Alumina extraction from fly ash by MgO modified soda sintering method: Waste reduction and utilization

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ABSTRACT

Bauxite import accounts for over 60% of the total consumption of China's alumina industry, and the domestic resource is to be soon depleted in about ten years. At the same time, coal-fired power plants have been generating fly ash in large amounts, which can be used to extract alumina among many applicaitons. Various methods for the alumina extraction from fly ash have been tested, developed and demonstrated in China. Generally, soda sintering methods can be more easily deployed than acid leaching methods, but it is also apparent that soda sintering methods tend to geneate more waste of little value. In this work, MgO has been added to replace CaO, and the replacement could reduce the output of extraction residue, spare a lot of energy by lowering the sintering termperature, and retain a high rate of alumina extraction. As a raw material for quality products such as heat insulator, the extraction residue, which is composed mainly of $MgO{\bullet}SiO_2$, could be more efficiently used than $CaO{\bullet}SiO_2$ or $2CaO{\bullet}SiO_2$.

Keywords: fly ash, alumina extraction, soda sintering, calcium oxide, magnesium oxide

1 INTRODUCTION

Aluminum is very important for morden civiliations. The well known Bayer method has been dominantly adopted across the world to extract alumina from bauxite, which would be further electrolyed to produde aluminum by the Hall-Héroult method. Bauxite is a rich resouce worldwide, but not for China. What's more, in the early of 2014, reliable supply of bauxite got even harder for China, due to export inhibitions enforced by some countries. As a result, the Bayer method may surrender its postion in China in future, despite its great advantages in many aspects.

It has to said that, some alumina reserves of low grade have long been identified in China, for which the Bayer method could not be applied. Since the foundation of P. R. China, the lime soda sintering method has been developed to extract alumina from alumina reserves of low grade, such as diaspore. After years of development, the conventional lime soda sintering method has been fully optimized with repesct to materials, energy and economy.

It has been well establised the conventional lime soda sintering method follows the following formula (1) and (2):

$$\frac{[Na_2O]}{[Al_2O_3]+[Fe_2O_3]} \approx 1.0 \qquad (1)$$

$$\frac{[CaO]}{[SiO_2]+0.5\times[TiO_2]} \approx 2.0 \qquad (2)$$

In the sintering process at 1300-1400 ^oC, $Na_2O{\bullet}Al_2O_3$ and $Na_2O{\bullet}Fe_2O_3$ $2CaO{\bullet}SiO_2$ and $CaO{\bullet}TiO_2$ would form, and in the dissoluiton process, $Na_2O{\bullet}Al_2O_3$ would enter the solution. By reacting the solution with CO_2, $Al(OH)_3$ precipitates and by further baking, alumina is obtained.

In addition to the hight cost of energy, $2CaO{\bullet}SiO_2$ is massively generated in the process. Up to now, it seems $2CaO{\bullet}SiO_2$ can only be used as raw materils for cement.

In addition to diaspore, there is another increasingly recognized alumina source in China: the fly ash from coal-fired power plants, 80-90% of which could be alumina and silica. As shown in Figure 1, in past three decades, the output of fly ash has increased from almost zero to 0.54 billion tons in 2012. Though great efforts have been made for years to utilize the waste, a large amount of untreated fly ash is still continuously being piled up, and the total could reach up to about 3 billion tons in recent yeas.

In the eve of 21st century, the coal from the Zhungeer basin of Inner Mongolia has been found to generate a unique type of fy ash: the high alumina fly ash (HAFA).

The alumina in HAFA is as high as 40-60%, comparable to the bauxite of middle to low grades. The annual output of HAFA is over 25 million tons, and most of which has to be piled up, because there is no massive construction sites in the neigouring regions of many coal-fired power plants.

