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The degradation and corrosion characteristics of blended amine solution in the coal bed methane decarburization process

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For years, the degradation and corrosion of amine solutions has become an essential issue for the coal bed methane (CBM) decarburization process. And the degradation and corrosion characteristics of amine solutions are not clearly yet. Aimed to solve the sebarriersin this study, the degradation characteristics of blended amine solutions with or without antioxidants were studied in a rich oxygen environment. Results show without antioxidants here was a high oxidative degradation of amine solutions without antioxidants. While after adding certain antioxidants, such as sodium metavanadate (NaVO3), sodium sulfite or sodium potassium tartrate, the oxidative degradation ratio of blended amine solutions showed an obvious decrease. The amine solutions which added sodium metavanadate had the best antioxidant ability, followed by which added potassium sodium tartrate and then sodium sulfite. When added 1% sodium metavanadate, the oxidative degradation ratio of methyldiethanolamine (MDEA) +piperazine (PZ) (8:2) solution reduced 32%. And the corrosion characteristics of fresh amine solutions and rich amine solutions were investigated by the corrosion experiments at 90°C for 72 hours. Both the results of corrosion ratio test and the SEM show the corrosion ratio of rich amine solutions was much larger than that of fresh amine solutions. After adding 0.5% NaVO3 and 0.5% V2O5 as inhibitor, the corrosion of rich amine solutions were declined. According to the results of the degradation and corrosion characteristics, the decarburization agent for CBM process was recommended as MDEA+PZ(8:2) with 0.5% NaVO3 and 0.5%V2O5 .

Key words: blended amine, decarburization, antioxidant, oxidative degradation, corrosion.

INTRODUCTION

In the coal bed methane (CBM) utilization industry, it is essential to remove CO_2 before CBM liquefaction. And currently, amine-based absorption method is the most widely used to remove CO_2 from the natural gas and which is a well-proven commercial technology [1-4]. With the continuous studying on CO_2 absorbent by amine such as steric amine and enamine, the absorption characteristics of CO_2 absorbent is clearly known, and their different reactivity or rate for CO_2 absorption were investigated and reported [5]. Now, the research trend is shown to find a new blended solution which concludes all advantages of single CO_2 absorbents by studying the absorption of mixture absorbents.

MDEA is one of the most famous CO_2 absorbents and wildly applied in nature gas decarburization process. Although the corrosion that the MDEA single amine solution brought to piping equipment is much smaller than that of the other amine solutions [6,7], the influence of the degradation products of MDEA-based blended amine on the equipment system should not be underestimated[8,9]. During the decarburization process, accompany with the amine solution degradation the amine is gradually losing, as a result the absorption capacity of amine solution is decreasing. On the other hand, with the decomposition of amine the equipment corrosion caused by amine solution is raising, which will not only reduce the stability of absorption system, but also increase the construction costs and operating costs of the system, and result in direct economic losses. Furthermore, the degradation of amine solutions may lead to the erosion of the vessel wall, which result greater losses and more serious security risks. So in order to obtain a good strategy for the prevention of degradation of MDEA-based blended amines, a good understanding of the degradation process is necessary.

In the decarburization process, the two degradation types of organic amines are mainly oxidative degradation and thermal degradation [10]. The thermal degradation refers to the amine degradation that occurs in desorption tower, reboiler, heat exchanger and other high temperature regions, and does not require O_2 participation. While oxidative degradation refers to a redox reaction between organic amine and O_2 in the role of active groups [10]. The reaction balance of MDEA in aqueous solution is as follow [12-18].

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$$CH_3\text{-}N(CH_2CH_2OH)_2 + H_2O \leftrightarrow CH_3\text{-}NHCH_2CH_2OH + HOCH_2CH_2OH \quad (1)$$

When oxygen is present, the hydrolysis equilibrium products ethylene glycol will be further oxidized in the role of Fe^{2+} as catalyst, and oxalic acid and formic acid will be produced.

$$HOCH_2CH_2OH \rightarrow HOCH_2CHO \rightarrow OHCHO \rightarrow HOOCCHO \rightarrow HOOCCOOH \rightarrow HCOOH + CO_2 \quad (2)$$

The oxidative degradation products are acidic and have a strong corrosive effect on devices. And the smaller the molecular weight of organic acid, the greater the corrosive effect [9].

