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A review of the alumina recovery from coal fly ash, with a focus in China

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ABSTRACT: Coal fly ash, an industrial by-product, is derived from coal combustion in thermal power plants. It is one of the most complex and abundant of anthropogenic materials, and its improper disposal has become an environmental concern and resulted in a waste of recoverable resources. Coal fly ash is rich in alumina, making it a potential substitute for bauxite. With the diminishing reserves of bauxite resources as well as the increasing demand for alumina, recovering alumina from fly ash has attracted extensive attentions. The present review first describes the alumina recovery history and technologies, and then focuses on the recovery status in China. Finally, the current status of fly ash recycling and directions for future research are considered.

Keywords: coal fly ash; recycling; alumina; bauxite; recovery technologies

1. Introduction

Coal fly ash, a by-product of coal combustion in thermal power plants, is one of the most complex and abundant of anthropogenic materials. It accounts for 5~20 wt.% of feed coal and is typically found in the form of coarse bottom ash and fine fly ash, which represent 70~85 and 15~30 wt.% of the total ash generated, respectively. The generation of coal fly ash is anticipated to increase for many more years, as a result of the world's increasing reliance on coal-fired power generation. A more up-to-date estimate of annual worldwide generation of fly ash is 750 million tonnes [1]. In India, approximately 140 million tonnes is presently generated annually. Total generation in the U.S. and the E.U. is estimated to be around 115 million tonnes per annum. Figure 1 shows the generation of coal fly ash in China, from 2001 to 2015. Annual generation is still increasing and is anticipated to reach 580 million tonnes by 2015.

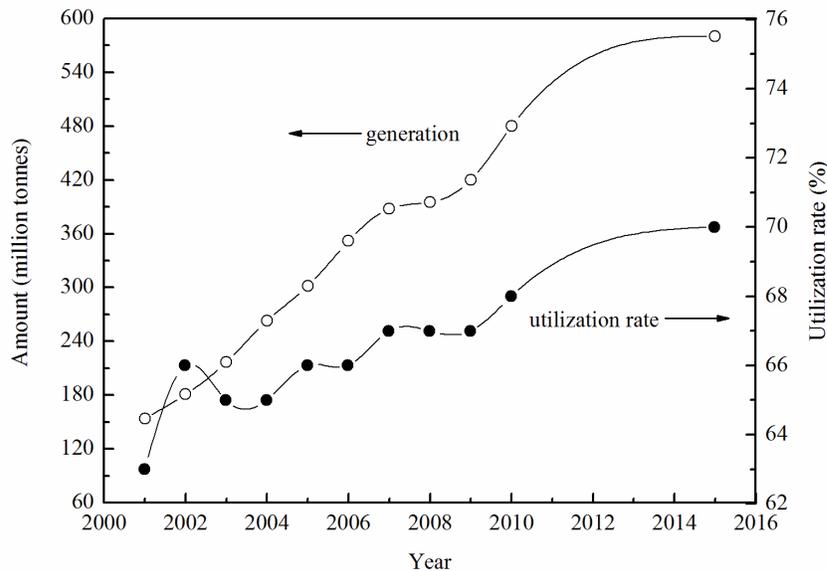


Fig. 1 The generation and utilization of coal fly ash in China

The environmental impact of coal fly ash is now being fully recognized. Most ash disposal methods ultimately lead to the dumping of fly ash on open land. Irregular accumulation and inappropriate disposal of fly ash will lead to its disposal over vast areas of land, with resultant degradation of the soil and danger to both human health and the environment. Fly ash particles are small enough to escape emission control devices, are easily suspended in air and have become a major source of gas pollution. Repeated exposure to fly ash can cause irritation of the eyes, skin, nose, throat and respiratory tract, and can even result in arsenic poisoning. Fly ash can even reach the sub-soil and ultimately cause siltation, clog natural drainage systems and contaminate the ground water with heavy metals. During coal combustion, most of U, Th and their decay products are released from the original coal matrix and are distributed between the gas phase and the solid combustion products.

Recycling coal fly ash can be a good alternative to disposal, and could achieve significant economic and environmental benefits as well. More aggressive efforts have been undertaken recently, to recycle fly ash [2, 3]. For example, about 20% of the fly ash generated is being used in concrete production. Other uses include soil amelioration [4-6], ceramic industry [7-9], catalysis and support for catalysis [10-13], adsorbents for removal of various pollutants [14], depth separation [15-17], zeolite synthesis [18-20] and valuable metals recovery [21-23]. The global average utilization rate of fly ash is estimated to be nearly 25% [24]. Current utilization rates have been estimated at 39% for U.S., 47% for the E.U. and 15% for India [25, 26]. For China, this rate has been increasing annually but has remained around 67% in recent years. It is expected to reach 70% by 2015 (see Fig. 1). However, there is a contradiction in the reported utilization

rate in China; Greenpeace reported that the practical utilization rate is only 30% [27]. Whatever the exact figure, it is clear that a significant proportion of coal fly ash will be left untreated and that there is an urgent need for developing new recycling methods for it.

