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Research on selectivity removing SO2 from flue gas with a novel absorbent

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Abstract:

Compared with the traditional methods of removal SO_2 from flue gas, the organic solvent absorption has some advantages as low investment, high SO_2 absorption efficiency and desorption efficiency. For the industrial application of organic solvent absorption as soon as possible, some laboratory research on selectively removing SO_2 and NOx from flue gas in the presence of CO_2 and an enlarged experiment has been done with a novel absorbent of Mn (II) + DMSO. The effect on desulfurization selectivity for absorbents is studied. And the regeneration capacities for absorbent are researched. The result shows that the novel absorbent has not only strong desulfurization efficiency, but also good selectivity for SO_2 and CO_2, the feasibility of desulfurization absorbent has been proved.

Keyword: selectivity; desulfurization; flue gas; the enlarged experiment; DMSO +Mn (II)

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1 Introduction

Removal of SO_2, CO_2 and NOx from flue gas is one of very important research projects in the world. In the previous literature [1], some laboratory research on removing SO_2 from flue gas with DMSO absorbent have been studied. But removing SO_2 and NOx from flue gas in the presence of CO_2 had not been reported. As we know, there is not only sulfur dioxide, but also a lot of CO_2 in flue gas from industrial emissions. Because SO_2 and CO_2 are all acidic gases, and the concentration of sulfur dioxide is much lower than carbon dioxide in the flue gas. If the absorbent has not selectivity for acid gas such as SO_2 and CO_2, it will lead to a serious decrease for desulfurization efficiency because the absorbent absorbs a large number of CO_2, therefore the good selectivity for SO_2 and CO_2 is necessary in order to reach higher desulfurization efficiency. Therefore, in this paper, based on our selected organic absorbent DMSO [2-7], a small amount of Mn (II) catalyst is added in the system of organic solvent absorption, it is found that the desulfurization efficiency with a small amount of Mn (II) catalyst has been much improved compared with pure physical solvent of DMSO, Mn (II) played a significant catalytic role [8]. In order to further verify the selectively desulfurization effect of Mn (II) + DMSO. Some laboratory research on selectively removing SO_2 and NOx from flue gas with Mn (II) + DMSO absorbent have been carried out. The research provides a basis for the industrial application of flue gas desulfurization technology.

2 Experimental Sections

The experiment includes two sections: (1) the selectivity absorption experiment of Mn (II) + DMSO on removal efficiency of SO2 and NOx in the presence of CO2. (2) the enlarged experiment.

2.1 The selectively absorption experiment of Mn (II) + DMSO on removal efficiency of SO_2 and NOx in the presence of CO_2.

The technological process of the selectivity SO2 removal experiment is shown in Figure 1. Sulfur dioxide with a mole fraction purity x (SO2)≥0.997, carbon dioxide with a mole fraction purity x (CO_2)≥0.99, NO and NO_2 with a mole fraction purity x (NOx)≥0.99, nitrogen of purity x (N2) ≥0.99999 are obtained from cylinders. Sulfur dioxide, carbon dioxide, NOx and nitrogen are mixed by a gas mixer with static agitation to simulate the flue gas. A flowrator is used to control the gas flow. CO_2 is analyzed by CO2 analyzer (type RD-7AG, Nanjing, China). Nitrogen Oxides is analyzed by NOx analyzer (type NA-721 Nitrogen Oxides Analyzer, China). O_2 is analyzed by AUS-gas analyzer with gas absorption method. A SO_2 analyzer (type NTS 100, Nanjing, China) is used for the SO_2 analysis of the gas phase from the inlet and tail gases. The SO_2 concentration in the gas phase before and after absorption is analyzed by SO2 analyzer, and then the removal efficiency is calculated.

The removal efficiency, % = $\frac{C_0 - C}{C_0} \times 100\%$ (1)

In which, C_0 - The SO_2 or NOx concentration before absorption;

C - The SO_2 or NOx concentration after absorption

All the chemical reagents used are AR grade. Purified and deionized water of conductivity <0.06μS·cm-1 is used in the measurements.

