Corrosion and degradation performance of novel absorbent for CO₂ capture in pilot-scale

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Abstract

The corrosion and degradation behavior of new blended amine absorbent specified by Toshiba were studied in the pilot plant under the condition of long-term operation. Three test campaigns of the CO₂ capture were completed. One campaign was the base experiment to evaluate the thermal and oxidative degradation and corrosion character of new absorbent. Other two campaigns were operated to evaluate the influence of SO₂ on the corrosion and degradation behavior of new absorbent.

The results show that the SO₂ removal efficiency is almost 100%. After addition of SO₂ to simulated flue gas, there will be more serious amine degradation and HSS formation. The greater the SO₂ concentration is, the more amine degradation and HSS formation. The point C which is outlet of the heat exchanger (rich liquid side) presents the most serious corrosion. Addition of SO₂ plays an important role to form the corrosion protect films. It was difficult to form protect film and easily be destroyed at the presence of SO₂ for stainless steel compared with carbon steel.

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Keywords: Carbon dioxide; amine absorbent; Corrosion; Degradation; Pilot plant

1. Introduction

It is well known that greenhouse gases, such as CO₂, CH₄, N₂O, HFC₃₃, PFC₅ and SF₆, contribute to global warming and climate change. Among these greenhouse gases, anthropogenic carbon dioxide from fossil fuel is the most important one because of its long life and large amount [1]. The power plant, cement plant, steel plant and refinery plant are all concentrate sources of carbon dioxide. The emission of CO₂ from fossil fuelled power plants...
accounts for above 30% of the total. So the CO₂ capture from fossil fuel power plants was concerned widely. Many technologies may be used to separating CO₂ from flue gas, including amine scrubbing, carbonation-calcination recycle technology (CCR), O₂/CO₂ recycle combustion technology and chemical-looping combustion technology (CLC), and so on[2-6].

In effect, amine-based scrubbing technology has been used to separate carbon dioxide from natural gas in chemical industry for several decades. However, the flue gas from coal-fired power plant is large flow rate, high temperature and low CO₂ partial pressure with SO₂, NOₓ and fly ash, which is quite different with that from natural gas. Therefore, the technology must be further studied according to the condition of coal-fired power plants. Although facing to energy consumption and corrosion problems, amine-based scrubbing technology is still as timely solution for post combustion CO₂ capture compared other advanced technology[7].

A lab pilot plant has been built and operated based on theory studying for several years in Tsinghua University. The major work of this paper is to test the corrosion and degradation performance of new absorbent in the pilot plant under the condition of long-term operation.

2. Experimental system and methods

2.1 materials and analysis methods

The N₂, O₂, CO₂ and SO₂ with more than 99.9% concentration were used to simulate flue gas. The chemical reagents were industry grade, and the concentration was more than 98%. The blended amine solvent specified by Toshiba was used for this research work.

The CO₂ concentrations of the absorber inlet and outlet were recorded by IR CO₂ analyzer which are ranged from 0~20% and 0~5%, respectively. The SO₂ flow rate was controlled by mass flow controller, and continuously adding to the whole system. A SO₂ IR analyzer (produced by Thermo Company) was used to analyze the SO₂ concentration. Meanwhile, O₂ concentration was detected by paramagnetic oxygen meter. The Dionex ICS-1000 and DX120 ion chromatographic instruments were used to analyze anion and cation respectively. The CO₂ loading was determined by total organic carbon analyzer (TOC-5000, Shimadzu).

Three kinds of steel were used for corrosion test, carbon steel, 304 (stainless steel), and 316L (stainless steel). Coupons and coupon holders are shown in Fig.1. Coupon holders are made of 304 (stainless steel). Coupons are flat rectangular samples, (25×10×2mm³ and 40×10×2mm³ for carbon steel and 304 (stainless steel), 25×10×1mm³ and 40×10×1mm³ for 316L (stainless steel)). PTFE gaskets were used to avoid electrochemical corrosion between carbon steel and stainless steel. The detailed chemical composition of material is shown in Tab.1.

