Research Development on Extracting of Aluminum from the Fly ash by Roasting Acid Leaching

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Abstract. The conditions of roasting activation of fly ash with NaF as assistant and extraction of Al_2O_3 by acid leaching were studied. The effects of conditions of roasting activation and acid leaching on the leaching rate of aluminum from fly ash were investigated of the pre- and post-extracted fly ash were analyzed by SEM.The results show that the optimal conditions of roasting activations were obtained as:mass ratio of coal fly ash to NaF 5:1, under time 60 min,temperature 850℃;the optimal conditions of leaching temperature80℃,leaching time120min, concentration of H_2SO_4 1.2 mol/L, liquid-to-solid ratio 12 mL/g, the dissolution rate of aluminum reached 94.1%. The preparation of Al_2O_3 was obtained after edulcoration and production.

1 Introduction

It has always been an important problem needed to be solved urgently to utilize fly ash comprehensively.At this moment, the main application of fly ash in domestic and oversea are concentrate on the aspects of industries of building and transportation and so on, which is low value-added exploit, with low use ratio. Therefore the future direction of utilization technology of fly ash is to improve the use ratio of fly ash and develop product of high additional value. Fly ash contains a large number of valuable elements,mainly are silicon and aluminum, especially the content of aluminum oxide ,which can be a good alternative of bauxite, is as high as 30% - 45% the highest purity may reach to 50 percent.In The Comprehensive Utilization Of Fly Ash Management Approach that has just been revised and was put into effective in 1st of March, 2013, there are a serial of specific encouraging policies to develop the technology to extract alumina oxide and related products that processes high added value.Accordingly,there is encouraging future to study the law of sulfide of aluminum oxide .

The process of extracting aluminum oxide from fly ash has been studied by both institutions in domestic and oversea, mainly are methods of alkali sintering and acid leading.Among them, acid leading method is the prime choice of comprehensive fly ash utilization.

2 Experimental

2.1 Agentia,Material and Instrument

Cup Chemical materials: NaF，H_2SO_4(analytical grade) .The coal fly ash was obtained from a thermal power plant in Shanxi, China. Chemical composition of coal fly ash was shown in Table1. The total content of SiO_2, Al_2O_3 and Fe_2O_3 reached above 87%.

Tab.1Chemical composition of coal fly ash（%，ω）

Chemical component	SiO_2	Al_2O_3	CaO	MgO	TiO_2	Fe_2O_3	Loss on ignition	Integral dose
Chemical constitution	43.28	39.00	1.30	1.15	0.65	5.43	8.90	99.56

The SEM in Figure 1 shows that fly ash contains a lot of needle like or rod like morphology of mullite crystal, and major aluminum silicate vitreous spherical.
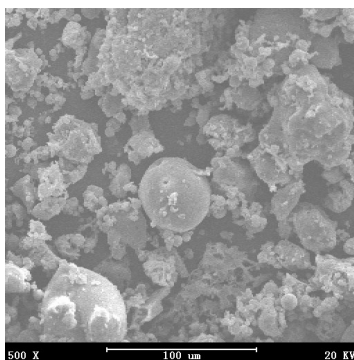
Fig.1 SEM photograph of the fly ash

Main instruments: HH-4 type digital constant temperature water bath pot, SHB-3 type circulating water vacuum pump, the type 722 visible light spectrophotometer, DHG-9070A type a thermostatic drum wind drying oven

2.2 Experiment design

Two key steps of extracting aluminum oxide are the process of calcination and acid leaching.

Calcination: weigh a certain amount of fly ash calcination, add the calcining additive NaF, mix evenly, put them in a silver crucible, and placed in calcination in a muffle furnace. The calcination temperature range is 500-1000℃. After a certain of calcination time, take out and cool to room temperature. The samples of acid leaching were obtained.

