

Recovery of Alumina from Coal Fly Ash by CaCl_2 Calcination Followed by H_2SO_4 Leaching

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Abstract

In this paper, a calcination-leaching method by using CaCl_2 and H_2SO_4 to recover alumina from coal fly ash (CFA) is developed. The process conditions including the parameters of CaCl_2 content, calcination temperature and time, acid concentration and leaching time are studied. Heat treatment under 900°C for 1 h of the ash with 80 wt.% CaCl_2 significantly enhances the alumina leachability (>96.6%) in comparison with the directing acid-leaching (2.31-4.78%) method. The recovery rate increases dramatically with the increasing of CaCl_2 content from 20% to 80%, and a H_2SO_4 leaching time from 10 minutes to 1 hour as well, but it remains near constantly as the increasing of CaCl_2 dosage >80% or acid-leaching time >1 h. The reaction mechanism is studied by X-ray diffraction (XRD) analysis to determine the crystalline phases change. The results indicate that quartz, mullite and amorphous phases have been destroyed after calcination with CaCl_2 and transformed to gehlenite, calcium aluminum silicate, andradite, wollastonite and mayenite, which are susceptible to acid leaching. The mineralogical characteristics of roasted clinker indicate that molten CaCl_2 can promote the incorporation of Ca into silica and silicates and result in the progressive susceptibility to acid attack. The potential chemical reactions during calcinating and leaching processes are also studied via chemical equations. The reuse and resource of coal fly ash can reduce the environmental impact of ash heap and the heavy metal pollution to the surrounding environment.

Keywords: Coal fly ash; Calcination; Leaching; Alumina recovery

Introduction

Coal-burning power plants consume pulverized solid fuels and produce a large amount of coal fly ash (CFA) as residues. The coal-fired generation accounted for 41% of the world electricity supply in 2006, while the share is projected to be 43% in 2030 [1]. In 2015, the generation of CFA in China reached 570 million metric tons [2]. The deposit of CFA causes severe environmental problems such as air, soil and ground water pollutions, and it's also a threatening to the health of the residents around the deposit site. Therefore, the treatment of CFA is becoming more and more significant. The reuse of CFA has been widely studied in recent years [3]. In the current state, the utilization of CFA is carried out mainly in the field of architectural materials [4,5], however, these materials are with low valued. High-value utilizations of CFA, such as soil reclamation, wastewater treatment and extraction of valuable metals have been applied in the industrial applications which are proved to be essentially useful [6-8].

Using CFA to produce alumina is one of the high-value utilizations of CFA. The recovery of alumina from coal ash or clay are based on the applications of hydrometallurgical processes such as acid or base leaching, precipitation, solvent extraction and re-crystallization [9-16]. Recently, Matjie [13] calcined the Sasol CFA from South Africa with calcium oxide under $1000\sim 1200^\circ\text{C}$, then the calcined mixture was leached with sulfuric acid at a concentration of 6.12 mol/L under 80°C for 4 h. The aluminium extraction efficiency was about 85%. Bai et al. [17] reported another acid leaching method by decomposing the mulite phases in CFA via calcining the CFA with the concentrated sulfuric acid at 300°C . The alumina extraction efficiency in this method was up to 85%, the same results are obtained with the method reported by Matjie [13]. Even though the process of extracting alumina has become feasible, there are a number of problems exist. Nitric acid and hydrochloric acid leaching processes for the recovery of alumina

and other minerals have been developed a long time ago, however these processes found little practical applications due to the highly corrosive nature of the concentrated chloride or nitrate solution [13], in addition, hydrochloric acid and nitric acid are expensive lixivants in terms of acid cost and large evaporative losses, which make these processes extremely uneconomic. In contrast, sulfuric acid is cheaper than nitric acid and hydrochloric acid and can be obtained easily. Therefore, from an economical point of view, using sulfuric acid as a lixiviant for the leaching processes, especially for industrial scale process is an optimal choice [18]. Moreover, large volume of residue arising from the sintering processes (normally 8 to 10 times to initial CFA) will cause the secondary pollutions [19].

