

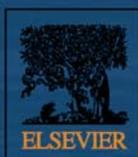
# JES

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## Could wastewater analysis be a useful tool for China?



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Review article

# Amine reclaiming technologies in post-combustion carbon dioxide capture

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## ABSTRACT

Amine scrubbing is the most developed technology for carbon dioxide (CO<sub>2</sub>) capture. Degradation of amine solvents due to the presence of high levels of oxygen and other impurities in flue gas causes increasing costs and deterioration in long term performance, and therefore purification of the solvents is needed to overcome these problems. This review presents the reclaiming of amine solvents used for post combustion CO<sub>2</sub> capture (PCC). Thermal reclaiming, ion exchange, and electrodialysis, although principally developed for sour gas sweetening, have also been tested for CO<sub>2</sub> capture from flue gas. The three technologies all have their strengths and weaknesses, and further development is needed to reduce energy usage and costs. An expected future trend for amine reclamation is to focus on process integration of the current reclaiming technologies into the PCC process in order to drive down costs.

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## Introduction

Carbon capture and storage (CCS) is a means of mitigating the contribution of fossil fuel emissions to global warming, based on capturing CO<sub>2</sub> and storing it away from the atmosphere by different means. Amine scrubbing is currently the most developed technology and is expected to be available commercially within the next decade to enable CO<sub>2</sub> capture from flue gas streams. Alkanolamines such as monoethanolamine (MEA), diethanolamine (DEA), N-methyldiethanolamine (MDEA), as well as amine blends traditionally have been investigated for this application. Other amines under active consideration for CO<sub>2</sub> capture are sterically hindered amines such as 2-amino-2-methyl-1-propanol (AMP) (Sartori and Savage, 1983; Mimura et al., 2000), and piperazine (PZ) (Rochelle et al., 2011), which is a cyclic diamine. MEA is so far the most studied solvent in this application and MEA based scrubbing is often used as a base case for evaluation of the PCC processes (IEAGHG, 2012; IPCC, 2005).

Fig. 1 illustrates a typical configuration of amine based process for PCC. A flue gas stream containing approximately 10 vol.% CO<sub>2</sub> and 5 vol.% O<sub>2</sub> is counter-currently contacted with the aqueous amine solution in an absorber column, which is operating at 55°C and 1 atmosphere pressure (Rochelle et al., 2001). The CO<sub>2</sub> rich amine solution exits at the bottom of the absorber column and is then sent through a counter-current heat exchanger, where it is pre-heated by the lean amine solution before being sent to the stripper column. The CO<sub>2</sub> is liberated from the amine solution in the stripper, which operates at 120°C and 1 atmosphere pressure. In the stripper, heat is provided by the steam from the reboiler. The gas leaving the stripper is dehydrated and compressed before transport and sequestration. The hot lean amine solvent is passed back through the cross-exchanger and back to the absorber for further CO<sub>2</sub> removal with a slip stream being sent to a reclaimer to remove solvent impurities.

Solvent losses often occur in an amine-based absorption/stripping system due to solvent volatility and degradation. Volatility is the loss of volatile amine off the top of the absorber in the exiting, treated flue gas. A well designed water wash

column can be used to recover the majority of amine losses through volatility.

All amine solvents are subjected to degradation as a result of the impurities either in the feed flue gas or those introduced to the amine system from other sources (ElMoudir et al., 2012). In PCC operations, the solvent degradation depends upon both flue gas composition and the type of pre-treatment operations. As the amine-based process was applied at first to natural gas sweetening, then to gas-fired flue gas, and finally to coal-fired flue gas, the impurities in the flue gas stream become more and more complex (Kohl and Nielsen, 1997; Dumée et al., 2012). Solvent degradation due to the presence of high levels of oxygen, SO<sub>x</sub>, NO<sub>x</sub> and fly ash in coal-fired flue gas causes increasing deterioration in long term performance.

Amine solutions are degraded with the impurities to form heat-stable salts (HSSs) and amine degradation products. These contaminants cause reduction of CO<sub>2</sub> absorption capacity, corrosion, foaming, fouling, and increase in viscosity and release of pollutants from toxic degradation products (Ciferno et al., 2009; Strazisar et al., 2003). To operate amine processes more effectively and reduce environmental pollution, these problems should be addressed. Maintaining proper amine solution quality in CO<sub>2</sub> capture plants is an important requirement. The solvent management strategies can be divided into two categories: degradation prevention and inhibition and solvent cleaning. Solvent degradation inhibition seems to be one method of protecting solvent (Soria, 1998) and more applications may be seen in the future (ElMoudir et al., 2012) but are beyond the scope of this work, and so solvent cleaning forms the focus of this review.

## 1. Amine reclaiming technologies

Heat stable salts refer to the salts formed by reactions of amine and its acidic degradation products and impurities. These salts are not regenerated under stripper conditions. Most acids and acidic gases that exhibit a lower pKa than CO<sub>2</sub> will react irreversibly with amines to form HSSs. These include

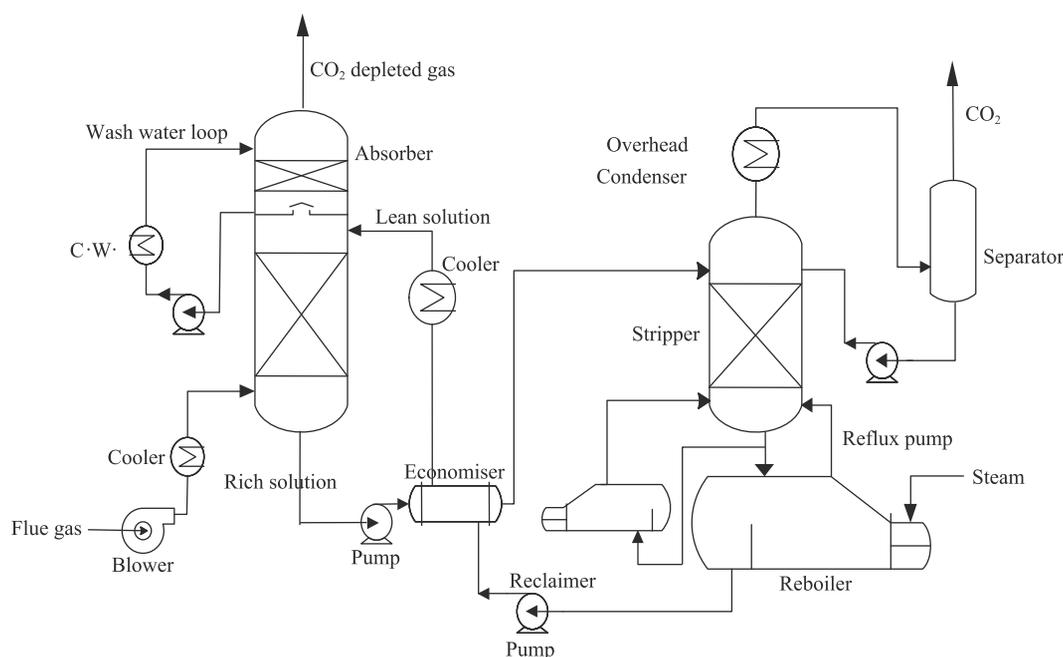


Fig. 1 – Schematic of the typical amine-based absorption-stripping unit for CO<sub>2</sub> removal.