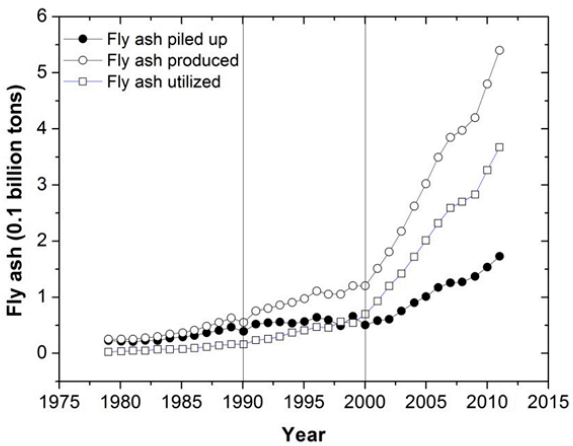

Figure 1: Fly ash from coal-fired power plants in China

To meet the double challenges by alumina shortage and environmental problem, alumina extraction has been considered as a preferred way for treatment of HAFA. Various methods for the alumina extraction from HAFA have been tested, developed and demonstrated in China, such as those adopted by Datang (conventional lime soda sintering method) and Shenhua (acid leaching method).

Generally, the conventional lime soda sintering method can be more easily deployed than acid leaching methods, but the method also generates more waste of little value. To reduce the waste output, a modified lime soda sintering method has been proposed to folow formula (3) and (4):

$$\frac{[Na_2O]}{[Al_2O_3]+[Fe_2O_3]+[SiO_2]} \approx 1.0 \qquad (3)$$

$$\frac{[CaO]}{[SiO_2]+[TiO_2]} \approx 1.0 \qquad (4)$$

The sintering process would be made at 1000-1200 ^oC for the formation of $Na_2O•Al_2O_3$, $Na_2O•Fe_2O_3$, $Na_2O•CaO•SiO_2$ and $CaO•TiO_2$, and in the dissolution process, $Na_2O•Al_2O_3$ would enters the solution. By reacting the solution with CO_2, $Al(OH)_3$ precipitates and by further baking, alumina is obtained. By a de-alkaline process, $CaO•SiO_2$ could be generated from extraction residue $Na_2O•CaO•SiO_2$, and Na_2O is recyled. It has been claimed that $CaO•SiO_2$ is more useful than $2CaO•SiO_2$, and could be used as wall materials or added in paper milk.

In contrast to the conventional lime soda sintering method, the improved lime soda sintering method could greatly reduce the waste output by cutting 50% CaO input. But the question remains whether the waste output could be cut further, and be more effectively used. Our solutions is based on the following formula (5) and (6):

$$\frac{[Na_2O]+[K_2O]}{[Al_2O_3]+[Fe_2O_3]+[SiO_2]} \approx 1.0 \qquad (5)$$

$$\frac{[CaO]+[MgO]}{[SiO_2]+[TiO_2]} \approx 1.0 \qquad (6)$$

By comparison with the improved lime soda sintering method for the alumina extraction from fly ash, our formula suggests the partial or full replacement of CaO by MgO. In general, CaO and MgO coexist in many alumina resources, and in some times, MgO can be a major component.

The replacement does not alter the reaction mechanisms, and because MgO has a smaller molecular weight than CaO, the input of raw materials and the output of waste would be further reduced. The sintering temperature could also be decreased by 100-200 ^oC. What'more, $MgO•SiO_2$ has very attractive properties with variety of applications, such as heat insulating materials, paints, and glass-ceramics.

2 EXPERIMENTAL

2.1 Materials and chemicals

The high alumina fly ash (HAFA) used in this work has been collected from GUOHUA power plant, which fires the coal dug from the Zhungeer basin of Inner Mongolia

The alumina in HAFA can be close to 50%, as given in Table 1, which will make it econocmially feasilbe for alumina extraction. By comparison, the average alumina is only about 15-20% in the fly ash across China.

Sodium carbonate (soda), calcium oxide (lime), sodium hydroxide and magnesium oxide are all of analytical grade, and deionized water was always used in the experiments.

SiO_2	Al_2O_3	TFe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	MnO	LOI	Total
40.92	49.21	1.91	0.47	2.85	0.12	0.5	1.57	0.03	1.81	99.39

Table 1: Compositions of HAFA from the coal of Zhungeer basin of Inner Mongolia

2.2 Methods and procedures

To make the formua, weighted HAFA and chemicals have been grounded to filter through a 200 mesh sieve. Some water was added to mix up the materials for manual pelletization. The pellets was subsequenly placed in crubiles for heating sevearl hours in a furance

As the sintering was completed, the pelletes were crushed, and then gournd to filter thourgh a 200 mesh sieve. A standard method for alumia extraction was applied, and the alumina extraction rate is accordingly calculated.

