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Development of a facile reclaiming process for degraded alkanolamine and glycol solvents used for CO₂ capture systems



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ABSTRACT

Post-combustion CO_2 capture based on alkanolamine solvents is currently the most developed and ready-to-use technology to reduce CO_2 emission into the atmosphere. The CO_2 gas captured by this method usually displays a moderate level of moisture, which requires dehydration through the use of glycol solvents. However, due to exposure to impurities in the flue gas stream and high temperatures, these solvents can experience chemical and thermal degradation. The build-up of degradation products can lead to plant operational problems and increase consumption of utilities such as gas and electricity.

A new reclaiming process was therefore developed to separate degradation products and other types of impurities from these solvents. A detailed analysis of the feed stream, the recovered product stream, and the waste stream showed that this novel reclamation technology is capable of removing most of the undesirable impurities and degradation products and restoring the solvent to almost its original purity at a high recovery rate with minimal energy consumption. The data generated by this study will be useful for scaling-up and designing commercial reclaimers that can meet the solvents' cleanup targets with low expenditure, low energy consumption, and minimal waste for disposal.

1. Introduction

Carbon dioxide (CO_2) is one of the most impactful greenhouse gases due to its having, after water vapor, the second largest emission volume (Songolzadeh et al., 2014). Fossil fuel combustion is the main contributor to CO₂ emissions to the atmosphere (Quadrelli and Peterson, 2007). Consequently, various kinds of CO₂ removal methods have been under intensive research and development, such as absorption, adsorption, membrane-based separation, and cryogenics, among which chemical absorption based on alkanolamine is the most widely developed and ready-to-use technology (Aaron and Tsouris, 2005; Strazisar et al., 2003; Duke et al., 2010; Aboudheir and Elmoudir, 2013; ElMoudir et al., 2014). Large amounts of data and information have been published on operating plants utilizing chemical absorption based on alkanolamine solvents to remove CO₂ from flue gas (Critchfield and Rochelle, 1987; Fytianos et al., 2016; Jassim et al., 2007; Kierzkowska-Pawlak, 2010; Lee et al., 2013). However, the gas captured by this method usually displays a moderate level of moisture, which requires dehydration before delivering the CO₂ to the export pipeline in order to prevent potential hydrate formation and corrosion in the export line.

Glycol solvents provide an effective means for gas dehydration (Kohl and Nielsen, 1997). However, alkanolamine solvents like monoethanolamine (MEA) and glycol solvents like monoethylene glycol (MEG) can never work trouble free. Exposed to impurities in the flue gas stream and high temperatures in the reboiler, alkanolamine solvents can experience chemical and thermal degradations (ElMoudir, 2012; Bougie and Iliuta, 2014; Davis and Rochelle, 2009; Gouedard et al., 2012; Gouedard et al., 2014). Glycol solvents are also susceptible to thermos-oxidative degradation reactions (Collins, 1964; Brown et al., 1987; Clifton et al., 1985).

For alkanolamine solvents, the most significant degradation products are heat stable salts (HSSs), which have a great impact on plant equipment and operation. These salts arise mainly from the formation of ionic degradation products of organic acids such as acetic and formic acids. These organic acids derive from the solvent degradation reactions with O_2 and other impurities (Bacon, 1987; Blanc et al., 1981). Once formed, these acids react immediately with the solvents to form complex salts called HSSs (formate or acetate with amine solvent). The major kinds of degradation products for glycols are also organic acids. Any accumulation of degradation products and impurities can give rise

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to great operating challenges and problems in the entire process of CO_2 capture such as an increase in solvent corrosivity, foaming tendency, and fouling formation as well as in consumption of utilities such as energy/steam and power.

Currently, the most widely used reclaiming technologies include ion exchange, electrodialysis and thermal reclamation. Ion exchange and electrodialysis are only capable of removing ionic degradation products such as HSSs and organic acids (ElMoudir et al., 2012). These technologies require feed filtration prior to feed processing. In addition, they sometimes require degassing the feed to remove or reduce acid gas residual in the solvent in order to minimize interference between the acid gas and these two reclamation systems as in both systems the acid gas (i.e. CO_2) will be neutralized along with HSS and other ionic species. Failure to remove non-ionic degradation products can still lead to operational problems (ElMoudir, 2012). Thermal reclamation, using heat energy to evaporate solvent from high-boiling degradation products, can remove not only ionic and non-ionic contaminations, but also solid impurities (ElMoudir et al., 2012). Therefore, this form of thermal reclamation is the only feasible option for solvent reclamation.