Acid leaching: calcined product was ground and sieved to 200 mesh size. Acid leaching experiments were done in the constant temperature water-bath water (500 ml three-necked flask was used for leaching container), and were mixed in a flask with agitation equipment. To prevent acid volatile and moisture evaporation, three-necked bottles were needed to connect condenser device). Under the condition of considering four influencing factors, the pickling time, acid concentration, solid-liquid ratio, reaction temperature and so on, sulphuric acid condenser device was applied to dissolve out of Al_2O_3. After reaction fully, impurity was removed, products were made into Al_2O_3 powders preparation stage.

2.3 Analytic method

The measurement of each component in fly ash adapts GBT 1574-2007 component analysis of coal fly ash.

3 The Experiment Result and the Discussion to It

3.1 Activation of Fly Ash and Factor Analysis   Influencing it

Aluminum oxide and silicon exist in fly ash in the form of complicated double salt   aluminum vitreous and alusite, whose acid solubility is extremely poor, for it need powerful energy to break the silicon and aluminum key to transform from stable aluminum to mineral substance soluble to acid. Take calcination time, temperature and dosage of activator as impact factors, the orthogonal experiment was designed to conduct with three different amount. To ensure better condition for process of calcination and activation, the parameter of acidleach should be fixed in: temperature:80℃;concentration of H_2SO_4,1.2mol/L;liquid-solid ratio,20:1（ml：g）.

Result can be represented as Chart 2, from the experiment designed according to orthogonal table. It can be seen that the three factors impacting fly ash activation are calcination temperature, the ratio of Fly Ash between NaF in fly ash and calcination time in sequence according to the importance. It is acknowledged from Analysis of Means that optimum condition for activation calcination is to maintain the temperature at 850 ℃, the ratio between Fly Ash and NaF being 20:4 and keep calcination time 120min.

Factor analysis shows that the longer calcination time is, the higher dissolution rate of Al_2O_3 will be. But taking practical reasons into account, calcination time is designed as 60 min since that calcination time impacts activation less obviously, thus the preferred process condition for

activation calcination is to maintain the temperature at 850 ℃, the ratio between Fly Ash and NaF being 20:4 and keep calcination time 60min.

Tab.2   The result of orthogonal experiments

Number	Calcination time （min）	Calcination temperation （℃）	Caol ash/NaF （ω）	Al_2O_3 solubility （%）
1	60	650	10:1	61.91
2	60	750	10:1.5	81.72
3	60	850	10:2	96.10
4	90	650	10:1.5	74.81
5	90	750	10:2	89.70
6	90	850	10:1	79.99
7	120	650	10:2	80.81
8	120	750	10:1	73.21
9	120	850	10:1.5	92.25
mean1	79.910	72.510	72.000	—
mean 2	81.797	81.543	81.927	—
mean3	82.090	89.743	88.870	—
range	2.190	17.273	16.890	—

3.2 Acid Leaching of Coal Ash and Factor Analysis   Influencing It

The experiment has studied key factors affecting dissolution rate of Al_2O_3 such as temperature of acidleach, time of acidleach, concentration of H_2SO_4 and ratio of solid and liquor, adapting the method of with one single factor changed and other fixed.

3.2.1 Influence of Temperature to Dissolution Rate of Al2O3

Fixed experiment condition is setting acid leaching time as 120min, concentration of H_2SO_4 as1.2mol/L and ratio of solid and liquor as 20:1. Given the demand of low energy of experiment,the experiment conducting six single factor analysis in the temperature below 100℃, obtains the result as following graph.

Tab.3   Influence of the temperature to alumina dissolving ratio

Temperature/℃	50	60	70	80	90	100
Dissolving ratio/%	66.1	79.8	89.9	94.1	94.5	94.6

Tab.3 shows that, as the increase of reaction temperature, the dissolving ratio rises, too, because with the temperature rises, the move speed of molecule adds, viscosity of solution decrease and diffusivity increases hence lead to accelerate reaction speed. The change will be more obvious in the temperature of 50℃~80℃. When temperature is above 80℃, there are still the rising trend of dissolving ratio, while a slow one. Considering to decrease energy consuming, the suitable temperature is 80℃.

