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Effect of Combined Forms of Al and Si on the Acid Leaching Performance of Fly Ash

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Abstract

Research on the leaching performance of fly ash of Shanxi, Chongqing and Western Inner Mongolia. Analyze the existing forms, crystallinity and package situation of Al-Si phase in fly ash from different areas by using SEM and XRD. Effect of fractionation of Al-Si phase in fly ash on the leaching performance from the view of mechanism was investigated as well. Leaching experiments and analysis indicate that: the leaching rates of Al2O3 in fly ash from the there different areas are 97.41%, 68.94% and 23.61% respectively, under the conditions of solid-liquid ratio 1:20, rotary speed 500rpm, leaching time 120min, sulfate concentration 20%, particle sizes -74μm. Leaching performance of fly ash in Western Inner Mongolia is better than that in other two areas. The main reason for different leaching performance of fly ash from different areas is the difference in crystallinity, encapsulated glass phase of Al-Si phase in fly ash. The crystallinity for Western Inner Mongolia is 75.98%, while there is no non-crystalline phase in fly ash from other tow areas, The average FWHM of XRD diffraction peak of Al-Si phase are 0.641, 0.3324 and 0.1107, respectively. The crystallinity of fly ash in Western Inner Mongolia is worst among the there areas, and its content of glass phase is also lowest among them, so its activity is obviously higher than that of other two areas.

Introduction

China is one of the biggest coal producer and consumer in the world. Nowadays, coal is primary energy resource in our country and this situation will last long. Although there are significant progress in new power technology like waterpower, wind power and nuclear power these years, coal fired electricity still occupies a dominant position, the fly ash emission is more than 200 million tons at the present stage in our country. Fly ash has been used in building operation、architecture and many other field, but most of it is used in an extensive way which has low added value and little technology. The alumina content in fly ash is 17%~35%, it can be as high as 40%~60% in some areas. The fly ash is an important kind of unconventional aluminum resource. As the environmental policy of the nation becomes more strictly and the short of high grade alumyte intensifies, leaching alumina from high-alumina fly ash has become research focus[1~11].

The way to extract alumina from high-alumina fly ash includes: alkali process, acid process, ammonia process and acid and alkali combination process. The alkali process used for high-alumina fly ash has long technological process, low efficiency of comprehensive utilization of resources, high energy consumption, large quantity of leaching residue and other shortcomings. In contrast with it, acid process has significant advantages of the utilization of valuable elements and energy consumption. In this paper ,by studying the existing form of valuable element, crystallinity and apparent morphology in high-alumina fly ash from different areas, and the influence of these factors on the leaching performance of alumina in fly ash, theoretical foundation is provided for industry application[12~14].

Experiment

Material

The high-alumina fly ash used in leaching experiment comes from Chongqing, Shanxi and Western Inner Mongolia, the chemical composition of fly ash in different region is shown as Table1.

Table 1 Chemical composition of fly ash in different regions(mass fraction, %)									
Component	Regions	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	TiO_2	SO_3	K_2O
Content/%	Western Inner Mongolia	36.72	3.97	39.78	7.66	-	2.37	1.83	0.96
	Chongqing	41.25	17.48	26.26	3.66	1.94	-	0.88	-
	Shanxi	46.98	3.85	27.83	3.37	-	1.11	1.26	1.33

Sulfuric acid leaching

Reaction kettle KCF02-10 is used for sulfuric acid leaching experiment, the sulfate concentration、solid-liquid ratio （g：ml）, temperature and other factors that have influence on the leaching performance are studied. The alumina leaching rate of fly ash is determined by analyzing the alumina content in leaching residue, the formula is as follows：

$$\eta = 1 - \frac{M_{residue} \times A_{residue}}{M_{ash} \times A_{ash}} \quad (1)$$

In the formula, Mresidue、Mash-stand for the quantity of leaching residue and fly ash；Aash、Aresidue-stand for the content of alumina in leaching residue and fly ash；η-stands for the alumina leaching rate.

Phase and surface texture analysis

X-ray diffractometer type PW3040/60（copper plate）of Holland Panalytical is used for analysing raw ore and roasting mineral, diffraction angle range 5 °<2θ<90 °, scanning rate 7 °/s. Scanning electron microscope SSX-550 is used for observation of mineral's micro structure.

Calculation of crystallinity of fly ash

Jade software 5.0 is used for analysis of crystallinity of fly ash from different areas：first, smooth the XRD pattern of the sample in order to get rid of all kinds of chance fluctuation（noise）；second, fit the strength of amorphous peak in the whole pattern；then fit manually until all the diffraction peak in XRD pattern fit；last, calculate the crystallinity of fly ash in different areas according to Jade formula.