At present, the knowledge of the corrosion and oxidative degradation of the blended amine solutions for CO2 absorption was limited. There are a few reports on the degradation of organic amines from University of Regina [5, 19-22], University of Texas at Austin, French Petroleum Institute, Norwegian Technology University and Dow Chemical Company [11]. While in China, reports on the degradation problems of organic amine solution in CO_2 absorption process are rare, only Chen Changhe [11], Lu Jiangang [23], Zhang Chengfang [24], Zhang Yongchun [25] and several other scholars did researches on that. So there is no enough date to optimizing industrial design and calculating CO_2 fraction. Thus, it is particularly necessary to conduct investigations to reduce the oxidative degradation of MDEA amine solutions effectively by strict controlling the operating conditions and adding corrosion inhibitors or antioxidants.

This study aimed to understand the degradation characteristics and corrosion characteristics of amine solutions in the decarburization process, and realized by testing the degradation ratio of amine solutions and the corrosion ratio of steel sample sheets immersing in the amine solutions. Finally improved the CO_2 absorption ability of amine solution for, and certain antioxidants and inhibitors were added into the solutions to reduce the degradation and corrosion ratio.

METHODS AND MATERIALS

The materials and equipment used in the degradation and corrosion experiments are listed in Table 1 and Table 2 as below.

Table 1. The materials for degradation experiments and corrosion experiments

Name	Specification	Resource
CO_2	99.999%	Chengdu Hong Jin chemical (gas) Co., Ltd.
MDEA	99%AR	Chengdu Kelong Chemical Reagent Factory
DETA	99%AR	Chengdu Kelong Chemical Reagent Factory
MEA	99%AR	Chengdu Kelong Chemical Reagent Factory
PZ	99%AR	Chengdu Kelong Chemical Reagent Factory
sodium sulfite	AR	Chongqing Chuandong Chemical (Group) Co., Ltd
Sodium aluminate	AR	Chengdu Kelong Chemical Reagent Factory
sodium potassium tartrate	AR	Chengdu Kelong Chemical Reagent Factory
V_2O_5	99%	Chengdu Jinshan Chemical Reagent CO,.LTD
Steel sheet	Q235	Cutting by subcontractor into the size of 40*40*2 （mm ）
abrasive paper	GRIT No.CW800	NAMKYUNG ABRASIVE IND.CO,.LTD
H_2SO_4	AR	Chongqing Chuandong Chemical (Group) Co., Ltd
acetone	AR	Chongqing Chuandong Chemical (Group) Co., Ltd
HNO_3	AR	Chongqing Chuandong Chemical (Group) Co., Ltd

Table 2. The apparatus for degradation experiments and corrosion experiments

Name	Model	Resource
Electronic balance	FA-2004N	Shanghai Minqiao Precision Scientific Instruments Co., Ltd.
Automatic titration analyzer	ZD-2	Shanghai Dapu Instrument Co., Ltd.
Precision pH meter	PHS-3C	Shanghai Dechuan Precision Instruments Co., Ltd.
Constant temperature convection oven	101	Shanghai Dongxing Test Equipment Co., Ltd.
Constant temperature water bath	HH-S11-NI6	Beijing Scientific Instruments & Materials Corp
Vernier caliper	0-150MM	Guilin Guanglu Measuring Instrument Co., Ltd
SEM	Tescan Vega	FEI Nova400, China

Degradation experiments

In the coal bed methane decarburization process, the temperature in the absorption tower usually is 45°C and the pressure is 0.4MPa, while in the desorption tower, the temperature usually is 115°C and the pressure is 0.06MPa. The degradation of amine solutions caused by thermal or chemical is very slight that it is not necessary to consider them separately. So in this study, the thermal degradation and chemical degradation were tested together in the thermal degradation experiments, while the oxidation degradation of amine solutions was tested alone. And according to the results of Idem R. O.'s research [5] ,that there was no significant degradation of MEA and MDEA which induced by CO_2 at both lower and higher total amine concentrations at a temperature range of 328-393 K.

We assumed that the thermal degradation of CO_2 loaded amine solution was similar with the thermal degradation of fresh amine solution. Thus we did not investigate the thermal degradation of CO_2 loaded amine solution here, and it will be investigated in our next work.

Thermal degradation experiments

In the thermal degradation experiments, reactors containing a certain amount of fresh amine solutions were sealed and put in a constant temperature convection oven, and were heated at 95 °C constantly for a period of time. And during the heating, for every designed time interval1 mL sample were taken out from the reactors, and the total amine concentration of the samples were determined by an automatic titration analyzer. After the measured total amine concentration in the solutions reduced to a constant value and changed slightly, the thermal degradation experiments would be stopped. The thermal degradation of the fresh amine solutions and the rich amine solutions were tested respectively. By the analysis of the total amine concentration in the solutions at different time periods under high temperature heating conditions, the thermal degradation characteristics of amine solutions were obtained.