3.2.2 The Influence of Time of Acid Leaching to Dissolving Ratio of Al3O2

Fixed experiment condition is setting acid leaching temperature as 80℃, concentration of H_2SO_4 as1.2mol/L and ratio of solid and liquor as 20:1. The result of experiment changing acid leaching time as single factor is demonstrated as Tab.4.

Tab.4   I Influence of the time treated by H_2SO_4 to alumina dissolving ratio

Time /min	30	60	90	120	150	180
Dissolving ratio/%	76.8	85.0	94.1	94.1	94.1	94.3

It can be learned that with the increase of acid leaching time, the alumina dissolving ratio rises constantly. And it would be up to maximum when the leaching time is 120 minutes. While aluminum oxide dissolution rate was not significantly increase as it continued to increase the reaction time. That is because at reaction initial stage, sulfuric acid was in high concentration, the reaction product layer was not completely healed, the activity site of the solid reaction can be sufficiently in contact with the sulfuric acid, and then the dissolution rate of aluminum increased substantially. As the reaction proceeded, the reaction interface healed, the rate of inner diffusion slowed, the concentration of sulfuric acid was reduced, therefore, the dissolution rate would not substantially increase even if the time was extended[7]. The extension of acid leaching time would result in losses of equipment and energy, and therefore 120min was chosen for leaching time.

3.2.3 The Influence of the Concentration of Sulfuric Acid to Dissolving Ratio of Al2O3

Owing to the strong oxidized characteristic of the sulfuric acid,the chemical reaction will be more intense than hydrochloric acid.

Fixing experiment condition is setting leaching time as 120 minutes and ratio of solid and liquor as 20:1.The result of experiment changing concentration of sulfuric acid is demonstrated as Tab.5 .

Tab.5   Influence of the time treated by H_2SO_4 to alumina dissolving ratio

H_2SO_4 /mol/L	0.6	0.9	1.2	1.5	1.8	2.1
Dissolving ratio/%	75.8	85.0	94.1	94.2	94.3	94.0

Tab.5 shows that,with increase of sulphuric acid concentration,the dissolving ratio rises.As the concentration of sulfuric acid is up to 1.5mol/L,the dissolving ratio is up to 96%.However the dissolving ratio would reduce as the concentration of sulfuric acid continues to increase.This is because as the increase of the oxidizing property of solution,the dissolving ratio would rise if the concentration of sulfuric acid is less than 1.5mol/L.And if sulphuric acid concentration is more than 1.5mol/L,part of the aluminum sulfate in the form of crystal exists in filter residue which result in the decrease of the dissolving ratio.aluminum oxide dissolution rate was not significantly increase as the concentration of sulfuric acid is from 1.2mol/L to 1.5mol/L.Thus considering to decrease energy consuming ,the suitable sulphuric acid concentration is 1.2mol/L.

3.2.4 The Influence of Ratio of Solid and Liquor to Dissolving Ratio of Al2O3

Fixed experiment condition is setting leaching temperature as 80 centigrade and concentration of H_2SO_4 as 1.2 mol/L .The result of experiment changing ratio of solid and liquor as single factor is demonstrated as Tab.6 .

Tab.6   Influence of NaF/ash ratio to alumina dissolving ratio

L:S /mL/g	0.6	0.9	1.2	1.5	1.8	2.1
Dissolving ratio/%	75.8	85.0	94.1	94.2	94.3	94.0

Tab.6 shows that,as the increase of the ratio of liquid-solid ,the speed of dissolving ratio rises when the ratio of liquid-solid is less than 12.As the ratio of liquid-solid is more than 12,the increase trend of dissolving ratio become slower.This is because as the increase of the ratio of liquid-solid,the solid-liquid interface increases which lead to the the rises of dissolving ratio.Considering to decrease energy consuming,the suitable ratio of liquid-solid is about 12:1.

