Reclaiming of degraded MEA solutions by electrodialysis: Results of ED pilot campaign at post-combustion CO₂ capture pilot plant

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A study of the behavior of heat stable salts (HSS) during electrodialysis (ED) reclaiming of monoethanolamine solvent (30 wt.% MEA) is reported in detail. Degraded lean MEA samples with a loading of approx. 0.2 mol/mol were taken from the solvent loop of post-combustion capture (PCC) pilot plant after 400, 535 and 972 h of operation at real conditions. The specially designed conventional pilot ED unit equipped with cation-exchanged membranes and anion-exchanged membranes was used. Before and after ED reclaiming, all streams were analyzed for specific solvent components. A quite uniform removal of all analyzed HSS anions (except for nitrate ions) during the ED treatment prevents accumulation of any specific undesirable compound in the solvent loop. Visual inspection of the ion-exchange membranes revealed the deposition on the membrane surface having reddish-brown color. It was experimentally confirmed that such deposition did not noticeably affect on membrane performance in ED process. Furthermore, it was demonstrated on the laboratory level that selected membranes possess a good long-term stability after being contacted with fresh and degraded MEA for approx. 2 years.

1. Introduction

Oxidative degradation by the presence of free oxygen in flue gases (approx. 6 vol.%) forms a wide range of degradation products including organic acids (e.g. formic, acetic, oxalic acids), amonia, amides and aldehydes (Goudard et al., 2012; Lepaumier et al., 2009; Fredriksen and Jens, 2013). Amine-based solvents can also react with inorganic, acidic impurities in flue gases (SO₂, NO₂, HCl, etc.) aside to the carboxylic acids to form heat stable salts (HSS) decreasing the CO₂ capacity of amine due to lower pKa value (Dumée et al., 2012; Strazisar et al., 2003).

Since HSS cannot be regenerated in the stripper under normal operation conditions, continuous build-up of HSS in the solvent loop needs certain countermeasures because of:

• Reduction of CO₂ absorption capacity of the amine solvent and deterioration of the overall system performance;
• Change of macroscopic properties of the solvent – increase of viscosity reduces the mass-transfer efficiency and leads to increased solvent circulation costs (Cummings et al., 2007; ElMoudir et al., 2012);
• Corrosion of equipment due to chelating effect of HSS (Rooney and DuPart, 1996–1997; Tangapanichakoon and McCarvey, 2006); furthermore, dissolved metals such as Fe, Cr, Ni can catalyze further oxidative degradation (Goff and Rochelle, 2006; Sexton and Rochelle, 2009);
• HSS and products of corrosion lead to stable solvent foam reducing gas–liquid surface area (Jouravleva et al., 2000; Cummings and Mecum, 1998);

To overcome the problem of HSS presence, different techniques have been proposed to reclaim amine-based solvents. Thermal reclaiming (amine distillation) is the most widespread HSS removal method (Sexton et al., 2014). Ion exchange (IX) reclaiming as an alternative method for removal of HSS anions (Jouravleva et al., 2000) was adapted from acid and metal removal process used in the water treatment (Zagorodni, 2006). Electrodialysis (ED), a mature membrane-based technology, is also considered as a promising alternative approach for the reclaiming of amine-based solvents. Preferential removal of charged species from the liquid stream
takes place through ion-exchange membranes in the presence of the electric field as illustrated in Fig. 1.

The ED process is based on the Donnan exclusion effect that consists in a reduction of the mobile ion concentration within an ion exchange membrane due to the presence of fixed ions of the same sign as the mobile ions. As a result, HSS ions are removed through anion-exchange membranes from the feed flow cells (diluate) to the concentrating cells. The purified solvent (diluate) is returned to the main solvent loop. The ED process is believed to be less energy-consuming technique than thermal reclaiming (Dumée et al., 2012) and with lower chemical consumption and waste level in contrast to IEX process (Wang et al., 2015). However, the principle of this method does not allow to remove non-charged degradation products.