Oxidation degradation experiments

In this study, different kinds of fresh amine solutions with or without adding antioxidants were prepared for oxidation degradation experiments. A certain amount of amine solutions were taken into the reactor, and the reactor was fed in oxygen for a while, then the reactor was sealed and placed in a heated convection oven to keep a constant temperature. Samples were taken at different time periods. By using an autoburette, the total amine concentration in the sample can be analyzed, and then the oxidative degradation characteristics of amine solutions would be obtained. By comparing the oxidative degradation characteristics of different amine solutions with different antioxidants, the amine formulations with excellent stability will be selected out.

Corrosion experiments

Q235 steel sheets with a size of 40×40×2(mm) were selected as the specimens for corrosion experiments. And the steel sheets were immersed in different amine solutions in different 250mL beakers. These beakers were sealed and placed in a constant temperature water bath for heating at 90 °C for 72 hours. The mass of each specimen before and after the corrosion experiments were measured. The corrosion characteristics of the decarburization amine solutions were quantitative and qualitative analyzed by using the gravimetric method and scanning electron microscopy (SEM). The corrosion rate of specimens can be calculated by Equation(1).

$$\overline{\mu} = \frac{m_0 - m_i}{t \times s} \tag{3}$$

Where,

$\overline{\mu}$ is the metal corrosion rate, g/(m^{2}h);

m_0 is the first mass of specimen before corrosion test, g;

m_i is the final mass of specimen after corrosion test for a certain period and the corrosion products on the surface of specimen was removed , g;

S is the surface area of specimen exposed to the corrosive environment, m^2;

And *t* is the corrosion time, h.

RESULTS AND DISCUSSION

Thermal degradation

Six different kinds of fresh amine solutions of 30% mass fraction were prepared. 100 mL amine solutions were put into different beakers. Then sealed the beakers and placed them at a constant temperature of 95 °C for 44 hours. During this period, every 12 hours 1mL amine solution sample was taken out for analyzing. 0.5 mol/L hydrochloric acid solution was used for titration analyzing, the consumption volume of hydrochloric acid were measured when the pH value of the amine solutions reached 7. Then the total amine concentration in the amine solution can be calculated, and the amine thermal degradation ratio were obtained.

Table 3. The hydrochloric acid consumption amount of each 1 L amine solutions (mol/L)

Time	MDEA	MEA	DETA	MDEA+MEA 7 : 3	MDEA+DETA 8 : 2	MDEA+PZ 8 : 2
0h	2.565	5.005	5.935	2.968	3.194	2.616
12h	2.540	4.929	5.703	2.917	3.169	2.616
24h	2.490	4.829	5.734	2.917	3.169	2.590
44h	2.490	4.653	5.659	2.842	3.144	2.565

The results are shown in Table 3 and Fig. 1.

It can be seen in Table 3, the hydrochloric acid consumption amount of each 1L amine solutions decreased slightly with time. This is because that under the constant heating environment at 95 °C, the amine degraded, and the total amine concentration of the amine solutions decreased with time, which resulted in the decrease of hydrochloric acid consumption amount.

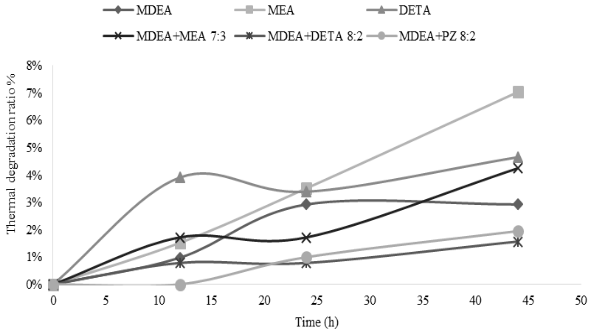

Fig.1. The change of thermal degradation ratio of amine solutions with time

In Fig.1, the thermal degradation ratio of MEA solution had the fastest increasing rate with heating time, and after 44 hours heating the ratio is 7.03%. Then the thermal degradation increasing rate turned to slower for others amine solutions with an order as: DETA> MDEA+MEA (7:3)> MDEA+ DETA (8:2)> MDRA+PZ (8:2). And it can be found that the thermal degradation ratio of MDEA+PZ(8:2) blended amine solution was just 1.6% after 44 hours, which indicated that the thermal degradation of this blended amine solution is so slightly that can be ignored.