Fig.1. coupon holders and coupons for corrosion test
Before every experiment, the coupons were firstly polished and grinded with 120- or 150- grit water abrasive paper (this is according to GB/T 2481), then degreased with magnesia and acetone, rinsed with alcohol many times, dried, weighed, measured of surface area. After that, these coupons were carefully stored in a dry bottle and sealed in nitrogen environment, to be further mounted. The corrosion degree was tested by weighting the losses of coupons based on the method regulated by Chinese standard JB/T7901-1999 “Metals materials- Uniform corrosion method of laboratory immersion testing”. The corrosion rate (R) can be calculated using the following equation:

\[ R = \frac{8.76 \times 10^7 \times (M - M_1)}{STD \times mpy} \]

Where \( M \), \( M_1 \), \( S \), \( T \) and \( D \) denote weight before reaction (g), weight after reaction (g), sample area (cm\(^2\)), reaction time (h), sample density (kg/m\(^3\)), respectively.

<table>
<thead>
<tr>
<th>Material</th>
<th>C</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>Mn</th>
<th>Mo</th>
<th>N</th>
<th>Cr</th>
<th>Ni</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>316L</td>
<td>0.02</td>
<td>0.76</td>
<td>0.031</td>
<td>0.0022</td>
<td>1.22</td>
<td>2.15</td>
<td>0.04</td>
<td>17.16</td>
<td>10.5</td>
<td>Balance</td>
</tr>
<tr>
<td>304</td>
<td>0.045</td>
<td>0.49</td>
<td>0.033</td>
<td>0.001</td>
<td>1.05</td>
<td>/</td>
<td>0.057</td>
<td>18.32</td>
<td>8.4</td>
<td>Balance</td>
</tr>
<tr>
<td>carbon steel</td>
<td>0.053</td>
<td>0.031</td>
<td>0.016</td>
<td>0.034</td>
<td>0.25</td>
<td>/</td>
<td>/</td>
<td>0.025</td>
<td>0.012</td>
<td>Balance</td>
</tr>
</tbody>
</table>

2.2 Lab pilot plant

Fig.2 shows the scheme of the small loop pilot plant for capture CO\(_2\) using aqueous blended amine solvent in Tsinghua University, which is same with conventional industrial amine-based CO\(_2\) recovery plant except for recycled flue gas. No fresh solvent and water was added into the system during the experiment, so this design can keep water balance. The absorber and stripper, with an internal diameter of 0.207 meter, were filled with 700Y gauze structured, 3-meter height packing. The major equipment and pipeline are made of 316L stainless steel. The heat input to the stripper is supplied by electrical heater (with the power of 60kW). Liquid sample for degradation testing was collected per 100 hours during the operation. The plant can be operated continuously and all the testing data can be collected automatically.
The corrosion test was performed using weight loss coupons installed at six different locations and three different material coupons at every position, as shown in Fig. 2. These test points were lean solvent inlet of the absorber (A point), rich solvent outlet of the absorber (B point), rich solvent outlet of the heat exchanger (C point), lean solvent outlet of the stripper (D point), CO₂ outlet of the stripper (E point) and treated gas outlet of the absorber (F point).

Three campaigns have been conducted in this pilot plant. The flue gas of campaign1 contains about 12vol% CO₂ and 18vol% O₂. The experiment condition of the campaign2 was identical to the first campaign exclude adding 200ppm SO₂, and 300ppm for the last campaign. The average flue gas flow rate of the three campaigns was about 86m³/h, and liquid solvent flow rate was ranged from 0.2m³/h to 1.2 m³/h. The average temperature of absorber and stripper bottom was 46℃ and 116℃, respectively. The continuously operating time was around 500 hours for campaign1, 430 hours for campaign2, and 345 hours for campaign3. If the CO₂ removal efficiency was reduced to 60% below or the CO₂ concentration out of the absorber reached 5%, the experiment was finished. Hence, the operating time of the last two campaigns was short.

3. Results and discussion

3.1 Accumulation of SO₂ in solution

![Fig.3. SO₂ concentration of absorber outlet](image)

![Fig.4. Sulfate and sulfite concentration of two campaigns](image)

The SO₂ concentration out of absorber was analyzed by IR SO₂ analyzer ranged from 0 to 20ppm (Model 43C, Thermo). This value was recorded per 12 hours. The Fig.3 shows that the SO₂ concentration out of absorber of two campaigns. With the increasing of SO₂ concentration from campaign2 to campaign3, the outlet SO₂ concentration was dramatically increased. However, the maximum value was very small compared with the inlet SO₂ concentration. It is means that the SO₂ removal efficiency is almost 100%. Therefore, SO₂ was accumulated gradually in new absorbent under this research condition.

