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RESEARCH ARTICLE

FORMATION OF HEAT STABLE SALTS DURING THERMAL DEGRADATION OF AQUEOUS METHYLDIETHANOLAMINE (MDEA) SOLVENT AND CORROSION STUDIES WITH DIFFERENT ALLOYS

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ABSTRACT

The objective of this research work was to study the formation of heat stable salts (HSS) during thermal degradation of Methyldiethanolamine (MDEA) solvent and to check the corrosion rates for different alloys. HSS such as acetate, formate, sulfates, thiosulfate, glycolate, nitrate etc. were formed with varying concentrations during thermal degradation of MDEA. The corrosion rates of three different specimen of alloys, namely SS-304, SS-321 and Hastelloy-x, under thermal degradation of lean MDEA (46.34 weight %) from Gasco, Habshan (Abu Dhabi) and 46 weight% fresh MDEA loaded with H_2S and RSH at 130ºC were observed. The corrosion rate using lean MDEA at a stirring speed of 700 rpm and at 130°C were observed as SS-321 (0.2977 millimeter/year as 'mmy'), Hastelloy-x (0.1859 mmy) and SS-304 (0.11396 mmy). The fresh MDEA solutions were degraded at 130ºC with and without stirring pat 700 rpm. Formation of HSS was much higher when fresh MDEA degraded thermally without stirring. Thermally degraded fresh MDEA solution without stirring has no effect on SS-304 but corroded the Hastelloy-x at 1.0214 mmy. Thermally degraded fresh MDEA solution loaded with H_2S and RSH and stirred at 700 rpm corroded the specimens most as SS-321 (64.7144 mmy), SS-304 (60.8032 mmy) and Hastelloy-x (0.2678 mmy).

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INTRODUCTION

Corrosion is a ubiquitous problem in gas treating in the petroleum and natural gas industries. The primary impurities removed in the treating process are carbon dioxide and hydrogen sulfide. The corrosion of equipment and piping is an inevitable consequence of removing these gases with alkanolamines. As corrosion is an inevitable result of dealing with acid gases, aqueous alkanolamine solutions which contain CO_2 and H_2S are corrosive to carbon steel and corrosion rates are increased by high alkanolamine concentration, high acid gas loading, high temperatures, degradation products, and foaming (Dow Chemical, 1998).The area most susceptible to corrosion in any amine sweetening plant (Fig. 1) are lean/rich heat exchanger, reboiler, stripping column, reflux condenser and rich solvent let-down valve. The principle contaminants of an MDEA solvent includes hydrocarbons, iron sulfide, heat stable salts (HSS), alkanolamine degraded products, hydrogen sulfide, fluid velocity and temperature of the process (Cummings *et al*., 2003 and 2005).

Strong acid anions such as formate, thiosulfate, acetate, thiocyanate and chloride can bind amine molecules to form salts that are non-regenerable even with addition of heat and are referred to as Heat Stable Salts (HSS) (Kadner and Rieder, 1995). Common HSS species present in gas sweetening units are listed in Table 1 (Stewart and Lanning, 1994). These anions appear mainly from the water dilution and keep on accumulating. Organic acids are typical degradation products from the alkanolamine (due to thermal and oxidative degradation) solution. It is well known that the presence of HSS increases the corrosivity of amine solutions. The disadvantages of forming such salts not only tie up the amine and trim down the acid gas capacity but also considered corrosive as well (Randy, 2001). The presence of HSS increase solution viscosity and decrease acid-gas carrying capacity which may increase the operation cost of amine unit (Dow chemical, 2013).

The major cause of corrosion is the oxidation of iron and producing corrosive agents which may interact with the surrounding environment. In amine sweetening plants the corrosive agent is a form of an acid gas in solution, either a molecular form of H_2S or CO_2 in solution. These acid gases are dibasic and can give up two protons to produce different ions in solution. The ions from H_2S are bisulfide (HS^-) and sulfide (S^{-2}) while bicarbonate (HCO_3^-) and carbonate (CO_3^{-2}) are produced from CO_2 (Cummings *et al*., 2005).