Oxidative degradation

The oxidative degradation characteristics of single amine solutions and blended amine solutions without anti-oxidants

Prepared different kinds of fresh amine solutions of 30wt%. 150mL amine solutions were put into a volumetric flask and then fed pure oxygen for 2 minutes. Then sealed the volumetric flask and placed it at room temperature for a design time. During this period, every 96 hours took 1mL of amine solution sample for analyzing. 5mol/L hydrochloric acid solution was offered for titration analyzing, the consumption volume of hydrochloric acid were measured when the pH value of the amine solutions reached 7.Then the total amine concentration in the amine solution could be calculated, and the amine degradation ratio were obtained. The results are shown in Table 4 and Fig. 2.

Table 4 shows that the total amine concentration declined before held for 303 hours. This was due to the amine in solutions was oxidized in oxygen-rich condition. The oxidative degradation of single MEA amine solution and MDEA+MEA blended amine solution is larger than that of single MDEA amine solution and MDEA+PZ blended amine solution. And all amine concentrations declined slightly with time.

In Fig. 2, it can be seen that, the oxidative degradation ratio of MDEA+MEA blended amine solution raising fastest with holding time, and also had the highest ratio after held for 399 hours compare with other amine solutions. Then is that of MEA single amine solution. Then the single MEA amine had a lower oxidative degradation ratio than MDEA+MEA (7:3) blended amine. Lowest oxidative degradation ratio was found for single MDEA after 399 hours oxidization, and MEDA+ PZ (8:2) has a little higher ratio than MDEA which was found as 24.63%.

According Table 4 and Fig. 2, a conclusion can be obtained that the in these four amine solutions, MDEA +PZ blended amine solutions was affected by oxygen a little, whose oxidative degradation ratio is only 3.8% at the first 44 hours, but still

Table 4. The hydrochloric acid consumption amount of each 1 L amine solutions（mol/L）

Time	MDEA	MEA	MDEA+MEA	MDEA+PZ
0h	2.565	5.030	3.471	3.93
96h	2.515	4.829	2.842	3.8052
192h	2.389	4.552	2.766	3.7204
303h	2.414	4.389	2.641	3.6156
399h	2.414	4.276	2.616	3.607

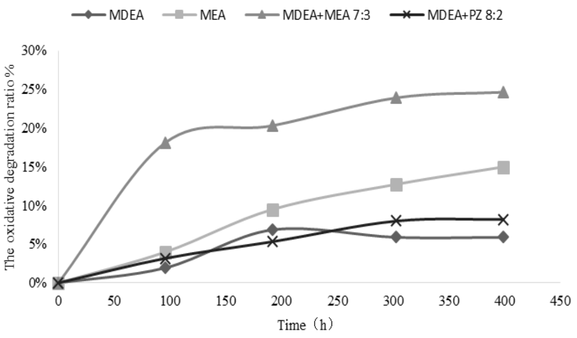

Fig. 2. The change of oxidative degradation ratio of amine solutions with time

more larger than its thermal degradation ratio of 1.6% at the first 44 hours. As the effect of oxygen on amine solutions exists almost in the whole decarburization process, while the effect of heat exists only in the amine solution recovery process, the influence of oxygen on amine degradation is much larger than that of thermal.

The oxidative degradation characteristics of blended amine solutions with anti-oxidants

The 30% amine concentration solution which contained by MDEA+PZ (8:2) blended amine was reported had a good CO2 absorption ability with a high CO2 absorption rate and regeneration ratio[15]. Moreover, the above thermal degradation experiments and oxidative degradation experiments proved that the MDEA+PZ (8:2) had a reliable stability even in high temperature and high oxygen content atmosphere.

Therefore, the blended amine solution MDEA+PZ (8:2) was selected as an optimization CO2 absorption compound of the investigation for studying the effect of anti-oxidants. 1wt% of three kinds of antioxidants, namely potassium sodium tartrate tetrahydrate, sodium sulphite and sodium metavanadate was added in the blended amine solution. The oxidative degradation characteristics study results are shown in Table 5 and Fig. 3.

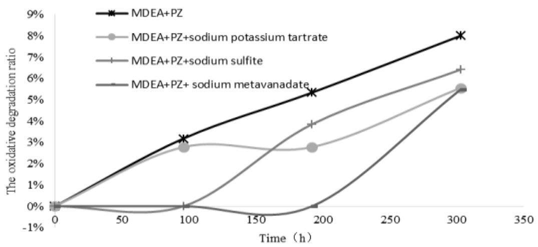

Fig.3. The change of oxidative degradation rate of blended amine solutions with time

Table 5 shows that the hydrochloride consumption amount of each 1 L amine solutions reduced with increasing of held time, which means the total amine concentration decreased gradually with time, and indicates that the oxidative degradation occurred in the amine solution. But the total amine concentration of MDEA+PZ (8:2) blended amine solutions with anti-oxidants did not change significantly.

