

Experimental and mechanism studies on seawater flue gas desulfurization

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Abstract: Seawater flue gas desulfurization (Seawater FGD) process has a number of advantages, but the study on mechanism of seawater FGD is little. The effects of absorbing efficiency of SO₂ by the constant component and part of trace transition elements in seawater are studied by the experiment. The results indicate that the effect factors of absorption of SO₂ by seawater are alkaline, ion intensity, catalysis of Cl⁻ and transition metal ions Fe²⁺, Mn²⁺. The degree of effect is alkaline > the catalysis of Cl⁻, Fe²⁺ and Mn²⁺ > ion intensity. The mechanisms of catalysis oxidation for S(IV) by Cl⁻, Fe²⁺ and Mn²⁺ are discussed. According to the results, some measures can be used to improve the capability of desulfurization.

Keywords: seawater; flue gas desulfurization; catalysis

Introduction

Installation of scrubbers or the use of low sulfur-containing coal are two options used by power plants to reduce SO₂ emissions. The majority of power plants control SO₂ emissions using lime based scrubbing, although this desulfurization process has a number of advantages, it also has some serious disadvantages. Alternates will have to be found. It is known that SO₂ is absorbed by seawater as one of alternates. Bromley (Bromley, 1972) first proposed the method of using the seawater as the absorbent for flue gas desulfurization in 1972, which is applicable mainly to coal fired boilers where seawater is available. In this time, ABB Environmental Company started the development of a FGD (flue gas desulfurization) process using seawater for the absorption of SO₂ from flue gases. About this process had been reported very little during 1970's—1980's, until 1990's, the principles and operation conditions for the process have been studied (Grgic, 1991; Barrie, 1976; Purnendu, 1979), the investigation of the apparatus and applications for flue gas desulfurization using seawater have been carried out, but further research about the absorbing mechanism of seawater FGD has not been reported, hence the process is not significantly improved in the efficiency of desulfurization.

Absorbing capacity of seawater for SO₂ is affected by some factors due to its complex chemical component (Wu, 1982). Absolute alkaline is a very major factor. It is affected by some other factors such as ion intensity, the catalysis of Cl⁻ and transition metal ions Fe²⁺, Mn²⁺ and so on.

According to the investigated results of the acid rain formed from SO₂ in the atmosphere, the effects of the conversion of SO₂ had been studied by using some components of seawater. Kaplan (Kaplan, 1981) had studied all kinds of soluble salt. Further research about the catalysis oxidation of the trace metal on the surface and inside the particulate matter in the atmosphere for SO₂ had been done. The conditions of manganese(II) catalyzed sulfur dioxide in aqueous solution at environmental concentration were studied by Takashi *et al.* (Takashi, 1984). The research on catalysis oxidation of the heavy metal ions in water drops was carried out by Barrie (Barrie, 1976). Purnendu (Purnendu, 1979) studied the transition metal ion-sulfur(IV) system. Based on the study results of SO₂ oxidation in atmospheric environment, the study on mechanism and experiment of seawater FGD are carried out. According to this result, some measures for example adding some metal salt into absorbing solution of seawater can be used to improve the capability of desulfurization system, such as higher efficiency of desulfurization, lower running cost and so on.

1 Experimental devices and methods

1.1 Experimental devices

The experimental devices are shown in Fig. 1.

1.2 Experimental methods

In order to study the effect of the different components contained in seawater on the desulfurization, the solutions containing the concerned components were made up with deionized water. A certain volume of the solution was taken to carry out the experiment according to the process of Fig.

1. A simulated stack gas containing 1000—4000 mg/m³ SO₂ and 10% O₂ was used throughout the experimental program, the carrier gas used in the experiments was N₂.

KNS-400 flue gas analyzer was used to record concentrations of SO₂ and O₂.

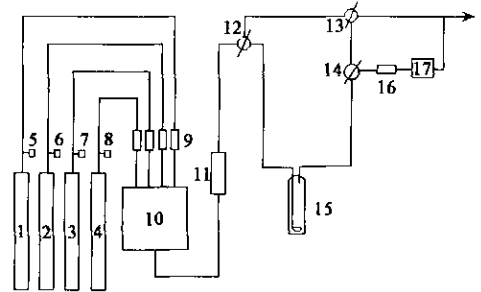


Fig.1 Schematic diagram of flue gas desulfurization using seawater

1. SO₂ metal flask; 2. N₂ metal flask; 3. CO₂ metal flask; 4. O₂ metal flask; 5, 6, 7, 8. reducing pressure valve; 9. flux meter; 10. mixed flask; 11. gas flux meter; 12, 13, 14. valve; 15. bubbling reactor; 16. drying pipe; 17. KNS-400 flue gas analyzer