The efficiency of ED reclaiming can be further optimized by a prior dosage of strong alkali base for desalting of the amine-based solvent. In 1990s, Unio Carbide (now The Dow Chemical Company) tested ED reclaiming with prior dosage of NaOH to the methyl diethanolamine (MDEA) solution on a pilot scale (Price and Burns, 1995), that allows to achieve approx. 90% of reduction of total HSS content. This process and specially developed polytetrafluoroethylene ion-exchange membranes were patented (Cohen and Gregory, 1999) and later commercialized for refineries under UCARESEP™ trade name (Burns et al., 1995). ElectroSep™ is another patented (Byszewski, 2003) and available ED process based on engineering solution of modified electrodialysis configuration of Dow’s technology (Hakka et al., 1994). ElectroSep™ providers retrofitted the conventional scheme by such techniques as alkali base addition directly to the modified arrangement membrane stack without its mixing with solvent and recirculation of the salt mobile phase. This solution helped to reduce the utility consumption and amine losses and enhance separation (Parisi and Bosen, 2006a, 2006b). The ED approach is currently being tested in Alstom-Dow Advanced Amine Process post-combustion CO₂ capture pilot plant using UCARSOL™ series of solvents (Vitse et al., 2011; Babuaro et al., 2014).

Despite to the fact that some companies have already implemented and tested ED for HSS removal, there is very limited information published in the literature. The work of Meng et al. (2008) seems to be one of the first scientific publication with detailed focus on evaluation of operating conditions and estimated energy consumption of HSS removal from 35% aqueous MDEA solution. Vasilevsky et al. (2009) described the lab- and pilot-scale test of ED unit for reclaiming of diethanolamine (DEA) used for natural gas sweetening. The authors stated that 89% of HSS were removed with relatively low DEA losses (<6%) although the amine alkalinization step was not applied as contrasted to work (Cohen and Gregory, 1999). S. Kentish et al. intensively investigated the potentials of ED reclaiming of MEA (Lim et al., 2014b), and the prior concentration of HSS by nanofiltration was proposed (Lim et al., 2014a).

As a part of FP7 project “OCTAVIUS”, ED reclaiming was demonstrated under real operating conditions at the post-combustion CO₂ capture pilot plant operated by EnBW AG and located at Heilbronn, Germany. In the recent publication (Bazhenov et al., 2014), some of the results of this ED pilot campaign and ED process parameters like specific concentrate volume and specific energy consumption as a function of initial HSS content were briefly presented and discussed. The primary goals of this work were as follows:

- Get an insight about the transport of the different compounds which are dissolved in the degraded MEA solvent during its ED reclaiming process;
- Investigate the impact of increasing heat stable salt concentrations on membrane performance/ED-performance in time;
- Determine the MEA loss under the available operation conditions;
- Evaluation of the ion-exchange membranes after ED reclaiming of real degraded MEA;
- Study of the membrane stability with regards to degraded MEA solvent contained dissolved, chelated heavy metals and HSS anions.

The results of ED reclaiming of three different samples of MEA taken from post-combustion capture (PCC) pilot plant after 400, 535 and 972 h of operation were selected for detailed investigation and discussion.

2. Experimental: materials and methods

2.1. Reclaiming of MEA by the ED unit

A flue gas slip-stream of about 1500 Nm²/h was taken from the bituminous coal-fired power plant downstream of the FGD. The PCC pilot plant was designed to capture 7.2 tons of CO₂ per day at average CO₂-concentrations of the power plant and a capture rate of 90% with 30 wt.% aqueous MEA solution (Rieder and Unterberger, 2013). The lean MEA-solvent at 35 °C with a loading of about 0.2 mol CO₂/mol MEA was collected after the cartridge filtration (5 μm) in the separate tank with a volume of 1001, taken after 400, 535 and 972 h of continuous operation of PCC pilot plant (so called solvent cases). The lean solvent was reclaimed by electrodialysis without dosage of strong alkali base (e.g. NaOH) since all MEA samples taken were required to be returned to the solvent loop with a minimal impact on PCC pilot plant performance.