The leading company in the design and development of thermal reclamation is Canadian Chemical Reclaiming (CCR) Technologies. The reclaimers developed by CCR have five versions. In the first version of the reclaimer, the amine solvents co-evaporate with some of its degradation products. The waste volume also needs to be reduced for easy handling and disposal (Beasley and Merritt, 1992). The second version can have high solvent recovery and low solubility of inert liquid-like paraffinic oil in amine and reduced thermal degradation during the reclamation process. However, it has two separation steps and the contamination of the inert liquid is very likely to cause foaming and plugging problems (Meisen et al., 1996). The third version is complicated as it has two heating zones (Abry et al., 1999). The fourth version of the reclaimer needs to mix recovered solution with degraded feed to enhance the solvent recovery rate (Razzaghi et al., 2003). However, no data is available about the fourth or fifth versions. Thus, the currently existing thermal reclamation technologies need further improvements to reduce the complexity of the reclaimer, eliminate contaminants from the recovered solvent, increase the solvent recovery rate, and reduce solvent loss and utility consumption.

In this study, a novel thermal reclaimer is presented. It is a simple vacuum unit that is able to remove most undesirable impurities from degraded alkanolamine/glycol solvent and restore these solvents to their original purity at a high recovery rate and minimal energy consumption. To demonstrate the efficiency of this reclaimer, degraded solvents of monoethanolamine (MEA) and monoethylene glycol (MEG) obtained from two Canadian working plants were used as feeds of the novel reclaimer. Detailed analysis of the feed stream, the recovered product stream, and the waste stream were carried out and the results are presented and discussed in this paper.

2. Experimental: materials and methods

2.1. Reclaiming of MEA and MEG by the thermal reclaiming unit

The process flow diagram of the new reclaimer is shown in Figs. 1 and 2. This reclaimer included a feed tank, which stored the degraded feed of MEA or MEG. Degraded MEA solvent was mixed with a chemical solution of 50% (mass weight) sodium hydroxide (NaOH) in advance to liberate amines from HSSs in the degraded solvent. The amount of NaOH added depended on the HSSs content of the degraded MEA solvent. The reclaimer also included an evaporator where thermal distillation took place under vacuum. The heat energy was provided by hot oil, which came from the recycling oil bath and then travelled in the jacket of the evaporator. Because degradation products and contaminants have higher boiling points, they could be left in the evaporator when the target solvent and water evaporated. The reclaimed product was condensed in the condenser unit and finally collected in the product flask. The setup also included a recycling cooling system, which could efficiently condense all the vapors.

At the beginning of the reclamation process, the production rate was high while the concentration of the solvent in the product was low. After a while, the production rate slowed down while the solvent concentration increased gradually. The system reached steady state when the production rate remained almost stable and the solvent concentration of the reclaimed product was almost equal to the feed concentration.

During the reclamation process, the liquid inside the evaporator (waste) gets darker and darker. After an extended period of operation, the liquid shows two layers. The upper layer is dark brown liquid while the bottom layer is dense with a black creamy color. The upper layer has a much greater volume than the bottom layer. When the waste is collected for sampling, the upper layer travels much more easily as it is less dense.

Most of the alkanolamine and glycol solvents cannot be reclaimed in the atmospheric pressure because their boiling points are higher than their degradation temperatures under the atmospheric pressure. For instance, MEA and MEG are thermally unstable at or above 421 K (Dow, 1962) and 464 K (Guide, 2008) respectively. A vacuum pump was thus used to maintain the vacuum pressure. When the waste became highly concentrated, it was withdrawn from the bottom of the evaporator and collected. During the steady state of the reclamation, feed was frequently added to the evaporator to make the liquid level inside the evaporator almost stable. The main operating parameters of the test campaigns for degraded MEA and MEG solvents are summarized in Table 1.

2.2. Analysis of the solvent samples

To validate the efficiency of the new reclaimer, 10 reclaimed products during the steady state were collected for analysis, along with one feed sample and two samples of the processing fluids. The routine analysis included the physical property measurements of density, viscosity, and refractive index. For MEA samples, MEA concentration, HSSs content and CO_2 loading were also routinely analyzed.

