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Evaluation of Utilizing Sulfur Black in Magnesia Regeneration from Mg-based Desulfurization Gypsum

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Abstract: Sulfur black was employed as the precursor to yield reductive gases for simultaneously regenerating magnesia from the magnesium gypsum and producing high level of sulfur dioxide. The experiments were performed in a successive evaporation-regeneration system to determine the SO_2 concentration during the regeneration and evaluate the desulfurization activity of the regenerated MgO. The peak value of SO_2 concentration increased gradually with the increase of regeneration temperature, evaporation temperature, and the loading of bed materials while the maximum of SO2 concentration was even higher than 20% when the loading of bed materials was 16 g. Additionally, the desulfurization activity of the regenerated MgO at 750 °C was higher than the light burned MgO, which was likely to be due to the forming of more pores and the increase of the specific surface area of the regenerated MgO. The results of X-ray diffraction spectroscopy, specific surface area analyzer and X- ray photoelectron spectroscopy confirmed the successful regeneration of MgO with a high activity using sulfur black as the precursor of reductive gases to decompose the magnesium gypsum.

Keywords: Magnesia; sulfur black; regeneration; SO_2 concentration

1. Introduction

Sulfur dioxide (SO_2) are released from the combustion of sulfur-containing fuels such as coal and petroleum[1]. They contribute to several environmental issues such as acid rain, as well as secondary aerosols [2]. Wet flue gas desulfurization (WFGD), which mainly removes SO_2 by contacting the gases with an aqueous solution or slurry containing an adsorbent, is an effective technique for removing SO_2 from gas streams. Lime/limestone desulfurization method was dominantly employed in coal-fired power plants due to the low investment, abundance of Ca-based desulfurizers, and high SO_2 removal efficiency. However, some practical engineering problems have arisen in the process of application. Such as the disposal of the substantial desulfurization byproducts, i.e., flue gas desulfurization gypsum (FGDG). And the scaling and wear of nozzles and trays in the desulfurization units, which affects the continuous operation of desulfurization system[3]. In this case, the magnesia (MgO)-based WFGD method has been increasingly used as an alternative for lime/limestone method. The solubilities of the magnesium salts in the byproducts of MgO-based WFGD process, which was commonly called as magnesium gypsum, are much higher than those of the corresponding calcium salts[4]. Thus, both the clogging and scaling were effectively inhibited for the MgO-based WFGD method.

Magnesium sulfate ($MgSO_4$) and magnesium sulfite ($MgSO_3$) are the main components of magnesium gypsum[5]. Actually, MgO can be regenerated after the thermal decomposition of the magnesium gypsum at the temperature higher than 900 °C [6]. Such a high temperature not only resulted in a great energy consumption in the regeneration but caused a drastic deterioration of their desulfurization activities[7]. Although the addition of some reductive gases was beneficial to reduce the decomposition temperature of the magnesium gypsum, some byproducts were likely to be

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generated during the decomposition, such as carbonyl sulfide (COS), hydrogen sulfide (H_2S) and so on [8].

A method was proposed by our group to overcome the above problems. In this method, the regeneration of MgO and the generation of high level of SO_2 were simultaneously achieved. In our works, sulfur black [9] was employed as the precursor to yield sulfur vapors. In this work, the feasibility

of the utilization of sulfur black as the reductive agent in decomposition of magnesium gypsum was studied. The effects of the reductive decomposition parameters, including the reaction temperature, the gas hourly space velocity (GHSV) and the loading of sulfur black, on the SO_2 concentration was investigated as well. In addition, the reduction mechanism of sulfur vapor and $MgSO_4$ in magnesium gypsum was revealed.