Although the O₂ content of two campaigns was about 18%, SO₃²⁻ was still observed, which is shown in Fig.4. As the SO₂ concentration increased, SO₃²⁻ and SO₄²⁻ concentration climbed slowly. After 200 hours, SO₄²⁻ was more than SO₃²⁻ for campaign 2. But for campaign3, this time is after 300 hours.

3.2 Amine degradation
A serious problem associated with chemical absorption of CO$_2$ from coal-fired power plant flue gas streams is solvent degradation caused by SO$_2$ and O$_2$, as well as by heating the solution. The campaign1 evaluated the influence of both O$_2$ and temperature on the degradation of the absorbent. The campaign2 and campaign3 evaluated the contribution of SO$_2$ to absorbent degradation by comparing with campaign1. The amine concentration – time plots of three campaigns are shown in Fig.5. For the amine-H$_2$O-CO$_2$-O$_2$ system in campaign 1, the amine concentration reduced from the initial 4.6mol/L to 4.3mol/L during 500 hours, decreased by 6.5%. But for amine-H$_2$O-CO$_2$-O$_2$-SO$_2$ system, it is decreased by 11.82% during 430 hours and 34.7% during 345 hours for campaign2 and campaign3, respectively. That is to say, with the increasing of SO$_2$ concentration, the tendency of amine degradation was accelerated. Addition of SO$_2$ may compete with CO$_2$ to react with amine, which retarded the inhibited role of CO$_2$ and caused an increase of amine degradation [10].

![Fig.5. Effect of SO$_2$ on amine degradation](image1)

3.3 Heat stable salts

![Fig.6. Effect of SO$_2$ on Heat Stable Salts formation](image2)  
![Fig.7. Formation Rate of Heat Stable Salts](image3)

The Fig.6 shows the mass percent of total heat stable salts (HSS). Four kinds of organic acid were detected, including formate, acetate, oxalate and glycolate. And the formate and acetate were mainly products of amine
degradation. The content of HSS can be used to evaluate the solvent degradation extent and to analyze the degradation mechanism. For campaign1, the New absorbent contained approximately 0.14 mass% HSS after operating 500 hours. However, for campaign2 and campaign3, this value was 0.98 mass% for 430 hours and 0.92 mass% for 345 hours, respectively. In campaign1, the HSS was accumulated slowly in solvent with the time elapsed. However, SO2 accelerated the process of HSS accumulation that was obtained from campaign2 and campaign3. As the SO2 concentration increased, the content of the HSS rose too. As shown in Fig.7, formation rate of HSS has small fluctuate for campaign1, and the whole trend was decreased. But with the increasing of SO2 concentration from campaign2 to campaign3, the formation rate of HSS enhanced. The thermal and oxidative degradation has a small influence to HSS formation compared to SO2.

3.3 Corrosion results

<table>
<thead>
<tr>
<th>Test point</th>
<th>Temperature (°C)</th>
<th>Flow rate (m/s)</th>
<th>Corrosion rate (µm/a)</th>
<th>Temperature (°C)</th>
<th>Flow rate (m/s)</th>
<th>Corrosion rate (µm/a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>42(14~47)</td>
<td>0.36</td>
<td>3.784</td>
<td>45(44~46)</td>
<td>0.33</td>
<td>2.339</td>
</tr>
<tr>
<td>B</td>
<td>43(26~47)</td>
<td>0.09</td>
<td>0.504</td>
<td>48(45~50)</td>
<td>0.09</td>
<td>29.404</td>
</tr>
<tr>
<td>C</td>
<td>99(78~102)</td>
<td>0.37</td>
<td>99.878</td>
<td>101(99~103)</td>
<td>0.32</td>
<td>59.575</td>
</tr>
<tr>
<td>D</td>
<td>116(93~120)</td>
<td>0.21</td>
<td>0.392</td>
<td>116(115~118)</td>
<td>0.84</td>
<td>1.987</td>
</tr>
<tr>
<td>E</td>
<td>107(80~109)</td>
<td>1.61</td>
<td>4.940</td>
<td>103(96~108)</td>
<td>1.08</td>
<td>1.115</td>
</tr>
<tr>
<td>F</td>
<td>39(25~42)</td>
<td>11.92</td>
<td>3.076</td>
<td>43(42~45)</td>
<td>11.51</td>
<td>2.410</td>
</tr>
</tbody>
</table>