- Densities were measured using an Anton Paar density meter (DMA 4500) at a temperature of 293.15 K. Viscosity measurements were performed with a rotational viscometer (model SMART, Fungilab S.A.). The instrument contains a measuring cell, which is connected with a thermostatic bath to allow the samples to be tested under a standard temperature of 293.15 K. The refractive indices of the solvents were measured using a digital refractometer (model PA230X, MISCO Refractometer) at a temperature of 293.15 K.
- The exact solvent concentration of MEA was determined by volumetric titration with a standard solution of 0.1 N hydrochloric acid (HCl) to the endpoint determined by both methyl orange indicator and pH meter. CO₂ loading was determined by volumetric titration with a standard solution of 0.1 N sodium hydroxide (NaOH) to the endpoint determined by pH meter. The same titration method of CO₂ loading was employed to determine the heat stable salts (HSSs) contents in the solvents, after a full reflux distillation to strip all CO₂ in these samples.
- Further detailed analysis was conducted in the Polaris Laboratories, Edmonton, Alberta, to determine total hardness, freeze point, pH waters, visual test, specific conductance, boil point, and total dissolved solids. The elemental contents and degradation products were measured using inductively coupled plasma (ICP) and ion chromatography (IC) respectively. The concentration of MEG in each sample was also determined by ion chromatography (IC). The methods used by the Polaris Laboratories can be found at www2.eoilreports.com/CompleteTestList.



Fig. 1. Process flow diagram of the new reclaiming unit.

3. Results and discussion

3.1. Monoethylene glycol (MEG)

Solvent color is a visual indicator of solvent purity. Fig. 3 shows the colors of the waste, the reclaimed product, and the feed. The fresh MEG solvent, whether pure or dissolved in water, should be clear and colorless. As shown in Fig. 3, the reclaimed product is clear, which indicates the removal of degradation products and impurities. Darker color of a sample usually indicates a higher level of degradation. Because the waste has the highest solvent contamination, it is observed as opaque black. The visual tests also show that there is no non-magnetic precipitation in the reclaimed solvents. However, the feed and the waste showed minor flocculant and flake.

The element concentrations of impurities in 10 reclaimed products, feed and two waste fluids are summarized and listed in Table 2. As seen from Table 2, the reclaimed products are free of corrosion metals Fe, Al, Pb and Zn, contaminants Ca and Mg, corrosion inhibitors B and Mo, and carrier salts Na and K. Although corrosion inhibitors Si and PO_4^{3-} still

Operating parameters of the test camp vents.	paigns for degra	ded MEA and	d MEG sol-
Parameters	Unit	Value	

Parameters	Unit	value	value		
		MEA	MEG		
Hot oil temperature Absolute operating pressure of reclaimer Cooling water temperature	K kPa K	413 38.00 281	445 20.00 279		

exist in the reclaimed products, their concentrations are very low compared with those in the degraded feed. Moreover, the value of each element concentration is quite stable in different reclaimed products, which proves that reclaimed solutions collected during the steady state are almost the same. The silicon concentrations of the reclaimed products range from 3 to 7 mg/L and the phosphate concentrations are also within a narrow range of 6–15 mg/L.

To better evaluate the performance of the reclaimer, Fig. 4 presents



a) the vacuum pump, cooling system and feed tank b) principal part of reclaimer Fig. 2. General view of the reclaimer.



Fig. 3. General view of the waste (left), the reclaimed product (middle), and the feed (right).

Element concentrations (mg/L) of the reclaimed products, the feed and the wastes for MEG solvents.

Element	Element Product #										Feed	Waste #	¥	
(mg/L)		1	2	3	4	5	6	7	8	9	10		1	2
Fe		0	0	0	0	0	0	0	0	0	0	7	8	9
Al		0	0	0	0	0	0	0	0	0	0	4	0	0
Pb		0	0	0	0	0	0	0	0	0	0	1	2	2
Zn		0	0	0	0	0	0	0	0	0	0	9	12	12
Ca		0	0	0	0	0	0	0	0	0	0	51	1	7
Mg		0	0	0	0	0	0	0	0	0	0	9	10	10
Si		6	6	7	3	4	6	6	7	7	6	32	98	143
PO_4^{3-}		12	12	12	9	12	12	15	9	12	6	1907	4507	5301
В		0	0	0	0	0	0	0	0	0	0	457	1334	1616
Mo		0	0	0	0	0	0	0	0	0	0	80	231	283
Na		0	0	0	0	0	0	0	0	0	0	2690	7200	8760
K		0	0	0	0	0	0	0	0	0	0	3720	10230	12490
10000														
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Fig. 4. Change of element concentrations found in the product, the feed and the waste.

the average values for element concentrations found in the product, feed and waste. Fig. 4 shows that most element concentrations are higher in the waste than in the feed. This phenomenon makes sense as those impurities could not be evaporated during the reclamation process and thus gradually got accumulated in the waste. However, the concentrations of Al and Ca are higher in the feed. When the waste was collected for analysis, the upper layer was easier to collect as it had lower viscosity. The Al and Ca impurities may accumulate more easily in the lower layer and thus have a lower concentration in the collected waste.