Understanding the chemical and mineralogical properties of coal fly ash is important, as these properties influence its use and disposal. Coal fly ash is one of the most complex of the materials that can be characterized [28]. The major crystalline phases characterized are mullite and quartz for most ash and major components are metallic oxides with varying contents of unburnt carbon. The contents of principal oxides are, in descending order: $\text{SiO}_2 > \text{Al}_2\text{O}_3 > \text{Fe}_2\text{O}_3 > \text{CaO} > \text{MgO} > \text{K}_2\text{O}$. Coal fly ash is rich in aluminium, making it a potential source of alumina. With the diminishing of bauxite resources as well as the increase in alumina demand, the profitable industrial utilization of coal fly ash in alumina recovery has attracted extensive attentions.

2. Alumina recovery

2.1 History

The recovery of alumina from coal fly ash was pioneered by Grzymek in Poland in the 1950s [29], and was developed mainly because of the bauxite embargo during the Cold War. The recovery process was based on the auto-disintegration of sinter containing calcium aluminates and dicalcium silicate [30]. The sinter was mixed with sodium carbonate and underwent a series of complicated chemical treatments including carbonization and water scrubbing to produce alumina and Portland cement. In 1953, a demonstration plant for recovering 10 thousand tonnes of alumina and producing 100 thousand tonnes of Portland cement was established in Poland. At the end of the 1970s, a

second plant was established with the capability of producing 100 thousand tonnes of alumina and 1.2 million tonnes of cement. In the early 1970's, there was widespread concern about an impending producers' cartel of bauxite exporters, leading to higher prices. This concern led the U.S. Bureau of Mines to undertake a major program of research into potential alternatives to bauxite. The processes studied included variations of existing leaching and sintering processes. Since the 1980s, more researches have been conducted and new recovery technologies developed as well.

2.2 Recovery technologies

All commercial production of alumina from bauxite is performed by a process patented by Bayer in 1888 [31]. As bauxite is sufficiently rich in aluminum hydroxide minerals and low in impurities, and the alumina can be extracted relatively easily and inexpensively, any alternate methods for extracting alumina must be economically competitive with the Bayer process. Unlike bauxite, fly ash shows the characteristics of relatively low content of alumina, high content of silica, and the presence of aluminum mainly in the form of chemically stable mullite, which may lead to a low alumina recovery rate and high capital and operating costs. Recently, a number of processes for recovering alumina from coal fly ash have been reported, which can be grouped into three types: the sinter process, the acid leach process and the HiChlor process (see Table 1).

Table 1 The comparison of different alumina recovery technologies

Recovery technologies	Advantages	Disadvantages	
Sinter processes	Lime sinter process	The auto-disintegration of the sinter avoids the need for grinding; the lime costs less	A considerable amount of calcium silicate residues are generated
	Lime-soda sinter process	Fewer residues are produced as compared with the lime sinter process	The energy cost is relatively high and the process is complex; the soda costs more
	Predesilication and lime-soda sinter combination process	Offers the advantages of simultaneously extracting silica and reducing the solid residues to some extent	Filtration and the washing of desilicated liquor are confronted
	Calsinter process	It cost less lime as compared with the lime sinter process; dissolves aluminium and other metals with dilute acid	The process is complex; a proportion of soluble impurities are introduced into the pregnant solution
	Direct acid leach (DAL)	Simultaneously dissolves and recovers aluminium and other metals	Requires acid-resistant and air-tight processing equipment; excessive use of acid and low extraction rate
Acid leach processes	Enhanced acid leach	Relative high extraction efficiency with dilute acid	The energy cost is relatively high
	Sinter-acid leach combination process	Relative high extraction efficiency with dilute acid	The process is complex and energy cost is relatively high
	HiChlor process	Not applying acid or alkali; simultaneously recover aluminium and other metals	The energy cost is relatively high; low extraction rate

I. Sinter processes

According to the sintering mediums, the sinter processes can be classified into: lime or lime-soda sinter, the Calsinter process and other sinter processes (e.g. salt-soda sinter, ammonium sulfate sinter and fluorides sinter). The sinter processes involve a high-temperature reaction of coal fly ash with powdered sintering agents to form soluble

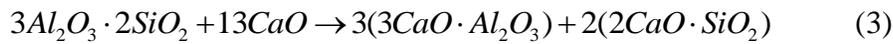
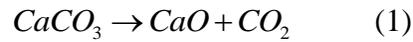
alumina compounds. The sinter is then leached to separate aluminium, and the pregnant solution is subsequently treated to prepare alumina with high purity.