In this paper, we report a new process to recover alumina from CFA. The CFA sintered with CaCl_2 as additive over $900\sim 1000^\circ\text{C}$ and leached with H_2SO_4 at optimal conditions. The advantages of the process including: (1) lower sintering temperature than widely used lime-sinter process and lime-soda-sinter process. (2) the unreacted CaCl_2 can be easily removed by water washing, which can effectively reduce the acid consumption in acid leaching. (3) the high extraction efficiency of alumina (more than 95%).

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Received December 22, 2016; **Accepted** December 28, 2016; **Published** January 09, 2017

Citation: Sun Y, Liang Z, Sun F, He S, He M, et al. (2017) Recovery of Alumina from Coal Fly Ash by CaCl_2 Calcination Followed by H_2SO_4 Leaching. J Environ Anal Toxicol 7: 427. doi: [10.4172/2161-0525.1000427](https://doi.org/10.4172/2161-0525.1000427)

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Methods and Materials

Materials

The CFA sample was obtained from Junliangchen coal-fired power plant, located in Tanggu District, Tianjin. 10 kg CFA sample was obtained from the electrostatic precipitator collection bins of the power plant. The sample was dried at 105°C for 24 h to a constant weight, crushed into small particles that passed through a 10-mesh sieve, and the resulting sample was then ground by using a planetary ball mill (QM-3SP2, Nanjing University Instrument Factory, China) to produce a 200-mesh powder, which was then homogenized prior to use and further analysis. CaCl₂ and H₂SO₄ (special reagent grade) were purchased from Beijing Modern Oriental Fine Chemicals Corporation (Beijing, China). All reagents were used as received. The deionized water which prepared by a laboratory water purification system (DW 100, Shanghai Hitech Instrument Co., Ltd, Shanghai, China), was used in all experiments and sample analysis.

H₂SO₄ direct leaching test

A total amount of 10.00 g CFA powder was added to 100 mL H₂SO₄ solution (1, 2, 3, 4, 6 or 8 M) in a beaker, the mixture was heated to 80°C, then stirred magnetically at 300 rpm for 2 h to ensure that the slurry mixed homogeneously and the leaching process proceeded sufficiently. The slurry was centrifuged at 10,000 rpm for 10 minutes, and the supernatant was finally collected. The volume of the supernatant and its alumina concentration were determined. The solid residue was washed with distilled water until no aluminum was detected, dried at 105°C for 24 h, and the weight was recorded. The leaching test was performed in duplicate.

CaCl₂ roasting combined with H₂SO₄ leaching

A total amount of 10.00 g CFA powder was mixed with measured amounts of powdered CaCl₂ (2.00, 4.00, 6.00, 8.00, 10.00, 12.00, 14.00, 16.00 and 18.00 g) using an agate mortar. The mixture was transferred to a corundum crucible and heated in a SX-GD7123 muffle furnace (Tianjin Central Experimental Furnace Co., Ltd., Tianjin, China). The temperature protocol was as follows: 30 to 900°C with a heating rate of 10°C/min, followed by constantly heating under 900°C for 120 minutes. The clinker was then allowed to natural cool down to room temperature (RT). The weight of the roasted clinker was recorded to evaluate the loss on ignition (LOI) prior to washing with distilled water and drying at 105°C. The procedure used for the H₂SO₄ leaching of the clinker at room temperature was similar to that for the direct H₂SO₄ leaching described in Section 2.2, except that the H₂SO₄ concentration was 1, 2, 3, 4, 6 or 8 M, or the slurry was obtained at certain time intervals including 10, 20, 30, 60, 90, 120, 150 and 180 min. All the experiments were performed in duplicate. The concentrations of Al, Si, Fe, Ti and Ca in the solution were determined.

