Remediation of monoethanolamine after exposure to brown coal flue gases

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ARTICLE INFO

ABSTRACT

Monoethanolamine (MEA) is the solvent most commonly considered for post-combustion capture. However, the solvent will accumulate a range of contaminants during use, notably heat stable salts, that reduce its performance. This work considers the removal of these contaminants from MEA solutions that had been exposed to over 50 and 1800 h of post combustion capture of flue gases from a brown coal-fired power station. Analysis indicated that these MEA solutions contained significant quantities of heat stable salts including iron, potassium, sulphate, nitrate and organic anions, particularly in the older sample. Both solutions were initially neutralised to free the protonated amine, which led to precipitation of some impurities within the older solvent. Nanofiltration was considered as an approach to further concentrate impurities, but was ineffective due to low permeation rates and low rejection of monovalent salts, at less than 20%. It was effective in concentrating metal contaminants and may be useful into the future for this reason. Conversely, electrodialysis was effective in removing up to 91% of the ionic content of the solutions, although the current efficiency fell at low feed conductivities. Monovalent salts such as sodium, potassium and nitrate were removed more readily than multivalent salts such as iron and sulphate. MEA loss was consistent with our prior work at around 0.15 g/m^2 s and was predominantly as the free amine rather than the carbamate salt.

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1. Introduction

The use of monoethanolamine (MEA) to capture carbon dioxide is a common operation in natural gas sweetening and is considered as the baseline solvent for the large scale capture of this greenhouse gas from post combustion flue gas streams (Boot-Handford et al., 2014). However, over time, the MEA accumulates impurities (Dumée et al., 2012; Reynolds et al., 2012). Anionic impurities include heat stable salts such as formate, oxalate and acetate from reactions with residual oxygen (Goff and Rochelle, 2004), sulphites, sulfates from reaction with SOx and nitrates and nitrites from reaction with NOx (Supap et al., 2009). Chlorides can also accumulate from residual HCl in the flue gas stream (Strazisar et al., 2003). These anions are generally associated with protonated amines (MEAH$^+$), but ammonium cations may also form and metal cations such as Fe, Cu and Ni can also accumulate through corrosion (Chi and Rochelle,

2002a). Oligomers and polymers can also form through thermal degradation (Strazisar et al., 2003). These impurities impair operation by reducing the total MEA strength and also by increasing the solvent viscosity. Further, they lead to increased rates of equipment corrosion, which ultimately results in necessary replacement.

In natural gas sweetening operations, these impurities are often removed simply by routine solvent replacement. However, this approach is unlikely to be economic for large scale carbon capture. The addition of NaOH or a similar alkali can be used to release the protonated amine and recover this solvent component. This process is referred to as neutralisation, although the pH of the total solution actually deviates further from neutrality during this step (Eq. (1)):

$$MEAH^+ + OH^- \rightarrow MEA + H_2O \tag{1}$$
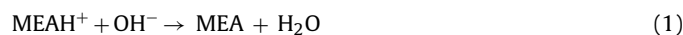
Neutralisation may also result in some conversion of the carbamate anions to bicarbonate and carbonate species, as these are more stable at the elevated pH (Conway et al., 2011). In turn, this may lead to precipitation of some salts (Liu et al., 1995). The salts precipitated during neutralisation and other solid impurities can

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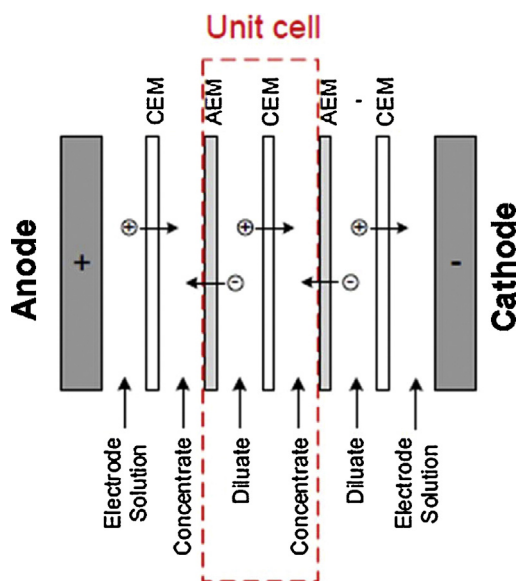 E-mail address: sandraek@unimelb.edu.au (S.E. Kentish).

