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STUDY ON ABSORPTION OF LOW-CONCENTRATION SO_2 WITH BASIC SLAG INTENSIFIED BY ULTRASONIC WAVE

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Abstract

Both the low-concentration SO_2 and Bayer red mud do harm to the environment seriously.

In this paper, it focuses on the absorption of low-concentration SO_2 with red mud. It studies on the absorption by roasted red mud and non-roasted red mud, and the experiments are intensified by ultrasonic wave of 20 kHz at different ultrasonic power. Through the single factor experiment and orthogonal test, the results were analyzed by the chemical and XRD analysis technology. The conclusion shows that the desulfurization and dealkalization processes can be intensified by ultrasonic wave. The amount of desulfurization reaches 36.7 ml/g. The optimal conditions are: liquid-solid ratio is 9:1; stirring speed of impeller is 250 rpm; gas flow is 0.1 m^3/h; the ultrasonic power is 550 W. But the alkali amount of red mud dealkalizated still can not meet the national standard of cement production, and it needs the further processing to subsequent use.

Introduction

It is well known, SO_2 flue gas and its acid deposition cause serious environmental problems, which bring great harms to the environment and human beings[1]. Flue gas desulfurization (FGD) is one of the most effective technologies to control sulfur dioxide pollution. For the high concentration SO_2 (vol>3.5%), it can be treated by producing sulphuric acid directly; but for the low concentration SO_2 (0.05%<vol<3.5%), it is still a difficulty facing by industrial enterprises and the environmental community because of its very low concentration, wide waste sources and high cost of the treatment etc [2,3], Currently, FGD technology commonly used have some problems of abandonment or low utilization of most desulfurization by-product and secondary pollution for environment, which hinder the development of these existing FGD technologies. Therefore, the development of new FGD technology with small waste production and SO_2 resources recovery is particularly important[4].

The red mud suspensions usually exhibit a caustic pH in the range 10.5-11. A further fact to consider is that red mud is filtered from an aqueous phase that is a strongly caustic solution due to the presence of sodium hydroxide and sodium carbonate remaining from the caustic attack to bauxite. According to the chemical properties previously described make the red mud suspensions suitable to be used as sorbents in a flue gas desulfurization process, a property that is due to both the caustic solution surrounding the solid and the ability of the DSP to exchange Na+ ions with the solution[5]. Presently, the alumina companies both world wide and China dump the red mud directly in the disposal field, and only less than 15% of red mud has been reused[6]. This method trends to make the waste lye penetrate into the agricultural field, thereby leads to the groundwater polluted, soil alkalization and soil salinization etc [7]. Moreover, it is more or less have some effects on the environment such as air pollution, clay liner pollution and because of its radioactivity, it is harmful to the human being and their living environment[8].

Ultrasound has great effects due to its mechanical, thermal, and physiochemical properties on the mass transfer process, so as to provide a new method of accelerating the phase mass transfer[9]. In this paper, it studies on a new method, which is absorption of low concentration SO_2 with Bayer red mud intensified by ultrasonic wave[10,11], that is, enhancing the absorption by red mud suspension by using its cavitation, dispersion and mechanical crushing effects etc. Furthermore, the effect of mechanical agitation coupling ultrasonic wave is also studied systemically.

Experimental Principle and Equipment

Materials and thermodynamic calculation

In this paper, Bayer red mud from Zhengzhou aluminum plant, Henan Province, China. The chemical composition shows as bellow (Table 1):

Table 1 Chemical components of Bayer red mud of Henan Zhengzhou alumina factory

Composition	Weight percentage content (%)
Na_2O	4.51
Al_2O_3	23.01
SiO_2	18.64
Fe_2O_3	12.38
CaO	15.69
TiO_2	4.09
MgO	1.61
K_2O	1.76
Ignition loss	12.45

The main reactions during this process shows as bellow, and Gibbs free energies ($\triangle G$) are obtained by thermodynamic calculation at different temperature.