As a follow-up of the lab-scale prototype testing (Volkov et al., 2014), the pilot ED unit was designed and manufactured by A.V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences (TIPS RAS), and then delivered to the PCC plant in Heilbronn for further operation. The electrodialyzer with active surface area of about 1.1 m² was equipped with commercial cation-exchange membranes MK-40 and anion-exchange membranes MA-41 (Shchekin/Azot Ltd., Russian Federation). In the beginning, all the cells in the electrodialyzer were filled with the same solution, so the transport of charged species from diluate to concentrate stream during the operation of the ED unit was caused by the presence of electric field and not by concentration gradient across the membranes. ED-reclaiming was carried out for 60 min and then the diluate stream was replaced by the new batch of degraded solvent from the solvent tank. Such cycles were repeated 5 times for each solvent case in order to collect sufficient amount of the concentrate stream for further analysis. The detailed protocol of the ED unit operation can be found elsewhere (Bazhenov et al., 2014). Some characteristics of ED unit electrodialyzers and ion-exchange membranes used are summarized in Tables 1 and 2, respectively.
Table 1
Some characteristics of ED unit electrodialyzer.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>MK-40</th>
<th>MA-41</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode and cathode</td>
<td>Ruthenium oxide coated titanium</td>
<td>Ruthenium oxide coated titanium</td>
</tr>
<tr>
<td>Active membrane area, m²</td>
<td>1.1</td>
<td>1.1</td>
</tr>
<tr>
<td>Spacer type, material</td>
<td>Single spiral-type, LDPE</td>
<td>Single spiral-type, LDPE</td>
</tr>
<tr>
<td>Flow path length per spacer, cm</td>
<td>560</td>
<td>560</td>
</tr>
<tr>
<td>Spacer thickness, mm</td>
<td>1.2</td>
<td>1.2</td>
</tr>
<tr>
<td>Number of desalting cells</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>Number of concentrate cells</td>
<td>24</td>
<td>24</td>
</tr>
<tr>
<td>Solvent flow, l/h</td>
<td>150</td>
<td>150</td>
</tr>
<tr>
<td>Linear liquid velocity, m/s</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Voltage mode, V</td>
<td>40–80</td>
<td>40–80</td>
</tr>
<tr>
<td>Current mode, A</td>
<td>2–5</td>
<td>2–5</td>
</tr>
</tbody>
</table>

Table 2
Some characteristics of ion-exchange membranes (n-azot, 2014; Kesore et al., 1997).

<table>
<thead>
<tr>
<th>Membrane</th>
<th>MK-40</th>
<th>MA-41</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type</td>
<td>Composites formed from the cation-exchange resins</td>
<td>Composites formed from the anion-exchange resins</td>
</tr>
<tr>
<td></td>
<td>KU-2 (polystyrene matrix cross-linked with divinylbenzene and fixed groups), polyethylene binder and nylon reinforcing net.</td>
<td>AV-17 (polystyrene matrix cross-linked with divinylbenzene and fixed groups), polyethylene binder and nylon reinforcing net.</td>
</tr>
<tr>
<td>Fixed groups</td>
<td>–SO_4^−</td>
<td>–N'(CH_3)_3</td>
</tr>
<tr>
<td>Rupture strength, MPA</td>
<td>&gt;11.0</td>
<td>&gt;11.0</td>
</tr>
<tr>
<td>Surface electrical resistance, Ohm/cm²</td>
<td>&lt;10.0</td>
<td>&lt;10.0</td>
</tr>
<tr>
<td>Transport number, fraction</td>
<td>&gt;0.98</td>
<td>&gt;0.94</td>
</tr>
<tr>
<td>Total static exchange capacity, relative to 0.1 M HCl or NaOH, of dried membrane, meq/g</td>
<td>2.6 ± 0.3</td>
<td>2.0 ± 0.3</td>
</tr>
<tr>
<td>Humidity content, %</td>
<td>5.6</td>
<td>6.5</td>
</tr>
<tr>
<td>Dry:</td>
<td>29.3</td>
<td>28.5</td>
</tr>
<tr>
<td>Swollen:</td>
<td>1.25</td>
<td>1.27</td>
</tr>
<tr>
<td>Density, g/cm³</td>
<td>1.16</td>
<td>1.16</td>
</tr>
<tr>
<td>Change in volume during swelling, %</td>
<td>8 ± 2</td>
<td>8 ± 2</td>
</tr>
<tr>
<td>Length:</td>
<td>30 ± 5</td>
<td>30 ± 5</td>
</tr>
<tr>
<td>Thickness:</td>
<td>5 ± 2</td>
<td>5 ± 2</td>
</tr>
</tbody>
</table>

The removal efficiency (η, %) for different solvent cases was used to study the behavior of individual HSS anions. This parameter was calculated as follows:

\[ η = \frac{ΔC_{t=0}}{C_{t=0}} \times 100% = \frac{C_{i,t=0} - C_{i,t=60}}{C_{i,t=0}} \times 100% , \]

where \( C_{i,t=0} \) is the initial concentration of \( i \) individual HSS anion before ED treating, meq/l; \( C_{i,t=60} \) is the concentration of \( i \) individual HSS anion after 60 min of ED operation, meq/l (meq/l = milliequivalent/liter).

