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Desulphurization Characteristic of Industry Alkaline Wastes during Coal Combustion

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ABSTRACT

The desulphurization characteristics of four sorts of industry alkaline wastes and one sort of limestone were studied by means of flue gas analyzer and the high temperature tube reactor. Pore structure and desulphurization product characteristic were investigated respectively by mercury porosimeter and XRD diffraction technology. The reasons why wastes and limestone hold the different desulphurization capability were deeply discussed. The result shows that white clay and carbide slag could capture the release of sulfur at 800-1100℃. Salt slurry and red mud could capture the release of sulfur at first stage at 800-900℃. But when the experimental temperature rises to 1000℃, the sulfur capture abilities of them depress. Pore structures of waste are higher than that of limestone. This makes the sulfation reaction goes further. To sum up, wastes have better sulfur capture ability.

Keywords: Industry Alkaline Waste, Desulphurization, Pore Structure, XRD, Limestone

1. Introduction

Combustion desulphurization technology has been concerned as an important development direction of coal clean technology. Natural limestone has been widely used as desulphurization sorbent because it contains a great amount of CaO. But the actual operating result is that limestone's desulphurization efficiency and CaO conversion fraction are not high in the fluidized bed furnace, and in other combustion mode, its efficiency is even lower [1]. When the limestone is added excessively, ash and CO_2 in the flue gas will increase greatly.

With the rapid development of Chinese industry, the accumulation and discharge of industry wastes become more and more serious, which pollutes the environment. Only a small number of wastes are used as building material. And some useful matters are reclaimed from these wastes. Many industry alkaline wastes contain a great deal of CaO and alkali Oxide [2,3,4,5,6,7], which can react with SO_2 directly. If these alkaline wastes can be used as desulphurization sorbent, the purpose of using waste to treat pollution will be achieved. The desulphurization characteristics of four sorts of industry alkaline wastes and one sort of limestone are studied by means of flue gas analyzer and the high temperature tube reactor in this paper. Pore structures of industry alkaline wastes and limestone are investigated by mercury porosimeter. Desulphurization product characteristics are analysed by

XRD diffraction technology.

2. Experiments

2.1 Materials

Four sorts of industry alkaline wastes and one sort of limestone are used as samples in this experiment. White clay comes from Laiwu. Red mud comes from Zibo. Carbide slag comes from Jinan. Salt slurry comes from Binzhou. Limestone comes from Zibo. The samples' chemical composition is analysed according to GB3286. The results are given in Table 1. The coal sample is lean coal which comes from Huangtai. Proximate and sulfur form analysis of the coal is shown in Table 2.

2.2 Procedure

The desulphurization characteristics of sorbents were studied in desulphurization experimental reactor (Figure 1). The mass of the coal sample is 100±0.1mg. The coal sample is added into the sorbent at the rate of Ca/S=2. The SO_2 of flue gas was analyzed by MSI flue gas analyzer.

The phase composition of desulphurization product was analyzed by target D/MAX-B X-ray diffractometer. The pore structure was studied by Poromaster60 mercury porosimeter.

Sulfur capture ability of sorbent is judged by the variable amount of SO_2 released from the coal after adding desulphurization sorbent. The ratio of SO_2 released is calculated by the formula (1):

$$V_{SO_2} = \frac{M_S \times \int_{t_0}^{t} C_{(t)} V_t dt}{M \times S_t \times M_{SO_2}} \times 100\% \qquad (1)$$

Where M_S is the mole mass of sulphur, M_{SO2} is the mole mass of SO_2, $C_{(t)}$ is the concentration of SO_2 at time t_0, V_t is flux of flue gas, M is the mass of coal and S_t is the sulphur containing ratio in coal.

3. Results and Discussion

3.1 Desulphurization Characteristics of Wastes

The desulphurization characteristics of sorbents were studied at 800-1200℃, as is shown in Figure 2.