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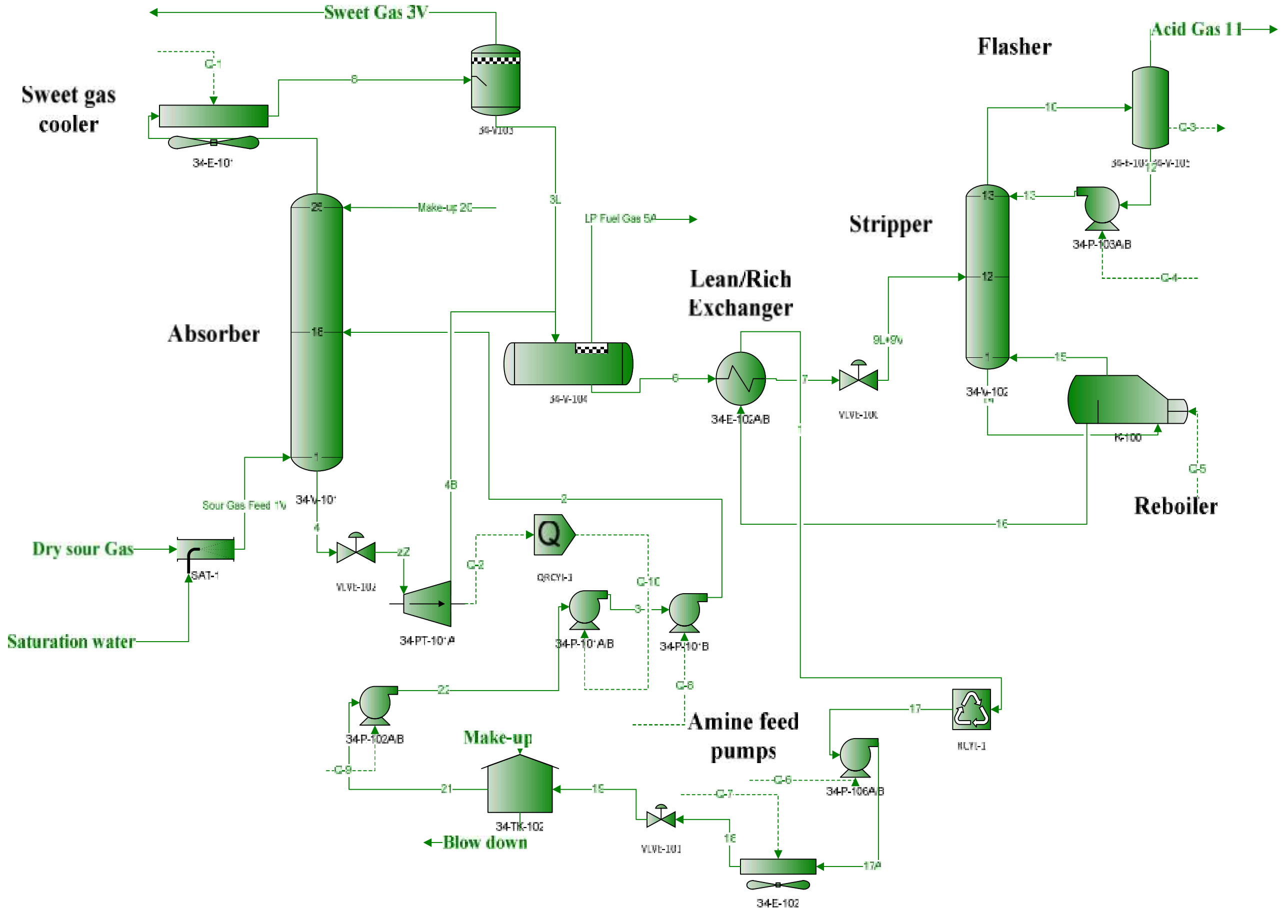

Fig. 1. Process flow diagram of natural gas sweetening unit

Table 1. HSS species present in amine solution

Name	Formula	Limit (ppm)
nitrate	NO_3^-	-
nitrite	NO_2^-	-
formate	$HCOO^-$	500
oxalate	$C_2O_4^{2-}$	250
acetate	CH_3COO^-	1000
sulfate	SO_4^{2-}	500
sulfite	SO_3^{2-}	500
phosphate	PO_4^{3-}	-
thiosulfate	$S_2O_3^{2-}$	10,000
thiocyanate	CNS^-	10,000
glycolate	$C_2H_3O_3^-$	500
malonate	$C_3H_2O_4^{2-}$	1000
succinate	$C_4H_4O_4^{2-}$	1000