From Fig.3, it can be seen that, after adding three different anti-oxidants, the oxidative degradation ratio of MDEA+PZ (8:2) solutions was decreased. This indicated that the anti-oxidants did effort on protecting the amine solutions from degradation caused by oxygen. Results show sodium metavanadatehad the best ability to reduce the degradation caused by oxygen in these three anti-oxidations, and the degradation ratio reduced 32% after 303 hours reaction compare with the blended amine solution without any anti-oxidations. And it was found that t sodium potassium tartrate had a better ability to reduce the degradation than sodium sulfite.

Corrosion results

Corrosion characteristics of fresh amine soliotions

The corrosion characteristics of six different fresh amine solutions of 30wt% total amine concentration were investigated by the corrosion experiments at the same temperature of 90°C for 72 hours. The results are shown in Table 6.

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Table 5. The hydrochloric acid consumption amount of each 1 L amine solutions (mol/L)

Time	MDEA+PZ + sodium potassium tartrate	MDEA+PZ + sodium sulfite	MDEA+PZ + sodium metavanadate	MDEA+PZ
0h	3.7728	4.0872	3.8252	3.93
96h	3.668	4.0872	3.8252	3.8052
192h	3.668	3.93	3.8252	3.7204
303h	3.5632	3.8252	3.6156	3.6156

Table 6. Corrosion characteristics of fresh amine solutions

Fresh amine solutions	Amine Concentration wt%	Surface area 10^{-6} m^2	Specimen mass before erosion g	Specimen mass after erosion g	Corrosion rate $g/(hm^2)$
MDEA	30%	3568	32.5308	32.5269	0.01518
MEA	30%	3446	31.3111	31.3071	0.01612
DETA	30%	3616	32.7790	32.3841	1.51668
MDEA+PZ	30%(8：2)	3524	31.8979	31.8921	0.02286
MDEA+DETA	30%(8：2)	3585	31.7671	31.7603	0.02634
MDEA+MEA	30%(8：2)	3450	31.3799	31.3734	0.02617

Among these three single amine solutions, the lowest corrosion rate was found on the specimen immersing in the MDEA single amine solution, while that in DETA single amine solution had a highest corrosion rate, which indicated that the corrosion rate of specimen in amine solutions has a positive correlation with the alkalinity of amine solutions. That means the better CO_2 absorption characteristics, the stronger corrosion characteristics. After adding different activators (PZ, DETA and MEA) in the MDEA solutions, the specimens in these three blended amine solutions had a larger corrosion rate than that in the MDEA single amine solutions, but still much lower than that in the DETA single amine solutions. And the specimen in the MDEA+PZ blended amine solutions had the lowest corrosion rate among these three blended amine solutions.

Corrosion characteristics of rich amine solutions

The rich amine solutions were prepared by piping CO2 into the fresh amine solutions for enough time. Then the corrosion characteristics of rich amine solutions were studied by the corrosion experiments at the same temperature of 90°C for 72 hours. The results were as shown in Table 7. From Table 7 it can be seen that, the largest corrosion rate of specimen immersing was found in the MEA rich amine solitions, while that in MDEA rich amine solitions is the lowest. The corrosion rate of specimen in MDEA+PZ rich amine solutions is 0.0999 gm-2/h, which is slightly higher than that in MDEA rich amine solitions. Compared with Table 6, it is obviously that the corrosion rate of specimen in rich amine solutions is much higher than that in the relative fresh amine solutions, which indicated that the corrosion characteristics of rich amine solutions is much stronger than that of fresh amine solutions. And in these blended rich amine solutions, the specimen in the MDEA+PZ rich amine solutions still had the lowest corrosion rate.