$$Na_2O + SO_2 \rightarrow Na_2SO_3 \qquad (1\text{-}1)$$

$\triangle G_{25°C}$= -78.230KJ/mol

$\triangle G_{45°C}$= -77.292KJ/mol

$\triangle G_{65°C}$= -76.542KJ/mol

$$4SO_2(g) + 4Na_2O \rightarrow 3Na_2SO_4 + Na_2S \qquad (1\text{-}2)$$

$\triangle G_{25°C}$= -345.981KJ/mol

$\triangle G_{45°C}$= -343.206KJ/mol

$\triangle G_{65°C}$= -339.738KJ/mol

$$4.5SO_2(g) + Al_2O_3 \rightarrow Al_2(SO_4)_3 + 1.5S \qquad (1\text{-}3)$$

$\triangle G_{25°C}$= -39.884KJ/mol

$\triangle G_{45°C}$= -35.222KJ/mol

$\triangle G_{65°C}$= -31.492KJ/mol

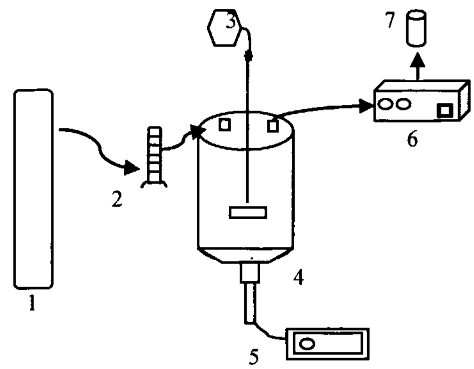
$$4CaO + 4SO_2(g) \rightarrow 3CaSO_4 + CaS \qquad (1\text{-}4)$$

$\triangle G_{25°C}$= -198.792KJ/mol

$\triangle G_{45°C}$= -194.716KJ/mol

$\triangle G_{65°C}$= -191.455KJ/mol

When $\triangle G<0$, the reaction can be proceeded spontaneously. The thermodynamic calculations (1-1), (1-2), (1-3) and (1-4) indicates that the reaction can be carried out by themselves and has stronger trends. Therefore, it is theoretically feasible to treat SO_2 flue gas by Bayer red mud as the absorbent.



1) SO_2 cylinder 2) Rotameter 3) Motor 4) Reactor 5) Ultrasonic Generator 6) SO_2 analyzer 7) Absorption cell

Fig1 Equipment devices connection diagram

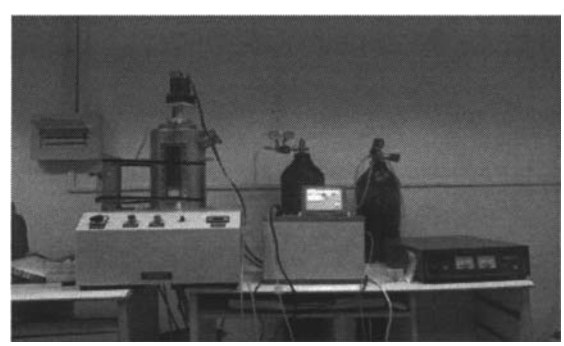


Fig. 2 Equipment devices schematic diagram

Ultrasonic wave adopted in this experiment is at frequency 20KHZ and acoustic intensity 1~6 W/cm^2。The equipment devices connection diagram shows as Fig.1 and Fig.2. When the concentration of SO_2 tail gas reaches to 140ppm stably (that is the national discharge standard: 400 mg/m^3), the experiment is stopped.

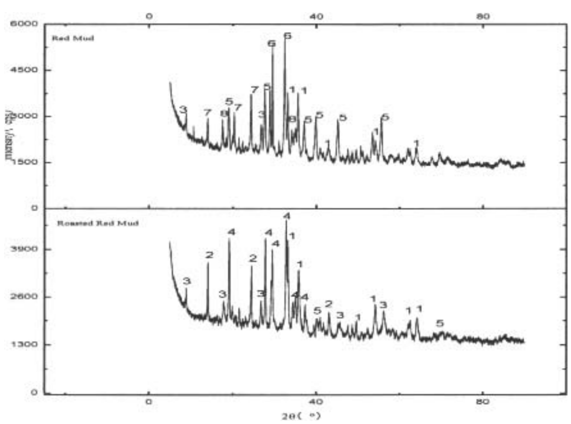
Results and Discussion

Bayer red mud modification experiment

Experimental condition: roasting at temperature 600℃ for 5 hours, the chemical and mineralogical phases are analyzed, which are compared with the composition unmodified, see table 2 and fig.3.