The main corrosion compound in gas sweetening system is iron sulfide which is fairly insoluble in aqueous solution and tends to distribute uniformly over the surface of oxidized iron. This uniform distribution results in minimal porosity to the solution, therefore the layer creates a significant barrier to further corrosion by blocking the access of the corrosive agent to the free metals (Cummings *et al.*, 2003). During gas sweetening, H_2S enters the aqueous MDEA phase and undergoes a two-step reaction sequence, losing H^+ to form HS^- followed by S^{-2}. Only small fraction of the HS^-undergoes the second step (Cummings *et al.*, 2005). In the simplest stoichiometric forms, the basic corrosion reactions of dissolved H_2S with iron are as follows:

$$H_2S + Fe = FeS + H_2 \quad \text{.........................}(1)$$

$$2HS^- + Fe = FeS + H_2 + S^{-2} \quad \text{........................}(2)$$

In gas sweetening unit, in presence of H_2S the diatomic hydrogen molecule is produced which attacks the metal surface making the metal brittle, known as sulfide stress cracking (Kelland, 2009). On the other hand S^{2-} reacts with Fe^{2+} to produce sulfide scales(Madsen, 2011). The iron sulfide forms scales to the surface of the process equipment, piping, heat exchanger tubes and absorber/stripper trays leading to blocking the flow. Another type of corrosion known as erosion corrosion occurs on a metal surface because of the relative movement between the metal surface and corrosive medium (DuPart *et al.*, 1993). In absence of H_2S, carbonic acid and bicarbonate corrosion dominates analogously to H_2S mechanisms. Iron carbonate ($FeCO_3$) forms corrosion-inhibiting protective layers but lesser than iron sulfide layer. The pH ranges in which the carbonic acid ionic forms dominate differ from H_2S. Also in the pH range of alkanolamine solution a significant fraction of CO_2 in solution are in the carbonate (CO_3^{-2}) form in lean alkanolamine solution. Thus, corrosion rates in CO_2 systems is much more pH dependent (Cummings *et al.*, 2005) than H_2S

systems. Different researchers (Kennard and Meisen; 1985, Kohl and Riesenfeld; 1985) reportedthat dissolved CO_2 was a primary corroding agent in alkanolamine gas treatment plants.For CO_2, the reactions are as follows:

$CO_2 + Fe + H_2O = FeCO_3 + H_2$ …………………..(3)

$2HCO_3^- + 2Fe = 2FeCO_3 + H_2$ ………………………(4)

Hamah-Ali *et al*., (2011) reported that primary amines are more corrosive than the secondary amines, which in turn are more corrosive than tertiary amines. However, all amines are equally non-corrosive when there is no acid gas presents. MDEA differs from the other aminesas it does not produce CO_2 degradation products. Gunasekaran *et al.* (2013) tested carbon steel 1018 in 5.0 kmol/m^3 alkanolamine concentration with CO_2 saturation at 80ºC where the solvents included monoethanolamine (MEA), diethanolamine (DEA), MDEA, 1-amino-1-propanol (AMP), piperazine (PZ) and their blends. It was observed that corrosion rate ranked in the order MEA > AMP > DEA > PZ > MDEA. Duan *et al.* (2010) reported the relative corrosivity of different systems of MDEA solutions and ranked them as MDEA/CO_2/O_2/HSS > MDEA/CO_2/O_2> MDEA/CO_2. Thus MDEA containing CO_2 was least corrosive while maximum corrosion was occurred in presence of CO_2, O_2 and HSS.

Corrosion has also negative impact on the industries economy as the equipment needs to be replaced regularly and the production may be lost due to unexpected plant outages. Corrosion can be minimized by altering certain design features (Dow Chemical, 1998). Some of them are listed below:

1. Solution velocities should be less than 1.1 m/s.
2. The rich solution should be on the tube side of the lean/rich heat exchanger.
3. The exchanger should be maintained under pressure to prevent acid gases from flashing.
4. A low temperature heating medium should be used in the reboiler, so as to prevent accelerated corrosion rates and thermal degradation of the amine.
5. All equipment should be stress relieved.

