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Desulfurizing absorbent for flue gas and its absorption mechanism

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Abstract: A new desulfurizing absorbent for flue gas, i.e., an organic physical solvent of DMSO(dimethyl sulfoxide) mixed with a relatively small amount of chemical solvent(Mn^{2+}) was studied. Compared with pure physical solvent of DMSO, the purification efficiency of the new absorbent was improved. And its absorption and reaction mechanism are discussed.
Keywords: liquid absorption; desulfurization; flue gas

Introduction

Removal of SO_2, CO_2 and other acidic gas from flue gas is one of very important research projects in the world. In order to find effective method, various desulfurization technique(Zhu, 1998; Li, 1996; Lin, 1992; Chen, 1997; Tai, 1999; Yeh, 1992; Tan, 1999), such as activated carbon, molecular sieve, the electron-beam radiation technique, chemical method, physical solvents etc. are all attempted. Compared with these methods, organic solvent absorption has some advantages as low investment, high SO_2 absorption efficiency and desorption efficiency and worth to further research. In this paper, we study and select a liquid organic absorbent with a high absorption and desorption efficiency for high selectivity to SO_2 with low toxicity and low price. And this absorbent will be used to remove SO_2 from flue gas to solve industrial problem for flue gas purification.

1 Experimental

The experiment includes two sections: (1) the solubility experiments and the optimum absorbent selection; (2) technological condition experiment.

1.1 Experimental apparatus

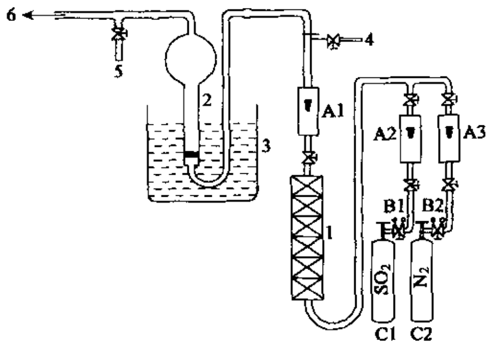

Fig.1 The technological process of SO_2 absorption
C1: SO_2 cylinder; C2: N_2 cylinder; B1 - B2: walve; A1 - A3: flowrator;
1. a gas mixer with static agitation unit; 2. absorption tube; 3. constant temperature bath; 4. inlet gas to SO_2 analyzer; 5. outlet gas to SO_2 analyzer; 6. to fume hood

The apparatus for SO_2 solubility and regeneration (Li, 1987). The technological process is shown in Fig.1. The absorption apparatus of technological condition is an absorption tube with sandglass. The sulfur dioxide with a mole fraction purity $\times$ (SO_2) $\geqslant$ 0.997, pure nitrogen with a purity $\times$ (N_2) $\geqslant$ 0.99999; are both from cylinders. The sulfur dioxide and nitrogen are mixed by a gas mixer with static agitation unit to simulate the flue gas. A flowrator is used to control the flow. The SO_2 analyzer with SO_2 sensor(type NTS 100, Nanjing, China) was used for the SO_2 analysis of the gas phase from the feed gas and the tail gas. The SO_2 concentration in the gas phase before and after absorption is analyzed by SO_2 analyzer, then the purification efficiency is calculated.

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The purification efficiency(η) is: $\eta = \frac{C_0 - C}{C_0} \times 100\%$, where, C_0 is the SO_2 concentration before absorption; C is the SO_2 concentration after absorption. All the chemical reagents used are AR grade. The water is purified and deionized with a conductivity < 0.06 μs/cm.

1.2 Determination method

SO_2 solubility determination: The whole apparatus is evacuated and flushed several times with nitrogen to ensure complete exclusion of oxygen and carbon dioxide, then it is evacuated again. A known amount of degassed absorbent is sucked into the absorption tube, the weight of which is initial weight W_1 . Put it in the thermostatic bath, and let SO_2 go through the absorption tube at a rate of 25 ml/min at different temperatures till its saturation(constant weight is W_2).

$$SO_2 \text{ solubility}(gSO_2/g \text{ solvent}) = \frac{W_2 - W_1}{V \times d}.$$

Where, W_1 is the initial weight(g) = solvent + absorption tube; W_2 is the end weigh(g) = solvent + absorption tube + SO_2; V is the solvent volume(ml); d is the solvent density(g/ml).