Table 2 Chemical components of roasted Bayer red mud

Composition	Weight percentage content (%)
Na_2O	4.77
Al_2O_3	25.02
SiO_2	20.06
Fe_2O_3	13.07
CaO	16.68
TiO_2	4.35
MgO	1.58
K_2O	1.75
Ignition loss	9.75



1—Fe_2O_3, 2—Sodatite, 3—Muscovite, 4—Cancrinite, 5—Calcium Aluminum Silicate, 6—$CaCO_3$, 7—Vishnevite, 8—$CaSiO_3$

Fig 3 XRD analysis of roasted red mud and red mud

After roasting at temperature 600℃ for 5 hours, the color of the roasted red mud was apparently changed, the reason should be the water evaporation and other original valence states of iron is oxidized at high temperature into ferric iron; The weight percentage content of chemical composition for the roasted red mud are increased, it is because of the evaporation of bound and adsorbed water; CaO content is increased might be due to the decomposition of part calcite; from the mineralogical phase of roasted red mud, the physiochemical properties also changed in certain level, such as the amount of Fe2O3 is increased, but the amount of calcite is decreased.

Fig.2 shows, the part of $CaSiO_3$ and $CaCO_3$ decomposed at high temperature into CaO, so that their contents are reduced after being roasted. Therefore, it can conclude that SO_2 absorption capacity of roasted red mud is improved compared with the original red mud.

Effect of roasted red mud on desulphurization

Table 3Amount of SO_2 absorbed by roasted red mud and red mud with and without ultrasonic wave

No.	Material	Power(W)	Amount of SO_2(ml/g)
1	Red Mud	0	25.1
2	Red Mud	500~ 550	27.3
3	Roasted Red Mud	0	30.2
4	Roasted Red Mud	500~550	46.9

Table 4 shows that the amount of SO_2 absorbed by roasted red mud is more than the original red mud per unit, and the absorption can be intensified by ultrasonic wave. But both of the original and roasted red mud, the dealkalization is quite low, the highest rate still doesn't exceed 35%. The reason is that, with the development of aluminum production technologies, most of sodium ions are transferred to sodium silicon slag ($Na_2O \cdot Al_2O_3 \cdot 1.7SiO_2 \cdot nH_2O$), which is fixed as the formation of a stable mineral phase and very difficult to be dissolved. So, the soda adherent to the red mud mainly acts during SO_2 absorption. That is why alkali content of reaction slag is still very high, correspondingly the dealkalization of red mud is lower.

Effect of ultrasonic wave intensification on SO2 absorption by red mud

Based on the mechanical agitation experiments, it studies the SO_2 absorption intensified by ultrasonic wave under the condition of frequency 20KHZ, power between 400~700W, and the amount of SO_2 fixation per unit red mud are obtained at different ultrasonic powers (Fig.4).

The curve of SO_2 absorption by red mud under different ultrasonic powers shows the tendency, the optimal power range is between 500~600W, the amount of SO_2 absorption reaches the best level in this range.

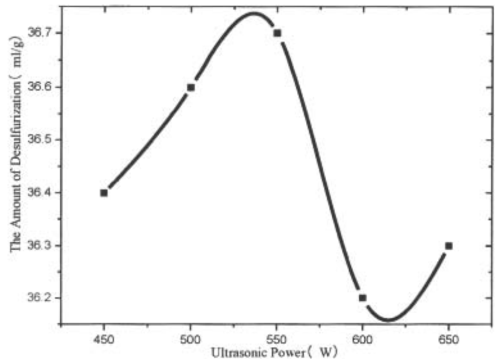


Fig 4 Curve of SO_2 absorption by red mud under different ultrasonic powers

When the ultrasonic power gets to 550W, the effect of ultrasonic wave on SO_2 absorption is most intensified, the amount of SO_2 fixation is 36.7 ml/g.