SO$_2$ is released through two stages in coal combustion. The rate curve shows tow-peak structure. FeS and aromatic sulfur in the coal will release when temperature is above 1000℃. The rate curve shows one-peak structure at 800-900℃ [8].

Only SO$_2$ at first stage is released at 800℃ (Figure 2). The rate curve shows one-peak structure. The ultimate ratio of SO$_2$ released is 53%. When limestone is added into coal, the amount of SO$_2$ released decreases. When the industry alkaline wastes are added into the coal, the amount of SO$_2$ released decreases obviously. Salt slurry's effect is the most outstanding. There is almost no SO$_2$ released and the ultimate ratio of SO$_2$ released is only 11.7%. White clay's effect is obvious and the rate is 13.5%. Red mud and carbide slag also can capture the release of SO$_2$ at first stage. Wastes can resist SO$_2$ released. Sulfur capture ability of wastes higher than limestone's always. According to XRD pattern of sulfur retention at 800℃ (Figure 3), it is clear that after adding white clay, carbide slag and red mud, the main desulphurization product is CaSO$_4$. The diffraction maximum of CaSO$_4$ is clearly higher than that of desulphurization product caused by adding limestone. It shows that white clay, carbide slag and red mud are more easily react with SO$_2$ directly. Besides CaSO$_4$, there is MgSO$_4$ in the sulfur retention with salt slurry. MgSO$_4$'s diffraction maximum is high. It shows that magnesium-based matters in salt slurry can capture the release of SO$_2$ at first stage, which improves salt slurry's sulfur capture ability. Least CaSO$_4$ is produced after limestone is added, and CaO still exists in great amount. It is because limestone's calcinations speed is slower, which results in worst desulphurization efficiency.

At 900℃, the amount of SO$_2$ released increases obviously and the ultimate ratio is 94%. When experimental samples are added into the coal, the amount of SO$_2$ released decreases greatly. But the change of each material's effect is greatly different. White clay's desulphurization effect is the most outstanding, and the ultimate ratio of SO$_2$ released is about 21%. 73% is reduced compared with coal's ratio. Carbide slag shows better desulphurization efficiency at such temperature, and its ratio is about 38%. 56% is reduced compared with coal's ratio. When red mud and salt slurry are added into the coal, the ratios reduce 39% and 47% respectively.

At 1000℃, since FeS and aromatic sulfur in the coal begin to release in great amount, the late stage appears in the process of SO$_2$ released. Limestone doesn't reduce SO$_2$ released amount at first stage, but no SO$_2$ is released at late stage. The ratio of SO$_2$ released reduces 54%. After white clay and carbide slag are added, the amount of SO$_2$ released reduces obviously at first stage and no SO$_2$ is released at late stage nearly. The ratios reduce 70% and 66% respectively. Red mud and salt slurry have better desulphurization performance at first stage, but have no efficiency at late stage, which makes their desulphurization efficiency depress, and the ratios reduce 35% and 36% respectively.

At 900-1000℃, white clay can capture the release of sulfur at first and last stage. White clay's desulphurization performance is the best. This is because its represents better micro-structural characteristics, which prepares for rapid pyrolysis of CaCO$_3$, adsorption of SO$_2$ and sulfation reaction. Carbide slag also has better sulfur capture ability, only second to white clay. The reason is that carbide slag contains rich Ca (OH)$_2$. Ca (OH)$_2$ will be decomposed into CaO at about 400℃. So it can react with SO$_2$ early and capture SO$_2$. Carbide slag represents better micro-structural characteristics of inner pore similarly. Salt slurry and red mud contains magnesium-based matter and so they can react with SO$_2$ directly at lower temperature. They represent better micro-structural characteristics, which is good for the full sulfation reaction. Therefore they can capture the release of sulfur at first stage. But the stability of MgSO$_4$ is poor. The sulfate is
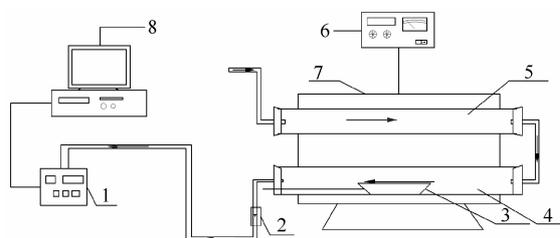

