



A technology review for regeneration of sulfur rich amine systems

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ABSTRACT

Reducing the capital cost of post combustion CO₂ capture by eliminating flue gas desulfurisation (FGD) pre-treatment, requires management of the amines preferential SO₂ absorption. Novel technologies such as CS-Cap restrict the impact of SO₂ to only a small fraction of the amine inventory resulting in high sulfate burden amines. Traditional thermal reclamation of these spent absorbents has advantages regarding simplicity, but ranks poorly for industrial ecology around PCC. These amines require low energy regeneration technologies compatible with their physico-chemical properties that also maximise the potential for valorising by-products. This review summarises the sulfur chemistry and outlines several amine reclamation processes. It assesses the status of established and novel regeneration technologies for their applicability to high sulfur loaded amines. Should deep sulfur removal be required, a hybrid approach with initial bulk removal (as product) followed by a polishing step to further reduce sulfur is prospective. A preliminary estimation of the relative cost of using standard reclamation methods for treating Sulfur loaded CS-Cap absorbent revealed the cost would increase due to its higher sulfate burden despite comparable treatment volumes. Research gaps are identified which would enable better comparison between the costs of traditional FGD versus higher reclamation costs for combined capture technologies.

1. Introduction

Given its wide availability, low cost and high energy density, coal will remain an important global energy source into the near future (MIT, 2007; Takeshita and Yamaji, 2006). In 2015, the Paris Agreement was adopted under the United Nations Framework Convention on Climate Change (UNFCCC). This agreement aims to limit global average temperature increase to below 2 °C above pre-industrial levels. To meet this target with continued coal use, methods for lowering or removing CO₂ emissions from coal-fired power stations are required. Recent studies suggest that the 2 °C target will not be achievable without the deployment of large-scale Carbon Capture and Storage (CCS) (Peters et al., 2017; Rogelj et al., 2016; IPCC, 2014).

Currently, the most technologically advanced method for removing CO₂ from coal-fired power station flue gas is the amine based post combustion capture process (PCC) (Liu et al., 2017). Major drawbacks of this process include the large infrastructure requirements and parasitic load on generation (resulting in prohibitive costs without offsets or CO₂ product sales) (Zhang et al., 2017). This is especially true for coal PCC processes, which have the highest incremental cost relative to a

similar plant without CO₂ capture (Folger, 2013).

The implementation of amine based PCC technology to power plants requires flue gas pre-treatment to remove reactive acid gases, i.e. SO_x and NO_x, prior to CO₂ absorption to maintain capture efficiency (Liu et al., 2017). SO₂ is the second most abundant acid gas present after CO₂ and despite flue gas SO₂ concentrations typically 1000 times lower than CO₂, it is comparatively more soluble and forms a much stronger acid in aqueous solution. Flue gas SO₂ concentrations < 10 ppm are recommended (Davidson, 2007) for PCC operation. As SO₂ is a stronger acid gas than CO₂, its absorption into the basic solutions used for CO₂ capture is faster and dominant over CO₂ absorption (Beyad et al., 2014). This also means that release of SO₂ during amine regeneration does not occur thermally at the same conditions used for CO₂ stripping. This leads to accumulation of absorbed SO₂ as heat stable salts (HSS) over time, progressively neutralising the capture solution, reducing its capacity to absorb CO₂ (Beyad et al., 2014). In an operating amine plant, it is desirable to limit the level of HSS in solution as they can affect operation through reduced capacity, increased corrosion and absorbent foaming. Consequently, flue gas desulfurization (FGD) is an essential requirement for PCC (Adams, 2010).

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Absorption of SO₂ in water is summarised in reactions (1)–(5) below. It is a function of pH change as the absorption of SO₂ is a combination of gas absorption (reaction (1)) and a sequence of reactions rapidly attaining equilibrium (reactions (2)–(5)). Bisulfite is also in acid/base equilibrium with sulfite according to reaction (4) (Puxty et al., 2014). Moreover, due to the presence of O₂ in the flue gas, S (IV) is irreversibly oxidized to form S (VI) (e.g. sulfuric acid, bisulfate and sulfate). In the oxidation of sulfite to sulfate (reaction 6) the sulfate (VI) formed is more stable and less soluble than sulfite (IV).



MEA reacts and acts as a weak base as shown in reaction (7) below.



A laboratory study did not detect any direct reactions between SO₂ and MEA under controlled laboratory conditions (Beyad et al., 2014) and unlike CO₂ reacting with aqueous amines to form carbamates, there was no formation of analogous sulfurous acid amide under the conditions tested.

The net reaction of SO₂ in aqueous amine solutions is to form sulfite with the release of two protons. When exposed to O₂ sulfite will oxidise to sulfate (SO₄²⁻), which is a stronger acid and less soluble than its S (IV) precursor (Puxty et al., 2014).