The optimal reaction parameters of alumina extraction process

More than 95% of alumina in the CFA has been recovered through the steps mentioned above. In order to get the optimal leach rate, a series of experiments are operated to optimize the reaction parameters. The parameters include the CaCl₂ dosage of 10 grams CFA (2-24 g), calcination temperature (700-1100°C), calcination time (10-180 min), acid concentration (1-8N), and leaching time (10-180 min).

Analytical methods and characterization of CBA

Chemical compositions of the coal bottom ash were determined by an X-Ray Fluorescence (XRF) (XRF-1800, Shimadzu Company). All the compounds in the ash were evaluated in form of oxides.

The solid samples were crushed and ground with a pestle and mortar, and each powdered sample was subjected to XRD analysis using a D8 Advance X-ray diffractometer system with Cu K radiation. Scans were run from 10° to 90° (2θ) with the increment of 0.02°, operating at the voltage of 40 kV and the current of 40 mA.

Results

Characterization of CFA

Table 1 shows the chemical compositions of CFA, which indicates that the major components are Al₂O₃ and SiO₂. In CFA, Al₂O₃ accounts for 37.9%, which is characterized as high-alumina CFA. Figure 1 is the XRD pattern of CFA, it can be seen that the main components are mullite (the JPCDS card number: 15-0776), quartz (the JPCDS card number: 46-1045) and amorphous phase

H₂SO₄ leaching of alumina in CFA

CFA is directly leached by H₂SO₄ according to the orthogonal test below. The results of orthogonal test are shown in Table 2. It can be seen that the alumina extraction rate increases with the reaction time rising, and decreases with acid concentration declining. However, liquid/ash has little effect on the alumina extraction rate. The effects of reaction time, H₂SO₄ concentration and liquid/ash weakened according to the order. The alumina extraction efficiency remains less than 5% without calcinated addition, which is confirmed by Nayak [20]. Therefore, it can be seen that in CFA, mullite, quartz and glass phase can't be destroyed by sulfuric acid without calcinating with additive.

Effect of CaCl₂ roasting and H₂SO₄ leaching of alumina in CFA

The main procedure of recovery alumina from CFA is shown in Figure 2, which indicates produce of Al₂O₃ is feasible under this experiment condition.

CFA is calcinated by CaCl₂ and leached with H₂SO₄ at different conditions, including the CaCl₂/CFA ratio, calcination temperature, calcination time, acid concentration and leaching time are shown in Figure 3a-3e respectively.

Components	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	TiO ₂	CaO	MgO	LOI
Mass fraction (%)	37.9	48.0	4.3	1.3	6.1	0.1	2.3

Table 1: Chemical composition of CFA.

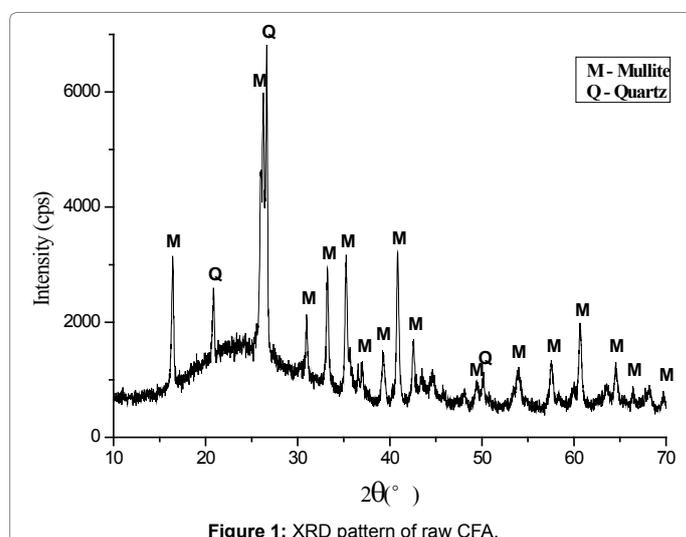


Figure 1: XRD pattern of raw CFA.