Property measurements for the reclaimed products, the feed and the wastes of MEG solvents are presented in Table 3, which shows that the solvent concentration of each reclaimed product is equal or very close to the feed concentration, thus demonstrating the low solvent loss of this reclaimer. The freezing point of the feed is slightly lower than that of the reclaimed product due to the higher level of degradation

products, as degradation products, especially organic acids, can decrease the freezing point of the solvent. Hence, the relatively higher freezing point of the reclaimed product may confirm that some degradation products have been removed. The specific conductance can also be used to demonstrate product quality. The specific conductance values of the reclaimed products range from 66 to 127 μ S, while the specific conductance of the feed is much higher, 4550 μ S. The decreased specific conductance of the reclaimed product was caused by the removal of ionic degradation products like organic acids that can conduct electricity.

Table 3 also shows that the total hardness of the reclaimed product is 0 mg/L, confirming the complete removal of divalent cations of mainly calcium and magnesium. The physical properties of refractive index, density and viscosity are closely related to the degradation products content of the solvent. For the physical properties of refractive index and viscosity, there was not much difference between the reclaimed product and the degraded feed. Both refractive index and viscosity of the product are slightly lower than those of the feed. However, the density of the product is much lower than that of the feed due to the removal of the heavy degradation products and impurities. Because the degradation products content of the waste is much higher than that of the feed or the product, the refractive index, density, and viscosity of the waste are much larger than those of the feed or the product.

The organic degradation products contents for 10 reclaimed products, feed and two wastes are summarized and presented in Table 4. As seen from Table 4, the degradation product anions of glycolate and nitrite have been eliminated in all reclaimed products. The anion of acetate has been totally removed in most of the products. For all reclaimed products, the concentration of sulfate or chloride is almost the same, around 6 mg/L. The concentration of nitrate is also stable in each product, at 13 mg/L. However, the concentration of the formate is not stable in different products, ranging from 0 to 42 mg/L.

To better evaluate the removal efficiency of the reclaimer for the individual degradation products, Fig. 5 presents the average values for the product and the waste. Although the anions of sulfate, chloride, nitrate, formate, and acetate are still present in the reclaimed products, their concentrations in the products are much lower compared with those in the feed. For most of the ionic degradation products, their concentrations are much higher in the waste than in the feed. This phenomenon is most obvious for the anions of nitrate and glycolate, with concentrations in the feed lower than 1000 mg/L and concentrations in the waste around 3000 mg/L. However, the measured concentration of nitrite is higher in the feed than in the waste, possibly because this kind of degradation product accumulates more in the lower layer of the liquid inside the evaporator (waste), while upper layer of waste is collected for sampling.

3.2. Monoethanolamine (MEA)

The colors of the waste, recovered product and the feed are shown in Fig. 6. The clean MEA solvent, whether pure or dissolved in deionized water, is pure and colorless. As seen from Fig. 6, the reclaimed product is pure and colorless, which indicates the removal of degradation products and contaminants. The feed is clear fluorescent orange while the waste is opaque dark red. Darker color of the solvent normally results from a higher level of degradation. Thus, higher level of degradation products in the waste can be assumed.

The feed also shows a slight foaming tendency, while the reclaimed products do not show any foaming tendency at all. The foaming tendency of the degraded feed results from the high level of degradation products and contaminants. The fact that the reclaimed products do not foam indicates that the degradation level in the product is quite low.