Desorption capacity determination: The above-mentioned saturated sulfur dioxide absorption tube(the weight is W_2) is regenerated by heating at 60℃ and bubbling nitrogen at a rate of 25 ml/min till a constant weight occurs(the weight is W_3).

$$SO_2 \text{ desorption efficiency}(\%) = \frac{W_2 - W_3}{W_2 - W_1} \times 100\% .$$

1.3 Test of apparatus

In order to ensure proper operation of the apparatus, the solubility of SO_2 in water is measured and compared with the values reported in the literature (John, 1999). The experimental measurements agreed with the reported values with a mean deviation of 0.67%. The measured result is listed in Table 1.

Table 1 Comparison between experimental data for SO_2 solubility in water and literature data

Temperature, ℃	Experimental data, g/100gH$_2$O	Literature data, g/100gH$_2$O (John, 1999)	Deviation, %
20	11.2933	11.28	0.12
25	9.4234	9.41	0.14
30	7.8086	7.80	0.11
35	6.5132	6.47	0.67

2 Result and discussion

2.1 The selection of absorbents

2.1.1 Solubility and desorption of SO_2 in different solvents

The experiment results in Fig.2 and Table 2 show that the solubilities of SO_2 in different solvents in sequence are: DMSO > DMF > DMA > SuHinol > PEG400 > TBP > DEA. Thus there are good solubility and good regeneration for SO_2 in DMSO. Therefore DMSO is fit for as a desulfurizing absorbent for flue gas purification, and worth further studies.

2.1.2 The effect of additive on the removal of SO_2

In order to increase purification efficiency, some additives such as Fe^{3+} , Mn^{2+} and thiophene were added to liquid absorbents to test the effect of additives on SO_2 removal.

Experiment conditions: temperature: 24℃, gas flow rate: 80 ml/min, inlet SO_2 concentration: 0.1798%. The experiment result is shown in Fig.3.

The result mentioned above showed that the addition of Mn^{2+} in DMSO can increase purification efficiency; the addition of Fe^{3+} increases removing efficiency only at the beginning of absorption, but decreases as the time goes; the addition of thiophene to DMSO showed negative effect on the removing efficiency compared with pure DMSO. The addition of Mn^{2+} in DMSO can increase purification efficiency.

Table 2 SO_2 solubility and desorption in different solvents

	Temperature, ℃	DMF	DMSO	DMA	SuHinol	PEG400	TBP	DEA
SO_2 solubility,	22	1.3500	1.3550	1.0213	0.4844	0.4706	0.3542	0.2353
g/SO_2 solvent	30	1.1180	1.1420	0.9062	0.4063	0.4018	0.3025	0.1961
	35	0.9910	1.0000	0.8055	0.3594	0.3208	0.2292	0.1870
	40	0.8790	0.9091	0.7143	0.2969	0.2564	0.1875	0.1373
	45	0.7890	0.8000	0.6122	0.2656	0.1887	0.1667	0.1250
	50	0.7130	0.7455	0.5714	0.2031	0.1487	0.1458	0.1072
Desorption efficiency of SO_2, %		88.68	98.95	86.14	99	99	99	57.15

Notes: DMF: N,N-dimethylformamide; DMSO: dimethyl sulfoxide; DMA: N,N-dimethyl acetamide; PEG400: polyethyleneglycol; TBP: tributyl phosphate; DEA: diethanolamine

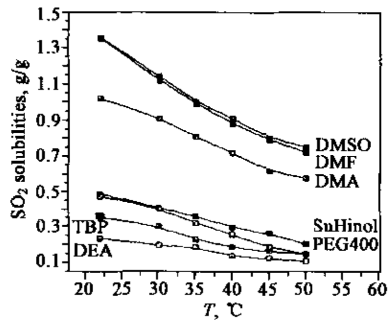

Fig.2 SO_2 solubility in different solvents

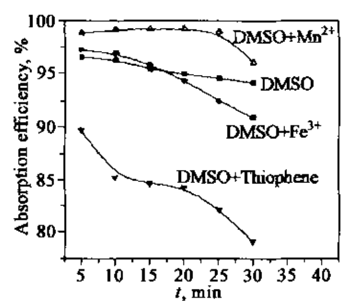

Fig.3 The effect of additives on the removal of SO_2

2.1.3 The effect of Mn^{2+} concentration on purification efficiency

The experiment conditions: t = 30℃, inlet SO_2 concentration: 0.1806%, gas flow rate: 80 ml/min, Mn^{2+} concentration: 0.03—0.1 mol/L. The result is shown in Fig. 4.