Leaching Performance

The influence of sulfate concentration on the alumina leaching performance in fly ash

When different concentration of sulphuric acid is used for leaching fly ash from different areas, the alumina leaching rate and alumina content in leaching residue are different, the results are shown as figure1 and figure 2.The leaching experimental results indicate that for each kind of fly ash from these area, alumina leaching rates increase as sulfate concentration increases, when solid-liquid ratio and leaching temperature stay the same. When the concentration of sulfuric acid is 20%, leaching temperature is 150 ℃, particle size of fly ash is -74μm, solid-liquid ratio is 1:20, rotary speed is 500rpm and leaching time is 60min, the alumina leaching rate of fly ash from Western Inner Mongolia can reach up to 97%, and the alumina content of leaching residue are about 2%, while the leaching rate of Chongqing and Shanxi is 40.61% and 21.53%.

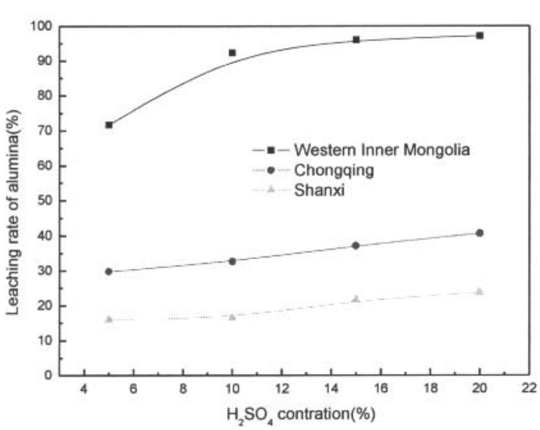

Fig.1 Effect of sulfate concentration on leaching rate of alumina
Leaching conditions: temperature150℃, solid-liquid ratio 1: 20, rotary speed 500rpm, leaching time 60min, particle size -74μm

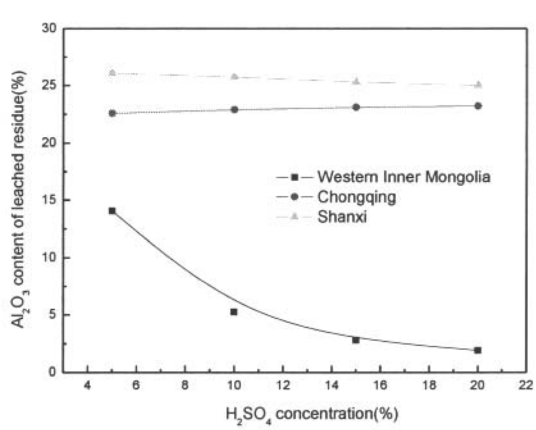

Fig.2 Effect of sulfate concentration on alumina content of leached residue of fly ash
Leaching conditions: temperature150℃, solid-liquid ratio 1: 20, rotary speed 500rpm,leaching time 60min, particle size-74μm

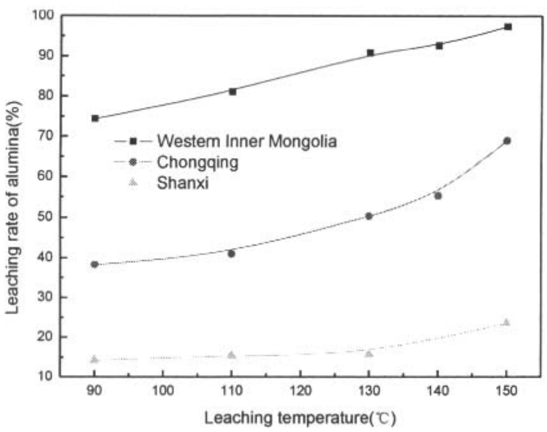

Fig.3 Effect of leaching temperature on leaching rate of alumina
Leaching condition: solid-liquid rate 1: 20, rotary speed 500rpm, leaching time 120min, sulfate concentration 20%, particle size -74μm

