



Reduction of chloride in amine from gas sweetening unit using a continuous virtual countercurrent ion exchange setup

Mehrdad Manteghian*, Javid Haddad

Department of Chemical Engineering, Faculty of Engineering, Tarbiat Modares University, Tehran, Iran

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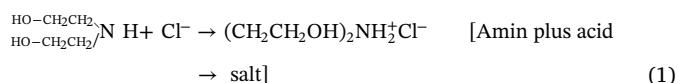
ABSTRACT

In this work, continuous chloride reduction was studied using a Continuous Virtual Countercurrent Ion Exchange setup (CVCIE). With this new laboratory scale setup constructed, ion exchange process which is inherently batchwise was conducted continuously. Lewatit Monoplus M800 OH and Amberjet 4500 OH resins were used for the first time for amine reclamation. According to the resins' critical properties, Lewatit Monoplus M800 OH showed a better performance in chloride separation. The resin performance is pH-dependent. In this regard, amine-to-resin ratio at different influent chloride concentrations showed that Lewatit Monoplus M800 OH has the potential for higher chloride exchange at a pH of 10.5–11. During several experiments, the optimum amount of caustic needed for regeneration of the saturated resins was determined. Setup results showed that chloride concentration in amine tank was reduced to 50 ± 10 ppm and the pH increased to 11.85 ± 0.15 which were the averages of three different tests.

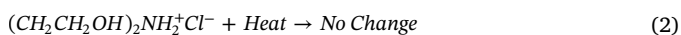
1. Introduction

Diethanolamine (DEA) is a chemical absorbent used in the sweetening of sour gases in refineries and petrochemical plants (Maddox, 1982; Sheilan et al., 2008). This process is carried out in a closed circuit and accumulation of contaminants such as chloride anions in compounds known as Heat Stable Salts (HSS) takes place in aqueous amine solutions. The presence of chloride in amine solutions produces a strong bonded salt which does not break up by heating amine in the regeneration column of a gas sweetening unit. Formation of chloride heat stable salts is very undesirable, mostly resulting in amine solution loss and corrosion (Gouedard et al., 2012; Supap et al., 2011; Islam et al., 2011).

• Chloride HSS formation reaction



• Desorber column reaction



Heat stable salts such as chloride, due to their anionicity lead to decreased pH of the solution, increased conductivity and also dissolution of the thin protective layer of surface named rust or carbon

monoxide ($\text{Fe}(\text{OH})_2$) (Kittel et al., 2009; Lemire et al., 2013; Gao et al., 2012; Mesgarian, 2014). Creation of corrosive products will result in fouling, priming, erosion, foaming etc. These salts also reduce the absorption capacity of DEA. Adding more amine to compensate for amine deficiency will increase the solution viscosity and so the absorption and desorption of the system will be affected. Total heat stable salts' concentration should not exceed 0.5% of the solution (5000 ppm) (Davoudi et al., 2014; Hajilary et al., 2011; Verma and Verma, 2009). The amine in gas sweetening units is exposed to contaminants introduced through chemical injection, sea water leakage in heat exchangers and makeup water. The amount of chloride increases gradually because of water evaporation at high temperatures. The only remedy is to remove these contaminants by amine reclamation. Among different methods of amine reclaiming has ion exchange shown better results in terms of cost and energy requirements (Wang et al., 2015; Dumée et al., 2012; Cummings et al., 2007; Pal et al., 2013).

Corrosion and fluid loss in the oil and gas industry cause staggering costs which have been reported to be 5.1 billion dollars and around 95 million pounds per year in the United States, respectively (Tems and Al-Zahrani, 2006; Koch et al., 2002; Abedinzadegan Abdi and Meisen, 1999; Stewart, 1991). This shows the necessity of amine reclamation. Decomposition of materials in corrosion is inevitable in many cases and its occurrence and related costs cannot be eliminated completely. With proper and optimal management, about 25–30% of annual corrosion costs are reversible. Also, the rest is considered as reducible costs by

* Corresponding author.

E-mail addresses: manteghi@modares.ac.ir, a.sameni@modares.ac.ir (M. Manteghian).

improvement of the process in amine systems (Tems and Al-Zahrani, 2006; Koch et al., 2002).

High amounts of chloride have been stated as an amine contaminant by Verma and Verma (2009), Hajilary et al. (2011), Mesgarian (2014), Davoudi et al. (2014), and Niazmehr et al. (2016). Hajilary et al. (2011) reduced the pressure drop of the absorber column from 0.272 ATM to 0.136 ATM by decreasing chloride and HSS levels and controlled the quality of sweet gas. Reduction of steam and energy consumption due to removal of chloride has been reported by Davoudi et al. (2014) and Hajilary et al. (2011). Improvement of the amine process along with internal corrosion rate reduction by chloride removal has been stated by Hajilary et al. (2011) and Niazmehr et al. (2016).

Ion exchange resins optimal performance have crucial role in CVCIE setup. Gode and Pehlivan (2006) showed better performance of resin Lewatit S 100 for Cr (III) separation at pH 4.5–3.5. Studies by Gode and Pehlivan (2006) and Rengaraj et al. (2001) indicated that pH reduction would significantly increase the resin capacity and lead to better resin performance. Alyüz and Veli (2009) have also showed similar results and obtained the optimal pH range.