SO<sub>x</sub> and NO<sub>x</sub> present in the flue gas, mineral acids arising from chloride and fluoride present in the feed fuel (Strazisar et al., 2003), as well as carboxylic acids, such as formic-, acetic-, and oxalic-acids generated by oxidative degradation of amines (Rooney et al., 1998; Lepaumier et al., 2009) and other anions introduced in makeup water.

Heat stable salts are the cause of the most problems in amine system (Verma and Verma, 2009). The recommended HSS level in amine solution is less than 10% of the amine concentration (Bacon, 1987), but levels should be controlled below 5000 ppm of total HSS for the most trouble-free operations (Cummings et al., 2007). The experimental results of carbon steel coupons in 50 wt.% MDEA solutions indicate that the total HSS concentration should not exceed 0.5 wt.% of the total solution (Rooney et al., 1997). While Kohl and Nielsen (1997) recommend that the content of total contaminants should be less than 10% of the active amine concentration; otherwise, the contaminants should be removed. Many efforts have been made to control the impurity level, especially the HSS level in the amine system. The various options for controlling the contaminants include solution purging, neutralization, and amine reclamation.

In solution purge, also called “bleed and feed”, a portion of contaminated solvent is removed and replaced with fresh solvent to reduce the contamination. Due to loss of useful solvent, increased disposal cost and environmental concerns, this approach may not be a permanent solution.

Online neutralization of HSSs involves the addition of caustic to the amine system. The addition of the strong base raises the pH of the system and converts the amine salt to the inorganic salt, with the benefit of releasing the amine trapped by HSSs available for CO<sub>2</sub> removal again. However, this method does not remove the acid anions from the solution and the addition introduces another impurity into the system which heightens solution viscosity, corrosivity and scaling potential (Strazisar et al., 2003).

The previous techniques are useful, but do not address the contamination problems on a long-term or continuous basis. Reclaiming the amine is a more permanent and environmentally friendly technique. A number of reclaiming processes have been used to manage corrosion and solvent purification by separating HSSs and other degradation products from amine solvents including thermal reclamation (distillation), ion exchange and electro dialysis.

### 1.1. Thermal reclamation

Thermal reclamation uses heat energy to purify an amine solvent by the evaporation of amine from the high-boiling degradation products, as well as suspended solids. Distillation is usually conducted on a small side stream, which is withdrawn from the solution leaving the stripper reboiler and fed to a steam-heated or direct fired kettle or reclaimer. The reclaiming system also can be performed off-site at the reclaiming plant.

#### 1.1.1. Traditional thermal reclamation

Fig. 2 illustrates a traditional design of an amine thermal reclaiming process in the case of nature gas sweetening (Blake and Rothert, 1962). Usually 1%–3% of the circulating

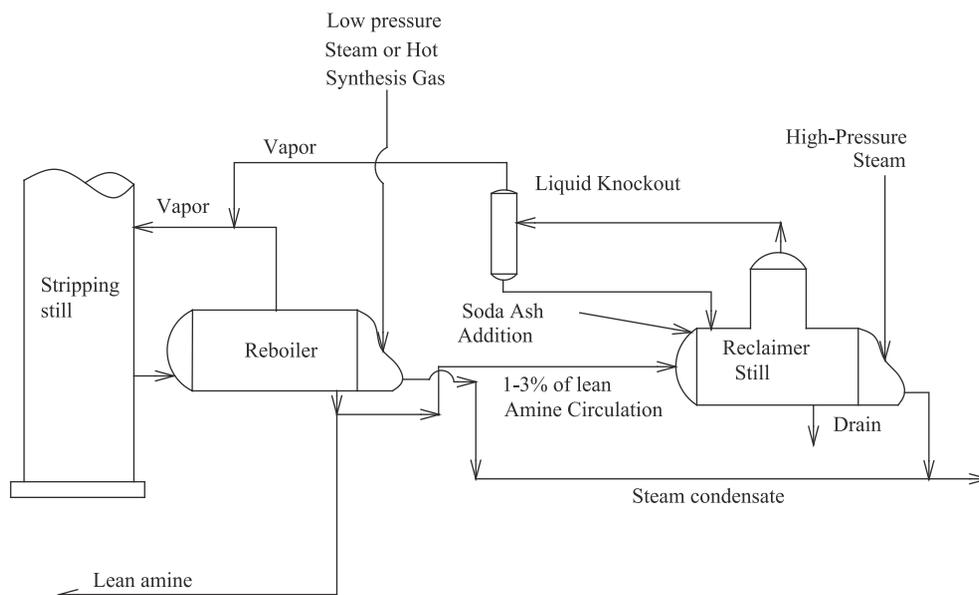
lean solution is fed into the reclaimer through liquid inlet in continuous mode. The slip ratio can be varied according to the amount of contamination in the amine solvent and amount of solvent inventory (Wonder et al., 1959). Purified amine is returned to the system through the overhead vapor line. In most designs, a high-pressure stream enters the reclaimer tube bundle and when leaving can be tied into the condensate line from the reboiler. In some cases, direct fired tubes are used. A drain on the reclaimer bottom is to remove and dispose the concentrated contaminants. A manhole facilitates cleaning the reclaimer with a water hose without having to pull the tube bundle.

Typically, the contaminated amine is mixed with a strong base such as caustic soda or soda ash to liberate the amine from HSSs (Blake and Rothert, 1962; Pottia and Verbeest, 1972; Rooney, 1999). To prevent distilling any of the stronger acids, the strong base is added to free the amine in advance of the thermal reclaimer (Blake and Rothert, 1962; Blake, 1963). Then the mixture is either allowed to settle for some time to remove the solids and precipitate matters or sent to the reclaimer directly. An excess of strong base will not affect the amine solution itself but a very large excess will raise the boiling temperature and also result in additional sludge accumulation (Blake, 1963). Therefore, the added amount of sodium carbonates or hydroxide is slightly more or less than the stoichiometric amount of HSSs present in the degraded amine. A strong base such as soda ash can be added as an aqueous solution.

The conventional horizontal kettle configuration is utilized in most reclaimer designs as it minimizes the metal surface to liquid volume ratio (Jefferson, 1963). Kettle size is usually set at a shell capacity in 50–100 times the amount of solvent flow to the reclaimer per minute (Blake and Rothert, 1962; Blake, 1963; Jefferson, 1963). Large values are used for small reclaimers and small values for large reclaimers. The amine plant size, economics and expected solvent degradation rate determine how large the reclaimer should be.