In most industrial processes, corrosion is a serious problem, especially for CO2 capture from coal-fired power plant flue gas, for amine absorbent is used, and complex flue gas composition, as well as heat stable salts (HSS) that are the products of absorbent degradation [11-14]. The amine-CO2-O2-HSS system was used as basis to evaluate the corrosion characteristics of this whole system. The amine-CO2-O2-SO2-HSS system was used to evaluate the influence of SO2 on corrosion at six typical positions. The Tab.2 shows that corrosion rate of carbon steel for six test positions and operating condition of two test experiments. It has small difference of operating condition for every test position between campaign1 and campaign2. The highest corrosion rate of two tests is all at the point C which is outlet of the heat exchanger (rich liquid side). But the corrosion rate of campaign2 is lower than campaign1 though 200ppm SO2 was added continuously in campaign2. The possible reason is that the protect film was formed on the surface of test coupons. Under the temperature of point C, a part of CO2 will be stripped from rich liquid, so there will be gas-liquid two phase flow. And this has ever been detected by glass float flow meter. The corrosion rate can be accelerated by gas-liquid two phase flow [15]. The high CO2 loading solution with CO2 bubbling is the main reason to result in high corrosion rate. Comparing point B and point D in campaign1 and campaign2, it is concluded that addition of SO2 will accelerated corrosion at low temperature and inhibited corrosion at high temperature. From point E in campaign1 and campaign2, the quicker gas flow speed of CO2, the higher corrosion rate. As to point A and F, some condition such as temperature, flow rate and CO2 concentration are similar, corrosion rate is also similar. The temperature, gas or liquid flow rate, solvent with HSS, SO2 and CO2 loading are all contribute to corrosion.
Tab.3 Corrosion rate of stainless steel

<table>
<thead>
<tr>
<th>Test point</th>
<th>Campaign1 304</th>
<th>Campaign 2</th>
<th>Campaign1 316L</th>
<th>Campaign 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.16248</td>
<td>NA</td>
<td>0.14447</td>
<td>NA</td>
</tr>
<tr>
<td>B</td>
<td>0.33116</td>
<td>0.14003</td>
<td>NA</td>
<td>0.50398</td>
</tr>
<tr>
<td>C</td>
<td>0.19498</td>
<td>NA</td>
<td>0.25283</td>
<td>0.25199</td>
</tr>
<tr>
<td>D</td>
<td>0.37171</td>
<td>0.64833</td>
<td>0.1361</td>
<td>1.02869</td>
</tr>
<tr>
<td>E</td>
<td>0.18586</td>
<td>0.12006</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>F</td>
<td>NA</td>
<td>0.3282</td>
<td>0.11068</td>
<td>0.48903</td>
</tr>
</tbody>
</table>

Tab.3 shows the corrosion rate of 316L stainless steel and 304 stainless steel in two test experiments. The highest corrosion rate is at point D at the presence of SO$_2$. The corrosion rate was retarded at the presence of SO$_2$ excluding point D and F. It was difficult to form protect film and easily be destroyed at the presence of SO$_2$ for stainless steel compared with carbon steel. For stainless steel, the flow rate, SO$_2$, high temperature and high CO$_2$ loading may be the main reason to enhance corrosion. The corrosion rate of 304 stainless steel and 316L stainless steel are lower than carbon steel at every test point.

4. Conclusions

A pilot plant for capture CO$_2$ from coal-fired power plant was built in Tsinghua University. The pilot plant adopts amine-based chemical absorption process, including absorption and stripping. The gases out of the absorber and stripper were fed back to the absorber again, as well as the condensate. The whole system, therefore, is closed, which can keep the gas and water balance.

The major work of this paper is to test the corrosion and degradation performance of new absorbent in the pilot plant under the condition of long-term operation. The results indicate that SO$_2$ was accumulated gradually in new absorbent under the condition of 200ppm and 300ppm SO$_2$, and the SO$_2$ removal efficiency is almost 100%. Compared with thermal and oxidative degradation, the addition of SO$_2$ aroused more serious amine degradation. Meanwhile, the thermal and oxidative degradation has a small influence to HSS formation compared to SO$_2$. The highest corrosion rate for carbon steel is at the point C which is outlet of the heat exchanger (rich liquid side). Addition of SO$_2$ contributes to the formation of corrosion protect films. It was difficult to form protect film and easily be destroyed at the presence of SO$_2$ for stainless steel compared with carbon steel.

Acknowledgment

This work was carried out on collaboration research project between Tsinghua University and TOSHIBA.

References