2. Experimental

Sulfur black was used as raw material, sulfur vapor was obtained through a sulfur evaporator (SR). Then sulfur vapor entered the MgO regenerator, where it reacted with $MgSO_4$ to form MgO, and the SO_2 concentration was recorded at the same time. Both the sulfur black, quartz sands and magnesium gypsum particles were firstly manually grinded. Then, the magnesium gypsum and the quartz sands were mixed under a mass ratio of 1:1 while the mixture particles were filled into MgO regeneration reactor (MGR). At the beginning of the experiment, a stream of N_2 carried the saturated sulfur vapor into MGR under the atmospheric condition. The sulfur vapor was not fed into the MGR until the $MgSO_3$ in the magnesium gypsum was completely decomposed by calcining the magnesium gypsum at 550 °C for 30 min under N_2 atmosphere in the MGR. A cooler was placed after the MGR to condense the sulfur vapor from the exhaust gas. The exhaust gas from the cooler started to be collected immediately using a Teflon air bag every 5 min after the MGR temperature reached the desired value. The collected gases must be diluted 50-fold by N_2 because the SO_2 concentration in the air bag was far beyond the measuring range of the flue gas analyzer.

3. Results and discussion

The XRD patterns of the magnesium gypsum and the solid products after the regeneration at the temperature of 650 °C, 750 °C, and 850 °C were shown in Fig. 1. The magnesium gypsum was composed of $MgSO_3·6H_2O$, $MgSO_4·H_2O$ and $CaSO_4·2H_2O$ while the regeneration products mainly consisted of MgO, CaS and SiO_2. As observed in Fig. 1, a considerable peak of $MgSO_4$ was still distinctly present from the XRD pattern when the reaction temperature was 650 °C, implying that the total $MgSO_4$ was not sufficiently decomposed at 650 °C. When the regeneration temperature was 750 °C or 850 °C, all the peaks assigned to $MgSO_4$ were not displayed, manifesting the absolute decomposition of $MgSO_4$ into MgO. The presence of the peaks of CaS was most likely to be due to the reductive decomposition of $CaSO_4$ according to Eq. (1)[10].

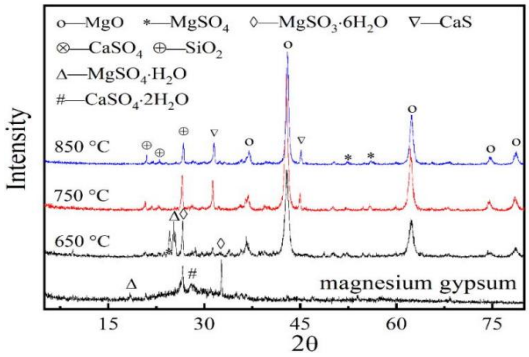

Fig. 1 The XRD patterns of the magnesium gypsum and the solid products after the regeneration at the temperature of 650 °C, 750 °C, and 850 °C

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$$CaSO4+S2=CaS+2SO2 \quad (1)$$

The release behavior of SO_2 with reaction time at different regeneration temperatures are given in Fig. 2(a) The peak value of SO_2 concentration increased gradually with the increase of regeneration temperature from 650 °C to 850 °C while it was even higher than 20 % at 850 °C. The occurrence of the peak indicated that the regeneration time was limited and the SO_2 concentration decreases quickly at the end of the regeneration. This was because that the reductive gas was continuously fed into the

reactor while the amount of magnesium gypsum was relatively insufficient compared with reducing gas in the latter part of the regeneration.