The operating conditions of thermal reclaimers depend on the type of solvents, which have certain temperature tolerations. When the temperature reaches the maximum allowable temperature, thermal degradation of the amine can occur. In the case of MEA, the temperature limit is set at 148°C to minimize thermal degradation (The Dow Chemical Company, 1998). The pressure at which a reclaimer operates can be either at atmospheric pressure or the stripper pressure, for example, MEA reclaiming is often carried out at the stripper pressure. The water and MEA vapor from the reclaimer can be injected to the regenerator bottom or mixed with the vapor from the reboiler. However, for high-boiling point amines such as DEA, diisopropanolamine (DIPA), MDEA, and some formulated solvent systems should be reclaimed under vacuum to avoid thermal degradation and maximize recovery (Bacon, 1987; Dumée et al., 2012). Secondary and tertiary amines or their blends are reported to be reclaimed by vacuum distillation with temperatures less than 204°C, for example, typical operating conditions for thermal reclamation of DIPA are 6.66–13.33 kPa absolute at 176.7°C (Kohl and Nielsen, 1997).

In the reclaiming cycle, initially the reclaimer is filled with the circulating amine solution. As the solution begins to distill, the overhead vapor is essentially water. As the distillation



**Fig. 2 – Traditional amine thermal reclaiming process.**  
Adapted from Blake and Rothert (1962).

continues, the amine concentration in the liquid will increase until the vapor composition will approximate the composition of the circulating solution. This ensures that the exiting vapor also contains the same concentration as the feed amine stream. This relationship can be explained by the vapor–liquid equilibrium graph for a binary system.

With a contaminated solution, there is a concentrating of high-boiling products in the liquid phase as the distillation proceeds. Its boiling temperature slowly rises as the boiling liquid becomes more concentrated with salts and degradation products (Kohl and Nielsen, 1997; Blake, 1963). When the boiling temperature reaches a predetermined limit, the feed to the reclaimer is to be shut off. The liquid phase contains a rather large proportion of high-boiling contaminants, some useful amine, and some water. To recover more of the remaining amine without raising the boiling point higher than the maximum allowable temperature, diluting water (usually from reflux water) is added and continues the distillation (Blake, 1963). The use of steam spargers is another effective way to recover additional amine without exceeding the tolerant temperature (Blake and Rothert, 1962; Blake, 1963), especially, if there is a considerable amount of sludge in the reclaimer (Blake and Rothert, 1962).

The reclaiming cycle is terminated when the temperature is close to the maximum allowable temperature or the amount of amine in the vapor stream falls sharply below the amine concentration in the feed (ElMoudir et al., 2012). This means that the maximum economic goal of amine recovery is achieved and can no longer be controlled by addition of water. Once the reclamation is terminated, the reclaimer bottoms are discharged, the reclaimer cleaned by flushing water, and prepared for the next cycle.

Due to potential plugging and fouling problems, it is imperative that enough solvent remains in the reclaimer bottom residue to avoid crystallization of solid salts (Simmons, 1991). The

discharged bottom waste is usually viscous liquid—about the viscosity of crude oil (Simmons, 1991). The amine remaining in the slurry waste results in solvent inventory loss. In one case reported by the Union Carbide Chemical Company, at least 74.6 wt.% of the residue waste from a MEA reclaimer could be MEA (Wonder et al., 1959). In principle, the concentration of the amine in the reclaimer waste should be as low as possible. Nevertheless, MPR Services Inc. claimed that the waste still contains high level of amine in the traditional reclaimer for MEA and diglycolamine (DGA) in many refinery industries (Cummings et al., 2007). Mitsubishi Heavy Industries claimed that the absorbent component remaining in the sludge can occupy 5% to 20% of the entire absorbent in the conventional reclaiming process (Iijima et al., 2011).

Thermal reclamation is an energy intensive process. Considerable heat is required since the amine and water both are carried overhead in the purification unit. IEA reported that the energy associated with thermal reclaiming is approximately 0.3 GJ/ton CO<sub>2</sub> for an USC PC (ultra supercritical pulverized coal) boiler reference case (IEAGHG, 2012). This reference case is based on standard supercritical design, 750 MW<sub>e</sub> nominal power output, with CO<sub>2</sub> capture and without limitation on water usage. For MEA based CO<sub>2</sub> capture process, the total heat consumption is about 3.0–3.7 GJ/t CO<sub>2</sub> (IPCC, 2005; Romeo et al., 2008; Abu-Zahra et al., 2007). These data indicate that approximately 10% of total heat consumption goes into thermal reclaiming unit. The typical advantages and limitations of thermal reclamation are given in Table 1.

#### 1.1.2. Modern improvements

A number of measures have been proposed to overcome the disadvantages or improve the performance of the classical distillation processes. Since the conventional reclaiming process that depends only upon heating and evaporation, a part of the absorbent component may remain in the reclaimer

bottom sludge. Mitsubishi Heavy Industries (Iijima et al., 2011) provides a patent reclaiming apparatus, as shown in Fig. 3, which can further separate the amine from the depleted materials. Compared with the conventional reclaimer, the MHI reclaimer includes a packed bed in which the absorbent is brought into gas-liquid contact with steam. The reclaiming apparatus further includes an absorbent distributing unit that extracts and distributes a part of the absorbent stored in the absorbent reservoir. A given example test illustrates that 7.3 wt.% absorbent contained in the sludge in a conventional facility, while the content of the absorbent contained in the sludge was 1.0% in the MHI reclaiming apparatus (The Dow Chemical Company, 1998).

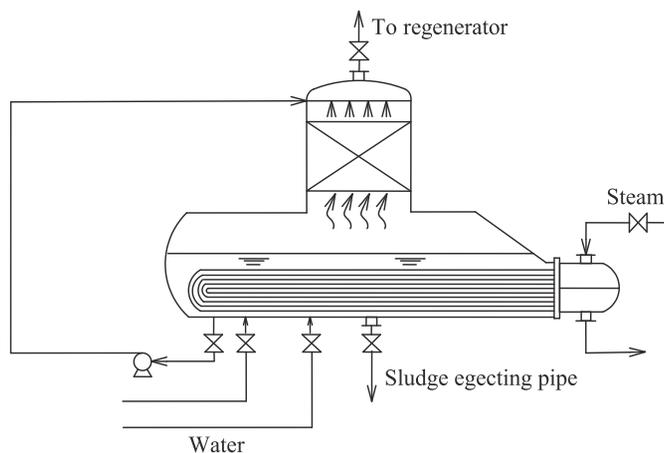
The conventional thermal reclaimers are operated at atmospheric pressure or above, while modern thermal reclaimers are generally operated at atmospheric pressure or vacuum (ElMoudir et al., 2012). The vacuum distillation process is designed to reclaim high boiling point amine solvents or their blends, which are sensitive to decomposition at high temperatures. According to Canadian Chemical Reclaiming (CCR) Ltd. (Millard and Beasley, 1993), numerous tests and evaluation of all the potential options showed that vacuum distillation is the most effective method for amine purification. CCR claimed that their processes could effectively clean contaminated amines with dramatically reduced operating cost. CCR is the leading company in developing vacuum thermal reclamation (ElMoudir et al., 2012). Below is a short description of modern thermal reclaiming

technology from the development of CCR reclamation apparatus and processes.