The element concentrations of 10 reclaimed products, feed and two waste fluids are summarized and listed in Table 5, showing only the element concentrations of Fe, Ca, Si, PO_4^{3-} and Na as Al, Pb, Zn, Mg, B,

Basic testing result of the reclaimed product	s, the feed and the wastes for MEG solvents.
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Testing	Unit	Product	#		Feed	Waste #								
		1	2	3	4	5	6	7	8	9	10		1	2
Freezing point	К	235	235	237	235	237	235	235	235	235	235	232	251	251
Boil point	K	380	380	380	380	380	380	380	380	380	380	381	428	428
Solvent concentration	wt%	51	51	50	51	50	51	51	51	51	51	51	< 99	< 99
pH		9.0	8.8	8.9	9.4	9.2	8.9	9.0	8.8	8.8	8.9	8.4	9.9	10.2
Total hardness	mg/L	0	0	0	0	0	0	0	0	0	0	159	2	21
Specific conductance	μS	127	76	73	67	66	85	91	80	76	89	4550	1525	1650
Refractive index	-	1.3849	1.3851	1.3848	1.3854	1.3846	1.3849	1.3855	1.3852	1.3850	1.3854	1.3868	1.4357	1.4379
Density	kg/m ³	1066.2	1066.5	1065.9	1066.8	1065.8	1066.6	1066.9	1066.5	1066.6	1067.0	1075.9	1135.5	1141.3
Viscosity	mPas	5.4	5.4	5.2	5.1	5.3	5.4	5.4	5.2	5.3	5.2	5.6	32.6	34.9

Mo and K are not present in the degraded feed. Compared with the MEG feed, the MEA feed shows lower levels of these impurities. In all the reclaimed products, the impurity elements Fe, Ca and PO_4^{3-} have been completely removed. Si concentrations are quite stable in the products, around 1 mg/L, but slightly lower in the feed. The concentrations of Na in the products range between 0 to 3 mg/L, almost half of the Na concentration in the feed. The differences of the element concentrations among the feed, product and the waste can be seen from Fig. 7, in which the average values for product and waste are applied.

Because impurities can get accumulated in the evaporator during the reclamation process, the concentrations of these elements in the wastes are much higher than those in the feed or reclaimed products. It also needs to be mentioned that the concentration of Na is very high in the wastes, much higher than in the feed. The addition of 50% sodium hydroxide (NaOH) in advance to liberate amines from HSSs in the degraded feed may be one of the reasons for this difference.

The properties of the reclaimed products, the feed and the wastes are presented in Table 6, which shows the freezing points of the reclaimed products to be almost stable, ranging from 264 to 265 K, slightly higher than that of the degraded feed. The relatively lower freezing point of the feed results from higher level of degradation.

Due to the large removal of degradation products, especially organic acids, the pH values of the reclaimed products are higher than that of the feed. The total hardness of each reclaimed product is 0 mg/L, which confirms the complete removal of divalent cations of mainly calcium and magnesium.

The physical properties of specific conductance, refractive index, density and viscosity are closely related to the degradation products content of the solvent. For 10 reclaimed products, the highest specific conductance value is $6540 \, \mu$ S. This value is much lower than the specific conductance of the feed, due to the removal of ionic degradation products, which can easily conduct electricity. Normally, larger values for density, viscosity or refractive index indicate a higher level of degradation. Table 6 shows that the density, viscosity and refractive index of each reclaimed product are smaller than those of the feed. This result also proves the removal of degradation products.

The results of routine analysis of the solvent concentration, HSSs content and CO_2 loading are presented in Table 7. For the degraded



Fig. 5. Change of ionic degradation products contents in the product, the feed and the waste.



Fig. 6. General view of the waste (left), the reclaimed product (right) and the feed (middle).

feed, the solvent concentration is 15.270 wt% (weight percent). The solvent concentrations of the products are within a narrow range of 14.942%–16.071%, close to the solvent concentration of the feed. However, the solvent concentrations of the wastes are very high, around 78%, which means that when the system reaches steady state,

Table 4

Deg	gradation	products	contents of	the	reclaimed	products,	the	feed	and	the	wastes	for	MEG	solvent	s.

Degradation products (mg/L)	Produc	ct#	Feed	Waste #	Waste #								
	1	2	3	4	5	6	7	8	9	10		1	2
Sulfate	7	6	6	6	6	6	7	7	6	7	123	308	292
Chloride	6	6	6	6	6	6	6	6	6	6	271	808	922
Nitrate	13	13	13	13	13	13	13	13	13	13	779	2839	3139
Glycolate	0	0	0	0	0	0	0	0	0	0	858	2683	3211
Formate	42	36	25	11	0	32	32	40	32	35	291	964	1121
Acetate	27	1	0	0	0	0	1	0	0	0	106	277	286
Nitrite	0	0	0	0	0	0	0	0	0	0	339	7	0

Element concentrations (mg/L) of the reclaimed products, the feed and the wastes for MEA solvents.