Figure 1. Schematic diagram of the experimental apparatus (1-flue gas; analyzer; 2-flowmeter; 3-test sample; 4-reactor; 5-preheater; 6-thermostat; 7-tube heater; 8-computer)

Table 1. Chemical composition analysis of test sample (%)

	Sample	LOSS	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	CaO	MgO	Σ
1#	white clay	36.2	10.7	0.86	0.21	48.5	1.8	98.27
2#	red mud	19.1	18.4	11.2	10.01	36.95	1.87	97.53
3#	carbide slag	28.5	2.8	1.5	0.2	66.4	0.1	99.5
4#	Limestone	43	2.1	0.46	0.2	51.6	2.5	99.86
5#	salt slurry	33.5	11.91	2.64	1.77	33.96	13.9	97.68

Table 2. Proximate and sulfur form analysis of coal

Proximate analysis (%)				Sulfur form analysis (%)				Net calorific power (Q$_{net,ar}$/kJ·kg^{-1})
M_{ad}	A_{ad}	V_{ad}	FC_{ad}	S_t	S_s	S_p	S_o	
1.14	32.31	14.41	52.14	1.88	0.06	1.16	0.66	20696

decomposed again at late reaction stage and SO_2 is released, which decreases sulfur capture ability of salt slurry and red mud. Limestone's desulphurization capacity increases with rise of temperature. This is because limestone's calcinations and decomposition needs a certain range of time and a certain temperature. At the initial stage, when adding limestone, SO_2 released ratio is higher than when adding wastes. As time extends, limestone is calcined into CaO of porous structure, good for sulfation reaction.
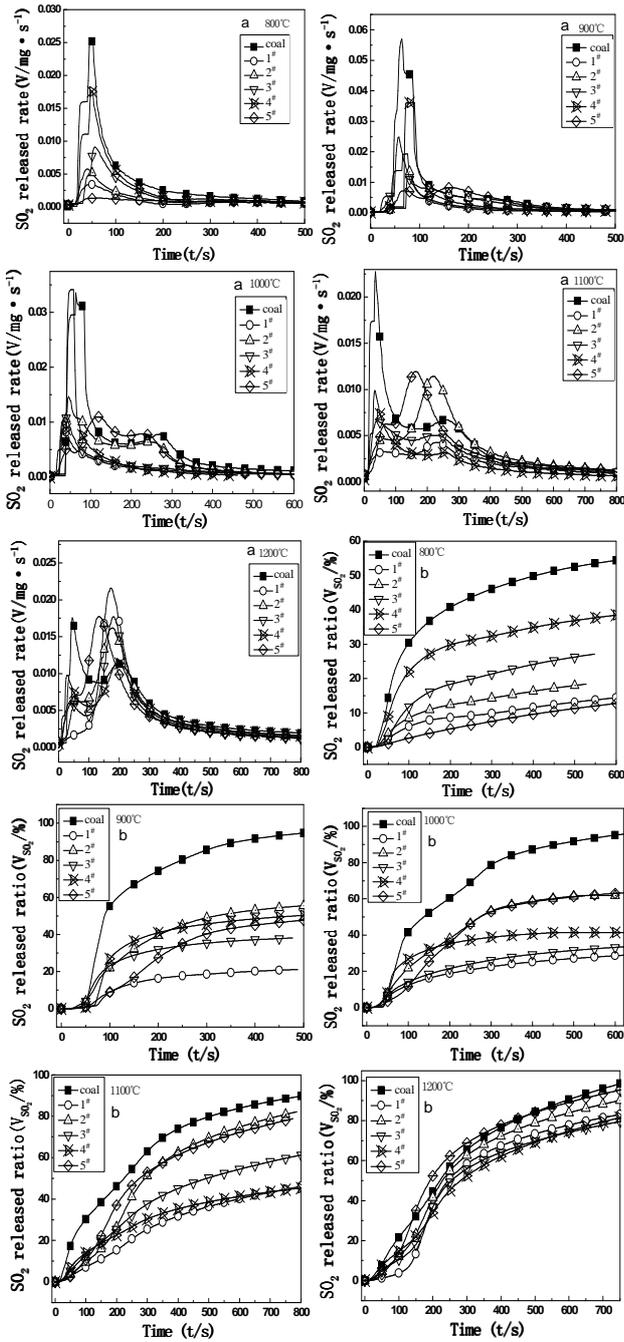