Standard method for alumia extraction: Weighted chemicals were dissoved in deionized water to prepare the solution of 15g/L Na_2O_K (NaOH in terms of Na_2O) and 5g/L Na_2O_C (Na_2CO_3 in terms of Na_2O). After that, weighted 8.00g sintered material was added in a beaker of 300mL, in which 100mL of prepared solution and 20mL of deionized water had been preheated to 90℃. The sintered material was stirred apart by a glass stick, and a magnetic stirrer was then dropped in the solution. Electric heating and stirring was applied, and the temperature was controlled at 85±5 ^{o}C. Vaccum filtration was made after 15 minutes, and boiling water was used to wash the beaker and filter cake for 8 times, 25mL for each time. The washed filter cake was dried with the filter paper. The sintered material and the red mud (dried filter cake) were then analyzed for chemical compositions. Alumina extraction rate could be calculated by the following formula (7):

$$\eta_{Al_2O_3}(\%) = [1-(\frac{A_{rm}}{A_{sm}})\times(\frac{MC_{sm}}{MC_{rm}})]\times 100 \qquad (7)$$

$\eta_{Al_2O_3}$ is standard alumina extraction rate in percentage, A_{sm} is alumina in percentage in sintered materials, MC_{sm} is MgO and CaO in percentage in sintered materials, and A_{rm} is the alumina in percentage in red mud, $MC_{rm}$is MgO and CaO in red mud in percentage.

3 RESULTS AND DISCUSSIONS

The MgO modified soda sintering method has been applied to the HAFA by full replacement of CaO wtih MgO. The modified soda sintering method has also been applied, and the results make a baseline. Some primary comparisons between the two methods were accoringly made.

3.1 MgO modified soda sintering method

In order to show the progress of the sintering process, the sintered material at 1050^{o}C for a half hour has been taken out for XRD analysis, as given in Figure 2. The appearance of a group of peaks assinged to Na_2MgSiO_4 indicates the occurrence of reactions, and the remaing peaks were attributed to MgO and complicated intermediates of sodium aluminium silicates. The total process may be represented by the following reactions formula (8) and (9):

$$Na_2CO_3 + Al_2O_3 = 2NaAlO_2 + CO_2 \qquad (8)$$

$$Na_2CO_3 + MgO + SiO_2 = Na_2MgSiO_4 + CO_2 \qquad (9)$$

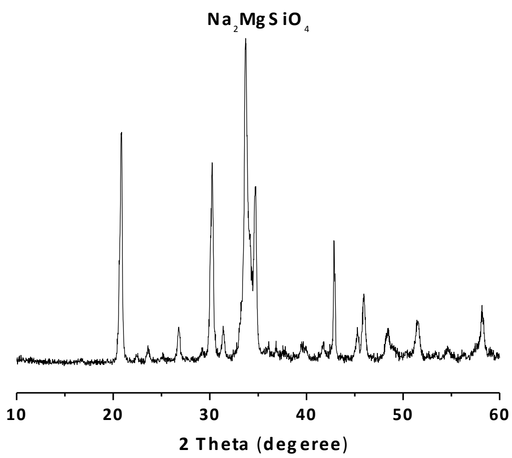

Figure 2. XRD spectra of sintered material at 1050^{o}C for a half hour by MgO modified soda sintering method

A fully sintered material was treated by the standard method for alumina extraction as detailed in the **section 2.2**, and the extraction rate was about 95.7%. The extraction solution was also analyzed for the chemical compositons, as given in Table 2. It should be noted that in the HAFA, the alumina to silica ratio is only slightly bigger than unity, as shown in Table 1, but in the extraction solutions, the said ratio is about thirty, which indicates a high separation efficiency of MgO modified soda sintering method.

3.2 Improved lime soda sintering method

The improved lime soda sintering method has also been applied to the HAFA, and the sintering process has been carried out at 1150^{o}C for two hours. The soda ratio of 0.95 has been used instead of the ideal requirement of 1.0.