The major aim of this work was to study the formation of HSS during thermal degradation of MDEA solution and check the corrosion rate. The corrosion rates of three different specimens of alloys, namely SS-304, SS-321 and Hastelloy-x under thermal degradation of lean MDEA (46.34 weight %) solution from Gasco, Habshan (Abu Dhabi) and fresh MDEA ((46 weight %)) solution loaded with H_2S and RSH at 130ºC, were observed. The fresh MDEA solutions were degraded with and without stirring at 700 rpm and at 130ºC.

Experimental

Metal alloy specimens

The metal alloy specimens used for the corrosion tests were Atlas Steels SS-304 (density 8.0 g/cm^3), Atlas Steels SS-321 (density 8.027 g/cm^3) and Hastelloy-x (density 8.22 g/cm^3, Haynes International Inc.). The compositions of these specimens are given in Table 2 and 3 and the schematic of the specimen used in the corrosion test is shown in Fig. 2.

Table 2. Composition of Hast-x alloy (Haynes International, Inc., 2013)

Hast-x	Cr	Fe	Mo	Co	W	C	Mn	Si	B
%	22	18	9	1.5	0.6	0.10	1	1	0.008

Table 3. Composition ranges for SS 304 and SS 321 grade stainless steel (Atlas Steels, 2013)

Grade		C	Mn	Si	P	S	Cr	Ni	N
SS 304	Min%	-	-	-	-	-	18	8.0	-
	Max%	0.08	2.0	0.75	0.045	0.030	20	10.5	0.10
SS 321	Min%	-	-	-	-	-	17	9	-
	Max%	0.08	2.0	0.75	0.045	0.030	19	12	0.10

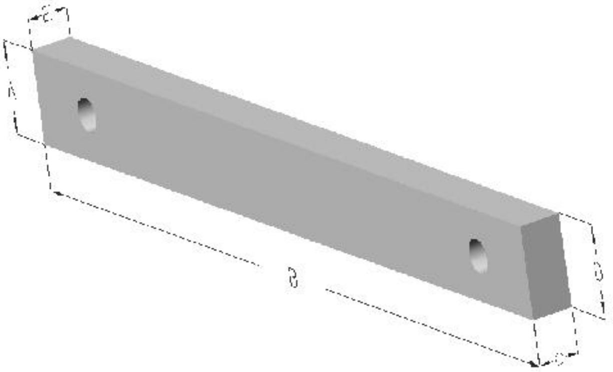

Fig. 2. Schematic of specimen used in corrosion tests

Thermal degradation of MDEA solution with corrosion studies

The metal sheets were cut into rectangular pieces forming specimens called “corrosion coupons” with two holes for suspension. Prior to use, the specimens were cleaned with acetone and soaked for 5 minutes in a sonicator and dried at 105ºC for 15 min. The specimens were kept in a desiccator before use. Finally, the coupons were immersed in aqueous MDEA solution in 250 ml round bottom flask having a vertical condenser mounted on it (Fig. 3) and left for fixed amount of time at 130°C as the reboiler temperature of the stripper used in the gas sweetening unit. The specimens were suspended in the solutions using filament yarn. In addition, small pieces (1 cm in length) of chopsticks were used to keep the specimens away from each other. After completion of the experiment, the coupons were soaked in ethanol for 30 minutes at 50°C-60°C in an ultrasonic bath and dried in an oven at 105ºC for 30 minutes. The experiment conducted with lean MDEA from Gasco, Habshan (Abu Dhabi) was continuously stirred at 700 rpm using magnetic stirrer. The freshly prepared MDEA solution loaded with H_2S and RSH were conducted without as well as stirring condition at 700 rpm. Stirring hot plate (Cimarec^{TM}) with a digital thermometer was used for heating and stirring the MDEA solution. The dimensions and weight of each coupon were measured before and after the experiment. The dimensions of the samples were measured using digital

Vernier calliper and each specimen was measured 4 times to take the average values.The corrosion rate of the coupons was carried out using the weight loss principle.