Canadian Chemical Reclaiming Ltd. began actively pursuing the reclaiming technology in 1986 (Millard and Beasley, 1993) and detailed their reclamation apparatus and process in a patent by its founders in 1992 (Beasley and Merritt, 1992a,b). The objectives are the removal of all impurities, permitting a 90%–95% solvent recovery from the contaminated solution, and reduction of the potential thermal degradation and corrosion. A flow diagram of the CCR process is shown in Fig. 4 (Meisen et al, 1996). The amine feed to the unit enters at atmospheric pressure and at a temperature of 5–24°C from a feed tank and is preheated in a shell and tube exchanger with the vapor from the still. This preheated feed is next mixed with hot recycled still bottom stream and then fed to an evaporator at vacuum pressure (typically 55–85 kPa). Water and some amine evaporate, and partial condensation occurs in the heat exchanger where the amine feed is preheated. The partially condensed stream is sent to a product separator to separate condensate from vapor. The condensate is sent back to the amine system after cooling and filtration. The separator top stream, consisting of water vapor, some amount of air and dissolved gas, and trace amounts of amine is cooled down in a water condenser for water and amine recovery. The waste gases are fed to the gas fired heater to destroy them before they can be released to the atmosphere. The still bottom stream is split into two streams. One stream is packaged for disposal, while the vast

**Table 1 – Comparison of commercially available amine reclamation technologies.**

	Distillation	Ion exchange	Electrodialysis
Main commercial providers	CCR Technologies, Chem Group	MPR Services Inc., Eco-Tec Inc.	Dow, ElectroSep
Applicability	Removal of solids and non-volatile species	Removal of ionic contaminants	Removal of ionic contaminants
Operation principle	Vaporization of volatile species (water, amine, etc.) from salts and degradation products	Ions captured by ion exchange resin	Ions removed by electrodialysis
Operation mode	Semi-continuous, on-line or batch. Mobile unit commercially available	Batch or on-line. Mobile unit commercially available	Continuous on-line or batch. Mobile unit commercially available
Waste type	Hazardous, non-aqueous	Aqueous	Non-hazardous, aqueous
Volume of wastes	Low (5%–15% inventory)	High (40%–50% inventory)	Moderate
Chemical usage	Stoichiometric NaOH	NaOH and H <sub>2</sub> SO <sub>4</sub> for resin regeneration	Stoichiometric NaOH
Feed requirements	Heat stable amine salts neutralized	Lean cool amine, hydrocarbon and particulate free	Lean cool amine, hydrocarbon and particulate free; heat stable amine salts neutralized
Energy demand	High	Low	Moderate
Overall amine recovery	85%–95%	~99%	~98%
Special requirements	Fuel gas or high temp. heat source	Regeneration chemicals and storage	DC power
Total cost	High	Moderate	Moderate
Advantages	Highly concentrated waste	Best for low feed salt concentration, very low product salt concentrations achievable; low energy consumption	Efficient for charged species; not affected by concentration in feed; lower chemical consumption
Limitations	High cost, low amine recovery; energy intensive; most amines need vacuum	Cannot remove non-ionic contaminants; high salt levels lead to frequent bed exhaustion and regeneration; expensive at large plant sizes anticipated for PCC.	Cannot remove non-ionic contaminants; membrane selection and durability



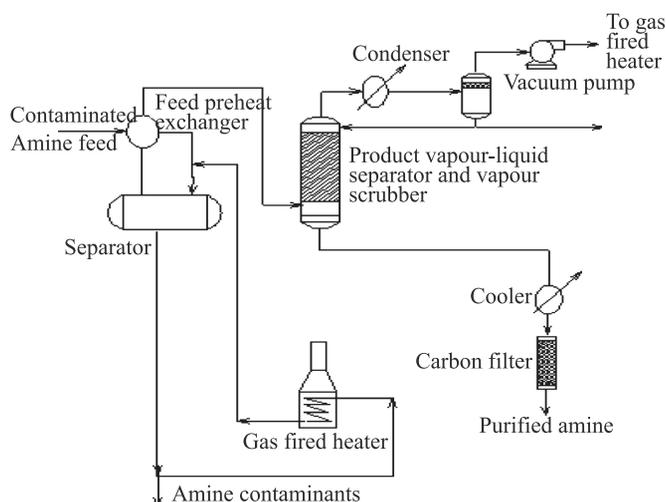
**Fig. 3 – A schematic of the Mitsubishi Heavy Industries (MHI) reclaiming apparatus.**  
Adapted from Iijima et al. (2011).

majority of the bottoms are recycled through the still heater to be heated and sent to the mixer. The still heater is a natural gas fired heater, which is designed to have a limited heat transfer, 30–60 sec of waste liquid residence time with velocity varying from 1.8 to 3.0 m/sec and a maximum temperature of 204°C. This CCR process has been successfully used to recover MDEA, ethylene glycol, and Sulfinol-M solution (Millard and Beasley, 1993).

Canadian Chemical Reclaiming Ltd. and the University of British Columbia (Canada) modified the aforementioned CCR process to overcome co-evaporation of amine and its degradation products which have similar boiling points as the amine. The product separator in the CCR process is replaced by a distillation column containing several theoretical stages in the modified process (Meisen et al., 1996). A suitable inert, high-boiling liquid is blended with the contaminated amine feed and sent to the distillation column to provide adequate liquid and vapor flow in the low section of the column. Laboratory experiments demonstrated that bis-hydroxyethyl

piperazine (BHEP), a major DEA degradation product, can be separated from aqueous DEA solutions with this modified process. However, this modified process has not been tested and unlikely will be (ElMoudir et al., 2012).

Based on operating experiences gained with the available CCR units, an improved process was invented by CCR at the end of 1990s. The improved process consists of two heating zones (Abry et al., 1999). The amine feed is first mixed with the heated recycled bottom liquid stream from the evaporator in a mixer. The hot mixture is fed to the evaporator operated at deep vacuum pressure (at least 55 kPa) in which most of the amine and water are evaporated. The bottom liquid is heated and recycled to enhance recovery of solvent as well as to heat up the amine feed. Some of the bottom liquid is recycled before heating and sprayed through a spray head in the evaporator to control formation of foaming. The vapor leaving the evaporator enters the second heating zone, which consists of a distillation unit used to separate amine and water, as well as the noncondensable gases. A contaminated DEA solution was reclaimed by the



**Fig. 4 – Flow diagram of the post combustion CO<sub>2</sub> capture process (PCC) (Meisen et al, 1996).**

different CCR mobile units. The improved process (unit #3) achieved the highest reduction in contaminants in the bottom waste and the greatest recovery of usable DEA solvent in the least amount of time on-site (Drake, 2000).