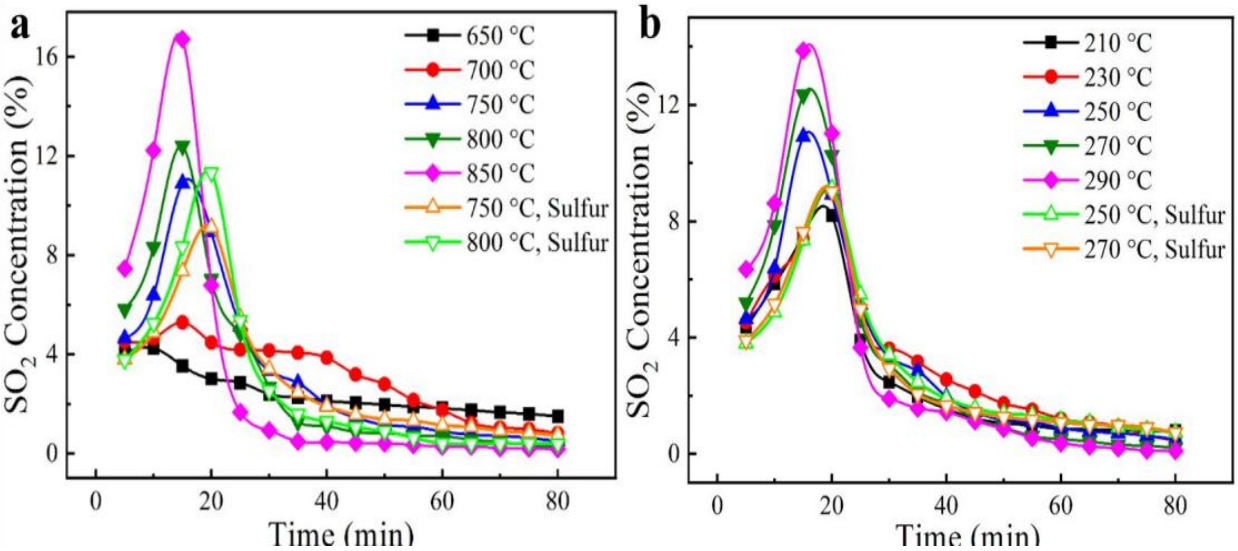

Fig. 2 Effects of (a) regeneration temperature and (b) evaporation temperature on the SO_2 concentration

Fig. 2(b) exhibited the effects of the evaporation temperature of sulfur black on the SO_2 concentration released in the reductive decomposition of magnesium gypsum. It was demonstrated that the peak value of SO_2 concentration increased monotonically with the increase of the evaporation temperature from 210 °C to 290 °C. The SO_2 concentration was the highest when the evaporation temperature was at 290 °C and reached a maximum of 14.2 %, which was higher than the SO_2 concentration at the same evaporation temperature using elemental sulfur as the precursor of the reductive gases. When the heating temperature of sulfur black is 250 °C, the peak concentration of SO_2

reaches 10.5%, which has met the requirements of manufacturing sulfuric acid. Considering the minimization of energy consumption in the evaporation period, the most reasonable evaporation temperature was set at 250 °C.

Fig. 3(a) highlighted the effect of GHSV on the SO_2 concentration. It was clearly displayed that the peak value of SO_2 concentration decreased gradually with the increase of GHSV. Additionally, the SO_2 concentration and the GHSV were basically inversely proportional, implying that GHSV scarcely affected the regeneration behavior between magnesium gypsum and the reductive gases from sulfur black. Consequently, the low SO_2 concentration at the high GHSV was caused by the dilution of more carrier gas fed into the sulfur evaporator.

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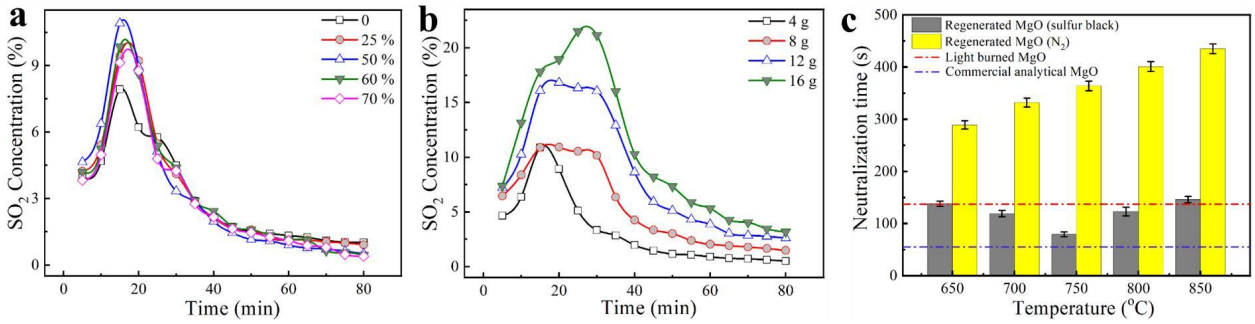