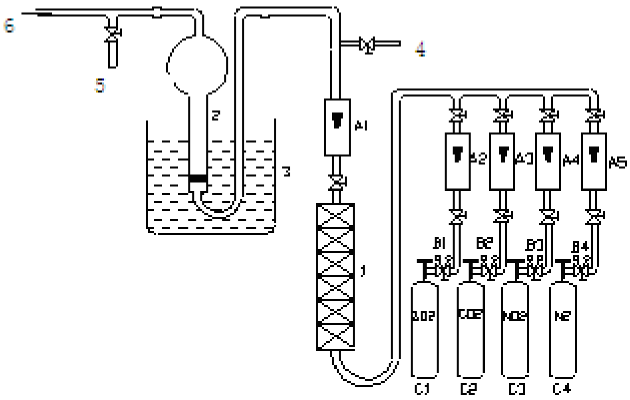

Fig. 1 The technological process of SO_2 absorption

C1: SO_2 cylinder, C2: CO_2 cylinder, C3: NO_x cylinder, C4: N_2 cylinder, B1-B4: walve, A1-A5: flowrator,

1- a gas mixer with static agitation unit, 2-absorption tube 3- constant temperature bath.

4-inlet gas to SO_2 analyzer, 5- outlet gas to SO_2 analyzer, 6- to fume hood

2.2 The enlarged experiment

The enlarged experimental apparatus is shown in Figure 2, the absorption tower is a packed tower, diameter is 25 mm, inside packing diameter is Φ= 5 mm×10 mm. The regenerative tower is a packed tower of 25 mm ×78 mm, with heat preservation jacket. The flow and the direction of the absorption solution at rectifier bottom are controlled by the recycle pumps. SO_2 , CO_2, O_2 and N_2 from cylinders are mixed by a gas mixer with static agitation to simulate the flue gas. A flowrator is used to control the gas flow. The mixed gas is absorbed through the saturation flask in absorption tower, A SO_2 analyzer (type NTS 100, Nanjing, China) is used for the SO_2 analysis of the gas phase. The SO_2 concentration of solution was measured by iodometric method.

The effect of ratio gas to liquid, rate of flow, temperature and inlet gas composition on the desulfurization selectivity is determined, and the absorption and desorption efficiency was measured.

Both SO_2 removal efficiency and desulfurization selectivity are used as the evaluation index. The desulfurization selectivity is defined as follows,

Desulfurization selectivity $=[SO_2]_l\ /[CO_2]_l$ (2)