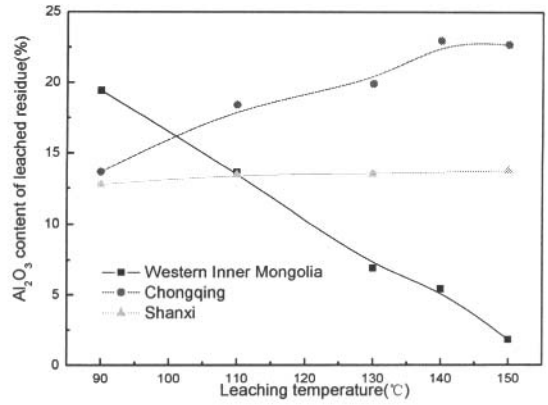

Fig.4 Effect of leaching temperature on lumina content of leached residue of fly ash
Leaching condition: solid-liquid 1:20, rotary speed 500rpm, leaching rate 120min, sulfate concentration 20%, particle size -74μm

The influence of temperature on alumina leaching performance of fly ash

The influence of temperature on alumina leaching performance is studied when temperature is 90~150℃, the results are shown as figure3 and figure 4, the results indicate that as temperature increases, alumina leaching rates of fly ash from different areas increase. When the leaching temperature is 150℃, the alumina leaching rates of fly ash from Western Inner Mongolia, Chongqing and Shanxi are 97.41%, 68.94% and 23.61%, separately. Alumina content of leaching residue is 1.79%, 13,63% and 12.73%, the leaching performance of fly ash from Inner Mongolia is much better than the other two areas.

Effect of leaching temperature on leaching performance of fly ash from West Inner Mongolia

After finding out the influence of leaching temperature and sulfate concentration on leaching performance of fly ash from different areas, further study is taken of factors which influence the alumina leaching performance and alumina content in leaching residue of fly ash from West Inner Mongolia, such as solid-liquid ratio, particle size and leaching time. The range of these factor is as follows: solid-liquid ratio 1:20~1:5, particle size -55~-150um, leaching time 30~120min. The results are shown as figure 5.

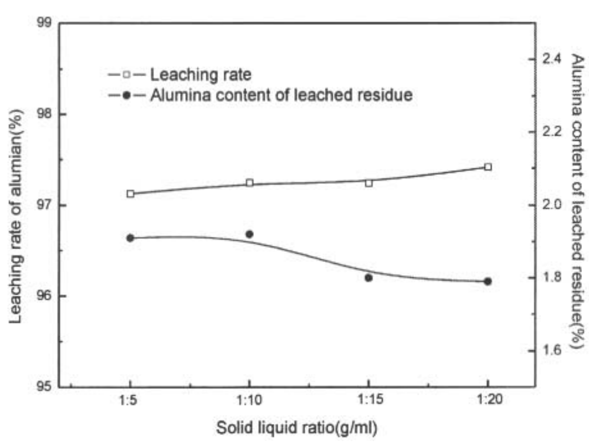

Fig.5 Effect of solid-liquid ratio on leaching rate of alumina
Leaching condition: rotary speed 500rpm, leaching time 120min, sulfate concentration20%, temperature 150℃, particle size -74μm

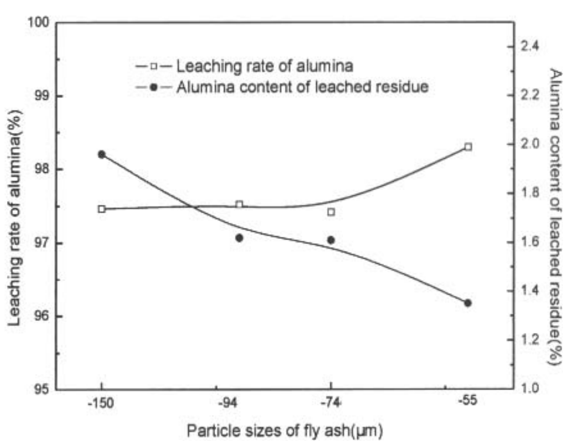

Fig.6 Effect of fly ash particle sizes on leaching rate of alumina
Leaching condition: rotary speed 500rpm, leaching time 120min, sulfate concentration 20%, temperature 150℃, solid-liquid ratio 1: 5

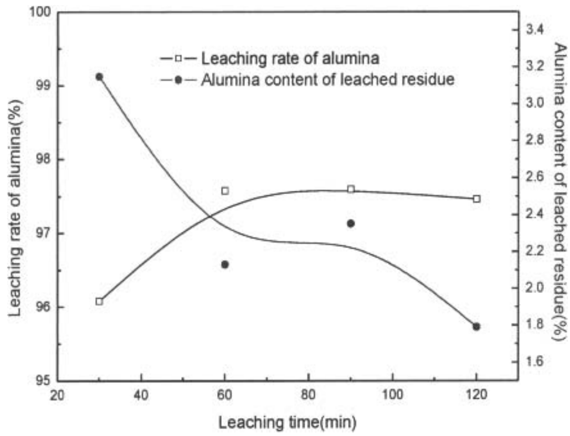

Fig.7 Effect of leaching time on leaching rate of alumina
Leaching condition: rotary speed 500rpm, solid-liquid ratio 1: 5, sulfate concentration 20%, temperature 150°C, particle size of fly ash-150μm

From the experiment results that figure5 show, when leaching temperature is 150°C, leaching time is 60min, solid-liquid ratio is 1:5, sulfate concentration is 20%, rotary speed is 500rpm and particle size is -150μm, alumina leaching rate of West Inner Mongolia can be still above 97%.