The improved CCR process was subsequently modified further (Razzaghi et al., 2003). Some of the recovered water or recovered amine is recycled in the modified process. This is believed to enhance solvent recovery and minimize the energy consumption (ElMoudir et al., 2012). However, no performance data on this modified process is available in open literature.

Vacuum reclaiming requires the introduction of a compressor system or vacuum pump system. Vacuum pump systems involve condensing most of the vapor and therefore are not energy efficient (Woodhouse et al., 2012). Using a compressor will reduce the energy consumption, but the investment cost for the compressor is high. Aker Clean Carbon AS (Woodhouse et al., 2012) proposed a method and a device for vacuum reclaiming with a reduced requirement compared to use of a vacuum pump but where the capital cost is lower than installing a dedicated compressor. The lean aqueous amine solution leaving the regeneration column is split in two portions. A part of lean absorbent is withdrawn and flashed to generate a vapor that is compressed and returned into the regeneration column. The other part of lean absorbent is introduced into a reclaiming column in which the lean absorbent is boiled to generate a gas phase and a liquid phase containing impurities. Then the gas phase is compressed together with the vapor from the flashing of the lean absorbent, to generate a low pressure in the reclaiming column. However, the company has not provided any performance data on this proposed process.

All the aforesaid vacuum distillation techniques should be considered as a single step process also when using partial refluxing or recirculation of the amine solutions in the reclaiming column. Praxair Inc. (Burgers et al., 2007) proposed a process with vaporization in two or more stages under decreasing pressures. A portion of lean absorbent leaving the stripper enters the first evaporator. The temperature in this evaporator is typically 121–149°C. The resulting first reclaimed vapor stream is sent to the bottom portion of the stripper. The fraction of the unevaporated liquid is sent through the valve to reduce the pressure to a value in the range of 3.5–35 kPa, and then is fed to the second evaporator. The temperature in the second evaporator can be about the same temperature as in the first evaporator. The resulting second reclaimed vapor is condensed in a cooler. The condensate is combined with the lean absorbent entering the absorber column. If noncondensable gases are present in the second vapor stream, a small vacuum pump would be needed to establish the desired low pressure in the second evaporator. The unvaporized residue in the second evaporator can be removed for further disposal. The third stage reclaiming column can be used to improve recovery of less volatile but still desirable components from this unvaporized residue. Before or during vaporization in the third evaporator, a small amount of steam is fed and combined with the residue. The temperature in the third vaporization stage can be about the same as in the first two units. The pressure is the same or less than that in the second evaporator. Third reclaimed vapor may be combined with the second reclaimed vapor. To reduce the steam duty, heat integration should be considered

during process design. No performance data is provided in this patent.

Shell (Van and Van, 2000) has a patent distillation process which comprises at least two stages. In the first step more than 95% of the water originally present is removed from the aqueous amine in a film-type evaporator. In the second step the aqueous amine is further purified in an agitated-film evaporator, which is operated at a temperature in the range of 120–200°C and a pressure in the range of 2 to 10 kPa. A pilot plant experiment showed that 96% di-isopropanolamine (DIPA) can be recovered from spent aqueous DIPA and approximately 90% HSSs were removed by applying a simple two step distillation process, if the sample was treated with stoichiometric amounts of NaOH prior to the first step.

Mobil Oil Corporation (Yan, 1992a) provided a patent reclamation process which consists of reactive and separation zones. Some degradation products are converted back to their parent amine in a regeneration reactor at an elevated temperature of about 243°C. The regenerated amine solution may be processed for removal of HSSs by distillation (or ion exchange). Although this process provides high solvent recovery from contaminated DEA as claimed by Mobil, thermal degradation of DEA could occur due to high temperature in the reactor (DEA is degraded once temperature exceeds 204°C). At the same time, Mobil Oil Corporation (Yan, 1992b) developed another process based on reactive distillation of amine solutions. A fraction of rich amine (e.g. DEA) solvent flowing from the absorber to the stripper is introduced to a vacuum distillation reactor column. Stripping steam is directly supplied to a low section of the distillation column for heating, control of the distillation temperature and hydration. The purified amine is taken from the top of the distillation column while the waste is withdrawn from the bottom. The process involves conversion of some amine degradation products (e.g. N,N-bis(2-hydroxyethyl) piperazine, BHEP) back to the amine in the presence of steam.

Operation of the reclaiming column is very important for a reclamation process performance. The reclaiming column will perform more efficiently if the operation is stable. To achieve a stable operation, liquid level should not undergo sudden variations, temperature control by addition of water should be adequate, temperature of the heating media should be as low as possible, and the reclaiming column should be designed with a proper L/D ratio (e.g. 3 to 4) (Yan, 1992b). Pre-removal of contaminants from the inlet streams of gas, makeup water and amine solution is also critical for reclaiming performance. The test results showed that reclaiming cycles (continuous operation between shutdowns for cleaning) were extended from four months to nine months under a more stable operation (Trovarelli et al., 2002).

### 1.1.3. Reclaiming waste

The quantity of reclaiming waste varies with a ratio of slip stream to total circulation rate of process solution. Thitakamol et al. (2007) estimated that 4–15 kg of waste per ton of CO<sub>2</sub> captured can be produced during thermal reclaiming. Similarly, approximately 3 L of reclaiming waste per ton of CO<sub>2</sub> captured in a commercial Econamine FG process was reported by Chapel et al. (1999).

Amine waste from CCS is a complex mixture of solvent, amine degradation products, other substances than CO<sub>2</sub> captured from the flue gas, and corrosion products. When

thermal reclaiming of the solvent is used the waste arises as the bottom product from distillation. According to EU regulations and directives it is the owner of a waste that is responsible for its classification. Waste shall be classified according to the European List of Wastes (EU, 2000). It seems reasonable to classify the waste as “07 01 Wastes from manufacture, formulation, supply and use of basic organic chemicals” subgroup “07 01 08\* other still bottoms and reaction residues”. The asterisk indicates that this type of waste is considered as hazardous pursuant to Directive 91/689/EEC on hazardous waste.

In the USA the Code of Federal Regulations Title 40: Protection of Environment is relevant for the classification and handling of waste. We have been informed from one operator of a carbon capture plant in the USA that they have classified their waste from thermal reclaiming as hazardous.

With regard to EU classification of liquids from the regeneration of ion exchange (see Section 2.2) columns or from electro dialysis (see Section 2.3), the actual composition will determine whether it is classified as hazardous or not. Such aqueous waste may also be handled on-site in a waste water treatment plant. This would have to be permitted by the authorities. Both the content of toxic metals and other hazardous inorganic and organic substances may contribute to the classification of the waste.

Amine reclaimer wastes generated in PCC processes demand suitable disposal means. Deshai et al. (2012) investigated the potential of using amine waste as a NO<sub>x</sub> reducing agent under laboratory conditions in a flow reactor. The amine waste was obtained from a distillation MEA reclaimer in an industrial CO<sub>2</sub> capture facility with a coal fired boiler. The result demonstrated that amine reclaimer waste is an attractive additive to reduce NO<sub>x</sub> in combustion processes, including cement industry kilns. Hauser et al. (2013) first demonstrated an efficient biodegradation of real amine waste from a PCC facility by pre-denitrification without external electron donor. The reclaimer waste was generated from a 30% (w/w) MEA solvent used for capturing CO<sub>2</sub> from flue gas from a coal-fired power plant. The biofilm system achieved 98% ± 1% removal of MEA and 72% ± 16% removal of total nitrogen.