Corrosion characteristics of rich amine solutions with inhibitors

According to the corrosion experimental results above, whether among the fresh amine solutions or the rich amine solutions, specimen in the MDEA+PZ(8:2) blended amine solutions had a relatively small corrosion rate. So the MDEA+PZ(8:2) blended rich amine solution was taken for investigation in this part of experiments. 0.5% -1% of sodium vanadate and vanadium pentoxide as corrosion inhibitors was added into the MDEA+PZ(8:2) blended rich amine solutions, the corrosion experiments were carried out at 90 °C for 72hours. The corrosion rate of specimens in the MDEA+PZ(8:2) blended rich amine solutions with different inhibitors were measured, and the results were shown in Table 8. Compared Table 7 and Table 8, it can be seen that, afteradding inhibitors, the corrosion rate of specimens in the MDEA+PZ(8:2) blended rich amine solutions had a significant decrease, the corrosion rate decreased from 0.0999 $g/(hm^2)$ for the amine without inhibitors to 0.0026 $g/(hm^2)$ which was the largest corrosion rate after adding inhibitors. The anti-corrosion ratios of these six solutions with different inhibitors were larger than 97%. The anti-corrosion effect of inhibitor V_2O_5 was slightly better than that of inhibitor $NaVO_3$when same amount of inhibitors was added. And it was found the influence of inhibitor amount on the

Table 7. Corrosion characteristics of rich amine solutions

Rich amine solutions	Concentration wt%	Surface area $10^{-6}m^2$	Specimen mass before erosion g	Specimen mass after erosion g	Corrosion rate $g/(hm^2)$
MDEA	30%	3514	32.2393	32.2160	0.0896
MEA	30%	3429	31.2417	30.8665	1.4786
MDEA+PZ	30%(8：2)	3408	31.2460	31.2208	0.0999
MDEA+MEA	30%(8：2)	3566	32.4742	32.4338	0.1531

anti-corrosion effect is similar in the range from 0.5% to1%. And the he highestanti-corrosion ratio, 99.2%, was found in the solution which added 1% inhibitors of $NaVO_3+V_2O_5$(0.5%:0.5%)is t up to. The specimen surface corrosion characteristics were observed by using SEM at different scale, 5um,10um, 20um, 50umand 100um respectively. The SEM results of specimen before and after immersed in MDEA+PZ(8:2) blended rich amine solutions are shown in Fig 4-1a and Fig 4-1b respectively. Compared these two groups of images, it can be seen that, without adding any inhibitors, after immersing in the MDEA+PZ (8:2) blended rich amine solutions for 288h, that pitting appeared on the specimen surface was observed at 5um,10um and 20um scale, while at the 50umand 100um scale, that cracks increased on the specimen surface was observed. The results indicated that the rich amine solutions has a strong corrosion effect on the steel sample sheets, which is consistent with the results of corrosion ratio tests above. Fig 4-2a and Fig 4-2b show the SEM results of specimen before and after immersed in MDEA+PZ(8:2) blended rich amine solutions with inhibitors of $NaVO_3+V_2O_5$(0.5%:0.5%),respectively. Compared these two groups of micrographs, it can be seen that, with adding inhibitors of $NaVO_3+V_2O_5$(0.5%:0.5%),no significant difference can be observed on the specimen surface. This results indicated that the inhibitors of $NaVO_3+V_2O_5$(0.5%:0.5%) had an obviously anti-corrosion effect and protected the steel sample sheets from corrosion by rich amine solutions.

Table 8. Corrosion characteristics of MDEA+PZ (8:2) blended rich amine solutions with inhibitors

Inhibitor	Surface area $10^{-6}m^2$	Specimen mass before erosion g	Specimen mass after erosion g	Corrosion rate $g/(h*m^2)$	Anti-corrosion ratio %
$NaVO_3$(0.5%)	3654	34.2612	34.2605	0.0026	97.40
$NaVO_3$(1%）	3434	32.4299	32.4293	0.0024	97.60
V_2O_5(0.5%）	3623	34.1066	34.1069	0.0011	98.90
V_2O_5(1%)）	3534	33.1796	33.1790	0.0023	97.70
$NaVO_3 + V_2O_5$(0.25%:0.25%）	3506	32.6926	32.6920	0.0023	97.70
$NaVO_3+ V_2O_5$（0.5%:0.5%）	3441	32.1723	32.1721	0.0008	99.20

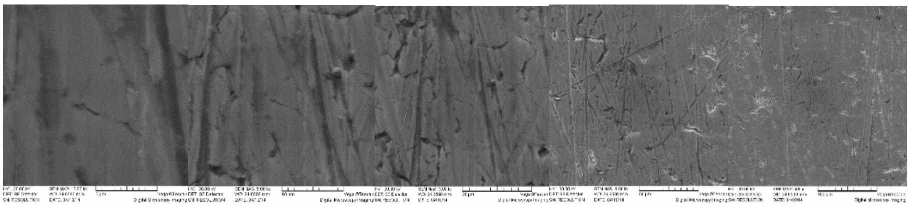

Fig 4-1a. SEM results of specimen before immersed in MDEA+PZ (8:2) blended rich amine solutions