Fig. 3 Effects of (a) GHSV and (b) the loading of bed materials on the SO_2 concentration; and (c) comparison of the neutralization time of the regenerated MgO and some typical MgO samples

The bed materials in MGR consisted of magnesium gypsum and quartz sands, and the mass fraction of quartz sands was constant at 50%. It was seen from Fig. 3 (b)that the peak value of SO_2 concentration increased steadily with the increase of the loading of bed materials. The peak value of SO_2 concentration was only 10.5% when the loading was 4 g while climbed to 21.5% when the loading rose to 16 g. In addition, it was observed that the peak duration of SO_2 concentration increased progressively with the increasing of the loading.

The desulfurization activity of regenerated MgO at different regeneration temperatures were evaluated according to the citric acid method from Chinese Standard YB/T 4019-2006 [11]. It was demonstrated in Fig. 3(c) that the neutralization time of MgO regenerated under the reductive atmosphere of sulfur black is much shorter than that of MgO regenerated during the thermal decomposition of magnesium gypsum under N_2 atmosphere, which was most likely due to the low decomposition rate of magnesium gypsum under N_2 atmosphere [12]. Additionally, the neutralization time of MgO regenerated under N_2 atmosphere increased with the increase of regeneration temperature while the neutralization time of MgO regenerated under the reductive atmosphere formed from sulfur black had a lowest value. The neutralization time of the MgO regenerated under the reductive atmosphere at 700 °C, 750 °C and 800 °C were even lower than that of the light burned MgO, which was used as the raw desulfurizers in power plants, suggesting that the desulfurization activity of the above three samples were higher than the light burned MgO. It was likely to be due to the forming of more pores and increase of the specific surface area of the regenerated MgO particles.

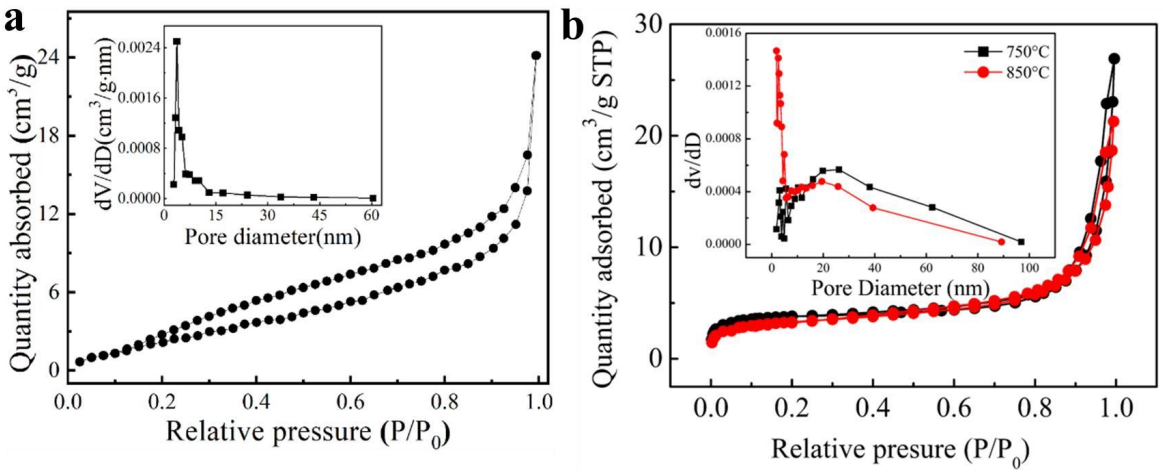

Fig. 4 N_2 adsorption-desorption isotherms and the pore size distribution plots of (a) the magnesium gypsum; (b) the regenerated MgO at 750 °C and 850 °C