$[SO_2]_l$: SO_2 concentration of rich solution

$[CO_2]_l$: CO_2 concentration of rich solution

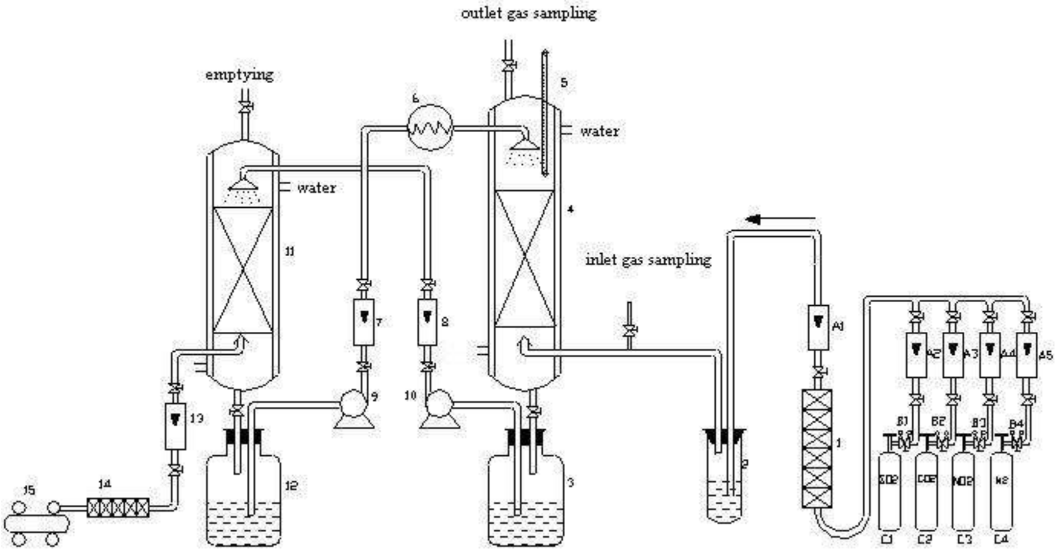

Fig. 2 The experimental apparatus of removing SO_2

1 a gas mixer with static agitation unit 2.saturation flask 3.absorption SO_2 flask 4.absorption tower 5.thermometer 6.heater 7. flowmeter 8. flowrmeter 9.pump 10.pump 11.regenerative tower 12. absorption flask after desorption SO_2 13. flowrmeter 14.filter 15. air compressor

3 Results and discussion

3.1 The selectively absorption experiment of Mn (II) + DMSO on removal efficiency of SO_2 and NOx in the presence of CO_2

3.1.1 The effect of Mn (II)+DMSO on the removal efficiency of SO_2

Experiment condition: temperature 303.15 K, gas flow: 80ml/min, inlet SO_2 concentration: 0.1792%. The effect of Mn (II)+DMSO absorbent on the removal efficiency of SO_2 is listed in Table 1, Mn (II) concentration is 0.03 mol/L.

Table 1 The effect of absorbent of Mn (II)+DMSO on the removal efficiency of SO_2

No	inlet SO_2 concentration, %	outlet SO_2 concentration, %	SO_2 removal efficiency, %
1	0.1806	0.0034	98.12
2	0.1670	0.0024	98.56
3	0.2608	0.0095	96.36

From Table 1, it can be seen that Mn (II)+DMSO absorbent have high the removal efficiency for SO_2, and the removal efficiency of SO_2 increases with the decrease of inlet SO_2 concentration.

3.1.2 The selectively absorption effect of Mn (II) + DMSO on removal efficiency of SO_2 in the presence of CO_2

Experiment condition: temperature 301.15 K, gas flow: 140 mL·min^{-1}, inlet SO_2 concentration: 0.1893 % SO_2, inlet CO_2 concentration: 11.3 % CO_2. The result is listed in Table 2

Table 2 Selectivity absorption effect of Mn (II) + DMSO on removal efficiency of SO_2 in the presence of CO_2

t,min	5		10		15	
	outlet concentration, 10^{-6}	removal efficiency, %	outlet concentration, 10^{-6},	removal efficiency，%	outlet concentration, 10^{-6},	removal efficiency ,%
SO_2	2	99.89	5	99.44	5	99.44
CO_2	8.9	21.23	9.2	18.58	9.4	16.81
t,min	20		25		30	
	outlet concentration, 10^{-6},	removal efficiency，%	outlet concentration, 10^{-6}	removal efficiency，%	outlet concentration, 10^{-6}	removal efficiency，%
SO_2	7	99.22	8	99.10	12	98.66
CO_2	9.6	15.04	9.8	13.27	10.2	9.73

From Table 2, it can be shown that the removal efficiencies of DMSO+Mn (II) absorbent for SO_2 are over 98% in the presence of CO_2 within the absorption time of 0 to 30 min, but only 9-21% removal efficiency for CO_2, it reveals that DMSO+ Mn (II) absorbents have a good selective removal for SO_2 in the presence of CO_2.

Meanwhile another experiment is also carried out to examine the absorption of SO_2 in the presence of CO_2 and SO_2 with pure DMSO and the similar results are obtained.