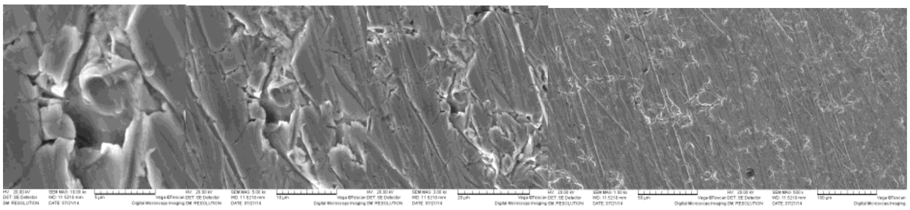

Fig 4-1b. SEM results of specimen immersed in MDEA+PZ (8:2) blended rich amine solutions after 288h

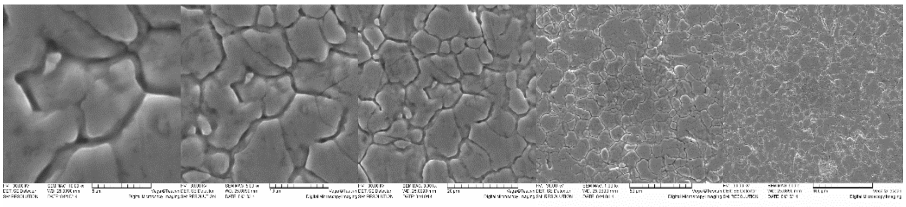

Fig 4-2a. SEM results of specimen before immersed in MDEA+PZ (8:2) blended rich amine solutions with inhibitor

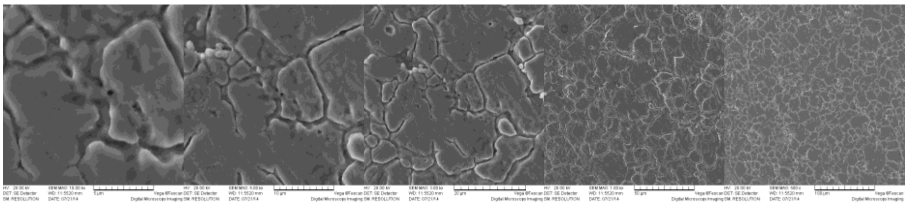

Fig 4-2b. SEM results of specimen immersed in MDEA+PZ(8:2) blended rich amine solutions with inhibitor after 288h

CONCLUSIONS

In the CBM decarburization process, amine degradation is mainly caused by oxygen, which result in low decarburization efficient and bring serious corrosion problems at the same time. Experiments were carried out to investigate the degradation and corrosion characteristics of amine solutions in the decarburization process. The results show that by adding certain antioxidants, the oxidative degradation ratio of blended amine solutions decreased obviously. The amine solutions with sodium metavanadate $NaVO_3$ has the most conspicuous antioxidant effects, followed by that with potassium sodium tartrate, and the last is with sodium sulfite. By adding 1% sodium metavanadate $NaVO_3$, the oxidative degradation ratio of MDEA+PZ (8:2) solution can be reduced by 32%. And the results of corrosion experiments show that the corrosion characteristics of rich amine solutions was much stronger than that of fresh amine solutions. The influence of inhibitor amount on the anti-corrosion effect is very small in the range of 0.5% to1%, and the anti-corrosion ratio of the solutions with 1% inhibitors of $NaVO_3+V_2O_5$(0.5%:0.5%)is the highest, up to 99.2%. The SEM results also show that with adding 1% inhibitors of $NaVO_3+V_2O_5$(0.5%:0.5%）the surface of specimen immersed in the MDEA+PZ blended rich amine solutions changed merely. The recommended decarburization agent formula is MDEA+PZ(8:2) with 0.5% $NaVO_3$ and 0.5% V_2O_5 as inhibitor.