The concentration coefficient (CE) for different solvent cases was used to compare transport efficiency of different species to the concentrate line and was calculated as follows:

\[ CE = \frac{C_{k,concentrate,finish}}{C_{k,diluate,star}} = \frac{ΔV_k/ΔV_{concentrate}}{ΔV_k/ΔV_{diluate,star}} ; \]

where \( C_{k,diluate,star} \) is the concentration of \( k \) individual compound in the diluate before ED treatment (equal to concentrate solution before ED treatment), mol/l or meq/l; \( C_{k,concentrate,finish} \) is the concentration of \( k \) individual compound in the concentrate solution after 5 cycles of ED treatment, mol/l or meq/l; \( ΔV_k \) is the total amount of transported compound to concentrate line during 5 cycles of ED treatment, mole or meq; \( ΔV_{concentrate} \) is the volume change of concentrate solution, l.

2.2. Chemical analysis of the solvent samples

To validate the ED reclaiming of MEA solvent under real operation conditions around 50 samples were chosen to be chemically analyzed for a better understanding of the behavior of different compounds. The wide spectrum of species, such as HSS anions, heavy metals, MEA and CO₂-loading were determined by the following methods:

- The concentrations of anionic species which could be analyzed were quantified by ion chromatography (IC) with a system from ThermoFisher ( Dionex ICS-2100, Dionex IonPac® AS15 column). During the measurements, the 8 mmol/l KOH was used as the eluent. For the anions detection, the conductivity measurement after AERS 500 suppressor technique from Dionex was used.
- The determination of heavy metals has been fulfilled by induced coupled plasma atomic optical emission spectroscopy (ICP-DES, Perkin Elmer Optima 3000 LX).
- The MEA concentration and the CO₂-loading of the solvent were determined by the titration of the samples with 1 N HCl using a commercial titrator from Xylem Inc. The first equivalence point (at pH = 7) allowed to calculate the MEA-loading, while the second one (at pH = 4) was attributed to reaction between HCl and CO₂–bonded MEA with complete removal of carbon dioxide and allowed to determine the overall MEA concentration. CO₂–loading was calculated from the difference between two values stated above.

2.3. Evaluation of membranes after ED reclaiming

The chemical composition of the membrane surfaces was determined by X-ray fluorescence analysis with a Thermo Scientific ARL PERFORM'X WDXRF spectrometer operating at 2.5 kW and using a Rh-tube. The method allows to detect all elements starting with Fluor (F) in the surface layer with the depth in the range of 4–30 μm. The contents of elements are half quantitative due to the absence of standard available for quantitative analysis.

2.4. Long-term membrane stability tests

The long-term stability of selected membranes was evaluated by using synthetically degraded MEA solvent and lab-scale electrodialyzer. Ion-exchange membranes MK-40 and MA-41 after continuous contact with non-degraded MEA during approx. 14.5 months were taken out from the lab-scale ED unit (Volkov et al., 2014) and placed in synthetically degraded 30 wt.% MEA for the next 7.5 months. The degraded MEA solvent was prepared in accordance with the following protocol: 30 wt.% aqueous MEA solution contained with CO₂ loading of 0.2 mol/mol and 2.4 g/l organic and inorganic anions as corresponding acids (Volkov et al., 2014) was placed into air- and leak-proof stainless steel vessel and conditioned at 120 °C (800) and 150 °C (2300). After the long-term exposure to the synthetically degraded MEA solvent, the ion-exchange membranes were washed with water and placed back to lab-scale ED unit. The protocol of reference ED tests for fresh and aged membranes was identical as described elsewhere (Volkov et al., 2014) except the use of 30 wt.% aqueous MEA solution with 0.2 mol CO₂/mol in the diluate stream and distilled water (101) in the concentrate stream.
3. Results and discussion

3.1. HSS accumulation during PCC pilot plant operation

Fig. 2 represents the build-up of HSS anions in MEA lean solution during the campaign at PCC pilot plant, measured by ion chromatography. Such acids react with free MEA to form heat stable salts. The content of HSS was constantly increasing in time (Fig. 2), and the major compounds of detected HSS were carboxylic acid anions such as formate, acetate, glycolate and oxalate, which are the products of oxidative MEA degradation (Gouedard et al., 2012). The formation of formic acid dominates compared to the formation of acetate, glycolate and oxalate.