3.1.3 The effect of absorbent of Mn (II)+DMSO on the removal efficiency of NOx

The effect of absorbent of Mn (II)+DMSO on the removal efficiency of NOx is listed in Table 3.

Table 3 The effect of absorbent of Mn (II)+DMSO on the removal efficiency of NOx

	inlet NO concentration ,10^{-6}	outlet NO concentration, 10^{-6}	NO removal efficiency ,%	inlet NO_2 concentration，10^{-6}	outlet NO_2 concentration，10^{-6}	NO_2 removal efficiency,%
DMSO	185	16	91.35	59	8	86.44
DMSO+0.03M$MnSO_4$	480	32	93.33	60	6	90.00

The results indicate that absorbent of Mn (II)+DMSO has high the removal efficiency for NOx, and the addition of Mn (II) in DMSO can increase removal efficiency of NOx.

3.1.4 The selectively absorption effect of Mn (II) + DMSO on removal efficiency of SO_2 and NO_x in the presence of CO_2

Experiment condition: temperature 301.15 K, gas flow: 130 mL·min^{-1}.The results are listed in Table 4.

Table 4 The selectivity absorption effect of Mn (II) + DMSO on removal efficiency of SO_2 and NO_x in the presence of CO_2

t, min	inlet concentration, 10^{6}	outlet concentration, 10^{6}	removal efficiency, %	inlet concentration, 10^{6}	outlet concentration, 10^{6}	removal efficiency, %	inlet concentration, 10^{6}	outlet concentration, 10^{6}	removal efficiency, %
SO_2	718	17	97.63	675	14	97.92	1274	21	98.35
CO_2	12%	9.5%	20.83	10.1%	8.5%	15.84	9.7%	7.8%	19.58
NO_2	85	8	90.59	70	6	91.42	50	5	90.00
NO	403	38	91.00	445	43	90.33	436	40	90.82

The results indicate that the removal efficiencies of DMSO+Mn (II) absorbent for SO_2 are over 97% in the presence of CO_2 , and for NO_x are over 90% in the presence of CO_2.

3.2 Result of the enlarged experiment

3.2.1 The effect of ratio of gas/liquid on the desulfurization selectivity

The suitable gas /liquid (G/L) ratio is the key factors influencing removal efficiency of SO_2. The effect of ratio of G/L on the selectivity removal efficiency of SO_2 is listed in Table 5. The results showed the suitable gas /liquid ratio is 1:40-1:500.

Table 5. The experimental result of removing SO_2 by Mn (II) + DMSO

No.	rate of flow/$m^3.h^{-1}$	ratio of G/L	temperature /℃	absorption solution concentration, mol/kg		inlet gas composition,%			outlet gas composition,%		removal efficiency,%		selectivity
				SO_2	CO_2	SO_2	CO_2	O_2	SO_2	CO_2	SO_2	CO_2	
1	0.04	40	25	0.0485	0.000910	0.45	9.8	2.3	0.0010	5.0	99.78	48.98	53.27
2	0.1	100	25	0.0610	0.00110	0.45	9.8	2.3	0.0060	5.2	99.67	46.94	55.45
3	0.2	200	25	0.129	0.00130	0.45	9.8	2.3	0.0194	5.8	95.69	40.82	99.46
4	0.25	250	25	0.132	0.00131	0.45	9.8	2.3	0.0274	7.0	93.9	28.57	100.92
5	0.04	40	30	0.0379	0.000801	0.45	9.8	2.3	0.0015	5.2	99.67	46.94	47.31
6	0.1	100	30	0.0551	0.000900	0.45	9.8	2.3	0.0072	5.5	98.4	43.37	61.20
7	0.2	200	30	0.129	0.00100	0.45	9.8	2.3	0.020	6.0	95.56	38.78	128.60