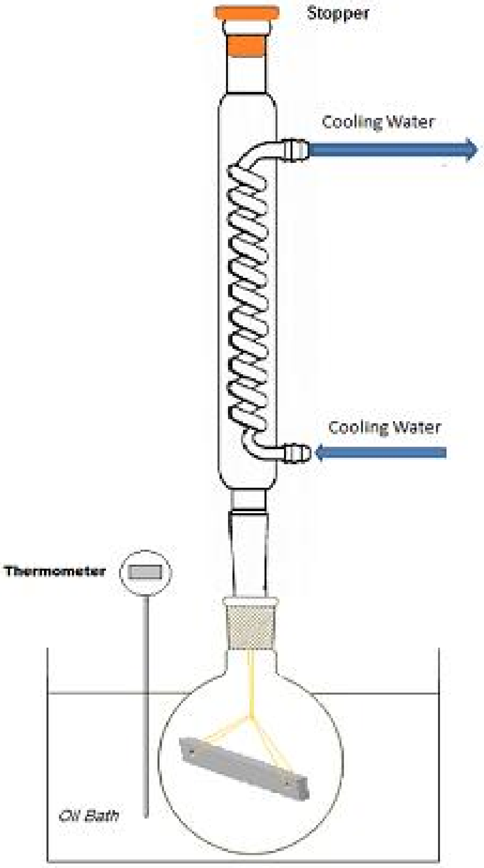

Fig. 3. Schematic diagram of the corrosion test

Analysis of HSS anions

The HSS anions present before and after thermal degradation studies was carried out using Ion Chromatography (ICS-3000 Dionex, Thermo Scientific Corporation).

Determination of Corrosion Rate (CR)

The simplest and longest-established method of estimating corrosion losses in plant and equipment is the weight loss test. A weighed sample (coupon) of the metal or alloy of interest is introduced into the process and removed after certain interval of time (Liang Hu, 2009). Finally, weight of the coupon was taken after cleaning all the corrosion products. The corrosion Rate (CR) can be calculated as (Alabama Specialty Products, Inc.):

$$CR = \frac{MassLoss\ (g)\ \text{x}\ K}{AlloyDensity\ \left(\frac{g}{cm^3}\right)\ \text{x}\ ExposedArea(A)\ \text{x}\ ExposedTime} \quad ..(5)$$

The factor K is constant and varied depending on the unit used to express the corrosion rate. The technique to calculate CR is simple and does not require complex equipment; merely an appropriately shaped coupon, a carrier for the coupon (coupon holder), and a reliable means of removing corrosion product without disruption of the metal substrate.

RESULTS AND DISCUSSIONS

Thermal degradation with lean MDEAsolution and corrosion studies

Thermal degradation studies was conducted for lean MDEA solution (46.34 weight% MDEA, 42 ppm H_2S and 9 ppm of RSH) at a stirring speed 700 rpmat 130ºC±5ºC. Table 4 showed the heat stable salts present in lean MDEA before and after the degradation experiment. It was observed that all the HSS anions were increased by thermal degradation of lean MDEA solvent except thiosulfate. Thiosulfates dissociates at room temperature to produce sulfite ions which may further oxidized to sulfate ions.

Table 4. HSS anion analysis of the lean MDEA solution using ICS-3000

HSS anions	In lean MDEA (ppm)	After experiment (ppm)
acetate	2906.5	2985.7
formate	203.80	219.90
sulfate	37.400	38.350
thiosulphate	44.401	28.350
glycolate	347.97	415.60
nitrate	0.4450	0.5170
chloride	5.330	5.310

The weight as well as the dimensions of the specimen on exposure to lean MDEA solution was changed as observed in Table 5. The corrosion rate (mmy) on lean MDEA exposure for the different specimen was observed as: SS-321 (0.2977) >Hastelloy-x (0.1859) > SS-304 (0.11396) The specimen SS-321 was corroded 2.5 times more than SS-304 and about 2/3 times more than Hast-x. The result showed in agreement with the previous studies on different metals under similar conditions (Roony *et al*., 1996 and 1997; Dow Chemicals, 2013) where SS-304 was mostly recommended material for the gas sweetening units. In addition, it was also noted that the corrosion rates in this test were higher than reported by Rooney *et al*. (1996 and 1997). This may be due to higher concentration of HSS present in lean MDEA solution as present in this study.