In most chemical engineering processes, there is an advantage to be gained by continuous operation as compared with classical batch technology. Batch process is segmented into many individual steps that are often performed at separate facilities, thereby, requiring frequent interruptions in production activities (Harrington et al., 2013). Batch production presents many disadvantages including long throughput times from start to finish (Calabrese and Pissavini, 2011), large raw material and intermediate inventories, extensive validation and scale-up activities with products often of lower and/or inconsistent quality (Goršek and Glavič, 1997; Kim and Lee, 1993). On the other hand, in a continuous process, raw materials are put into the automated system that is capable of carrying out complex chemical tests according to the predetermined quality parameters. These quality checks occur throughout the manufacturing process and most importantly without interruption. Rejected products may be handled through recycling loops, enabling the reuse of some or all component parts (Schaber et al., 2011). Continuous process is widely applied in petro-chemical and bulk chemical industry for its high production rate, automated operation and saving in cost by reducing inventory and transportation costs (Plumb, 2005).

CVCIE is more efficient than a simple batch contact (one resin bed) in that a large volume of amine passed through a relatively small plant and the interruptions to flow required for regeneration are eliminated in practice by using two or more parallel resin beds. In practice, the total resin inventory in a well design CVCIE plant (large enough to contain the exchange zone) is less than that of a corresponding batch unit (Dorfner, 1991). In batch setups with more than one resin bed, standby beds play a critical role, while in the CVCIE setup we have no standby resin beds. No material lingering and destruction will happen in resin beds of CVCIE setups. Timing schedule in standby beds of batch setups is somehow hard to control while there is no such a problem in CVCIE setup with three or more resin beds as interference of the running time of the beds does not occur. Batch operations prolong amine reclamation process because of the service of one resin bed with the other one in standby mode which is dangerous at the time of sudden pollution of amine. Continuous countercurrent IX has found a few large applications, of which uranium winning is the most notable (Rodrigues, 2012). Continuous countercurrent has been used for water purification in industries (Hendry, 1982; Marinsky and Marcus, 1981) in solid-liquid multi-stage countercurrent extractors or (leaching) systems, food processing (Marinsky and Marcus, 1981; Ruthven and Ching, 1989; Reverchon, 1997), though it has not been developed and used for amine reclamation.

Chloride has been identified as the main source of pollution in the 5th South Pars gas refinery. In this study, attempts have been made to improve the ion exchange technology for amine reclamation using a Continuous Virtual Countercurrent Ion Exchange setup (CVCIE). By

conducting the targeted tests, it was possible to remove chloride with greater recovery so this setup lead to a better outcome. The strong anionic commercial resins have been used with acceptable results in production of demineralized water in different industries. Comparison of the effectiveness of the two resins was also performed. Further, Lewatit Monoplus M800 OH resin was identified as a better choice.

2. Theory and formulation

Ion exchange is a chemically clean and eco-friendly process in which the fluid phase is in contact with the solid phase (Liang et al., 2015; Mondal et al., 2012; Crittenden et al., 2012). Ion exchange can be treated as an adsorption process. The continuity equation for the column process around a segment of solid adsorbent between the height (x) and (x + dx) in the bed, during time (dt) is (Nachod and Schubert, 2013; Marcus and SenGupta, 2001; Knaebel, 2011):

$$-\rho_b \frac{\delta \bar{q}}{\delta t} = \varepsilon \cdot \frac{\delta C}{\delta t} + u_s \cdot \frac{\delta C}{\delta x} - D_d \cdot \varepsilon \cdot \frac{\delta^2 C}{\delta x^2} \quad (3)$$

Where, (ε) and (ρ_b) are the bed porosity and bulk density, respectively, (u_s) represents the superficial liquid velocity, (D_d) denotes the axial dispersion coefficient, (C) is the solution concentration, and (\bar{q}) shows the mean concentration of the solute in the solid phase. The rate equation for this process is (Nachod and Schubert, 2013; Marcus and SenGupta, 2001):

$$\frac{\delta q}{\delta t} = \frac{K_f \cdot a_u}{\rho_b} (C - C^*) \quad (4)$$

Where, (q) is the volume of contaminated amine, (K_f) is the mass transfer coefficient between ion exchange particles and contaminated amine, (a_u) shows the total external solid surface area per unit bed volume, (C) represents the ionic pollutant concentration, (C^*) denotes the concentration of ionic pollutant in equilibrium with concentration q in the particle at time t.

Equation (3) can be integrated if the equilibrium isotherm is known, and by knowing that the mass balance at a generic time, t, can be solved. Langmuir (one-layer adsorption) and Freundlich (multi-layered adsorption) isotherm equations are the general equilibrium models used to understand the adsorption system which are expressed in Equations (4) and (5), respectively (Nachod and Schubert, 2013; Marcus and SenGupta, 2001; Knaebel, 2011).

$$\frac{q_e}{Q_M} = \frac{K \cdot C_e}{1 + K \cdot C_e} \quad (5)$$

$$\frac{q_e}{Q_M} = K \cdot C_e^{Fr} \quad (6)$$

Where, (q_e) is the solid-phase concentration in equilibrium with liquid-phase concentration C_e , (Q_M) is the ultimate sorptive capacity, and (K) as well as (Fr) are the equilibrium constants. The continuity, rate, and equilibrium equations are solved simultaneously using the appropriate initial and boundary conditions. Thomas-BDST model is also applicable to the design of ion exchange columns (Kapoor and Viraraghavan, 1998).

Determining the resin volume and the exchange capacity for resin beds in continuous systems depend on the operating period chosen between two regenerations (Eq. (7)). Ion exchange adsorption is much faster than carbon adsorption and as a result we can use equilibrium assumption in design calculations (Howe et al., 2012). How much amine can be treated per liter of resin and the total amount of Cl^- resin can exchange before the bed is exhausted would be obtained by Eqs. (8) and (9), respectively (Dorfner, 1991; Rodrigues, 2012; Nachod and Schubert, 2013; Marcus and SenGupta, 2001; Knaebel, 2011).

$$V = \frac{Q \cdot t \cdot S}{C} \quad (7)$$

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