2 Results and discussions

2.1 The effect of the alkaline in seawater

The pH value of deep seawater is about 8.0. According to the analysis results of the component of seawater, more HCO₃⁻ was detected but no CO₃²⁻. It is thought that the pH value of seawater is contributed mainly by HCO₃⁻, the solutions containing different content of NaHCO₃ (153 mg/L, seawater from Qinhuangdao Gulf) were made up. The results indicate that the SO₂ absorbing efficiency is obviously improved by the increase of NaHCO₃ concentration. Suggesting the alkaline for example HCO₃⁻ alkaline in seawater is very important to flue gas desulfurization.

2.2 The effect of Na₂SO₄ in seawater

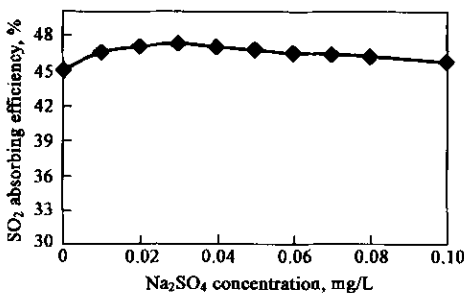


Fig. 2 Effect of concentration of Na₂SO₄ on absorption of SO₂

The solutions with different contents of Na₂SO₄ were made up depending on Na₂SO₄ concentration in seawater. SO₂ concentration in the simulated flue gas is 1240 mg/m³. 100 ml solution from prepared solutions were used, and the experiments were carried out. The results are plotted in Fig. 2. It is found that the absorbing efficiency of SO₂ has an increase in a certain range of the content of Na₂SO₄. This can be explained that the addition of Na₂SO₄ improves the intensity of ions in the solution, so promotes absorbing efficiency of SO₂. But absorbing efficiency shows a tendency of drop when the Na₂SO₄ content of the solution

exceeds that of seawater.

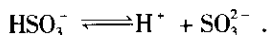
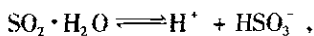
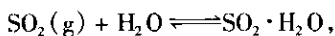
2.3 The effect of NaCl in seawater

The constant component in seawater is 99.8 to 99.9 percent of dissolved salt in seawater. And NaCl is about 85 percent of the constant component in seawater. It is very important to study the effect of NaCl on the absorption of SO₂ by seawater.

The simulated flue gas above-mentioned was used, and the absorbing experiments were carried out in the solutions of different NaCl concentration. The result is shown in Fig. 3.

Absorbing efficiency of SO₂ increases with the increase of NaCl concentration can be found from Fig.

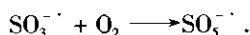
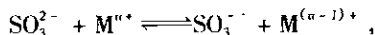
3. It shows good absorption of SO_2 even though the NaCl concentration is 0.8 mol/L. On the one hand the intensity of ions in solution possibly is improved by the presence of NaCl, on the other hand it may be the catalysis of Cl^- . The later factor may be the main effect factor. It is known that there is the balance of absorption of SO_2 in seawater:



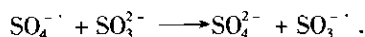
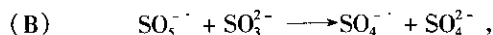
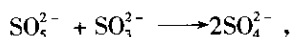
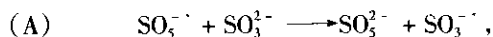
Part of SO_3^{2-} is oxidized to SO_4^{2-} . This is the key step to the balance which move right. Then the mechanism about the effect of NaCl is the catalysis oxidation of Cl^- to SO_3^{2-} .

The mechanism about the catalysis of Cl^- to SO_3^{2-} may be as follows.

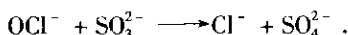
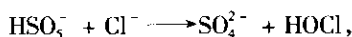
The first kind of mechanism is the transference of electron. SO_3^{2-} perhaps reacts with some trace metal ions and produces $\text{SO}_3^{\cdot -}$, and then combines with oxygen:



Then the reaction goes on by the way of the transfer of electron and forms the Caro's ions (SO_5^{2-}). And then forms SO_4^{2-} ions by transport of oxygen atoms.

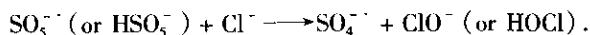


As a kind of strong oxidizer, Caro's ions usually exist as the form of HSO_5^- except in the solution of strong acid or strong alkaline. It can transfer oxygen to Cl^- according to the following reaction and then occur the oxidation reaction of SO_3^{2-} :

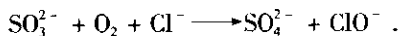


The above reactions may be the catalysis reaction mechanism of Cl^- because the speed of reaction is too slow.