Fig. 4 (a-c) showed photographs (a confocal Raman microscope; alpha model)) of thermally degraded specimens of SS-321, Hast-x and SS-304. These specimens were present in lean MDEA solution thermally degraded at a stirring speed of 700 rpm at 130ºC±5ºC.

Table 5. Corrosion test on lean MDEA solution

Properties	Hast x		SS304		SS321	
	Initial	Final	Initial	Final	Initial	Final
Mass (gm)	15.0669	15.0656	21.8243	21.8236	13.9175	13.9156
Total area(mm^2)	1826.8241	1825.5943	1643.0192	1643.0192	1707.0468	1707.0468
Duration (hr)	408					
Millimeters/yr (mmy)	0.1859		0.11396		0.2977	

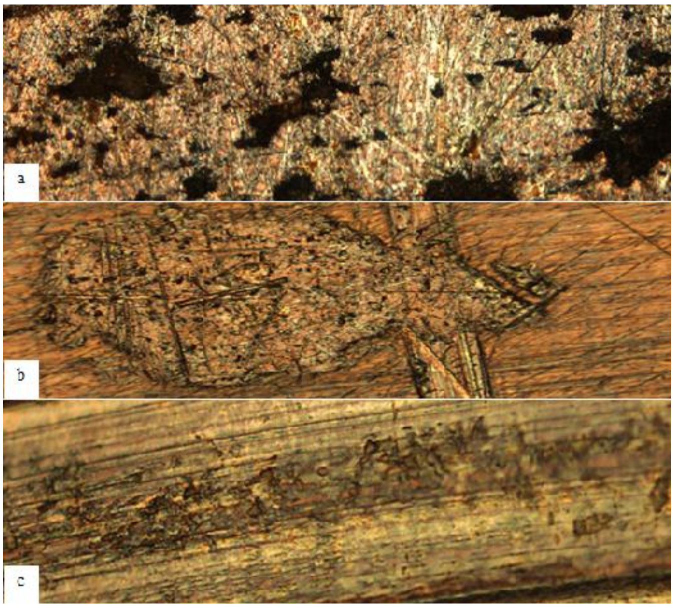

Fig. 4. Thermally degraded specimen of a) SS-304 b) Hast-x and c) SS-321

Thermal degradation with fresh MDEA solution and corrosion studies

Thermal degradation studies were conducted for fresh MDEA solution loaded with H_2S and RSH. Table 6 showed the heat stable salts present in fresh MDEA before and after the degradation experiment without stirring and with stirring at 700 rpm at 130ºC±5ºC. It was observed that all HSS anions amount were increased by thermal degradation of fresh MDEA solution loaded with H_2S and RSH.The HSS present in fresh and after thermal degradation studies with and without stirring (in brackets) are shown in Table 6.

Table 6. HSS on fresh MDEA loaded with H_2S and RSH for corrosion without stirring (with stirring)

HSS	In fresh MDEA (ppm)	After experiment (ppm)
acetate	-	532.2 (127.34)
formate	-	136.0 (59.89)
sulfate	0.250	5.90 (4.386)
thiosulphate	-	39.45 (20.45)
glycolate	-	390.2 (205.6)
nitrate	0.120	0.430 (0.530)

For the corrosion studies without stirring, the environmental conditions were fresh 46 weight % MDEA solution loaded with 37.65 ppm of H_2S and 40.24 ppm of RSH at 130ºC±5ºC using total reflux. This environment has no corrosion effect on SS-304 coupon as observed in Table 7 but corroded the Hastelloy-x specimen. Regarding the Hast-x specimen, it showed a higher corrosion rate (1.021 mmy) than that of the stirred lean amine solution (0.2678). In this case, crevice corrosion would probably occur which usually exists under deposits in stagnant medium (DuPart *et al*., 1993). Another factor that could attribute to such result is higher HSS anions formation in the system using fresh MDEA solution, which increase the corrosion rate significantly.