Nitrosamines, such as N-nitrosopiperazine (MNPZ), a class of carcinogenic or potentially carcinogenic compounds can be formed in CO<sub>2</sub> capture (Nielsen et al., 2013; Dai et al., 2012; Shah et al., 2013). Different nitrogen-containing species can cause nitrosation. NO<sub>x</sub> present in flue gas can form nitrosamine with secondary amines (Challis and Kyrtopoulos, 1977). Another possible nitrosation agent is nitrite in the solution. Nitrosation caused by aqueous nitrite has not been observed at pHs higher than 7.5 (Douglass et al., 1978), however CO<sub>2</sub> possibly accelerates the nitrosation from nitrite in basic conditions (Sun et al., 2011). Nitrosation of amine such as piperazine with nitrite is faster at higher temperature and/or lower pH (Goldman et al., 2013). Thermal distillation of amines is probably in favor of nitrosamine formation in the reclaimer.

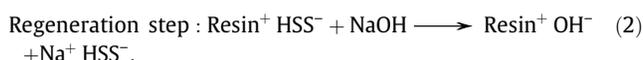
As a primary amine, MEA in itself is unable to form a stable nitrosamine. However, MEA can degrade into the secondary amine which is then nitrosated by reaction with nitrite. Nitrosamines were found to be present at a concentration of 2.9 μmol/mL in the lean MEA circulating solvent in a pilot plant in California (Strazisar et al., 2003). No detectable

amount of nitrosamines was found in the thermal reclaimer bottoms. However, this result does not mean that nitrosamines were destroyed in the reclaimer. They may be in the gas phase due to their low boiling points (Strazisar et al., 2003). Health and environmental risk assessment of nitrosamines should be further investigated based on data from real emission measurements.

## 1.2. Ion exchange

Ion exchange is a reversible exchange of ions between a solid and a liquid in which no substantial change in the structure of the solid occurs. The solid is the ion exchange material or resin particle. Ion exchange resins have been used to remove acidic contaminants from spent alkanolamine absorbent used in petroleum hydrocarbon fluids since 1950s (Taylor and Prielipp, 1957; Prielipp and Pearce, 1959).

The ion exchange action is similar to neutralization with strong base, but ion exchange occurs between liquid and solid. The ion exchange reclaimer was originally developed to remove non-volatile acid contaminated amine solvents used for removal of acidic gases in gas treating. The typical ion exchange process involves two steps, the loading step and the regeneration step, as shown in Eqs. (1) and (2). The loading step is to remove ionic contaminants from solution. In the regeneration step, the HSS anions are removed from the resin by replacing them with caustic, which produces biodegradable sodium salts, which are friendly to the waste water treatment systems. However, ion exchange resins are not capable of removing uncharged contaminants like those produced from amine thermal degradation.



Ion exchange seems chemically simple, and it has been claimed that ion exchange processes provide the optimum removal of HSSs with less chemical, energy consumption and less foaming (Cummings et al., 2007; Jouravleva and Davy, 2000). However, the practice of removing HSS from amine systems by ion exchange has presented many technical and operational challenges. For instance, previous ion exchange processes used in amine systems are ineffective and produce large quantities of diluted waste which requires neutralization and disposal. Poorly designed and/or operated ion exchange systems have caused significant amine losses which makes the waste untreatable in waste water plants in some cases (Cummings et al., 2007).

The ion exchange usually operates in a continuous or semi-continuous mode, but it can be operated at a batch mode in some cases. Continuous operation has proven to be more efficient than batch treatment, as acid anions are treated as they are formed, thereby instantly preventing operational problems (ElMoudir et al., 2012).

The thermal degradation of ion exchange resins at high temperature limits efficiency (Simister et al., 2004). The ion exchange process is favored by low temperature (less than 45°C)

and therefore the ion exchange reclaimer is typically located downstream of the lean amine cooler in an amine scrubbing process. Keller et al. (1992) have shown illustrations of the typical location of ion exchange unit in the amine plant.

An ion exchange process usually consists of a cation resin for cation removal and anion resins for anionic species removal (Yan, 1989, 1993; Keller, 1990; Veatch and Keller, 1991). Cationic resins are functionalized with either a sulfonic or carboxylic acid group (Yan, 1989). It has been found that the strongly sulfonic acid resins are preferred due to their greater stability, but the weakly acidic resins outperform the strongly acidic resins with carboxylic acid functionality (Audeh and Yan, 1994). The resin selection must be carefully considered since many standard resins cannot withstand the strongly alkaline nature of ethanolamine solutions (Dumée et al., 2012). A typical anion resin is a copolymer made of styrene and divinyl benzene. Strong base anion (SBA) resins are usually functionalized by chloromethylation followed by amination (Dumée et al., 2012). Type I SBA resins are aminated with trimethylamine, Type II SBA resins are aminated with dimethylethanolamine. These two types of resins are used for removal of acid anions in series (Cummings et al., 1992). Type II SBA exchange resins are easier to regenerate than Type I with NaOH (Coberly et al., 1998).

Resins degrade over time due to fouling by organic contaminants, suspended particles and oxidized iron in PCC service, and thus resins must be cleaned and replaced periodically. According to MPR Services Inc. (pers. comm.) anion exchange resins should be exchanged every second year.

The advances in ion exchange have led to reduced chemical and water consumption. Caustic utilization has reduced from typically 9–40 mol NaOH per mol HSS 20 years ago to just over 1 mol NaOH per mol HSS anion in 2007 (Cummings et al., 2007). Water consumption, depending on the application, now can be about 2/3 to 1/5 of the water demand in the beginning of 1990s (Cummings et al., 2007). Mobile and permanent units have become available throughout the world. Although the ion exchange process might be acceptable in natural gas treating services, the process alone cannot be considered an optimum solution for CO<sub>2</sub> capture application, particularly from flue gases (ElMoudir et al., 2012). In CO<sub>2</sub> capture, the high acid gas loading or high level of CO<sub>3</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup> in the amine solution could interfere and compete with HSS anions in the resin leading to reduced effectiveness of the HSS removal. To reduce the negative effect of the relatively high lean loading, Dow and Alstom (Handagama et al., 2012) have a patent process involving a stripper or flash drum for inexpensive, efficient and reliable removal of residual CO<sub>2</sub> from contaminated amine solution before the absorbent is fed to the amine reclaimer for separation of HSSs.

In natural gas sweetening, heat-stable salts are major degradation products to be addressed, while amine degradation products are minor to moderate in importance. However, in the case of CCS application, amine degradation products and HSSs are almost in equivalent ratio in terms of importance (ElMoudir et al., 2012). The amine degradation products include oxazolidinone, amides, and amino acids (Gouedard et al., 2012), which are difficult to remove by ion exchange.