Figure 3a shows the alumina extraction efficiency as a function of CaCl₂. The alumina extraction efficiency increases sharply from 43.72% to 95.56% as the CaCl₂ dosage increases from 20% to 80%, and then remains almost unchanged even 100% of CaCl₂ is added in.

Figure 3b shows the alumina extraction efficiency as a function of calcination temperature. The alumina extraction efficiency increases dramatically from 71.58% to 97.85% as the calcination temperature rises from 700°C to 900°C, and then stays stable under higher temperature which reaches 1100 °C during the test.

Figure 3c shows the alumina extraction efficiency as a function of calcination time. The alumina extraction efficiency increases steeply from 47.79% to 96.59% as the calcination time increased from 10 min to 60 min, and then remains nearly unchanged, despite more calcination

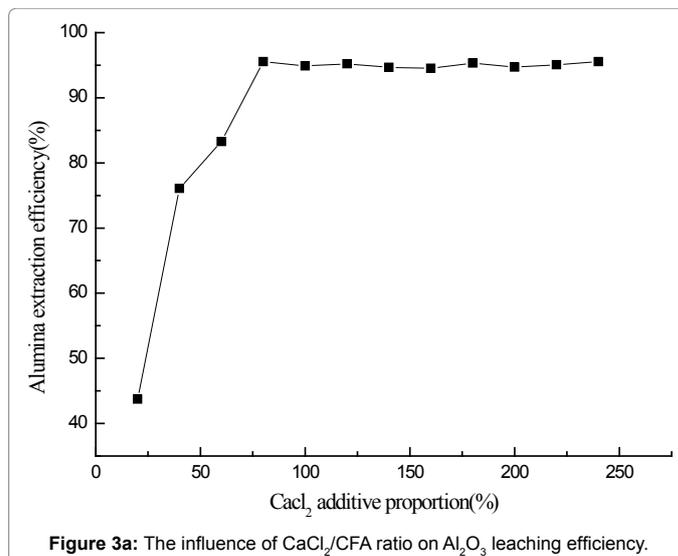


Figure 3a: The influence of CaCl₂/CFA ratio on Al₂O₃ leaching efficiency.

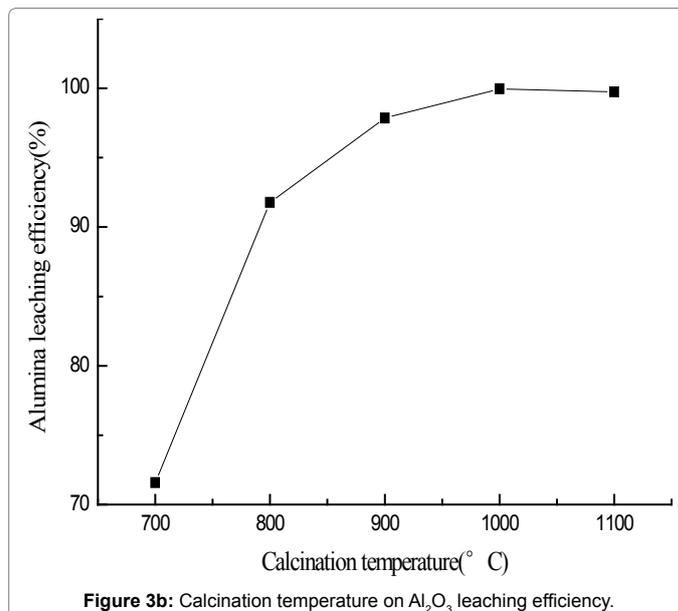


Figure 3b: Calcination temperature on Al₂O₃ leaching efficiency.