Fig 5 shows that the mineralogical composition of red mud is not changed much with and without ultrasonic intensification. Part of SO_2 is absorbed by soda adherent to the red mud, and the rest is fixed into $CaSO_3$ by Ca ions containing in the red mud that will be further oxidized into $CaSO_4$. Therefore, it can conclude that the ultrasonic wave intensifies the SO_2 absorption through its cavitation effects.

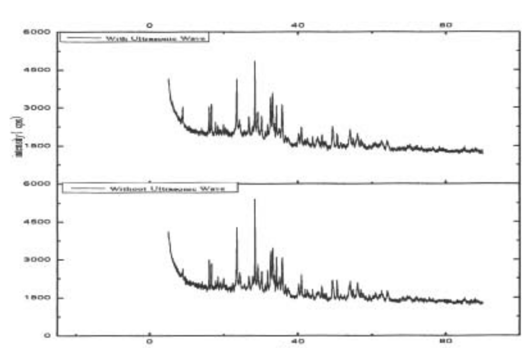


Fig 5 XRD analysis of the red mud slag with and without ultrasonic intensification

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Conclusion

(1) The SO_2 absorption capacity of the roasted red mud is much improved. The amount of SO_2 fixation by original and roasted red mud is respectively: 25.1ml/g and 30.2ml/g;

(2) The ultrasonic wave has great effect on well slurry state of red mud suspension and the red mud slay becomes finer. In the meanwhile, the ultrasonic wave also can increase the temperature of the whole system, as the power increases, the effect on temperature is more obvious;

(3) it is feasible that SO_2 absorption by red mud can be intensified by using ultrasonic wave. Under the condition of ultrasonic intensification, the optimal amount of SO_2 fixation is up to 36.7 ml/g, other optimal conditions are: liquid-solid ratio 9:1、agitation speed 250 rpm, gas flue 0.1 m^3/h、ultrasonic power 550 W. The order sorted by main influence factors: solid liquid ratio> gas flue>ultrasonic power>agitating speed;

(4) The dealkilization of red mud also can be intensified by ultrasonic wave, but the alkli content of red mud slag still can not meet the requirement of cement production for national standard. It needs further treatment to be reuse.

Reference

1. Xinxue Chen, Zhaojie Li, Xuejun Ma. Research progress on application of flue gas[J]. Journal of Pingdingshan Institute of Technology, 2005, 14(3):34-36.
2. Huijian Liu. A Study on Recovering Sulfur from Low-concentration SO_2 in Flue Gas[J]. Environmental Science Trends, 2003, (4):3-5.
3. Zhaoshuang Bian. Desulfurization Treatment Program on Low Concentration SO_2 Flue Gas[J]. Journal of Jianghan Petroleum Institute, 2004, 26(2):171-172.
4. Hui Xu. Research on SO_2 Desorption Method from Sodium Alkali Fuel Gas Desulphurization Rich Solution by Ultrasound[D]. Tianjin University, 2010, Doctor Dissertation。
5. Elisabetta Fois, Antonio Lallai, and Giampaolo Mura*. Sulfur Dioxide Absorption in a Bubbling Reactor with Suspensions of Bayer Red Mud. Ind. Eng. Chem. Res., 2007, 46 (21), 6770-6776.

6. Heng-long, Li. Exploration and Practice on Dry Red Mud Store Technology in Western Australia[J]. Non-ferrous, Metallurgy Part, 1993, (4):42~45.
7. Bei Chen, Suying Chen. Complex Utilization of Red Mud and its Safety Pile-up[J]. Technology & Development of Chemical Industry, 2006, 35 (12).
8. Xiangli Nan, Ting'an Zhang, Yan Liu. Main Categories of Red Mud and Its Environmental Impacts[J]. The Chinese Journal of Process Engineering, 2009, 9(z1).
9. Hui Zhang. Study on Process Intensification of Mass Transfer under Ultrasound Effects [D]. Zhejiang University, 2002.
10. Chang. C. S., Rochelle, G. T. SO_2 absorption into NaOH and Na_2SO_3 aqueous solutions [J]. *Ind. Eng. Chem. Fundam.* 1985, *24*, 7.
11. Yamada, K., Fukunaga, T., Harato, T. Process of SO_2 removal from waste gas by red mud[J]. Light Metals 1979, 1, 69.

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