The reaction of $\text{SO}_5^{\cdot -}$ or HSO_5^- may be faster than the series reactions of Caro's ions. Another reaction mode of reaction maybe occur:

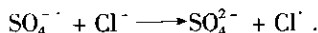


So the net reaction of free radical chain is:



The interactions show the possibility in the thermodynamics according to the data of electrode potential (negative change of the free energy). And it may be the main reaction mechanism in the situation of high concentration of Cl^- . This result is proved in the research of catalysis oxidation of Cl^- in the atmospheric environment(Clarke, 1983).

The other possible mechanism is the electron transfer of Cl^- .



Atom chlorine can further combine with Cl^- and produce $\text{Cl}_2^{\cdot -}$. The reaction is faster than reaction of

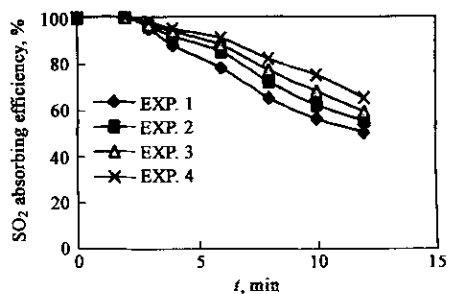
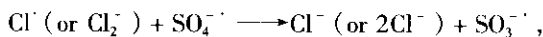


Fig. 3 Effect of concentration of NaCl on absorption of SO_2

EXP. 1: deionized water; EXP. 2: 0.1 mol/L NaCl; EXP. 3: 0.4 mol/L NaCl; EXP. 4: 0.8 mol/L NaCl

SO₄⁻ with SO₃²⁻ when the concentration of salt is higher than that of SO₃²⁻. Atom chlorine can multiply chain through the following reactions:



or the terminated step of the chain contains the following reaction:



The formed chlorine molecule will entirely be hydrolyzed, and SO₃²⁻ is further oxidized to SO₄²⁻. It is not the speed-control step because the reaction of SO₄⁻ with Cl⁻ and SO₃²⁻ is very rapid. The effect of Cl⁻ on the chain-increased of free radical is very little. The catalysis of Cl⁻ is consumed while SO₄⁻ react with other radicals or ion groups before it loses activity, reducing the speed of the termination of chain.

2.4 The effect of some transition metal elements

There are some rich trace elements in seawater. Some elements which possess higher activity were chosen, such as Fe, Mn, Cu and Co. Solutions containing Fe²⁺, Mn²⁺, Cu²⁺ and Co²⁺ were made up and absorbing experiments were carried out. The results are shown in Fig.4 and Fig.5.

In a certain range of absorbing time, absorbing efficiency of SO₂ is obviously improved with the increase of the concentration of Fe²⁺ or Mn²⁺ in the solution, when the concentration of Fe²⁺ is equal to that of Mn²⁺, the catalysis of Mn²⁺ is better than that of Fe²⁺ and so is that in high pH value.

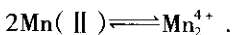
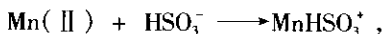
Absorbing efficiency of SO₂ is slightly promoted by Cu²⁺ and Co²⁺, but not obviously. Hence these are not the emphasis of catalysis mechanism.

It can be explained why Fe²⁺ and Mn²⁺ possess catalysis

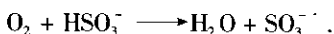
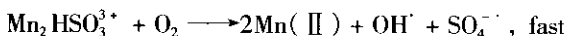
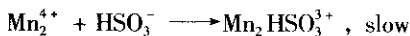
activity according to the fact that they have a series of oxidized states and reach easily high valance metal ions (Huss, 1982a). The following mechanism of catalysis can be proposed.

HSO₃⁻ in the solution will form intermediate product and induce catalysis reaction while there is Mn(II) in the aqueous solution.