Corrosion tests were also performed with fresh MDEA loaded with H_2S and RSH with stirring. 100 ml each fresh MDEA solution loaded with 53 ppm H_2S/7 ppm RSH and 24 ppm H_2S/8 ppm RSH were taken at a stirring speed of 700 rpm at 130ºC**.** The results are shown in Table 7. The corrosion test showed that the specimen used in this investigation corroded (mmy) at a rate was in agreement with the previous results (Dow Chemicals, 2013) and ranked as: SS-321 (64.7144) > SS-304 (60.8032) > Hast-x (0.2678). It was observed that the corrosion rate of SS-304 was less than that of SS-321. The maximum corrosion rate of SS-321 was observed both in lean as well as fresh MDEA solution. The rate of corrosion was much higher with stirring for fresh MDEA solutions as compared to lean MDEA as well as without stirring conditions.

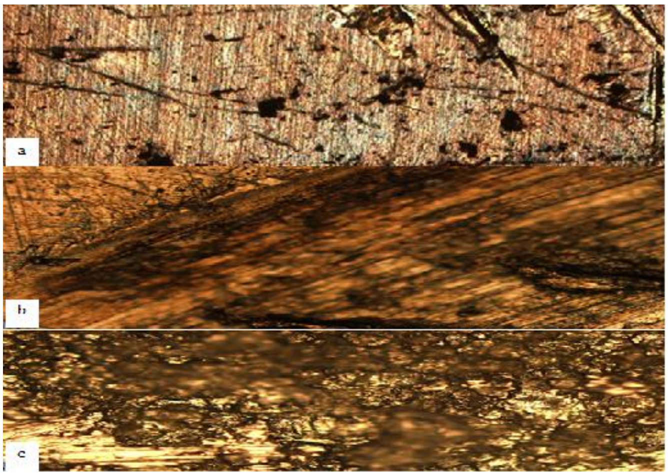

Fig. 5. Thermally degraded specimen of a) SS-304 b) Hast-xc) SS321

Table 7. Thermal degradation of fresh 46 weight % MDEA loaded with H_2S and RSH at 130℃

Properties	Hast x		SS304		SS321	
	Initial	Final	Initial	Final	Initial	Final
Mass (gm)	14.7650	14.7506	21.6035	21.6035	-	-
	(14.8506)	(14.8493)	(21.5096)	(21.250)	(13.9681)	(13.6757)
Area (mm^2)	1788.5991	1707.4412	1618.1214	1617.5538	-	-
	(1796.5251)	(1793.8702)	(1617.8432)	(1615.6684)	(1712.6506)	(1712.4296)
Duration (hour)	840 (288)					
Millimeters/year (mmy)	1.02142		0.00		-	
	(0.2678)		(60.8032)		(64.7144)	

The corrosion rate of Hast-x with the lean amine corroded at a rate of 0.1859 mmy, fresh MDEA loaded with H_2S and RSH with stirring corroded at a rate of 0.2678 mmy. Higher corrosion rate was achieved at stagnant conditions (1.0212 mmy) with the same solution of fresh MDEA solution loaded with H_2S/RSH. Fig. 5 (a-c) showed the photographs of thermally degraded specimens for SS321, Hast-x and SS304. Scratches were observed on SS304 specimen (Fig. 5a),which may be due to eroded particles bombarding during the corrosion test. Similarly, Fig. 5b and 5c display the effect of stirringon Hast-x and SS321 coupon by the MDEA solution.

Conclusion

It was observed that HSS such as acetate, formate, sulfates, thiosulfate, glycolate, nitrate etc. are formed during thermal degradation studies with varying concentrations for both lean as well as fresh MDEA solution loaded with H_2S and RSH. The corrosion rates using lean MDEA exposure at 700 rpm were observed as SS-321 (0.2977 mmy), Hastelloy-x (0.1859 mmy) and SS-304 (0.11396 mmy). The thermal degradation of the fresh loaded MDEA solution at 700 rpm corroded the specimens as SS-321 (64.7144 mmy), SS-304 (60.8032 mmy) and Hastelloy-x (0.2678 mmy). The stagnant medium of thermally degraded fresh MDEA solution did not affect the SS-304 but corroded the Hastelloy-x at 1.0214 mmy. Hastelloy-x showed lower corrosion rates in the fresh MDEA solution than SS-304. Moreover, SS-304 had lowest corrosion rate in lean MDEA solution.

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