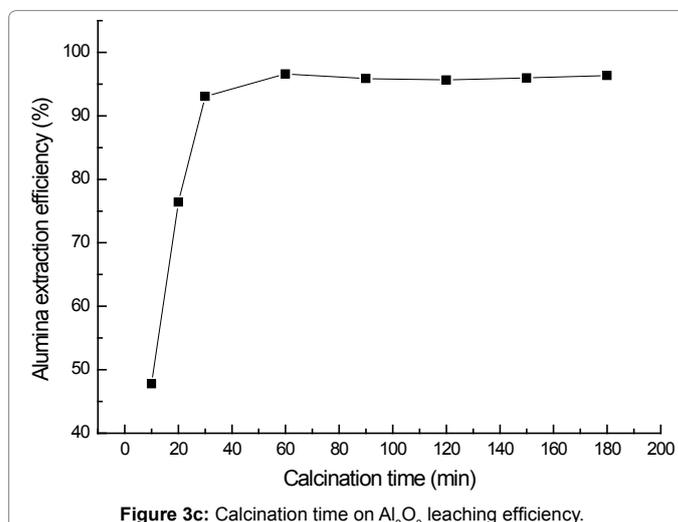


Figure 3c: Calcination time on Al₂O₃ leaching efficiency.

No.	Reaction time (h)	Acid concentration (mol/L)	Liquid ash ratio (ml/g)	Extraction efficiency of alumina (%)
1	2	8	5	2.31
2	2	4	10	2.88
3	2	2	15	3.14
4	2	1	20	3.6
5	4	8	10	2.34
6	4	4	5	3.27
7	4	2	20	3.48
8	4	1	15	3.62
9	8	8	15	2.75
10	8	4	20	3.6
11	8	2	5	4.16
12	8	1	10	4.06
13	16	8	20	3.52
14	16	4	15	4.32
15	16	2	10	4.78
16	16	1	5	4.68
Average 1	2.98	3.99	3.6	-
Average 2	3.18	3.89	3.52	-
Average 3	3.64	3.52	3.46	-
Average 4	4.33	2.73	3.55	-
Range	1.35	1.26	0.14	-

Table 2: The orthogonal test of direct acid leaching and results.

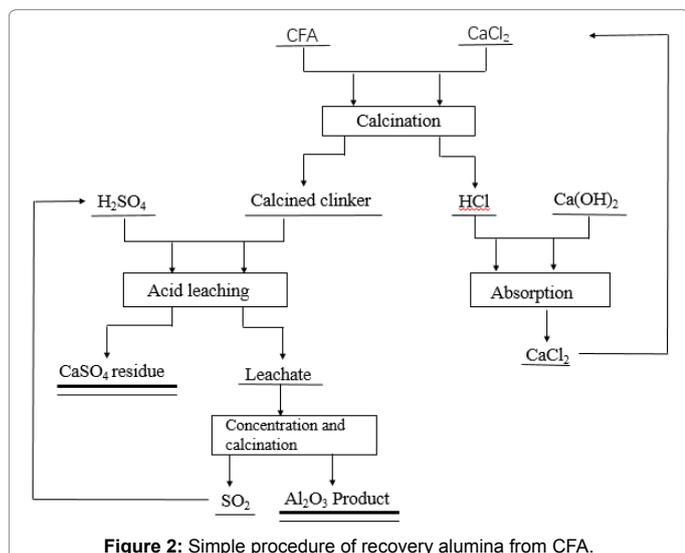


Figure 2: Simple procedure of recovery alumina from CFA.

time is reacted. The relationship between alumina extraction efficiency and leaching time is nearly linear (from 47.79% to 93.05%) from 10 min to 30 min, and after that, the alumina extraction efficiency only increases by 3.0% even when the calcination time is increased up to 3 h.

Figure 3d shows the alumina extraction efficiency as a function of H₂SO₄ concentration. The alumina extraction efficiency almost remains unchanged, from 94.89% to 96.77%, despite more H₂SO₄ concentration is added. This result indicates that the increase of H₂SO₄ concentration has little effect on the alumina extraction and at 1M H₂SO₄ the efficiency has reached the optimal condition

Figure 3e shows the alumina extraction efficiency as a function of leaching time. The alumina extraction efficiency increases from 79.78% to 93.20% as the leaching time increased from 10 min to 60 min, and then remains nearly unchanged, despite longer time is reacted.