From the above experiment results, it is found that the removal efficiency of SO_2 of mixed absorbents is better than pure DMSO, and optimum Mn^{2+} concentration is about 0.03 mol/L.

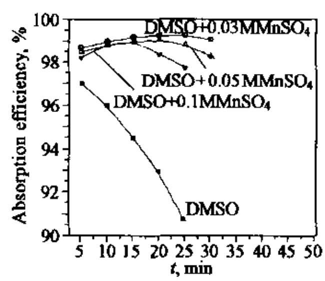

Fig.4 Results of the removal of SO_2 under different Mn^{2+} concentrations

2.1.4 The desulfurizing effect of Mn^{2+} and DMSO

The desulfurizing effect of 0.03 mol/L Mn^{2+} and DMSO are listed in Table 3.

Determination conditions: absorption temperature: 30℃, the gas flow: 80 ml/min.

2.1.5 Desorption determination of Mn^{2+} and DMSO desulfurization at different temperatures

The ideal absorbent should have a good SO_2 removal efficiency and a good regeneration. So the regeneration of DMSO + $MnSO_4$ (V/V = 1 : 0. 03) absorbent is determined. The results are listed in Table 4 and Fig. 5.

Table 3 The desulfurization effect of Mn^{2+} and DMSO

Liquid absorbent	Number of experiment	Inlet SO_2 concentration, $\times 10^6$	Outlet SO_2 concentration, $\times 10^{-6}$	Purification efficiency, %
DMSO + 0.03mol/L $MnSO_4$	1	1806	34	98.12
	2	1670	24	98.56
	3	2608	95	96.36

respectively.

Fig. 5 shows that the desorption of DMSO + $MnSO_4$ is influenced by the temperature. The higher the temperature, the higher the desorption efficiency. When the regeneration time is near 60 minutes, the regeneration efficiencies at different temperatures are all over 99, so the absorbent of DMSO + $MnSO_4$ has good desorption efficiency at a lower temperature.

Table 4 The desorption result of DMSO + $MnSO_4$

t, min	Desorption temperature, 60℃		Desorption temperature, 70℃		Desorption temperature, 80℃	
	SO_2 concentration, mol/L	Desorption efficienly, %	SO_2 concentration, mol/L	Desorption efficiency, %	SO_2 concentration, mol/L	Desorption efficiency, %
*	0.9700	0.00	1.204	0.00	1.2030	0.00
10	0.3200	67.01	0.3467	71.20	0.1336	88.89
20	0.1092	88.74	0.0680	91.61	0.0080	99.33
30	0.0227	97.66	0.0100	99.17	0.0018	99.85
40	0.0050	99.48	0.0045	99.63	0.0015	99.87
50	0.0043	99.56	0.0036	99.70	0.0014	99.88
60	0.0020	99.79	0.0020	99.83	0.0012	99.90

* Solution concentration before desorption

2.2 The effect of technological conditions on the removal efficiency of SO_2

This experiment mainly test the effect of absorbent concentration, temperature and gas flow on SO_2 purification efficiencies.

2.2.1 The effect of absorbent concentration on the removal efficiencies of SO_2

Experiment condition: temperature: 24℃, gas flow: 60 ml/min, inlet SO_2 concentration: 0.1792%. The results are shown in Fig. 6.

Fig. 6 shows that DMSO has a good purification efficiency for low SO_2 and SO_2 purification efficiency increases with DMSO concentration increase.