By comparing experimental results of the acid leaching performance of fly ash from different areas, we know the leaching performance of fly ash from West Inner Mongolia is the best. On the same leaching condition, the leaching rate of fly ash from West Inner Mongolia is 28.47% and 73.80% higher than the other two areas, when the leaching conditions are extended, the leaching performance of fly ash from West Inner Mongolia is still good.

Analysis of leaching mechanism

There are many kinds of mineral in raw coal in our country, such as kaolinite, boehmite, calcite, white mica, pyrite, marcasite, quartz, gypsum, etc. There are two reasons that cause great influence on the composition of the fly ash (phase, crystallinity, encapsulated effect between minerals), one is the differences of mineral composition in the raw coal, another is the different combustion conditions of the raw coal, and the influence plays a direct role in leaching performance of fly ash.[10] XRD patterns of the fly ash from these areas are shown as figure 8. As figure 7 shows, there are two main forms of Al element in West Inner Mongolia's fly ash: alumina (corundum type) and mullite, while there's mainly mullite in fly ash of the other two areas.

In the combustion process of raw coal, the decomposition processes of kaolinite in the fly ash are shown as following equation[11]

400~900°C

$$Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O=Al_2O_3{\cdot}2SiO_2+2H_2O \quad (2)$$

Above900°C

$$Al_2O_3{\cdot}2SiO_2=3Al_2O_3{\cdot}2SiO_2(mullite)+4SiO_2 \quad (3)$$

The related research results show that the fly ash from Inner Mongolia region contains a certain amount of boehmite [12], and this kind of the mineral in the combustion process reacts as follows:

$$\text{Above } 500°C \; 2AlO(OH)=Al_2O_3+H_2O \quad (4)$$

Under high temperature condition, alumina reacts with amorphous quartz decomposed from kaolinite and forms mullite:

Above 1200°C $3Al_2O_3+2SiO_2$ (amorphous) $=3Al_2O_3{\cdot}2SiO_2$ (5)

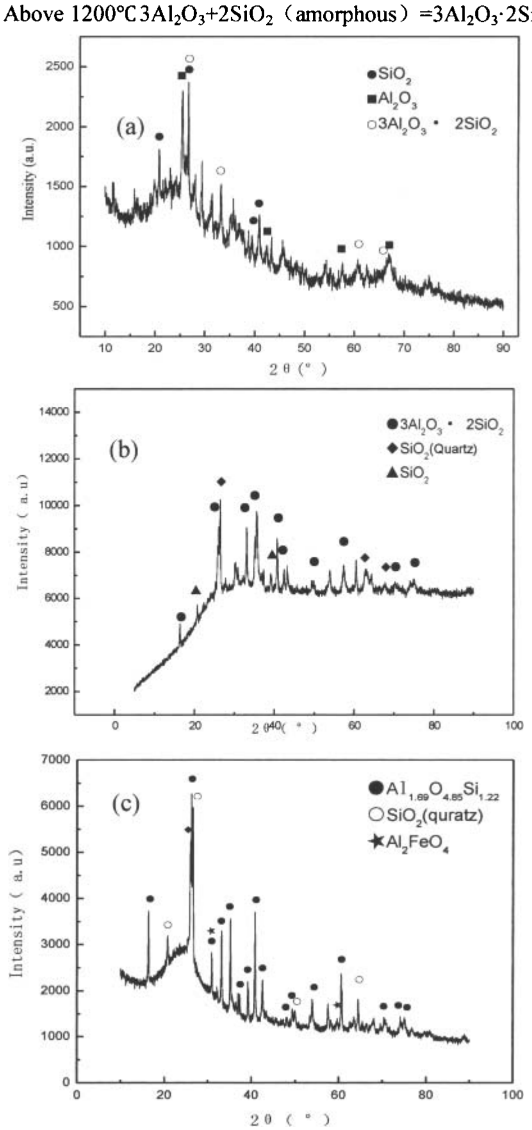

Fig.8 XRD patterns of fly ash in different regions
a- Western Inner Mongolia; b-Chongqing; c-Shanxi