As discussed above, the optimal as well as economic conditions for extracting alumina in the ash is a dosage of 80% CaCl₂ and calcinating at 900°C for 1 h, leaching with 1 M H₂SO₄ for 1 h, respectively. At those conditions, the leaching efficiency of alumina reaches as high as 96.6%.

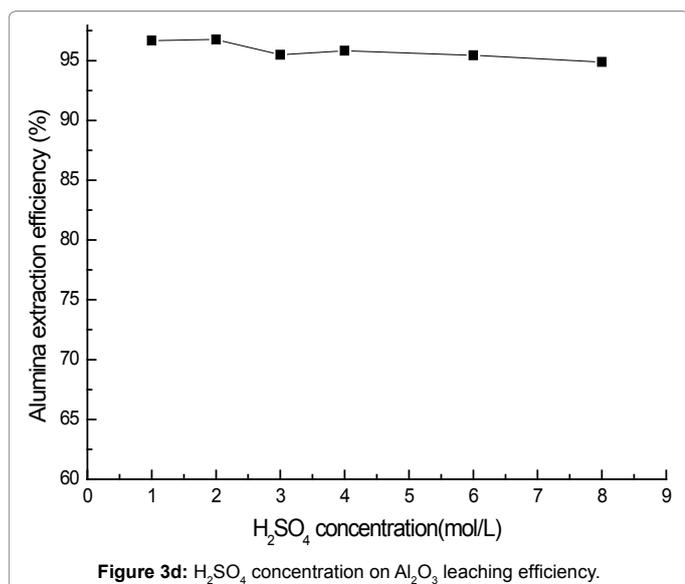


Figure 3d: H₂SO₄ concentration on Al₂O₃ leaching efficiency.

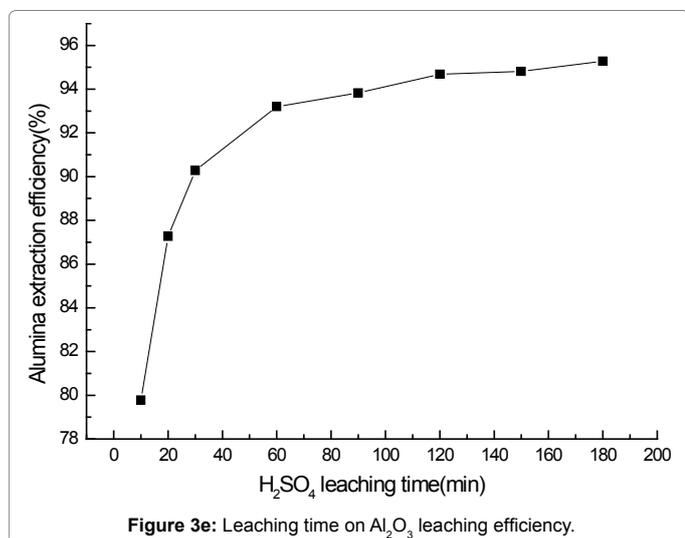


Figure 3e: Leaching time on Al₂O₃ leaching efficiency.

Possible reaction mechanism

The XRD pattern of raw CFA is shown in Figure 1, which indicates that the main crystal components in CFA are mullite and quartz, and the non-crystal component is amorphous glass. As mullite phase is a relative stable crystal and cannot dissolved in acid or alkali [21], so the extraction of alumina becomes difficult unless it has been destroyed.