3.3 Characteristics of fly ash and fly ash after acid leaching

The SEM(scanning electron microscope)morphologies of the pre-and post-extracted fly ash
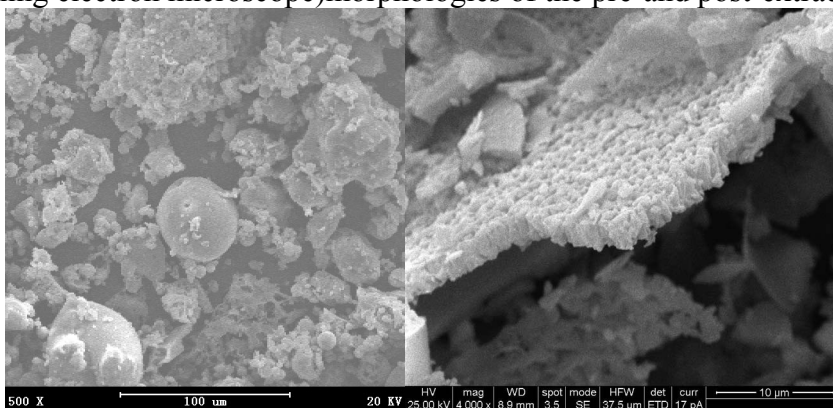

Fig 2 SEM morphologies of the pre- and post-extracted fly ash

Picture 6 indicates the morphology of fly ash changes a lot, the previous morphology, approximate sphere were destructed and formed nearly flake structure with high porosity in surface.

3.4 Product of Extraction and Manufacture

Through the reaction of acid leach, the alumina dissolving rate can reach to 94.1%, but elements in fly ash like Si, F, Ti,Ca and Mg have to be dissolved too in the meantime to ensure acquiring high quality alumina product by procedure of extraction and manufacture.

pH value of aluminum and iron complete precipitation was lower compared with that of other oxides, so it was considered that the pH range was controlled in order to remove iron. Sodium hydroxide solid was added to adjust pH value between 5-6, and then it was filtered to precipitate aluminum and iron, 8mol/L NaOH solution was added in the coprecipitation of aluminum and iron, the pH was adjusted between 12-12.5, then $Al(OH)_3$ precipitation was completely dissolved and $NaAl(OH)_4$ was generated, the iron was removed by filtration, and finally washed, iron precipitation was dried, iron was effectively recovered.

The obtained $NaAl(OH)_4$ solution by reaction consisted a bit of SiO_2 and Na_2SiO_3. The essence of sodium aluminosilicate solution desilication process is that SiO_2 was changed into compounds of small solubility. Saturated lime water could be added to the solution by using the method of depth desilication. An amount of lime was added so that SiO_2 was formed into garnet hydrate precipitation. CO_2 gas was bubbled into sodium aluminate solution through deep desilication for carbonation, and aluminum hydroxide precipitation was obtained. The precipitate was filtered, washed, ashed and heated 60min for dehydration in a muffle furnace at the temperature of 230℃. $Al(OH)_3$ product was obtained. The product was heated to 800℃ and continued calcined for 2h.Their chemical composition were analyzed (table7). The products met the requirements of metallurgical grade alumina and national secondary Al_2O_3 standard.

Tab.7 Chemical composition of Al_2O_3(%，ω）

Composition	Al_2O_3	SiO_2	Fe_2O_3	Integral dose
Content	99.15	0.03	0.002	99.182

4 Conclusion

Using NaF as auxiliaries to calcine and active fly ash, the orthogonality represents that factors impacting fly ash activation are calcination temperature, the ratio of Fly Ash between NaF in fly ash and calcination time in sequence according to the importance;Utilizing H_2SO_4 to dissolve fly ash, single-factor experiment indicates that :with the condition of temperature in 80℃,concentration of H_2SO_4,1.2mol/L;liquid-solid ratio being12:1, alumina dissolving ratio can reach 94.1%;The

morphology of fly ash changes a lot, from approximate sphere to flake structure with high porosity in surface.

Acknowledgement

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