Compared with the magnesium gypsum, the specific surface area slightly increased while the average pore diameter significantly increased for both the regenerated samples at the regeneration

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temperature of 750 °C and 850 °C. Fig. 4(a) and (b) showed the N_2 adsorption-desorption isotherm and the pore size distribution of the magnesium gypsum and the regenerated MgO, respectively. It was observed that both the N_2 adsorption-desorption isotherms of the regenerated MgO belonged to Type IV isotherms while H3 hysteresis loops appeared in the range of relative pressure of 0.30-0.99, indicating that the weak interaction between adsorbate and adsorbent [13]. Both the regenerated MgO samples exhibited microporous or mesoporous structure, and the pore was probably the slit pores formed by accumulation of particles [14].

HRTEM images of the regenerated MgO at 650 °C, 750 °C, and 850 °C were shown in Fig. 5, to study the changes of the apparent morphology of the products in the reductive decomposition of magnesium gypsum. It was seen in Fig. 5(a), (d), and (g) that the grain sizes apparently become larger with the increase of the regeneration temperature. Both the regenerated MgO at 750 °C and 850 °C exhibited a more significant crystalline structure than the regenerated MgO at 650 °C. The two- dimensional fast Fourier transform (FFT) patterns of the selected crystalline area from the HRTEM images of the above three samples were obtained from the lattice-resolved images of Fig. 5(c), 5(f), and 5(i), respectively. The inset photos indicated that the reciprocal lattice fringes matched well with the hexagon MgO structure. Fig. 5(c), (f), and (i) exhibited the regular arrays of highly ordered MgO nanostructures [15]. All the three samples showed (111) and (200) crystal planes corresponding to MgO. The moderate increase of the (200) crystal plane spacing was likely to be due to the sintering of the regeneration products at high temperature [16]

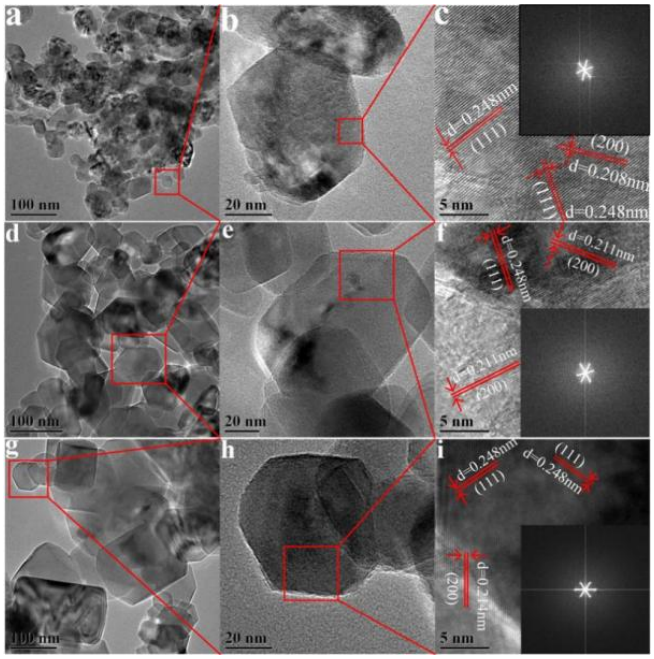

Fig. 5 HRTEM images of (a)-(c) the regenerated MgO at 650 °C, (d)-(f) regenerated MgO at 750 °C, (g)-(i) regenerated MgO at 850 °C

Fig. 6 showed the high-resolution XPS spectra of the O1s and S2p peaks for the magnesium gypsum and the regenerated MgO. The surface oxygen was divided into three categories, including lattice oxygen (O_I), vacancy oxygen (O_{II}) and adsorbed oxygen (O_{III}) [17]. The detailed quantitative parameters of the three characteristic oxygen peaks are listed in Table1. The peak area fractions of O_I, O_{II} and O_{III} changed from 21.30%, 70.68%, and 8.02% of the magnesia gypsum to 54.81%, 37.56% and 7.63% of the regenerated MgO. The peak area fraction of O_I was the highest for the regenerated MgO, indicating the presence of a lot of lattice oxygen on its surfaces. The decrease of the peak area fraction of O_{II} suggested that a considerable amount of O vacancies was still stable under the reductive atmosphere.