Figure 4 shows the XRD patterns of calcined CFA, calcined clinker at 900°C and leached residue. Quartz and mullite are the major crystalline minerals in the raw ash, accompanied by a moderate amount of amorphous glass phase [22,23]. After the raw ash underwent an intense mineralogical transformation via high-temperature solid-state reactions with CaCl₂, quartz and mullite were replaced by several new crystalline phases of silicates, aluminosilicates and aluminates during this procedure, which include wollastonite (CaSiO₃) (the JPCDS card number: 42-0550), calcium aluminium silicate (Ca_{0.88}Al_{1.77}Si_{2.23}O₈) (the JPCDS card number: 23-0105), mayenite (Ca₁₂Al₁₄O₃₃) (the JPCDS card number: 48-1882), andradite (Ca₃Fe₂(SiO₄)₃) (the JPCDS card number: 10-0288) and gehlenite (Ca₂Al₂SiO₇) (the JPCDS card number: 35-0755). After H₂SO₄ leaching, the acid decompositions of these new crystalline phases (namely “gelatinizing silicates”) were expected to involve silica dissolution and associated gelation [24]. Therefore, the new formed crystalline components were partly transformed to anhydrite (CaSO₄), which are sensitive to acid attack.

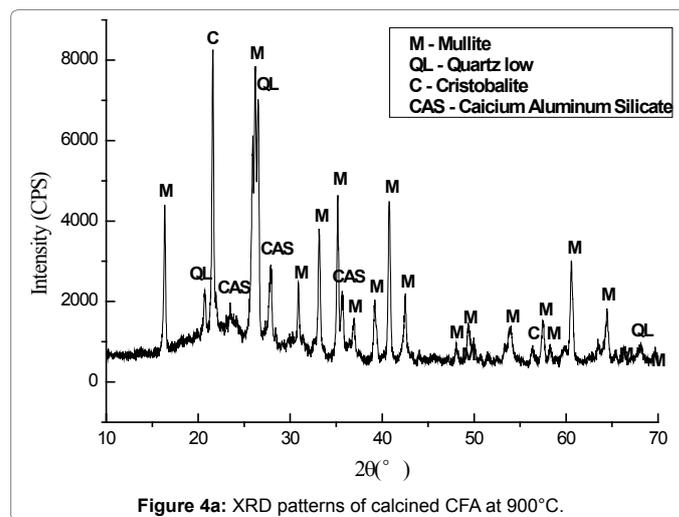


Figure 4a: XRD patterns of calcined CFA at 900°C.

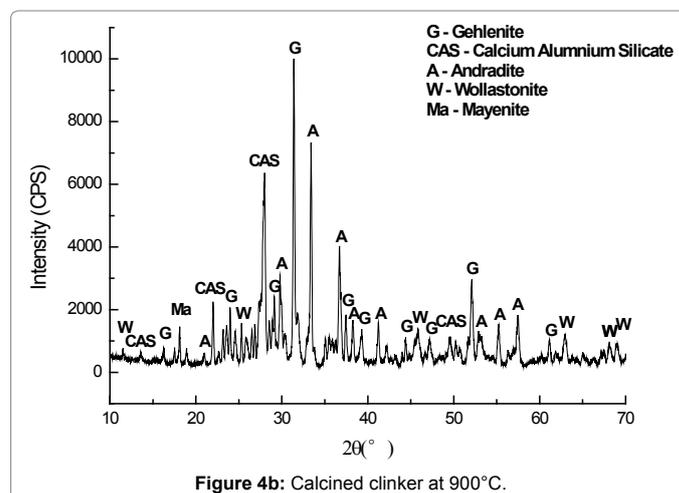


Figure 4b: Calcined clinker at 900°C.