Figure 2. Desulphurization characteristics of wastes in 800-1200℃ (a-the rate of SO_2 released with various samples; b-the ratio of SO_2 released with various samples)
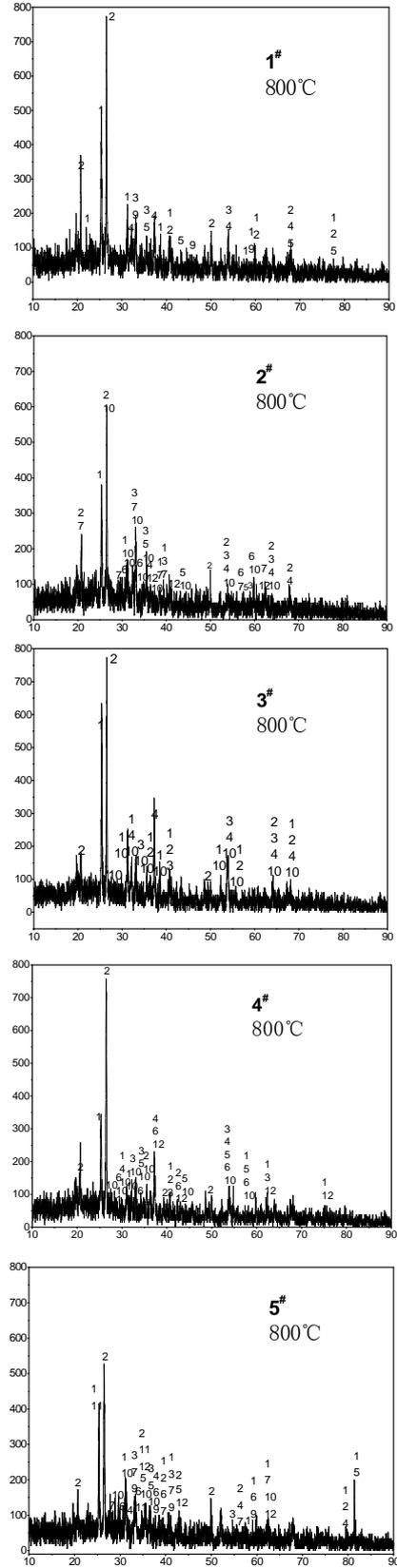