Inorganic anions were mainly represented by sulphate and nitrate ions due to absorption of SO₂ and NO₂ out of the flue gas. The domination of formate, oxalate and sulfate among the others was in common with another 30% MEA campaign at the PCC pilot plant at Heilbronn (Unterberger et al., 2013).

Since there is a trade-off between reclaiming cost and the desired HSS content in the solvent, three MEA samples with the initial HSS concentration of about 0.78 g/l (summed up concentration of the detected species after 400 h), 1.07 g/l (535 h) and 2.27 g/l (972 h) were taken to study the performance of ED unit toward HSS removal.

3.2. Behavior of HSS anions

The solvent was reclaimed by electrodialysis for 60 min, and then the diluate part was discharged and refilled for the next cycle with the solvent from 1001 feed tank taken as a degraded MEA sample from PCC pilot plant at a certain time. To simulate a continuous regime of operation, the reclaiming cycle was repeated 3 or 4 times while the concentrate stream remained in the system for all 4 or 5 cycles.

Fig. 3 presents the typical kinetics of the decreasing anion concentrations in diluate (feed) stream of the pilot ED unit for MEA (972 h) solvent case. All analyzed HSS anions were transferred through the membranes to the concentrate stream from the very beginning of reclaiming. All analyzed HSS anions achieved a reduction of about 50% within 1 h of ED operation with an active membrane area of 1.1 m² (see Table 3). The total reclaimed volume was approx. 291 for each solvent case. Besides the analytical errors in analysis for the individual species in the degraded MEA solvent, the deviations in the performance of ED unit at the first and the last cycle can be explained by combination of at least two effects: (i) enhancing of the ion transport due to the increase of the liquid temperature by about 21–24 °C (Bazhenov et al., 2014) as a result of partial dissipation of the electricity to the heat during 4 or 5 cycles of operation, (ii) back diffusion of charged species from the concentrate to the diluate in accordance with the concentration gradient caused by the increase of HSS anions in the concentrate during the operation.

The removal rates of the analyzed HSS anions from differently degraded MEA solvents are summarized in terms of removal efficiency (see Fig. 4). Since the mobility of individual compounds in the electrodialysis process depends on the charged form, the dissociation constants of corresponded acids pKₐ (Haynes, 2012) are listed in brackets. The highest removal efficiency (up to 90%) was achieved for nitrate ions that could be explained by its very low pKₐ value (very strong acid) and, hence, its complete dissociation
in the solution. The drop in removal efficiency for hydrochloric acid can be explained by its low concentration in the MEA solvent and the influence of chloride ions releasing from the anion-exchange membrane. Sulfuric acid is also a strong acid, but both the size of this anion and the double charge hindered its transport (Van der Bruggen et al., 2004). Generally quite small differences in removal efficiency were observed for all HSS anions except for nitrate regardless to remarkable differences in acid strength expressed by pKa. An explanation for this behavior is that the transport of bulky counter-ion [MEAH+] limits the mobility of anions in electrodialysis (Van der Bruggen et al., 2004). Taking into account the complexity composition of degraded MEA solution, the additional study of the mobility of the key compounds in the presence of other factors or chemicals by using more simplified model solutions is highly required. Meanwhile, it can be concluded from the obtained results that a quite uniform removal of all HSS anions during the ED treatment prevents accumulation of any specific undesirable compound in the solvent loop.

3.3. Behavior of heavy metals

As far as the ion-exchange membranes possess quite open porous structure with pore diameters up to 5 nm (Novikova et al., 2010), the rejection of isolated heavy metals by the membrane as a result of sieving effect is rather unlikely. Nevertheless, in all experiments, no transport of Fe, Cr and Ni through the membranes into the concentrate has been observed. This effect can be explained by a few reasons: (1) from different ED application fields it is widely known that multivalent ions (heavy metals ions in our case) are more strongly retained in the membrane material and thus thought to be transported more slowly (Van der Bruggen et al., 2004; Pérez et al., 1994; Andrés et al., 1995; Šimová et al., 2010); (2) due to relatively high pH value of solvent (pH>10) it is quite possible that determined heavy metals are presented as extremely fine particulate matter (e.g. iron hydroxide) or in charged, chelated forms like bulky complexes with MEA (Scheiman, 1962; Dixon and Williams, 1950; Salem, 1995) having a reddish-brown color, which transport is extremely hindered. The latter reason seems to be confirmed by the presence of the deposition of metals derived particles on the membrane surfaces (see Section 3.5). An enrichment of these heavy metals in the diluate took place (see Table 4) which might explain the dark reddish-brown color of the diluate compared to the lighter concentrate (Bazhenov et al., 2014).