Balance:

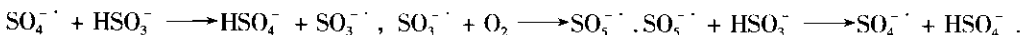


Initiation of chain:



Transmission of the chain:

(1) Main action role in the chain



(2) Secondary action role in the chain

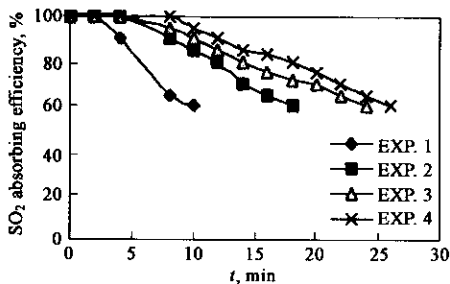


Fig.4 Effect of concentration of Fe²⁺ on absorption of SO₂

EXP. 1: [SO₂] 3420 mg/m³, deionized water; EXP. 2: [SO₂] 3560 mg/m³, [Fe²⁺] 5 × 10⁻⁵ mol/L; EXP. 3: [SO₂] 3790 mg/m³, [Fe²⁺] 1 × 10⁻⁴ mol/L; EXP. 4: [SO₂] 3650 mg/m³, [Fe²⁺] 5 × 10⁻⁴ mol/L

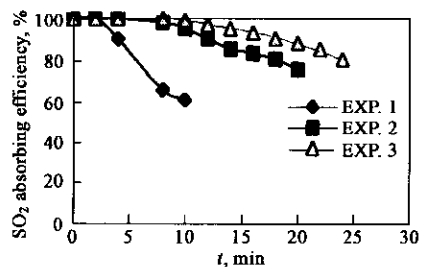


Fig. 5 Effect of concentration of Mn²⁺ on absorption of SO₂

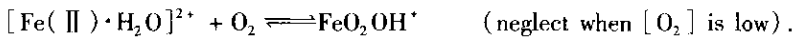
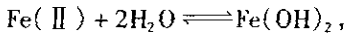
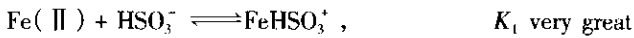
EXP. 1: [SO₂] 3590 mg/m³, [Mn²⁺] 5 × 10⁻⁵ mol/L; EXP. 2: [SO₂] 3700 mg/m³, [Mn²⁺] 1 × 10⁻³ mol/L; EXP. 3: [SO₂] 3500 mg/m³, [Mn²⁺] 5 × 10⁻⁴ mol/L

The termination of chain: $\text{SO}_5^{\cdot -} + \text{organic matter} \rightarrow \text{insert product}$.

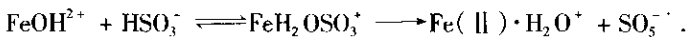
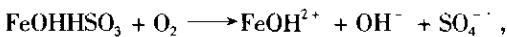
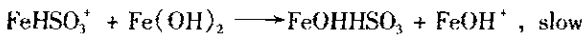
The characteristic of free radical in this mechanism is very obviously. All the free radicals involved have been proved by enormous research experiment separately (Coichev, 1992; Martin, 1991).

The mechanism of $\text{Fe}(\text{II})$ catalysis oxidation for SO_2 proposed by Huss (Huss, 1982b) is more complex than that of $\text{Mn}(\text{II})$. The specification is in the following:

Balance:

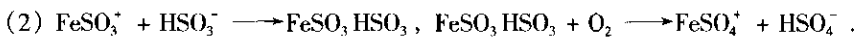
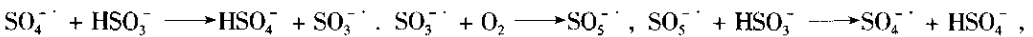


Initiation of chain:



Transmission of the chain:

(1) The process of free radical



The termination of chain:



It is thus clear from the above-mentioned that the catalysis of $\text{Fe}(\text{II})$ and $\text{Mn}(\text{II})$ is a complex process. The react step of them is very similar. Some authors (Christian, 1995) had dropped the same conclusions. HSO_3^- takes the important role of initiation and transmission of chain. Conditions must be controlled in order to bring catalysis of $\text{Fe}(\text{II})$ and $\text{Mn}(\text{II})$ into full play, and let SO_2 exist as the form of HSO_3^- as far as possible for the benefit of raising the desulfurization efficiency. This is closed to the control of pH value.

2.5 The effect of other constant matter in seawater

The solutions of KCl , MgCl_2 , CaCl_2 and H_3BO_3 were made up in the same concentration as them in seawater according to the above-mentioned method and the absorbing experiments were carried out. It is found that there is a certain favorable effect of KCl , MgCl_2 and CaCl_2 for absorption of SO_2 , but the effect is minor. H_3BO_3 decreased absorbing efficiency of SO_2 , since it may be acidity.

3 Conclusions

Absorbing experiments for SO_2 by seawater showed that the effect factors of absorption of SO_2 are alkaline, ion intensity, catalysis of Cl^- and transition metal ions Fe^{2+} and Mn^{2+} . The degree of effect is alkaline > the catalysis of Cl^- , Fe^{2+} and Mn^{2+} > ion intensity.

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