8	0.25	250	30	0.130	0.00110	0.45	9.8	2.3	0.041	7.2	90.88	26.53	118.45
9	0.04	40	40.5	0.0250	0.000600	0.45	9.8	2.3	0.0016	5.4	99.64	46.94	41.67
10	0.1	100	40.5	0.0380	0.000700	0.45	9.8	2.3	0.024	5.8	94.67	40.82	54.29
11	0.2	200	40.5	0.108	0.000899	0.45	9.8	2.3	0.0328	7.2	92.71	26.53	120.11
12	0.04	40	25	0.0414	0.000701	0.42	7.4	2.2	0.0006	3.8	99.86	48.65	59.09
13	0.1	100	25	0.0540	0.000900	0.42	7.4	2.2	0.0020	4.2	99.53	43.24	60.00
14	0.2	200	25	0.0864	0.00110	0.42	7.4	2.2	0.0041	5.0	99.03	32.43	78.55
15	0.04	40	30	0.0351	0.000601	0.42	7.4	2.2	0.0007	3.8	99.83	48.65	58.42
16	0.1	100	30	0.0510	0.000800	0.42	7.4	2.2	0.0023	4.8	99.46	33.33	63.78
17	0.2	200	30	0.110	0.000900	0.42	7.4	2.2	0.0046	5.2	98.91	27.78	122.33
18	0.04	40	40	0.0210	0.000600	0.42	7.4	2.2	0.0019	4.3	99.55	40.28	35.00
19	0.1	100	40	0.0350	0.000800	0.42	7.4	2.2	0.0065	5.1	98.46	29.17	43.75
20	0.2	200	40	0.0890	0.000900	0.42	7.4	2.2	0.010	6.3	97.63	12.50	98.89
21	0.04	40	25	0.0385	0.00110	0.41	19.0	2.0	0.0004	11.6	99.90	38.95	35.00
22	0.1	100	25	0.0510	0.00130	0.41	19.0	2.0	0.0024	15.1	99.41	20.53	39.23
23	0.2	200	25	0.0792	0.00160	0.41	19.0	2.0	0.0035	16.3	99.14	14.21	49.50
24	0.1	100	30	0.0301	0.000700	0.41	19.0	2.0	0.0006	12.0	99.85	58.33	43.03
25	0.2	200	30	0.0485	0.00100	0.41	19.0	2.0	0.0027	14.6	99.34	23.16	48.50

26	0.3	300	30	0.0980	0.00140	0.41	19.0	2.0	0.0243	16.0	94.04	15.79	70.00
27	0.1	100	40	0.0200	0.000500	0.41	19.0	2.0	0.0016	15.5	99.61	18.42	40.00
28	0.2	200	40	0.0364	0.000800	0.41	19.0	2.0	0.0060	15.9	98.53	16.32	45.50
29	0.3	300	40	0.0790	0.00100	0.41	19.0	2.0	0.0383	16.6	90.61	12.63	79.00

From Table 5, it can be found that removal efficiency of SO_2 is influenced by gas /liquid ratio. If liquid flow is kept constant, the alteration of gas /liquid ratio has very little influence on removal efficiency of SO_2, but the effect on the removal efficiency of CO_2 is obvious.

3.2.2 The effect of rate of gas flow on the desulfurization selectivity

The effect of rate of gas flow on the selectivity removal efficiency of SO_2 was studied with four rate of gas flow between 0.04 m^3/h -0.25 m^3/h, and the result is listed in Table 5. From Table 5, it indicates that the removal efficiency of CO_2 is lower; the selectivity is higher with the increase of the gas flow rate. Therefore, when the flue gas has high content of CO_2, we can decrease the absorption for CO_2 and increase the absorption of SO_2 by using the increase of the gas rate.

3.2.3 The effect of temperature on the desulfurization selectivity

The effect of temperature on the selectivity removal efficiency of SO_2 is listed in Table 5. The results indicate that the removal efficiency of SO_2 is high with the decrease of temperature; therefore high removal efficiency of SO_2 is obtained when SO_2 absorption is kept at suitable low temperature.