During the acid leaching process, leaching performance of mullite phase in fly ash is poor, because the crystallinity of mullite is high, it needs high energy destroying Al-Si key. This is the reason why latent solvent should be joined when dealing with fly ash, and in this way high leaching rate can be obtained. There's lots of alumina phase in fly ash from West Inner Mongolia, because the alumina, which is produced by boehmite combustion, doesn't react completely with the phase of amorphous quartz, and exist in free state. This is good for increasing the leaching rate of alumina in fly ash. Analysis results of aluminum silicon phase crystals of fly ash in different areas are shown in chart 2[14-16]. Crystallinity formula is as follows[15~17]:

$$X_c = \frac{\sum I_c}{\sum I_c + \sum I_a} \tag{6}$$

In the formula, $\sum I_c$ is the total diffraction integral strength for crystallization part; $\sum I_a$ is the total diffraction integral strength for amorphous part.

Table 2 Crystallization of fly ash in different regions

Rigions	$2\theta/°$	$d/10^{-10}$m	H	A	$I/\%$	F	Xc
Western Inner Mongolia	26.138	3.4064	593	18489	100.0	0.358	75.98%
	21.352	4.1579	358	4773	25.8	0.142	
	42.368	2.1316	345	9971	53.9	0.308	
	56.283	1.6630	132	4061	22.0	0.362	
	69.787*	1.3465	79	13673	74.0	3.105	
Chongqing	37.149	3.2818	1351	21386	65.3	0.489	100%
	27.583	3.2364	2999	32739	100.0	0.212	
	34.427	2.6029	1595	14371	43.9	0.255	
	37.127	2.4195	1628	32320	98.7	0.617	
	42.390	2.1305	1603	15751	48.1	0.294	
	63.127	1.4716	999	8209	25.1	0.256	
	78.355	1.2193	260	12541	38.3	0.541	
Shanxi	16.461	5.3806	1179	4817	47.5	0.121	100%
	26.026	3.4208	2044	10146	100.0	0.147	
	26.303	3.3855	4242	9261	91.3	0.065	
	26.606	3.3475	3928	9409	92.7	0.072	
	33.292	2.6890	1350	7361	72.6	0.162	
	35.230	2.5454	900	5698	56.2	0.083	
	40.881	2.2056	2398	8109	79.9	0.100	
	60.659	1.5254	1337	6372	62.8	0.141	

Note: * represent fitting results of amorphous phase; 2θ is diffraction angle; d is interplanar distance; I is relative strength; H is peak height; A is peak area; F is FWHM.

From the calculation results of table 2 , it is known that there is no amorphous phase in fly ash from Chongqing and Shanxi, the FWHM of XRD diffraction peak of aluminum silicon phase in fly ash from the three areas is 0.6411、0.3324 and 0.1107. The wider the FWHM of XRD diffraction peak of mineral is, the worse the crystallinity is, and the higher the activity of the minerals is, XRD results indicate that the activity of fly ash from West Inner Mongolia is best, the activity of fly ash from Chongqing take the second place, the activity of fly ash from Shanxi is the worst.

Conclusion

(1) The acid leaching results indicate: when solid-liquid ratio is 1:20, rotary speed is 500rpm, leaching time is 120min, sulfate concentration is 20%, particle size is -74μm, the leaching rate of these three areas are 97.41%, 68.94% and 23.61%, the

alumina content of leaching residue is 1.79%, 13.63% and 12.73%, when extending the leaching conditions, the leaching performance of fly ash from West Inner Mongolia is still good.

(2) The main reason that the leaching performance of fly ash from different areas is different is because the difference in crystallinity, encapsulated glass phase of Al-Si phase in fly ash, the crystallinity for Western Inner Mongolia is 75.98%, while there is no non-crystalline phase in fly ash from other two areas, the crystallinity are both 100%, the average FWHM of XRD diffraction peak of Al-Si phase in fly ash from the three areas are 0.6411, 0.3324, 0.1107, the crystallinity of fly ash from West Inner Mongolia is the worst.

(3) The structure of fly ash from West Inner Mongolia is loose and there is little glass phase, while there are lots of glass phase in the fly ash from Chongqing and Shanxi, in contrast with the fly ash from Chongqing, the surface of the glass phase in fly ash from Shanxi is more compact, so its activity is much lower, the analysis results of XRD and SEM verify the results of leaching experiments well.

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