3.4. Behavior of protonated MEA and CO2 loading

The study of electrodialysis reclaiming was conducted alongside with the long-term campaign at PCC pilot unit using lean MEA solution as delivered, and the reclaimed and concentrated solutions were mixed together and returned to the solvent loop to minimize the impact on the MEA campaign. Hence, the addition of strong alkali base or higher regeneration of the solvent to lower loadings was out of consideration. The lean MEA with CO2 loading in the range of about 0.2 mol/mol was used for the ED campaign without any pretreatment. Such an approach might have a certain drawback because the carbamate ions in the liquid phase might cause additional loss of MEA during electrodialysis process (Handagama et al., 2010; Parisi, 2015). One of the key process parameters is, of course, the absolute losses of MEA to the concentrate line during ED-process, which were under the circumstances of the PCC pilot relatively high. For 400 h solvent case, the amount of MEA transported to the concentrate through 5 cycles of ED reclaiming was 1.6 kg. Based on the total summarized amount of MEA introduced to the ED system with solvent to be reclaimed (8.6 kg) one can evaluate the relative MEA losses as 18.5%. Analogous results can be achieved for other degraded MEA samples: for MEA 535 h the amount of transported MEA was1.6 kg, the total amount of MEA before ED process was 8.7 kg, relative MEA losses were 18.3%; for MEA 972 h the amount of transported MEA was 1.3 kg, the total amount of MEA before ED process was 8.4 kg, relative MEA losses were 15.5%. Lower loss of MEA can be expected by treating the lean solution to lower CO2-loading.

From the process design point of view, the MEA losses were also represented as the direct MEA flow to the concentrate chambers and were evaluated in the range of 3.8–4.7 mol/m² h (see Table 5).

### Table 3
Total reclaimed volume of MEA and the kinetics of the sum of analyzed HSS anions in diluate (feed) stream for the first and the last cycle.

<table>
<thead>
<tr>
<th>MEA</th>
<th>Number of cycles</th>
<th>Total reclaimed volume, l</th>
<th>Sum of analyzed HSS anions, meq/l</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>First cycle</td>
<td>Last cycle</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0</td>
<td>20</td>
<td>40</td>
</tr>
<tr>
<td>400 h</td>
<td>5</td>
<td>29</td>
<td>15.6</td>
<td>14.4</td>
<td>11.5</td>
</tr>
<tr>
<td>535 h</td>
<td>5</td>
<td>29</td>
<td>21.4</td>
<td>19.8</td>
<td>15.1</td>
</tr>
<tr>
<td>972 h</td>
<td>5</td>
<td>29</td>
<td>47.5</td>
<td>36.1</td>
<td>25.3</td>
</tr>
</tbody>
</table>

### Table 4
Heavy metal content in feed compared to diluate (first cycle).

<table>
<thead>
<tr>
<th>MEA</th>
<th>Concentration change, mg/l</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe</td>
</tr>
<tr>
<td>400 h</td>
<td>19.0 → 20.0</td>
</tr>
<tr>
<td>972 h</td>
<td>311 → 334</td>
</tr>
</tbody>
</table>
The comparable values were found out by Lim et al. (Table 4 in Lim et al., 2014b): MEA flow for approx. 3.2 mol/m²h was calculated for MK-1 ED cell with membranes of comparable thickness (0.3–0.5 mm) from Membranes International Inc. At the same time, MEA losses during pilot-scale testing of EDM were much lower than that for FT-ED-40 ED cell with thin (<0.22 mm) membranes (10 mol/m²h for Neosepta membranes and 11.2–48.3 mol/m²h for Fumasep membranes) (Lim et al., 2014b).