3.2.4 The effect of inlet gas composition on the desulfurization selectivity

Three different gases, such as SO_2, CO_2 and O_2 was mixed in the process of the experiments. Inlet SO_2 concentration is about 0.4 %, O_2 concentration is 2% or so, the inlet CO_2 concentration is the change, the effect on the selectivity removal efficiency of SO_2 in the presence of CO_2 is studied. The result is listed in Table 5. From Table 5, it can be found that the removal efficiency of SO_2 of DMSO+ Mn (II) absorbents are over 90% when the concentration of CO_2 changed, therefore the selectivity for SO_2 removal does not decrease only increasing CO_2 concentration. i.e. absorbents still have high purification efficiencies for SO_2 in the presence of high content of CO_2.

3.2.5 The regeneration capacities of Mn (II) + DMSO

The solution of being absorbed was desorbed at room temperature at the rate of 100 ml/min, the desorption result of Mn (II) + DMSO is listed in Table 6 , it showed that the absorbents of Mn (II) + DMSO have good desorption efficiency , and the desorption efficiency are over 97% at room temperature.

Table 6 The desorption result of Mn (II) + DMSO

SO_2 concentration before desorption, mol/kg	desorption temperature, ℃	rate of flow, ml/min	SO_2 concentration after desorption, mol/kg	desorption efficiency , %
0.1081	25	100	0.0025	97.67
0.1101	25	100	0.0028	97.46

0.1863	25	100	0.0041	97.80

3.3. Mechanism Analysis

The absorption process for SO_2 containing DMSO + Mn (II) is a complicated mechanism coexisting of physical and chemical absorptions.

3.3.1. Physical absorption

DMSO is a polar aprotic organic solvent having a larger dipole moment (4.03 D). Its molecular structure is shown in Figure 3. SO_2 and NO_2 are polar gas molecules of V-type molecular configuration and their molecular structure are shown in Figure 3. However CO_2 is a symmetrical linear non-polar molecule, and its molecular configuration is shown in Figure 3.

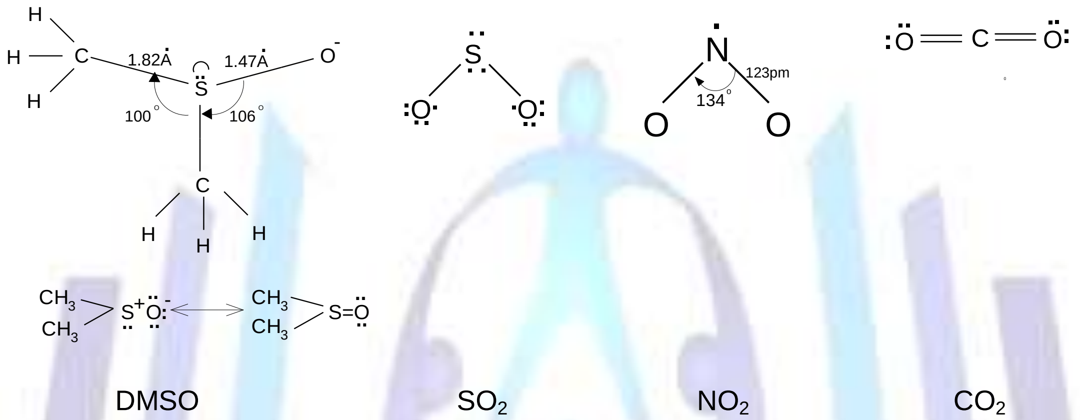

Fig. 3. Molecular structure for DMSO, SO_2, NO_2 and CO_2

DMSO is a polar organic solvent with a rather large dipole matrix, SO_2 and NO_2 are also polar gas molecules, while CO_2 is a non-polar gas molecule, therefore DMSO has a better absorption capacity on the polarity of the sulfur dioxide and nitrogen oxides, but less absorption capacity on the non-polar carbon dioxide. It agrees with the principle that like dissolves like.

