severity of each risk.

## 2. Causes of corrosion in alkanolamine plants

Corrosion problems in the Worldwide CO<sub>2</sub> capture process occur in most frequent failures. There is a great deal of experience from other industrial installations where high quantities of CO<sub>2</sub> are being handled, for example in the petrochemical industry or the oil and gas industry. However, the carbon capture process differs in one important aspect. It is not only the influence of CO<sub>2</sub> itself on the equipment, but also the presence of the oxidising acid species (NO<sub>x</sub> and SO<sub>x</sub>), that makes a significant contribution to the acidity of the flue gas. Due to the presence of free water, flue gas becomes corrosive to most parts of the installation's equipment. In the case of alkanolamine plants the proper selection of materials used for carbon capture unit strongly depends on the chemistry of the amine system. Most commonly, carbon steel will be used, as it is an economical solution. However, for some parts of the unit other types of materials must be considered, as the expected design life of the installation may not be sufficient.

According to Kohl and Nielsen (Kohl and Nielsen, 1997) corrosion of carbon steel in alkanolamine plants is influenced by high operating temperatures, rich and lean amine loadings (moles acid gas/mole amine), the ratio of CO<sub>2</sub> to H<sub>2</sub>S in the acid gas, amine solution contaminants including amine degradation products, amine solution concentration and amine type.

Two types of corrosion caused by wet acid gas and by amine solution were identified in the CO<sub>2</sub> post-combustion capture process with alkanolamines (Nielsen et al., 1995). The grade of corrosion mostly depends on the type and quality of material within the installation and the acidity of the environment.

Wet acid corrosion is encountered in all parts of the installation made of carbon steel and which have contact with the aqueous phase which contains a high concentration of dissolved acid gases CO<sub>2</sub>, H<sub>2</sub>S, as well as NH<sub>3</sub> and HCN (Ropital and Jones, 2009; Bosen, 2000). Strong acid corrosion involves a reaction between iron and hydrogen ions and, hence, largely depends on pH (IEAGHG, 2010). In wet environment conditions these gases convert into acids, which leads to pitting in different parts of the installation. Corrosion rates of carbon steel under wet conditions may vary from 1·10<sup>-3</sup> m/year to 18·10<sup>-3</sup> m/year (IEAGHG, 2010). These differences may be observed especially at the inlet to absorbers or coolers

<sup>1</sup> LSIPs projects are defined as projects involving the capture, transport, and storage of CO<sub>2</sub> at a scale of: at least 800,000 tonnes of CO<sub>2</sub> annually for a coal-based power plant, or at least 400,000 tonnes of CO<sub>2</sub> annually for other emissions-intensive industrial facilities (including natural gas-based power generation) – according Global CCS Institute.

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