Figure 3. XRD pattern of sulfur retention from wastes in 800℃ (1-$CaSO_4$; 2-SiO_2; 3-Fe_2O_3; 4-CaO; 5-Al_2O_3; 6-$Ca_3Al_2Si_3O_{12}$; 7-$Ca_3Fe_2(SiO_4)_3$; 9-$Ca_3Al_2O_6$; 10-$Ca_{1.8}Al_2O_{4.8}$; 11-$MgSO_4$; 12-MgO)
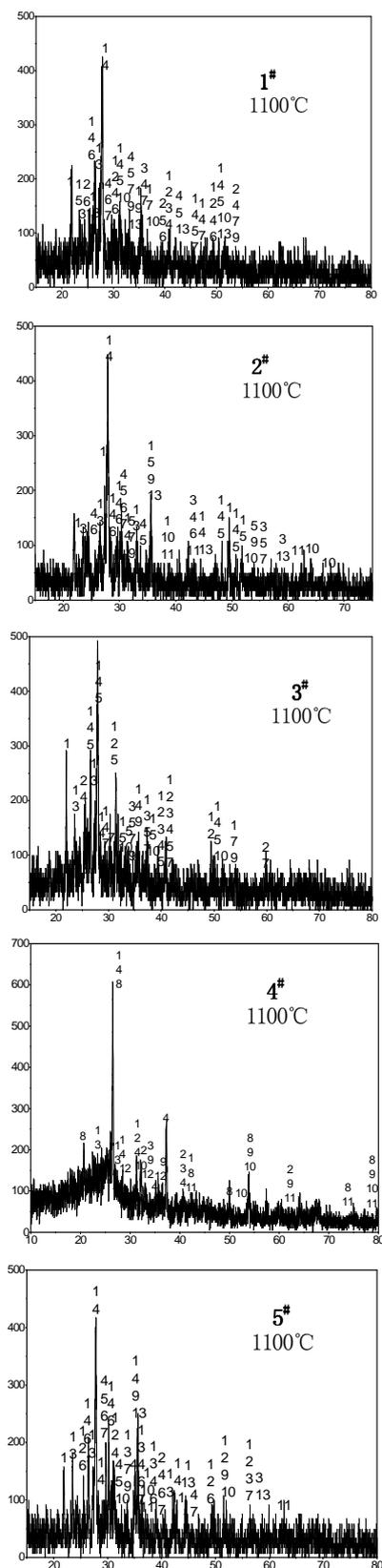
Figure 4. XRD pattern of sulfur retention from wastes in 1100℃ (1-CaAl$_2$Si$_2$O$_8$; 2-CaSO$_4$; 3-Ca$_3$Al$_6$O$_{12}$·CaSO$_4$; 4-2C$_2$ S·CaSO$_4$; 5-Ca$_2$ (SiO$_4$) ; 6-CaSiO$_3$; 7-Ca$_3$Fe$_2$ (SiO$_4$)$_3$; 9-Fe$_2$O$_3$; 10-CaO; 11-MgO; 12-Al$_2$SiO$_5$; 13- Al$_2$O$_3$)

At 1100℃, after white clay, carbide slag and limestone are added; SO$_2$ is captured at first and late stage. The ratios of SO$_2$ released reduce 54%, 38% and 53% respectively. After salt slurry and red mud are added, though they can capture the release of sulfur at first stage, they can do nothing to the sulfur released at late stage. The ratios of SO$_2$ released reduce only 3%-10%. Desulphurization efficiency is decreased significantly.

XRD pattern of sulfur retention at 1100℃ shows that the main desulphurization products of white clay and carbide slag are CaSO$_4$, Ca$_3$Al$_6$O$_{12}$·CaSO$_4$ and 2C$_2$S·CaSO$_4$ (Figure 4). The diffraction maximum of Ca$_3$Al$_6$O$_{12}$·CaSO$_4$ and 2C$_2$S·CaSO$_4$ is significant, showing large quantity. It is obvious that during the reaction process, considerable part of CaSO$_4$ forms thermal stable phases Ca$_3$Al$_6$O$_{12}$·CaSO$_4$ and 2C$_2$S·CaSO$_4$, which enhances the sulfur capture ability.