Element (mg/L)	Pro	oduc	t #			Feed	Waste #						
	1	2	3	4	5	6	7	8	9	10		1	2
Fe	0	0	0	0	0	0	0	0	0	0	49	399	397
Ca	0	0	0	0	0	0	0	0	0	0	7	39	38
Si	1	1	1	1	1	1	3	1	1	0	4	34	30
PO_4^{3-}	0	0	0	0	0	0	0	0	0	0	92	93	96
Na	0	3	3	0	3	3	0	3	3	0	6	4133	4081



Fig. 7. Change of element concentrations found in the product, the feed and the waste.

the liquid within the evaporator is highly concentrated. However, many solvent degradation products that are basic and similar to MEA could interfere in the solvent determination titration; therefore, the solvent concentration could be lower than 78 wt%.

The HSSs contents of the products are almost the same, around 0.061% (weight percent as MEA). This value is much lower than the HSSs content of the feed, which proves that this new reclaimer can efficiently remove most of the HSSs in the degraded MEA solvents.

Based on data in Table 7, the CO_2 loading of the degraded feed is 0.203 mol CO_2 per mol MEA solvent. The values of the CO_2 loading are very low, ranging from 0.004 to 0.048 mol per mol MEA solvent, within reclaimed products. Most CO_2 gas escaped from condenser and was vented out of the system by the vacuum pump.

The HSSs contents for the reclaimed products, the feed and two waste fluids are summarized and shown in Table 8. The concentrations of sulfate, chloride and nitrate are relatively low in the feed, below 100 mg/L. The sulfate concentration has been reduced by more than half. The concentrations of chloride and nitrate in the reclaimed products are around 6 and 13 mg/L respectively, lower than those in the feed.

Compared with the concentrations of sulfate, chloride and nitrate, the concentrations of glycolate, formate and acetate are much higher in the degraded feed. The formate concentration in the feed is 580 mg/L; however, this value has been largely reduced in the product. The glycolate concentration decreases from 325 mg/L in the feed to around 200 mg/L in the products. On the other hand, the acetate concentration decreases from 150 mg/L in the feed to around 50 mg/L in the reclaimed products.

To better evaluate the removal efficiency of the reclaimer, Fig. 8 presents the average HSSs values for the product, feed and waste. Although HSSs of sulfate, chloride, nitrate, glycolate, formate, and acetate still exist in the reclaimed products, their concentrations in the products are much lower, compared with their concentrations in the feed. The concentrations of most of the degradation products are much higher in the waste than in the feed. However, there are more glycolate and sulfate in the feed than in the waste. The reason might be due to the fact that these two kinds of HSSs accumulate more in the lower layer of the liquid inside the evaporator (waste), while the upper layer is collected for sampling. Moreover, these concentrations could be lower in reaction with caustic soda compared to other anions. Another reason may be that glycolate could suffer from thermal decommission at 352.15 K, leading to high boiling chemicals that are very likely to get accumulated in the waste (do Nascimento et al., 2017).

4. Conclusions

In this work, a novel thermal reclaimer was introduced and the degraded solvents of monoethanolamine (MEA) and monoethylene glycol (MEG) obtained from the working plant were used as feed of the reclaimer. The degraded feed, reclaimed products and wastes for each degraded solvent were carefully analyzed and compared to explore the removal efficiency of the reclaimer. The required absolute working temperature and pressure for MEA and MEG are 413 K and 38 kPa, and 445 K and 20 kPa, respectively. The results show that this reclaimer is able to remove most of the undesirable degradation products and impurities from the degraded solvent and restore each solvent to almost its original purity. Compared with existing thermal reclaimers, this newly developed reclaimer has several advantages. First, it has only one stage while some of the existing thermal reclaimers have multiple stages. This advantage will contribute to lower expenditure on construction and maintenance. In addition, the treated solvent will not degrade again during the reclamation process as the working temperature is lower than the degradation temperature of the solvent. The lower working temperature can also contribute to lower energy consumption. Furthermore, concentrating the waste can contribute to the reduction of waste quantity collected for disposal.