MPR Services Inc. provided a process for converting oxazolidones such as hydroxypropyloxazolidone (HPOZD) to alkanolamines such as DIPA and CO<sub>2</sub> (Turoff et al., 2008).

The conversion of HPOZD to DIPA and CO<sub>2</sub> requires 2 mol of hydroxide such as potassium hydroxide (KOH) for each of HPOZD present in the solution. Since the conversion reaction is carried out in a reaction vessel at preferably between 60 and 120°C, the slipstream of hot lean amine containing HPOZD exits the bottom of amine stripper. The entire reaction mixture including all cations from added caustic is then processed through the ion exchange resins after cooling. After cation removal, the solution goes to the anion removal resins (Keller et al., 1992). The overall process includes rinsing and regenerating the ion exchange resins by high quality water (clean, demineralized). The amounts of water needed for rinsing and regeneration can be considerable due to long washing time. Excess water into the amine circulation system must be removed by a distillation procedure. The need of considerable amounts of clean water and removal of excess water in the system might make energy consumption high when using ion exchange.

Amides can be hydrolyzed to corresponding amines and carboxylate anions in the presence of caustic (Sexton, 2008). The anions are expected to be removed by anion exchange. And therefore ion exchange removes organic acid anion from the equilibrium reaction of amide formation and drives the equilibrium to amine and acid anion. Amide formation has been reported to decrease after organic anions removed from the solution by ion exchange (Cummings and Mecum, 2000). Significant amounts of amino acids could be formed in CO<sub>2</sub> capture (Closmann, 2011), and the amino acids are difficult to clean out. However, the successful removal of bicine, an amino acid, has been reported (Cummings et al., 2007).

At present, the two major commercial providers of ion exchange for amine purification are MPR Services Inc. (Texas, USA) and Eco-Tec Inc. (Ontario, Canada). According to their websites, HSSX® and AmiPur®, are the commercialized reclaiming processes provided by MPR Services Inc. and Eco-Tec Inc. respectively (MPR Services Inc.; Eco-Tec Inc.). Both of the processes have been claimed to be successfully used in gas processing plants for amine purification, however, the performance of ion exchange reclaiming in CO<sub>2</sub> capture application has not been satisfactory so far. MPR Services Inc. has developed a new ion exchange process, known as Carbon Capture Amine Reclamation (CCAR™), to treat contaminated amine solvents used in CO<sub>2</sub> capture system. Eco-Tec Inc. also proposed a new ion exchange process, called AmiPur®-CCS, to purify amine solutions in CO<sub>2</sub> capture systems. However, no performance or testing data in any CO<sub>2</sub> capture plant has been reported.

### 1.3. Electrodialysis

Electrodialysis (ED) uses a direct current and ion-permeable membranes to remove ions from one solution chamber to another. ED as a technology for desalting water has been widely used in the water desalination industry since the 1950s (Katz, 1979; Shaposhnik and Kesore, 1997). The ED approach as a means to remove charged contaminants from aqueous ethanolamine solution was developed by Union Carbide Corporation (now The Dow Chemical Company) in the early 1990s (Kosseim et al., 1979; Gregory and Cohen, 1999). Different ED process configurations can be found in a

number of patents (Gregory and Cohen, 1999; Byszewski, 2002, 2003).

The separation of ionic degradation products from amine solutions by ED is done with a typical process setup consisting of a stack of alternating cation-selective and anion-selective membranes located between two electrodes. Commercial ED cells can contain hundreds of stacked membranes (Kohl and Nielsen, 1997). When a current is applied across the two electrodes, the cations and anions move toward their opposite electrodes and through the selective-ion membrane. The net effect is to remove both cations and anions from the feed stream and collect them in a concentrated waste stream. As with ion exchange, the ED process is only capable of removing ionic contaminants, neutral amine degradation products would be left in the amine solvent. Some of the carbamate anions, and/or the protonated amine could be transferred and therefore lost. A schematic diagram illustrating the principle of the ED process is shown in Fig. 5.

The salt removal rate in ED is primarily a function of the number of membrane cell pairs and the applied current. However, ion-exchange membrane type, surface area, and type of solution to be treated all play an important role on the ED process performance. The overall removal rate ( $R$ , g-eq/s) can be calculated from Eq. (3):

$$R = \frac{E \times n \times I}{F} \quad (3)$$

where,  $n$  is the number of membrane cell pairs,  $F$  is the Faraday constant (96480 C/g-eq),  $E$  is the efficiency factor, and  $I$  is the current (Amps), which is the main factor that affects the removal efficiency. Commercial membrane stacks have a current efficiency in excess of 90% (Dumée et al., 2012). Specially designed spacers are usually employed in each feed channel to increase mixing and thus reduce boundary layer effects (Dumée et al., 2012; Burns and Gregory, 1995).

Due to temperature sensitivity and limitation of the ion-exchange membranes, electro dialysis is best conducted on cold lean solvent. Thus, downstream of the lean amine cooler would be the best location to extract the slipstream. Additional cooling may be required to reduce the input temperature to around 40°C (Burns and Gregory, 1995). Neutralization with a neutralizing agent or caustic and microfiltration are usually used upstream of the unit (Kosseim et al., 1979; Liu et al., 1995). The filtration step could cause a loss of amine solution. The presence of dissolved iron, hydrocarbons

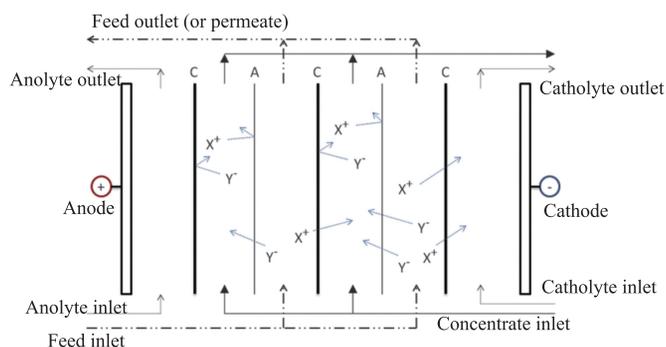
or suspended solids can result in fouling on the membrane surface, which increases the stack resistance and reduces the process efficiency (Dumée et al., 2012).

Commercial cationic and anionic ED membranes are based on the same styrene and divinyl benzene as ion-exchange resins, while functionalized aliphatic polymers are also used as these membranes can be more resistant to fouling and chloride oxidation (Hodgdon, 1992). Reported lifetimes of anion-exchange membranes are up to 10 years and cation-exchange membranes are up to 15 years. However, many membranes are designed for operation in a pH range of 2–9 which could be a problem for application at the typical pH range of lean amine solutions of pH 9–11 (Dumée et al., 2012).