REFERENCES

1. J. H. St. Clair, W. F. Simister, *Oil Gas J.*; (United States), **81**, 7 (1983).
2. J. Wen, C. X. Huo, B. Zhang, **864-867**, 194 (2014)
3. M. T. Sander, C. L. Mariz, *Energy ConVers Manage.*, **33**, 341 (1992)
4. F. A. Tobiesen, H. F. Svendsen, *Industrial & Engineering Chemistry Research*, **45**(8), 2489 (2006)
5. A. O. Lawal, R. O. Idem, *Industrial and Engineering Chemistry Research*, **45**(8), 2601 (2006)
6. P. C. Rooney, M. S. Dupart, T. R. Bacon, *Hydrocarbon Process*, **77**, 109, (1998).
7. J. H. Chen, Ju. Wen. *Guangdong Chemical Industry*, **42**(12), 45 (2015).
8. X. W. Feng, X. P. Guo, *Journal of Chinese Society for Corrosion and Protection*, **23**(2),79 (2003).
9. Q.G. Ye, F.Q. Lu. *Corrosion science and protection technology*, **12**(3), 173 (2000).
10. S. Chi, G. Rochelle, *Industrial & Engineering Chemistry Research*, **41**(17), 4178 (2002).
11. Sh. Zhou, Sh.J. Wang，G.T. Rochelle, C.G. Chen, *J. Tsinghua University* (Sci&Tech), **56**(1), 81 (2012).
12. M.X. Yang, C.C, Xu, X.R. Fang. *Corrosion & Protecion*, **28**(10), 519 (2007)
13. X.Q. Yan, *Chemical Engineering of Oil & Gas*, **38**(4), 308 (2000).
14. A. Chakma, A. Meisen, *Can. J. Chem. Eng*., **75**(5), 861 (1997).
15. P.C. Rooney, M.S. Dupart, T.R. Bacon, *Hydro Proc*., **77**(7), 109 (1998).
16. T. Supap, R. Idem, P.Tontiwachwuthikul, C. Saiwan, *International Journal of Greenhouse Gas Control*, **3**(2), 133 (2009).
17. T. Supap, R. Idem, P. Tontiwachwuthikul, C. Saiwan, *Industrial and Engineering Chemistry Research*, **45**(8), 2437 (2006).
18. M. Howart, A. Sargent, *Oil&Gas Journal*, **99**, 52, (2001).
19. A. O. Lawal, R. O. Idem, *Ind. Eng. Chem. Res*. **44**(4), 986 (2005).
20. O. Lawal, A. Bello, R. Idem, *Ind. Eng. Chem. Res*. **44**(4), 1874 (2005).
21. A. Bello, R. O. Idem, *Industrial and Engineering Chemistry Research*, **45**(8), 2569 (2006).
22. W. Tanthapanichakoon, A. Veawab, B. McGarvey *Industrial and Engineering Chemistry Research* , **45**(8), 2586 (2006),
23. C.F. Zhang, L.J. Chen, CN1367170, 2002.
24. J.G. Lu, Y.F. Zheng, M.D. Chen, H.C. Zhou, Z.B. Guo, CN101063207,2007.
25. Y.C. Zhang, G.M. Li, X.F. Wang, C. Guo, S. Chen CN102284229A, 2011.

ХАРАКТЕРИСТИКИ НА ДЕГРАДАЦИЯ И КОРОЗИЯ ЗА РАЗТВОР НА СМЕС ОТ АМИНИ ПРИ ОТНЕМАНЕТО НА ВЪГЛЕРОДА ОТ МЕТАН В СЛОЙ ВЪГЛИЩА

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(Резюме)

През годините деградацията и корозията от разтворите на амини са станали основен проблем за отнемането на метан от въглища (CBM). Тези характеристики на разтворите от амини досега не са изяснени. В настоящата работа са изследвани деградационните характеристики на смеси от разтвори на амини в среда, богата на кислород с и без антиоксиданти. Резултатите показват, че отсъствието на антиоксидани е налице висока окисилителна деградация. След добавянето на антиоксидант, т.е. натриев метаванадат (NaVO3), натриев сулфид или натриево-калиев тартарат се забелязва очевидно понижение на деградацията на разтворите. Най-добри антиксидантни свойства има натриевият метаванадат, след него натриево-калиевият тартарат и накрая – натревият сулфид. При добавянето на 1% натриев метаванадат степента на окислителна деградация на метил-диетаноламин (MDEA) + пиперазин (PZ) (в начално отношение 8:2) намалява до 32%.

Изследвани са корозионните характеристики на пресни разтвори от амини в експерименти при 90°C за 72 часа. Резултатите от тестовете за корозия и от сканираща електронна микроскопия (SEM) показват, че степента на корозия в богати на амини разтвори еп о-висока, отколкото в пресни разтвори. След добавянето на 0.5% $NaVO_3$ и 0.5% V_2O_5 като инхибитор корозията на разтворите, богати на амини намалява. Според получените резултати за деградацията и корозията за декарбинизиращ агент при for CBM-процеса се препоръчва разтвор на MDEA+PZ(8:2) с добавка от 0.5% $NaVO_3$ и 0.5%V_2O_5 .