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Table	6
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Properties of the reclaimed	products,	the feed and	l the wastes	for MEA solvents.
1	1 /			

-	-														
Testing	Unit	Product	Product #											Waste #	
		1	2	3	4	5	6	7	8	9	10		1	2	
Freezing point	К	265	264	265	265	265	265	264	265	265	265	260	251	251	
Boil point	K	375	375	375	375	375	375	375	375	375	375	376	428	428	
pН		11.5	11.4	11.3	11.0	10.9	10.9	10.9	10.9	10.8	10.7	10.3	11.3	11.2	
Total hardness	mg/L	0	0	0	0	0	0	0	0	0	0	17	108	105	
Specific conductance	μS	1329	1660	2010	4240	4780	4950	5220	5440	5450	6540	15480	596	851	
Density	kg/m ³	1005.4	1009.7	1007.9	1006.0	1005.6	1005.4	1006.8	1005.6	1005.4	1005.6	1030.0	1174.3	1195.4	
Refractive index		1.3522	1.3534	1.3530	1.3525	1.3524	1.3523	1.3529	1.3526	1.3522	1.3524	1.3622	1.4774	1.4743	
Viscosity	mPa s	4.2	4.5	3.7	3.8	3.9	3.7	4.2	4.2	3.9	4.1	5.3	440.1	444.5	

Testing	Unit	Product #									Feed	Waste #		
		1	2	3	4	5	6	7	8	9	10		1	2
Solvent Concentration HSSs content CO ₂ loading	wt% wt% as solvent mol/mol solvent	15.330 0.000 0.004	16.071 0.060 0.004	15.625 0.050 0.005	14.978 0.061 0.020	15.043 0.061 0.036	15.046 0.061 0.027	15.086 0.061 0.031	14.942 0.061 0.034	15.006 0.061 0.032	15.003 0.061 0.048	15.270 0.500 0.203	78.158 - -	78.429 - -

Table 8

HSSs contents of the reclaimed products, the feed and the wastes for MEA solvents.

Degradation products (mg/L)	Product #										Feed	Waste #	
	1	2	3	4	5	6	7	8	9	10		1	2
Sulfate	5	4	3	14	5	5	11	4	4	18	40	30	43
Chloride	6	6	6	0	6	6	6	6	6	6	9	52	50
Nitrate	0	13	13	13	13	13	13	13	13	0	54	426	418
Glycolate	0	136	135	194	210	205	230	242	207	233	325	163	158
Formate	0	3	2	5	17	7	6	11	16	8	580	687	674
Acetate	0	16	14	62	11	34	65	26	33	54	150	1264	1239



Fig. 8. Change of HSSs contents in the product, the feed and the waste.

References

- Aaron, D., Tsouris, C., 2005. Separation of CO₂ from flue gas: a review. Sep. Sci. Technol. 40, 321–348.
- Aboudheir, A., Elmoudir, W., 2013. Optimization of an existing 130 tonne per day CO₂ capture plant from a flue gas slipstream of a coal power plant. Energy Procedia 37, 1509–1516.
- Abry, R.G., Beasley, T.S., Carlson, S.W., Kresoyak, S.G., 1999. Process for recovering processing liquids. U.S. Patent 5,993,608.
- Bacon, T.R., 1987. Amine solution quality control through design, operation and correction. In: Proceedings-1987 Gas Conditioning Conference. The University of Oklahoma, Norman, Oklahoma.
- Beasley, T., Merritt, D.A., 1992. Process for reclaiming waste gas treatment chemical. U.S. Patent 5,152,887.
- Blanc, C., Elgue, J., Lallemand, F., 1981. MDEA process selects H₂S. Hydrocarbon Process 60 (8), 111–116.
- Bougie, F., Iliuta, M.C., 2014. Stability of aqueous amine solutions to thermal and oxidative degradation in the absence and the presence of CO₂. Int. J. Greenh. Gas Control 29, 16–21.
- Brown, P.W., Galuk, K.G., Rossiter, W.J., 1987. Characterization of potential thermal degradation products from the reactions of aqueous ethylene glycol and propylene glycol solutions with copper metal. Solar Energy Mater. 16 (4), 309–313.
- Clifton, J.R., Rossiter, W.J., Brown, P.W., 1985. Degraded aqueous glycol solutions: pH values and the effects of common ions on suppressing pH decreases. Solar Energy

Mater. 12 (1), 7786.