Dow's UCARSEP ED process has been used commercially for approximately 20 years. Dow reported that the UCARSEP has been successfully used to clean up UCARSOL solvents and DEA in different oil refineries (Byszewski, 2003; The Dow Chemical Company, 2004). The Dow's ED technology used in a MDEA plant was compared economically to solvent change-out and purging/feeding, ion exchange and vacuum distillation methods (Price and Burns, 1995). The ED process is economically and technically favored to solvent change-out or 'bleed and feed' options. Ion exchange and vacuum distillation could be used but there were concerns about the high chemical/utility consumptions and disposal of possible hazardous wastes (ElMoudir et al., 2012).

In ElectroSep™ process, which is developed by ElectroSep Technologies Inc., only anions are removed from the contaminated amine solution (Parisi and Bosen, 2006a,b). The ElectroSep process was likely adopted and modified from the Dow's ED technology. Instead of adding base directly to the amine solution in the UCARSEP process, base is added into the ED stack in the ElectroSep process (Parisi and Bosen, 2006b; Vitse et al., 2011). Arrangement of the membrane stack is also different, as shown in Fig. 6. It is reported that amine neutralization in the ED stack results in reduction of amine loss, and overall amine recoveries of 99.5% have been achieved (Parisi and Bosen, 2006a).

Although ED technology has been used successfully in removing HSSs in refineries, very little information is available for its use in the CO<sub>2</sub> capture process. However, this approach is currently being tested in post-combustion CO<sub>2</sub> capture pilot plant using UCARSOL™ FGC 3000 series of solvents (Vitse et al., 2011). Alstom and The Dow Chemical Company (Czarnecki et al., 2012) will continue to study the performance



**Fig. 5 – A schematic diagram of electro dialysis process (Dumée et al., 2012). A stack of alternating cation (C) and anion (A) exchange membranes are used to drive the ions ( $X^+$  and  $Y^-$ ) from the feed stream in to the concentrate stream.**

of ED reclamation in the Advanced Amine Process pilot plants for efficiency and waste stream characterization.

## 2. Comparison of reclamation technologies

A variety of reclaiming options are now available for amine purification. The use of purging or neutralization is unlikely to be sufficient to maintain amine purity in PCC systems. Other options, such as vacuum distillation, ion exchange, and electro dialysis, have matured and improved over the last two decades and are available as mobile service or permanent installations throughout the world. Some advantages and disadvantages of these processes are summarized in Table 1.

Distillation is only appropriate for MEA and other amines that are sufficiently volatile and stable at the temperatures that are required to distil the amine. Thermal reclaimers are operated at the PCC pilot plant using MEA or MEA blends as absorbents (Strazisar et al., 2003; Idem et al., 2006). However no detailed performance data of the reclaimers is available. For high-boiling point amines, distillation exposes the amine to high temperature and, hence, results in potentially further solvent degradation and carries energy penalty, which is particularly significant for PCC where energy efficiency is of paramount importance (Reynolds et al., 2012). In contrast, ion exchange and electro dialysis do not require high temperature and thus reduce the possibility of further thermal degradation. However, these two options cannot remove non-ionic contaminants. It is likely that vacuum distillation is best suited for applications where solvent degradation is an issue.

Ion exchange is ideal if the HSS concentration is low. However, higher HSS concentrations and total solution flow rates are likely to be present in a PCC scenario, and thus the equipment costs and scale become prohibitive (Dumée et al., 2012). According to MPR Services Inc. (pers. comm.) there is a limit to the size of a continuous ion exchange reclaiming unit. Until now MEA solvent for PCC cannot be handled in a full scale case. The amines with much higher resistance to degradation, such as AMP based solvents, could be better.

Electrodialysis has an advantage of lower chemical and water usage than ion exchange (Cummings et al., 2007; Byszewski, 2002). However, even a small quantity of  $\text{CO}_2$  in MEA solution can decrease the process effectiveness and increase the waste fraction. Specific energy consumption is linearly increased with the increasing  $\text{CO}_2$  loading (Volkov et al., 2013). In addition, the currently high costs associated with manufacture of selective membranes that are resistant to both high pH and amine solvents limit the application of ED

in PCC systems (Dumée et al., 2012). More work is required to match the membrane chemistry to the contaminated amine solution being treated.

## 3. Conclusions and prospects

The best approach to avoid amine solvent degradation is to address the conditions and circumstances which led to the degradation in the first place. However, it is not practical to eliminate all possible sources in an amine based PCC process. Hence a conscientious strategy for handling the issue of solvent contaminants, corrosion- and degradation products is the only option to limit waste handling/disposal and cost impact on PCC.

The root cause of solvent degradation in a PCC process is reaction of oxygen with the amine solvent. It is highly probable that solvent degradation products participate in in-process corrosion leading to dissolved metal contamination of the solvent. Such dissolved metal compounds speed up oxygen driven degradation reactions and hence lead to a vicious cycle. It is imperative that an effective solvent reclaiming process must be able to regenerate the solvent by removal of e.g. HSS, soluble metal ions (e.g.  $\text{Fe}^{2+/3+}$ ), and carbamate polymerization products. Hence a tailored solvent management strategy will be needed for each specific solvent in order to maintain optimal plant operation and cost reduction.

Three processes including distillation, ion exchange, and electro dialysis have been used in the natural gas sweetening industry for solvent reclaiming. Ion exchange- and electro dialysis reclamation processes can be utilized to reduce HSSs and some degradation products, but are not suitable for removal of the non-ionic degradation products. To date, solvent distillation (thermal reclaiming) is the only technology that can remove all degradation products. Therefore, at present, distillation is likely to be the most attractive solvent purification option for PCC. However, thermal reclamation still remains energy intensive, which is particularly significant for PCC where energy efficiency is of paramount importance. With the increasing focus on CCS, the current reclaiming technologies need to be continuously improved to achieve the highest recovery rate and quality of amine solvent at lowest possible cost.

An expected future trend for amine reclamation is to put focus on process integration of the current reclaiming technologies into the PCC process in order to drive down costs. Any of the currently available reclaiming technologies discussed above can be used for amine solvent regeneration, but each has advantages as well as significant limitations.

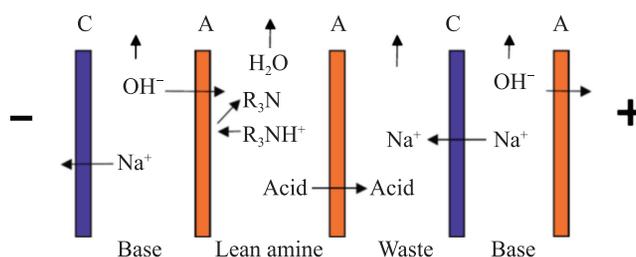


Fig. 6 – ElectroSep ED process (Parisi and Bosen, 2006a).

Integration of two or more reclaiming techniques is another approach to optimize the overall efficiency in removal of HSSs and degradation products. On the other hand, new and complex formulated solvents are expected to be developed to reduce PCC cost. Regardless of method types and operations, the new reclaiming techniques introduced must be able to handle all newly developed solvent systems.

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