SiO_2	Al_2O_3	TFe_2O_3	MgO	Na_2O	TiO_2
1.02g/L	32.5g/L	2.54mg/L	114.4mg/L	50.9g/L	0.05mg/L

Table 2: Chemical compositions of extraction solution for MgO improved alkali sintering method

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SiO_2	Al_2O_3	TFe_2O_3	CaO	Na_2O	TiO_2
0.65g/L	33.6g/L	9.04mg/L	69.0mg/L	64.0g/L	0.526mg/L

Table 3: Chemical compositions of extraction solution for modified alkali sintering method

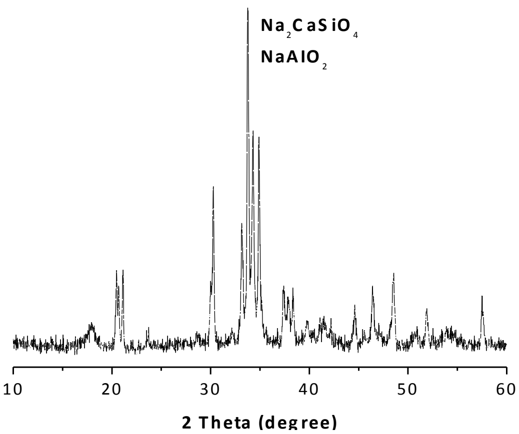
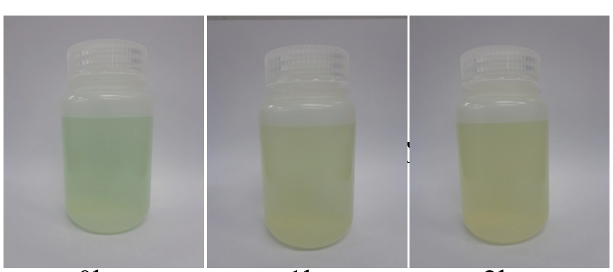


Figure 3: XRD spectra of sintered material at 1150°C for two hours by improved lime soda sintering method

The XRD spectra of sintered material, which has been fully sintered at 1150°C for two hours by the improved soda sintering method, is given in Figure 3. It can be seen that $NaAlO_2$ and Na_2CaSiO_4 become dominant components. The alumina extraction rate was about 96.5% by the method, and the extraction solution has also been analyzed for the chemical compositons, as given in Table 3.

3.3 Comparions of the two soda sintering methods

According to Table 2 and Table 3, for the two soda sintering methods, the extraction solutions are very similar in silica and alumina concentration. It cannot be expected the results would be precisely reproduced, because different conditions and formula have been adopted.



0hr 1hr 2hr

Figure 4: Color change of cxtraction solutions of alumina by the MgO modified soda sintering method

As shown in Figure 4, for the MgO modified alkali sintering method, the color of extraction soluiton was green at first, as time went by, it slowly changed into green-yellow, and finally 2 hours later, the color became yellow, which is then similar to the extraction soluiton for the improved lime soda sintering method. The color change may be due to the oxidation of Fe(II) to Fe(III), but the chemistry must be reserved for futher study.

Dilute NaOH solutions of 3-15% have been further used to dealkalize the extraction residues of two soda sintering methods at the temperatures of 160-300°C. Generally, a dealkalization rate of higher than 95% can be obtained.

4 CONCLUSIONS

The shortage of alumina is a long standing problem for China. Fly ash has been increasingly piled up, and high alumina fly ash (HAFA) has been considered as a new resource of alumina. Alumina extraction from HAFA could contribute to the solution of environmental problems.

Many methods have been tested, developed and demontrated for alumina extraction from HAFA, among which soda sintering methods could be more easily deployed than acid leaching methods. Conventional soda sintering method has been available, but the waste has to be massively generated. A modified soda sintering method has been introduced to partially solve the problem.

Our solution is to replace CaO by MgO in soda sintering formula, and the MgO modified soda sintering method reduces further the output of extraction residue which could be used as heat insulating materials, spares a lot of energy by lowering the sintering termperature, and retains a high rate of alumina extraction. The overall of results of our solution could be the waste reduction and utilization for the process of alumina extraction from HAFA.

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