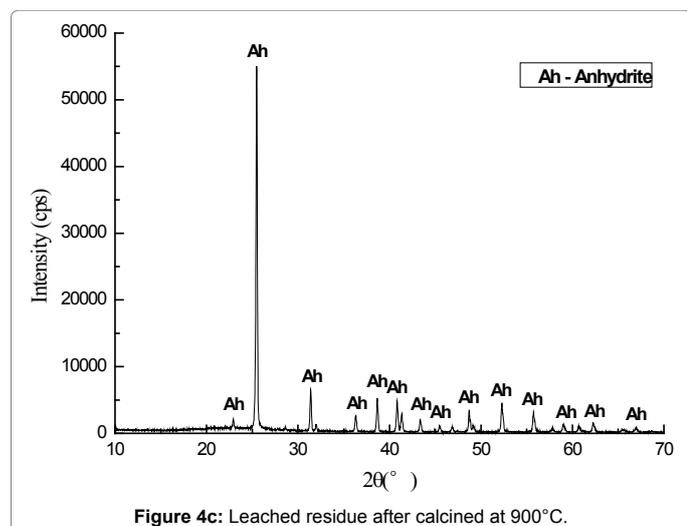
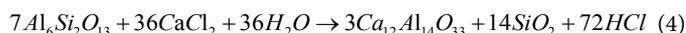
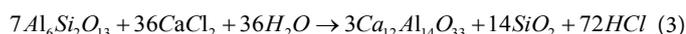
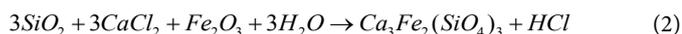
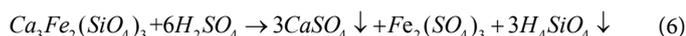


Figure 4c: Leached residue after calcined at 900°C.

The potential chemical reactions during the calcination are included as follows:



The relief of aluminum phases from mullite makes it easily dissolved in sulfuric acid solutions. In this way, the alumina is leached out from the solid phases to aqueous solution during H₂SO₄ leaching. The chemical reactions involved in the leaching procedure are as follows:



From the chemical equations of leaching process (Eqs.5~8), anhydrite(CaSO₄) can be found easily. Obviously, silicon oxide is the production of silicic acid sintering. And anhydrite is the production of calcination and be leached out in the leaching.

Discussion

Based on the discussion above, removal of alumina from CFA is feasible since the treatment procedure is simple and easy to be enlarged to industrial scale. The advantages of this procedure are the followings: firstly, the whole process is simple to conduct, addition of CaCl₂ and leaching with H₂SO₄ are easy to achieve. The extra CaCl₂ can be washed with water and do not affect the alumina leaching process. Secondly, the calcinating process is operated in dry state, which can avoid the clinker getting hard in wet process, making it easily operated during calcinating. Thirdly, the extraction efficiency of alumina reaches 96.6%, which is higher than the reported methods. The disadvantages of this process are also visible: firstly, the treatment process has no obvious economic feasibility, since the consuming of CaCl₂ and H₂SO₄ can hardly exceeds the values from selling the alumina products. Secondly, the reactive CaCl₂ consumes H₂SO₄ and generates CaSO₄ which is in precipitation and can't be recycled used.

Conclusion

A process of CFA roasting with CaCl₂ at 900°C prior to acid leaching to remove alumina is investigated. The treatment significantly enhances the alumina leachability (>95% when roasted with 80% CaCl₂ at 900°C for 1 h and leached by 1 M H₂SO₄ for 1 h) in comparison with direct acid leaching (2.31-4.78%). The removal efficiency of alumina steeply increases as the proportion of added CaCl₂ increases from 20% to 80% and the H₂SO₄ leaching time increases from 10 min to 30 min. However, the efficiency stays stable when the CaCl₂ dosage is further increased or the acid-leaching time is further prolonged. 1 M H₂SO₄ dissolves most of alumina (96.6%) within 1 h after the ash is roasted with 80% CaCl₂. The mineralogical characteristics of the roasted clinker indicates that CaCl₂ reacts with mullite and quartz in the CFA, and calcium is incorporated into the Si-O-Si network of silicates, which are susceptibility to acid attack. During the leaching processes, Al in the solid becomes Al³⁺ in the aqueous solution and silicon becomes silicic acid, which are easily leached in solution.

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