In order to document the high quality of the ED process under these limiting circumstances at the pilot plant a specific comparison in mol/mol has been placed. The analytical results of the diluate and concentrate samples show that MEA and carbamate are accumulated in the concentrate during electrodialysis. To understand the transport behavior of MEA, the mole ratio of permeated MEA to CO₂ was calculated for all solvents, and these values were in the range of 3.0–3.4 (Table 5). In contrast to Lim et al. (2014b), the direct diffusion of MEA and carbon dioxide through ion-exchange membranes was eliminated since the composition of the diluate and concentrate chambers were identical at the beginning of the process. Taking into account the accumulation of MEA as [MEA]⁺ and CO₂ as carbamate during the ED reclaiming, the migration of those compounds as the isolated species from the diluate to the concentrate compartment is concerned to the value of the CO₂ loading and leads to higher MEA losses with the reclaim rate.

The loss of MEA with regards to the removed amount of HSS anions is also important in view of indicating the trade-off between the solvent loss and desired level of remaining unwanted compounds. As expected, the increase of initial content of HSS anions in the solution lead to a significant drop in the relative loss of MEA per mole of the removed HSS anions – from 109 (MEA at 400 h) down to 33 (MEA at 972 h) as shown in Table 5. Despite the fact of noticeable difference in mole flow for MEA and HSS anions, the analysis of concentrate composition confirmed that the ED reclaiming still provides preferential removal of analyzed HSS anions resulting in about 4-fold increase of HSS anions in concentrate (see Fig. 5).

### Table 5

<table>
<thead>
<tr>
<th>MEA</th>
<th>Initial content of analyzed HSS anions, meq/l</th>
<th>Mole flow, mol/m²h MEA</th>
<th>CO₂</th>
<th>Sum of analyzed HSS anions</th>
<th>MEA/CO₂</th>
<th>MEA/analyzed HSS anions</th>
</tr>
</thead>
<tbody>
<tr>
<td>400 h</td>
<td>15.6</td>
<td>4.72</td>
<td>1.52</td>
<td>0.038</td>
<td>3.1</td>
<td>109</td>
</tr>
<tr>
<td>535 h</td>
<td>21.4</td>
<td>4.65</td>
<td>1.57</td>
<td>0.051</td>
<td>3.0</td>
<td>82</td>
</tr>
<tr>
<td>972 h</td>
<td>47.5</td>
<td>3.78</td>
<td>1.08</td>
<td>0.135</td>
<td>3.5</td>
<td>33</td>
</tr>
</tbody>
</table>

The X-ray fluorescence analysis of the surface of the MK-40 and MA-41 membranes before and after ED campaign were carried out for the identification of the inorganic part of the deposits. Table 6 lists the detected main elements on the surface of the MK-40 and MA-41 membranes. The cation-exchange membranes MK-40 have sodium as a counter-ion. During the ED process, Na⁺ ions were replaced by [MEA]⁺, which cannot be detected with the X-ray fluorescence analysis. Excess of sulfur is attributed to the presence of sulfonic-groups in ion-exchange resin of MK-40. As analogs, anion-exchange membranes MA-41 possess an excess of chloride as a counter-ions. The noticeable increase in iron (Fe) content for the MA-41 confirms the domination of iron-contained products at the surface of the membrane.

The observed deposition on the surface of ion-exchange membranes did not noticeable influence on the electrodialyzer performance as it was demonstrated recently by the control test of the
ED unit with the reference MEA solvent (Bazhenov et al., 2014). Nevertheless, the samples of MK-40 and MA-41 membranes used in pilot campaign were tested once again at the lab-scale ED unit (Volkov et al., 2014) with the model aqueous solution containing 30 wt.% of MEA and 2.4 g/l of oxalic acid as a typical HSS compound. Fig. 7 presents the results of this experiment with the fresh membranes of MK-40 and MA-41 alongside with the membranes taken from ED unit after the reclaiming campaigns. The similar character

Table 6
Element composition (wt.%) on the surface of MK-40 and MA-41 membranes before and after the ED campaign given by X-ray fluorescence analysis (minor elements are not given).