- Collins, H.H., 1964. Anti-corrosion work on cast iron. Anti-Corros. Methods Mater. 11 (10), 35–37.
- Critchfield, J., Rochelle, G.T., 1987. $\rm CO_2$ absorption into aqueous MDEA and MDEA/MEA solutions. In: AIChE National Meeting. Houston, TX.
- Davis, J., Rochelle, G., 2009. Thermal degradation of monoethanolamine at stripper conditions. Energy Procedia 1 (1), 327–333.
- do Nascimento, A.L.C.S., Teixeira, J.A., Nunes, W.D.G., Gomes, D.J.C., Gaglieri, C., Treu-Filho, O., Pivatto, M., Caires, F.J., Ionashiro, M., 2017. Thermal behavior of glycolic acid, sodium glycolate and its compounds with some bivalent transition metal ions in the solid state. J. Therm. Anal. Calorim. 130 (3), 1463–1472.
- Dow, 1962. Gas Conditioning Fact Book. Dow Chemical Company, Midland, Michigan.
- Duke, M.C., Ladewig, B., Smart, S., Rudolph, V., da Costa, J.C.D., 2010. Assessment of postcombustion carbon capture technologies for power generation. Front. Chem. Eng. 4 (2), 184–195.
- ElMoudir, W., Supap, T., Saiwan, C., Idem, R., Tontiwachwuthikul, P., 2012. Part 6: solvent recycling and reclaiming issues. Carbon Manage. 3 (5), 485–509.
- ElMoudir, W., Fairchild, J., Aboudheir, A., 2014. HTC solvent reclaimer system at searles valley minerals facility in Trona, California. Energy Procedia 63, 6156–6165.
- ElMoudir, W., 2012. Experimental Studies for Development of a Purification Process for Single and Mixed Amine Solvents. Ph.D. Thesis. University of Regina October.
- Fytianos, G., Ucar, S., Grimstvedt, A., Hyldbakk, A., Svendsen, H.F., Knuutila, H.K., 2016. Corrosion and degradation in MEA based post-combustion CO₂ capture. Int. J. Greenh. Gas Control 46, 48–56.
- Gouedard, C., Picq, D., Launay, F., Carrette, P.L., 2012. Amine degradation in CO₂

capture: I. A review. Int. J. Greenh. Gas Control 10, 244-270.

- Gouedard, C., Rey, A., Cuzuel, V., Brunet, J., Delfort, B., Picq, D., Dugay, J., Vial, J., Pichon, V., Launay, F., Assam, L., 2014. Amine degradation in CO₂ capture. 3: new degradation products of MEA in liquid phase: amides and nitrogenous heterocycles. Int. J. Greenh. Gas Control 29, 61–69.
- Guide, E.G.P., 2008. MEGlobal.
- Jassim, M.S., Rochelle, G., Eimer, D., Ramshaw, C., 2007. Carbon dioxide absorption and desorption in aqueous monoethanolamine solutions in a rotating packed bed. Ind. Eng. Chem. Res. 46 (9), 2823–2833.
- Kierzkowska-Pawlak, H., 2010. Carbon dioxide removal from flue gases by absorption/ desorption in aqueous diethanolamine solutions. J. Air Waste Manage. Assoc. 60 (8), 925–931.

Kohl, A.L., Nielsen, R., 1997. Gas Purification. Gulf Professional Publishing.

Lee, A.S., Eslick, J.C., Miller, D.C., Kitchin, J.R., 2013. Comparisons of amine solvents for

post-combustion CO_2 capture: a multi-objective analysis approach. Int. J. Greenh. Gas Control 18, 68–74.

- Meisen, A., Abedinzadegan, M., Abry, R., Millard, M.G., 1996. Degraded amine solutions: nature, problems and distillative reclamation. Proceedings of the 1996 Laurance Reid Gas Conditioning Conference.
- Quadrelli, R., Peterson, S., 2007. The energy–climate challenge: recent trends in CO₂ emissions from fuel combustion. Energy Policy 35 (11), 5938–5952.
- Razzaghi, M., Kresnyak, S.G., Keast, B.A., Giles, T.W., 2003. Process for recovering processing liquids. U.S. Patent 6,508,916.
- Songolzadeh, M., Soleimani, M., Takht Ravanchi, M., Songolzadeh, R., 2014. Carbon dioxide separation from flue gases: a technological review emphasizing reduction in greenhouse gas emissions. Sci. World J. 2014.
- Strazisar, B.R., Anderson, R.R., White, C.M., 2003. Degradation pathways for monoethanolamine in a CO₂ capture facility. Energy Fuels 17 (4), 1034–1039.