Accordingly, the absorption model of SO_2 in DMSO is shown in Figure 4 [9].

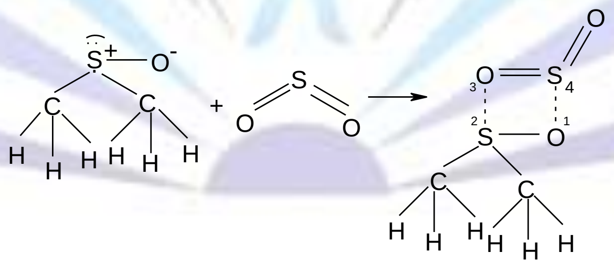

Fig. 4. The absorption model of SO_2 in DMSO

3.3.2. Chemical absorption

After adding Mn (II) in DMSO，SO_2 is oxidized to H_2SO_4 catalyzed by $MnSO_4$.

The chemical reaction is expressed as follows [10, 11, 12]:

$$SO_2 + \tfrac{1}{2}O_2 + H_2O \xrightarrow{M_nSO_4} H_2SO_4$$

The mixed absorbent has a good removal efficiency of SO_2 and a good regeneration. Therefore the selected absorbent has a good future in SO_2 removal.

4 Conclusions

The desulfurization selectivity experiment of DMSO + Mn (II) is studied. The result shows that the desulfurization absorbent has not only high desulfurization efficiency, but also good selectivity for SO_2 and NO_x in the presence of CO_2, the feasibility of desulfurization absorbent has been proved.

The effect of gas/liquid ratio, flow rate, temperature and inlet gas composition on the removal efficiency was determined, and the absorption and desorption experiment was investigated. The results indicated when liquid flow is constant, the alteration of gas /liquid ratio has very little influence on removal efficiency of SO_2, but the effect on the removal efficiency of CO_2 is obvious. The desulfurization absorbent still keep high desulfurization selectivity even if in high CO_2 concentration. The removal efficiency of SO_2 increases with the decrease of temperature; when the inlet gas composition changed, especially CO_2 concentrations vary from 7-19 %, there is no obvious influence on the removal efficiency of SO_2, it shows that the desulfurization absorbents still keep high desulfurization efficiencies in the presence of high content of CO_2.

The result provided a valuable reference for the industrial application of removal of SO_2 from flue gas.

References

[1] H. Li, W.R. Chen, D.Z. Liu, *Environ. Protect. of Chem. Ind*. 2002,**22**, 193-196.

[2] H. Li, W.R. Chen, *Phy. and Chem. of L*. 2006, **44**, 83-93.

[3] H. Li, W.R. Chen, *Phy. and Chem. of L*. 2006, **44,** 183-191.

[4] H. Li, W.R. Chen,. *Phy. and Chem. of L*. 2007, **45** 57-65.

[5] Li, H. *Phy. and Chem. of L.* 2009, **47,** 296-301.

[6] H. Li, W.R. Chen, D. Z. Liu, *J. of Environ. Sci.*. 2003, **15,** 92-96.

[7] H. Li, W.R. Chen, *Phy. and Chem. of L*. 2007, **45,** 207-213.

[8] H. Li, G. Q. Hu, X.S. Chen, *Phy. and Chem. of L*. 2010, **48,** 652-660.

[9] R.H. Huang, Z.Y. Li, P. S. Sun, *Yunnan Chemical Industry*,1991, **22,** 2-4.

[10] W. Pasiuk-Bronikowska, T. Bronikowski, *Chem. Eng. Sci*. 1981, **36,** 215-219.

[11] A. Huss, P. K. Lim, *J. Phys. Chem*. 1982, **86,** 4224-4228.

[12] C.M. Chen, Y. Zao, S.C. Ma, Y.C. Fu, *J. North China Electric. Power Univ.* 2001, **28,** 80-82.