<table>
<thead>
<tr>
<th>Element (wt.%)</th>
<th>Membrane MK-40</th>
<th>Membrane MA-41</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before</td>
<td>After (diluate)</td>
</tr>
<tr>
<td>Na</td>
<td>19.7 ± 0.3</td>
<td>2.5 ± 0.1</td>
</tr>
<tr>
<td>Si</td>
<td>0.9 ± 0.1</td>
<td>1.0 ± 0.1</td>
</tr>
<tr>
<td>S</td>
<td>72.8 ± 0.3</td>
<td>91.8 ± 0.3</td>
</tr>
<tr>
<td>Cl</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Ti</td>
<td>1.4 ± 0.1</td>
<td>1.0 ± 0.1</td>
</tr>
<tr>
<td>Cr</td>
<td>–</td>
<td>0.2 ± 0.1</td>
</tr>
<tr>
<td>Fe</td>
<td>0.7 ± 0.1</td>
<td>1.2 ± 0.1</td>
</tr>
<tr>
<td>Zn</td>
<td>0.4 ± 0.1</td>
<td>0.8 ± 0.1</td>
</tr>
<tr>
<td>Mo</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

ED unit with the reference MEA solvent (Bazhenov et al., 2014). Nevertheless, the samples of MK-40 and MA-41 membranes used in pilot campaign were tested once again at the lab-scale ED unit (Volkov et al., 2014) with the model aqueous solution containing 30 wt.% of MEA and 2.4 g/l of oxalic acid as a typical HSS compound. Fig. 7 presents the results of this experiment with the fresh membranes of MK-40 and MA-41 alongside with the membranes taken from ED unit after the reclaiming campaigns. The similar character

Fig. 6. General view of the cation-exchange membrane MK-40 (a – diluate side, b – concentrate side) and the anion-exchange membrane MA-41 (c – diluate side, d – concentrate side) after ED reclaiming campaign.
of curves confirms that the iron-contained deposition does not noticeably change the membrane performance for the electrodialysis.

### 3.6. Long-term membrane stability

It should be noticed that the overall contact time of the membranes of pilot EDM with real MEA solutions did not exceed 18 days. To evaluate the long-term membrane performance the lab-scale ED unit (Volkov et al., 2014) was assembled, and MK-40 and MA-41 membranes, which were in contact with MEA during last 440 days, were placed in synthetically degraded MEA solvent for the next 217 days at ambient conditions. A similar change of membrane color after contact with degraded MEA solvent and no visual membrane damage were observed. After washing the membranes in the water, MK-40 and MA-41 membranes were placed in the same lab-scale ED unit and the reference experiment (30% wt. MEA, 0.2 mol CO₂/mol MEA) was carried out as was done for the initial membranes. Fig. 8 shows that there is a slight decrease in performance (not more than 20%) for the membranes exposed to MEA solvents for approx. 2 years over the fresh membranes. Such a result should allow to expect long-term lifetime of the selected ion-exchange membranes in the ED-reclaiming process.

### 4. Conclusions

#### 4.1. Summary

To summarize the results of this study, the following remarks on the utilization of electrodialysis reclaiming of degraded MEA solvent used in the post-combustion process can be given. Five times repeated runs of ED reclaiming with the identical lean MEA solution confirmed the same removal behavior from dilute to concentrate. Three runs with differently degraded lean MEA solution after 400, 535 and 972 h of PCC pilot plant operation and increased HSS concentrations revealed a constant removal efficiency of HSS. Due to the constant lean loading of 0.2 mol/mol the loss of MEA with the concentrate was between 18.5% (400 h run) and 15.5% (972 h run), depending on the level of HSS. The autopsy of the membrane stack after the runs showed a brownish colored, thin layer at the surfaces of both membrane types, but more intensive at the anion exchange membrane surface. Iron is mainly enriched in this deposited layer. Lab test with the new and the used membranes revealed similar results, thus the deposited layer did not impact the efficiency of the membranes. A slight decrease of performance was determined when the membranes were exposed to synthetically degraded MEA solution for approx. 2 years compared to new ones in a lab test.

#### 4.2. Lessons learned

ED reclaiming provides quite uniform removal of HSS anions regardless the nature of such anions. Heavy metals cannot be removed by the electrodialysis. Long-term stability of ion-exchange membranes in the presence of amine-based solvents can be expected. At lower CO₂ loading values, an optimized operation of the ED pilot will possibly lead to lower MEA losses; the further decrease of MEA loss might be possible by dosage of NaOH resulting in the shift of the HSS bounded to MEAH⁺ to corresponded sodium salts and releasing of MEA in the neutral form.

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### References