Figure 4 shows that compared with desulphurization product at 800℃, the main desulphurization product of salt slurry and red mud are Ca$_3$Al$_6$O$_{12}$·CaSO$_4$ and Ca$_5$ (SiO$_4$)$_2$SO$_4$ at 1100℃, only with a small amount of CaSO$_4$. There is even no CaSO$_4$ in red mud. From the diffraction maximum value, the value of Ca$_3$Al$_6$O$_{12}$·CaSO$_4$ and Ca$_5$ (SiO$_4$)$_2$SO$_4$ is small, showing smaller amount and poor desulphurization efficiency. Salt slurry and red mud contains alkali metal compound and a considerable part of Ca^{2+} reacts with such compound and forms CaAl$_2$Si$_2$O$_8$, Ca$_2$(SiO$_4$), CaSiO$_3$ and Ca$_3$Fe$_2$ (SiO$_4$)$_3$ etc. as shown by Figure 4. It decreases calcium's active center and so it can't capture high-temperature sulfur and SO$_2$ decomposed by CaSO$_4$, which weakens sulfur capture ability.

At 1200℃, when experimental samples are added, desulphurization efficiency is poor and the ratios of SO$_2$ released reduce only 3%-19%. The reason is that because of serious high temperature sintering of experimental sample, sulfate produced at initial reaction stage is rapidly decomposed again, which deteriorates wastes' sulfur capture ability. Wastes basically cannot capture the release of sulfur at such temperature.

To sum up, after white clay and carbide slag are added, the amount of SO$_2$ released is reduced significantly at first and late stage. White clay and carbide slag could capture the release of sulfur at 800-1100℃. After salt slurry and red mud are added, the amount of SO$_2$ released is reduced significantly at first stage. Salt slurry and red mud could capture the release of sulfur at 800-900℃. But when the experimental temperature is above 1000℃, the sulfur capture abilities of them depress. After limestone is added, the amount of SO$_2$ released is hardly reduced at first stage. Its resistance to SO$_2$ precipitation is lower to experimental wastes at 800-900℃. But when the experimental temperature rises to 1000℃, limestone could capture the release of sulfur.

3.2 Temperature Characteristics of Wastes

As is shown by Figure 2, when white clay and carbide slag are added, the ratios of SO$_2$ released reduce over

50% and over 40% respectively at 800-1100℃. And at 900-1000℃, the ratios could reduce over 70% and 56% respectively. The range of optimum desulphurization temperature is wide and desulphurization performance is good. White clay and carbide slag represent good microstructure characteristics. So sulfation reaction could process in the inner particles and high temperature desulphurization phase is easily formed at high temperature, which makes their desulphurization performance better. When salt slurry and red mud are added, the ratios reduce over 40% at 800-900℃, showing better sulfur capture ability. When the temperature rises to 1000℃, because of poor sulfur capture ability at late stage, decomposition of desulphurization product and serious sintering, the sulfur capture abilities of them depress. Limestone has poor desulphurization capacity at 800-900℃, because of its hard calcinations and bad microstructure. With the rise of temperature, limestone is calcined fully, which improves the sulfur capture ability a little. When temperature rises to 1200℃, industry alkaline wastes and limestone hardly have any desulphurization capability because of serious sintering. So the optimum desulphurization temperature window of white clay is 800-1100℃, carbide slag's is 800-1050℃, and salt slurry and red mud's is 800-950℃.

3.3 Microstructure Characteristics of Wastes

The inner microstructure of desulphurization sorbent greatly influences its sulfur capture ability [9,10]. Micropore structure of samples was studied by mercury porosimeter in this paper. The samples include original samples and test samples after calcinations at 850℃ and 1050℃. The testing results were analyzed and characteristic parameters were got, including pore size distribution, porosity and specific area (Table 3 and Table 4).

Table 3 and Table 4 show that the pore structure of wastes' and limestone's original samples are greatly different. The pore size distribution of wastes is similar to that of limestone, with micropore and mesopore taking the main part. But porosity and specific area of wastes are higher than that of limestone.