Fig. 1. A schematic diagram of the ED rig. Diluate = the feed MEA solution that is gradually depleted of ionic impurities. Concentrate = the aqueous solution that is gradually gaining ionic impurities. CEM = cation exchange membrane, AEM = anion exchange membrane.

be removed by filtration. However, even with such neutralisation and filtration, the solvent inevitably builds in concentration of heat stable anions and undesirable metal cations, which can lead to increased corrosion rates. Further purification is required to remove these ionic impurities. Thermal reclamation is the most well known approach for solvent purification and involves evaporation of the amine solution, leaving behind a sludge containing the contaminants for disposal (Aboudheir et al., 2015). Alternatively, in ion exchange, the contaminated solvent is passed through a sequence of beds packed with ion exchange resin. The charged impurities are adsorbed onto the resin material, releasing either H^+ or OH^- ions in exchange. The bed is later regenerated through the passage of an acid or base, which releases the impurities into a wastewater stream and replaces the H^+ and OH^- ions on the resins. A third option is electrodialysis (ED), which operates by passing an electrical current across a stack of alternating cation selective and anion selective membranes (Strathman, 2004; Kentish et al., 2015) (Fig. 1). Charged impurities pass across the membranes in response to the electrical field, but their movement is restricted when they encounter a membrane of opposing selectivity. This causes these impurities to accumulate in every second channel, forming what is known as the concentrate stream. Conversely, charged impurities are depleted from the alternate channels, forming the diluate stream, which in the present case is purified MEA.

In our prior work, we have also considered nanofiltration (NF) to concentrate the salts within a contaminated solvent and thus reduce the scale and increase the efficiency of downstream electrodialysis. Nanofiltration is a pressure driven membrane process but one that also uses a charged membrane. In this case, the salts are concentrated in the retentate stream, as they are rejected from the membrane due to their charge. Clean neutral MEA permeates the membrane and can be returned to the main solvent process.

While the clean-up of these impurities will be an important component of any post-combustion capture process, there is little information on the efficacy of various approaches in practice. Sexton et al. (2014) provide a comparison based on desktop simulation, but do not provide any experimental data on these operations. Both Volkov et al. (2014) and our own prior works (Lim et al., 2014a, 2014b) present results based on synthetic solutions prepared in

the laboratory. However, data from experiments with amine solutions after exposure to real flue gases is very limited. Vitse et al. (2011) show that electrodialysis combined with mechanical filtration can be effective in maintaining the concentration of heat stable salts below 0.5 wt% in a proprietary advanced amine solvent (Dow UCARSOL™ FGC 3000), but provide no process information on the operation of the ED unit. Bazhenov et al. (2014) describe a two stage ED operation tested on an MEA solution that was capturing carbon dioxide from a bituminous-coal fired power station for up to 1000 h of operation. In single stage operation, the total anion concentration was reduced from 2.3 g/L to 0.9 g/L within an hour, with all anions including nitrate, sulfate, formate, acetate and oxalate reducing substantially in concentration. However, the concentration of heavy metal cations was not reduced.

In the present work, we test the viability of both nanofiltration and electrodialysis to clean up MEA solutions of around 25 wt% amine, that have been used for 50+ and 1800+ hours respectively in flue gas capture. The solutions were generated from the capture of carbon dioxide from the flue gases of the AGL Loy Yang coal-fired power station in the Latrobe Valley, Victoria, Australia by CSIRO. The aim of the work is to validate whether these processes can be effective when applied to amine solutions that have been exposed to post combustion flue gases and to provide data for future workers on the process parameters that provide optimum performance.

2. Experimental

2.1. Materials

Aged MEA (MEA1800+ (Azzi et al., 2014) and MEA50+) was sourced from the Post-combustion Carbon Capture pilot plant owned and operated by the CSIRO at AGL Loy-Yang power station and described in detail by Artanto et al. (2012) and Cottrell et al. (2009). This power station uses Victorian brown coal and the concentrations of NOx and SOx in the flue gas are substantial (150–250 ppm NOx (of which >98.5% is NO) and 120–200 ppm SOx) (Artanto et al., 2012). However, SO_2 and some NOx (the part that is not NO) is washed off in a pre-treatment column fed with 32 wt.% NaOH to keep the pH between 8.5 and 9.2, so that the concentrations that reach the MEA absorber are 120–245 ppm NO and <10 ppm SO_2.

The MEA had been stored for some months prior to delivery and hence it is possible that some carbamate anions had been converted to bicarbonate species. It is well known that carbamates will undergo such a reaction, but it is usually too slow to be relevant in active post-combustion capture operations (Astarita et al., 1964).

2.2. Solution pretreatment

Both NF and ED processes operate best at low CO_2 loadings (Liu et al., 1995), where the carbamate concentrations are minimised. While the CO_2 loading of the MEA1800+ was reasonably low as received (0.12, see Table 1), the CO_2 loading of the MEA50+ was 0.31, too high for effective ED or NF. Hence, this loading was reduced by simple boiling of the solution prior to use. In industrial practice, the solution for reclamation would be taken from the cool, lean solvent circuit, where the CO_2 loading should be less than 0.15.

Thermal boiling of MEA50+ solvent was carried out in batches using a 2 L round bottom flask with a condenser. The flask was filled with 1.5 L solvent and heated to a temperature of 110–120 °C at atmospheric pressure. Cold water (single pass) was used in the condenser to reduce the loss of MEA through evaporation. Small samples (approx. 5 mL) were taken periodically to monitor the loss of MEA and CO_2 from the solution. The boiling was continued until the measured CO_2 loading was less than 0.15 mol CO_2/mol MEA