Table 1 Calibration parameters of oxygen peak of Magnesium gypsum and the regenerated MgO at

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750 °C

Sample	Oxygen peak	Energy binding (eV)	Peak area fraction (%)
Magnesium gypsum	O_I	529.12	21.30
	O_{II}	530.40	70.68
	O_{III}	532.17	8.02
Regenerated MgO	O_I	529.86	54.81
	O_{II}	531.30	37.56
	O_{III}	532.92	7.63

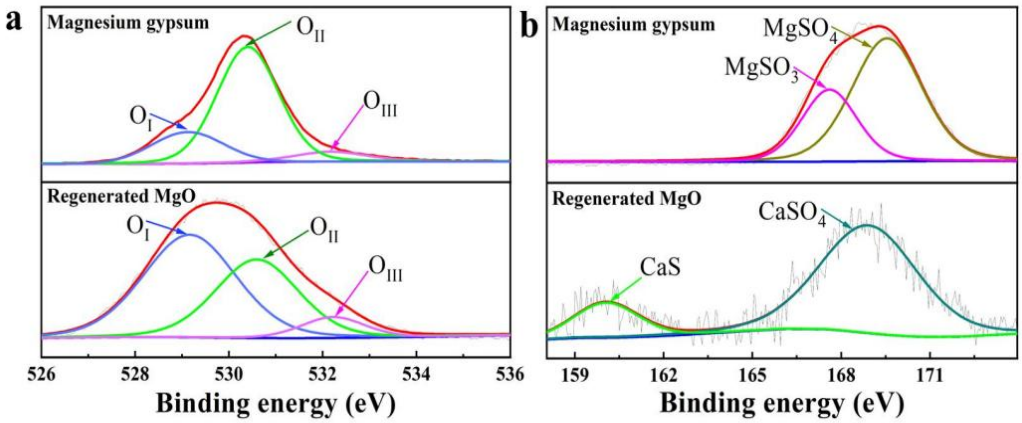

Fig. 6 High-resolution XPS spectra over (a) O1s and (b) S2p peaks of Magnesium gypsum and the Regenerated MgO at 750 °C

It can be seen in Fig. 6(b) that S2p peak consisted of two peaks, the binding energy of which was 160.05 eV (was attributed to the characteristic peak of CaS) and 168.93 eV (was ascribed to the characteristic peak of $CaSO_4$), respectively [18]. Consequently, $CaSO_4$ was reductively decomposed into CaS while $MgSO_4$ was reductively decomposed into MgO.

4. Conclusions

Sulfur black was employed as the precursor to yield reductive gases for simultaneously regenerating magnesia from the magnesium gypsum and producing high level of sulfur dioxide. The conclusions were given as follows:

(1) The feasibility of employing sulfur black as the precursor to yield reductive gases for simultaneously regenerating MgO from the magnesium gypsum and producing high level of SO_2 was confirmed. The maximum of SO2 concentration was even higher than 20% when the loading of bed materials was 16 g.

(2) The SO_2 concentration increased with the increase of regeneration temperature, evaporation temperature, loading of bed materials, and the decrease of GHSV.

(3) The regenerated MgO after the reductive decomposition of magnesium gypsum by the reductive gases generated from sulfur black showed a high desulfurization activity with the temperature at 700 °C, 750 °C and 800 °C. When the regeneration temperature was at 750 °C, its desulfurization activity was higher than that of the fresh light burned MgO owing to the forming of more pores and increase of the specific surface area of the regenerated MgO.

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