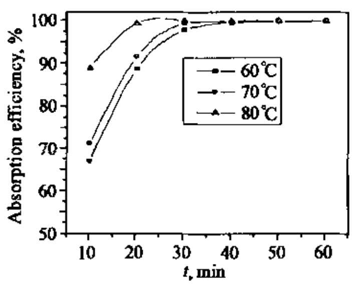

Fig.5 The desorption curve of DMSO + $MnSO_4$ at different temperatures

2.2.2 The effect of absorbent temperature on purification efficiency of SO_2

Experiment conditions: gas flow: 80 ml/min, inlet SO_2 concentration: 0.1783%. The results are shown in Fig. 7.

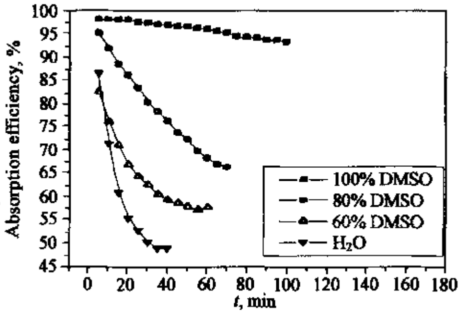

Fig.6 The effect of absorbent concentration on the removal efficiency of SO_2

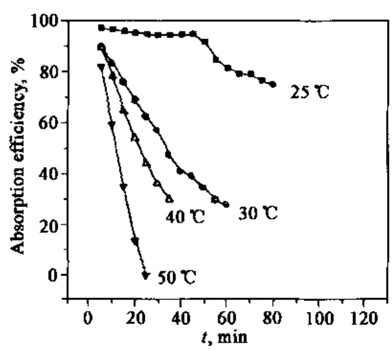

Fig.7 The effect of absorbent temperature on purification efficiency of SO_2

Fig. 7 shows that the temperature influences purification efficiencies. And the sulfur dioxide purification efficiency decreases when the temperature increases.

2.3 Mechanism analysis

DMSO is a polar organic solvent with a rather large dipole matrix, while SO_2 is also a polar gas molecule. DMSO has a strong solubility for SO_2. The absorption model of SO_2 in DMSO is shown in Fig. 8(Huang, 1991).

After adding Mn^{2+} in DMSO, the chemical reaction is expressed as follows (Pasiuk-Bronikowska, 1980):

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

DMSO has a rather large solubility for SO_2. After adding Mn^{2+} to DMSO, SO_2 is oxidized to H_2SO_4 catalyzed by $MnSO_4$. 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.

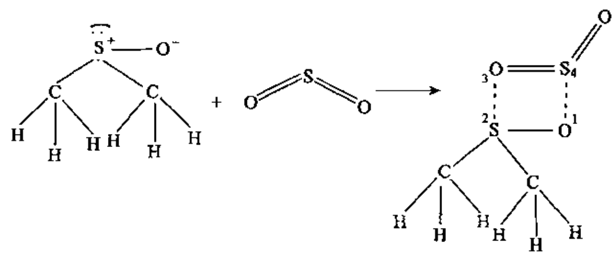

Fig.8 The absorption model of SO_2 in DMSO

3 Conclusions

DMSO is a colorless, non-toxic, polar organic liquid solvent, and has a large solubility for polar gas. After adding additives of Mn^{2+}, desulfurizing efficiency is increased, and the amount of $MnSO_4$ has not changed before and after chemical reactions. It is a cheap method for regeneration of sulfur. Therefore, desulfurization of DMSO and Mn^{2+} will have a good future.

It is a new idea to use organic solvent mixed with a relatively small amount of chemical solvent (Mn^{2+}) as sulfur dioxide absorbents. It has not only strong desulfurizing efficiency, but also good selectivity for SO_2 and CO_2, solving the problem that the present liquid inorganic compound absorbing sulfur dioxide can not be regenerated or the regeneration temperature is high. And this solvent can be regenerated at 60℃ and has high regeneration efficiency.

The major advantages of selected mixed solvents are that the method of regeneration is simple, and the operation is easy, compared with the absorption and regeneration of activated carbon, molecular sieve; it does not need too much power consumption compared with the electron-beam radiation techniques; it has stronger regeneration in compared with the traditional alkali methods. Therefore, the development and application of above solvents will have a great influence on the removal of SO_2 from flue gas.

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