Absorbed SO₂ is expected to rapidly oxidise to sulfate in the presence of dissolved oxygen (Reynolds et al., 2012). The HSS formation between flue gas SO₂ and MEA has been checked experimentally in pilot plant studies with 75% of the absorbed SO₂ being removed as sulfate (IEAGHG, 2012). Similarly (Lim et al., 2015) found the dominant sulfur species in a pilot plant MEA sample to be sulfate. The main impact of oxidation of SO₃⁻ to SO₄²⁻ is on the solubility of their salts concluding with the formation of the heat stable salt of sulfate with MEA (reaction (8)). Heat stable salts (HSS) are formed when a stronger acid than CO₂ is used to protonate MEA (Tanthapanichakoon Winyu and Veawab Amornvadee, 2006). The term ‘heat stable’ is used because the protonated MEA cannot be regenerated by heating, as the vapour pressure of the acid corresponding to the anion is too low (El Moudir et al., 2014). For this reason, it is desirable to reduce flue gas SO₂ concentrations to low levels (typically < 10 ppm) prior to the CO₂ capture process.

FGD is utilised primarily in the northern hemisphere to capture SO₂ from flue gases. However, existing FGD units cannot necessarily reduce SO₂ levels to or below 10 ppm without additional scrubbers. Where FGD is not currently utilised, additional voluminous pre-treatment contactors will be required, adding significantly to the overall cost of PCC (of the order of 100 s of millions of dollars in capital and operating costs for typical 500MWe boiler) (Kohl and Nielsen, 1997). Due to the typically low sulfur content in their coal, power stations in Australia do not currently utilise FGD or Selective Catalytic Reduction (SCR) (Yu et al., 2012). As a result SO₂ concentrations in power station flue gas emissions are in the prohibitive 100–600 ppm range (Reynolds et al., 2012). This imposes a serious barrier to the implementation of standard PCC technologies.

To mitigate the high cost involved in installing new FGD units or retrofitting the older FGD units, the concept of combined capture of

CO₂ and SO₂ is evolving as a next generation PCC technology. This approach utilizes the simultaneous removal of SO₂ and CO₂ in a single absorber column to remove both species. This concept has the potential to substantially reduce the capital and energy requirements of PCC.

1.1. Combined capture concepts

The Shell-Cansolv process is a combined capture process that removes SO₂ and CO₂ from gas streams (Shaw, 2009). This technology is employed on the first commercial PCC plant installed at SaskPower’s Boundary Dam coal-fired power station. SO₂ and CO₂ are removed in separate stages using different amine blends. The SO₂ and CO₂ rich streams are thermally regenerated, producing a sulfuric acid and concentrated CO₂ product streams respectively. Heat integration is possible between the SO₂ and CO₂ capture loops, improving the efficiency of the process. The combined capture process proposed by the Babcock and Wilcox Company similarly removes SO₂ and CO₂ from gas streams using two distinct stages (Paul S. Nolan, 2002).

The Netherlands Organisation for applied scientific research (TNO) has developed a combined capture process known as the CASPER process (Misiak et al., 2013) which was demonstrated in Australia by CSIRO. Here, an amino acid salt solution removes both SO₂ and CO₂ from the gas stream using a single absorbent, and single contacting column. Absorbed CO₂ is removed via a heated stripping column, producing a concentrated CO₂ product stream, and regenerated CO₂ lean absorbent. A slip stream of the CO₂ lean absorbent is treated to remove absorbed SO₂ via precipitation. The absorbent is cooled, initiating precipitation of the potassium sulfate product. This is filtered from solution, with the SO₂ lean absorbent recycled back to the absorber column for re-use. This process has been demonstrated at pilot-scale on a coal combustion flue gas. The conversion of absorbed sulfite to sulfate was determined to be a rate-limiting step. An economic analysis of the process suggested significant savings over a more conventional system employing FGD with CO₂ capture via 30 wt% Monoethanolamine (MEA) (Cousins et al., 2014).

The concepts for combined capture patented by Cansolv Technologies Inc. and The Babcox & Wilcox Company use absorbents that are physically separate and chemically different. SO₂ is removed in the bottom section of an absorber column using an aqueous tertiary amine or calcium carbonate solution and CO₂ is captured in the upper section using an aqueous primary or secondary amine solution (Beyad et al., 2014). Work completed at the CSIRO had observed that SO₂ retained its high affinity for absorption into amine absorbents, even when that absorbent was already fully loaded with CO₂ (Beyad et al., 2014). This understanding has led to the development of the CS-Cap combined capture process using a single absorbent for both the SO₂ and CO₂ capture steps.

1.2. The CSIRO CS-Cap process – A cost effective carbon capture solution for Australian coal fired power plants

This patented co-capture process uses a single absorbent and is SO₂ tolerant (Meuleman et al., 2012). Fig. 1 reveals a schematic of the process wherein the absorbent lean in CO₂ and SO₂ (blue stream) entering from the top of the absorber contacts with the flue gas entering the absorber from the bottom. As the gas stream moves up, SO₂ absorption occurs in the bottom section. However, instead of the full absorbent stream, only a small part of the total stream (bleed stream) is exposed to this part of the column. Though the absorbent is CO₂ rich (red stream) at this point, it absorbs SO₂ due to the absorbent’s selectivity for SO₂. Only between 0.01% – 3% of the total CO₂ rich absorbent is needed to remove SO₂ and produces a small but highly SO₂ concentrated (100–115 g/kg of SO₄) absorbent stream (green stream). This stream is sent for sulfur recovery and absorbent regeneration prior to its return to the top of the absorber (Puxty et al., 2014). As the CS-Cap process limits SO₂ contact with the bulk of the amine it will

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