Table 3. Aperture and porosity of test sample

Sample	Original sample		850℃ Calcined sample		1050℃ Calcined sample	
	Pore size (μm)	Porosity (%)	Pore size (μm)	Porosity (%)	Pore size (μm)	Porosity (%)
white clay	0.004-0.2	13.216	0.0045-0.3	19.665	0.005-1	22.329
carbide slag	0.004-0.2	25.083	0.0045-0.3	21.717	0.005-1	15.166
red mud	0.004-0.2	13.269	0.005-0.045	25.549	0.5-1	6.073
limestone	0.011-0.302	0.099	0.008-2.5	16.175	0.005-1	19.354

Table 4. Specific area of test sample (m²/g)

Sample	Original sample	850℃ Calcined sample	1050℃ Calcined sample
white clay	2.915	8.267	6.148
carbide slag	15.069	8.602	6.269
red mud	7.715	9.602	2.915
limestone	0.097	3.715	3.071

This makes wastes react with SO_2 more easily at initial reaction stage. Porosity and specific area of limestone are smaller, which makes limestone have poor sulfur capture ability at initial reaction stage.

The pore structure of white clay after calcinations at 850℃ is improved. The pore size distribution is wider. Porosity and specific area increase greatly, which makes SO_2 diffuse easily and sulfation reaction process goes further in the inner particles. With the rise of temperature, its pore size distribution becomes further wider, and porosity increases continuously. Because of sintering, its specific area decreases a little at 1050℃. But the general situation is better. This makes it still represents higher sulfur capture ability, which is in accordance with the above desulphurization experiment results. Carbide slag represents porous structure and its specific area is huge. With calcinations reaction and sintering reaction go simultaneously, the pore size distribution of carbide slag becomes wider, which makes SO_2 deep into the particles easily and makes sulfation reaction go further. Though its specific area and porosity decrease with rise of temperature, they are still higher, and so carbide slag still represents better sulphur capture ability. Red mud contains large amount of Al_2O_3 and Fe_2O_3. They react with produced CaO and form $CaO \cdot Al_2O_3$, $3CaO \cdot Al_2O_3$, $CaO \cdot Fe_2O_3$ and $2CaO \cdot Fe_2O_3$ at 850℃, which makes microstructure worse, the quantity of macropore and mesopore decrease. The pore size distribution of red mud becomes narrow after calcinations. Liquid eutectic solution accelerates ion migration and diffusion, which destroys crystal lattice of CaO. Irregular pore is formed. The specific area and porosity of red mud increase. With rise of temperature, $CaO \cdot Al_2O_3$, $3CaO \cdot Al_2O_3$, $CaO \cdot Fe_2O_3$ and $2CaO \cdot Fe_2O_3$ accelerate sintering. Pore structure of red mud changes, which causes plugging of pore or formation of molten pore or macropore. The specific area and porosity decrease rapidly and sulphur capture ability is reduced. The change of limestone's microstructure with rise of calcination temperature is similar to that of white clay's. But porosity and specific area of limestone are lower and its sulphur capture ability is worse than white clay's.

4. Conclusions

The desulphurization characteristics of samples had been studied at 800-1200℃. White clay and carbide slag could capture the release of sulfur at 800-1200℃. Salt slurry and red mud could capture the release of sulfur at first stage at 800-900℃, and when temperature rises to 1000℃, the sulfur capture ability of them decreases. Within the range of experimental temperature, industry alkaline wastes represent better temperature characteristics. The optimum desulphurization temperature window of white clay is 800-1100℃, carbide slag's is 800-1050℃, and salt slurry and red mud's is 800-950℃. According to the test of mercury porosimeter, the original samples and calcined samples of the wastes have better pore size dis-

tribution, higher porosity and specific area. This makes SO_2 deep into the inner particles and sulfation reaction go further. But because of sintering, specific area and porosity of red mud become smaller with rise of temperature. Sulfur capture ability of red mud decreases. Compared with limestone, industry alkaline wastes represent better desulphurization characteristics and temperature characteristics. They may be a new sort of desulphurization sorbent.

5. Acknowledgment

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