(1) Lime sinter process

The lime sinter process is a modification of the Pederson process which was used to produce pig iron and calcium aluminate slags from a mixture of bauxite, iron ore, coke and limestone [32, 33]. Alumina was recovered in the Pederson process by leaching the slag with a sodium carbonate solution. In the lime sinter process, the fly ash reacts with lime (added as limestone) at elevated temperature (>1100 °C) forming calcium aluminate, soluble in the extractant, and dicalcium silicate, insoluble in the same solution. The extraction of alumina from the sinter is carried out by dissolving the soluble alumina into the extractant and leaving the calcium silicate in the solid residues. The common extractants include water and dilute alkaline solutions, such as Na_2CO_3 and NaOH solutions [34]. After leaching, the aluminium in the pregnant liquor is subsequently precipitated as $\text{Al}(\text{OH})_3$ by contacting the solution with CO_2 . The next step is calcination of the precipitate to produce the final product α - or γ -alumina. The solid residues from the leaching step are sintered and mixed with gypsum during grinding to prepare cement. The schematic diagram of the lime sinter process is illustrated in Fig. 2. The major steps involved are described as follows:

Sintering of raw materials: The sintering step is conducted to activate the coal fly ash. The limestone is first dissociated into calcium oxide at high temperature. The inactive mullite and quartz in the ash then react with CaO , forming $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ and $2\text{CaO}\cdot \text{SiO}_2$, respectively. Forming $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ is the prerequisite of the lime sinter process. This sinter product is easily dissolved in the extractant, forming NaAlO_2 .

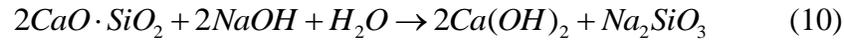
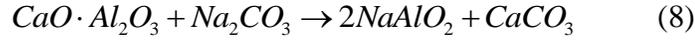
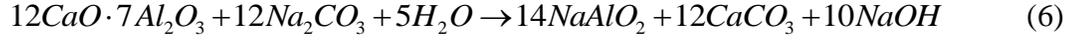
However, Hignett [35] reported $5CaO \cdot 3Al_2O_3$ as the most soluble aluminate, and the formation of other calcium aluminates is unavoidable in this process. $3CaO \cdot Al_2O_3$ and $CaO \cdot Al_2O_3$ can form depending on the availability of CaO in the mixture. These two compounds are not as soluble as $12CaO \cdot 7Al_2O_3$. The formed $2CaO \cdot SiO_2$ is hardly dissolved at all, which is helpful for the separation of aluminium and silicon. The chemical reaction equations involved in this process can be presented as follows:



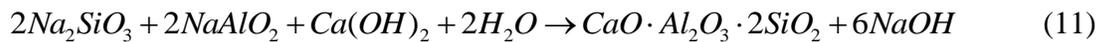
Auto-disintegration of the sinters: During cooling (temperature below 500 °C), auto-disintegration of the sinter occurs, a phenomenon attributed to the transformation from the metastable, monoclinic β polymorph of $2CaO \cdot SiO_2$ to the orthorhombic γ polymorph. The transformation is accompanied by an 11% volume increase, resulting in the matrix shattering into fine powder. This disintegration is helpful and avoids the need for grinding the sinters [36, 37].

Leaching of the sinters: The cooled sinter is leached by an Na_2CO_3 solution. After leaching, the aluminium remains in the leachate in the form of $NaAlO_2$, while most silicon is left as solid residue in the form of $2CaO \cdot SiO_2$, achieving the separation of aluminium and silicon. For the high levels of $3CaO \cdot Al_2O_3$ and $CaO \cdot Al_2O_3$ formed in

the sintering step, the extractant must contain an excess of Na_2CO_3 for maximum alumina extraction. The following equations represent these transformations:



Desilication of the crude leachate: Ideally all silica is fixed as insoluble residues in this process. However, the dissolution of small amounts of silicon during leaching is unavoidable, as is validated by the equations (9) and (10). It has been reported that a 2~3% (alumina basis) is the typical concentration of silica in the lime sinter process [38]. Hignett [35] reported the soluble alumina produced in the pilot plant as lower than that in the laboratory test. One of the major problems was the control of the silica content of the solution in the pilot plant. The silica concentration in the leachate could be decreased to less than 0.02% (alumina basis) by agitating the solution in the presence of lime at 70 °C. Therefore, the lime sinter process usually includes a step for Al-rich solution purification before the precipitation of aluminium. The desilication is conducted mostly by adding $\text{Ca}(\text{OH})_2$ suspensions to make the silicon transform into calcium aluminosilicates with relatively low solubility. The reaction is described as follows:

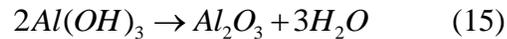


Carbonization of the refined solution: CO_2 gas is blown into the desilicated

NaAlO₂ solution from the bottom, followed by vigorous stirring. The NaAlO₂ hydrolyzes to form the precipitate Al(OH)₃ when the pH falls to a certain value. The initially formed Al(OH)₃ particles are easy to aggregate due to the high surface activity, which could induce the small particles to grow into larger ones. The addition of dispersing agents with high performance (e.g. polyethylene glycol, polyvinyl alcohol) can control the shape of the precipitate and make filtration easy. Lin et al. [39] added 0.1% dispersing agent prepared from ammonium acrylate and acrylamide into the enriched NaAlO₂ solution, and ultrafine Al(OH)₃ powder was obtained. The following equations represent these transformations:



Calcination of the precipitate: The obtained Al(OH)₃ is calcined based on the Thermo-Gravimetric/Differential Thermal Analyzer (TG-DTA) and X-ray diffraction (XRD) analysis to transform into Al₂O₃ with high purity. The chemical reaction that occurs is:



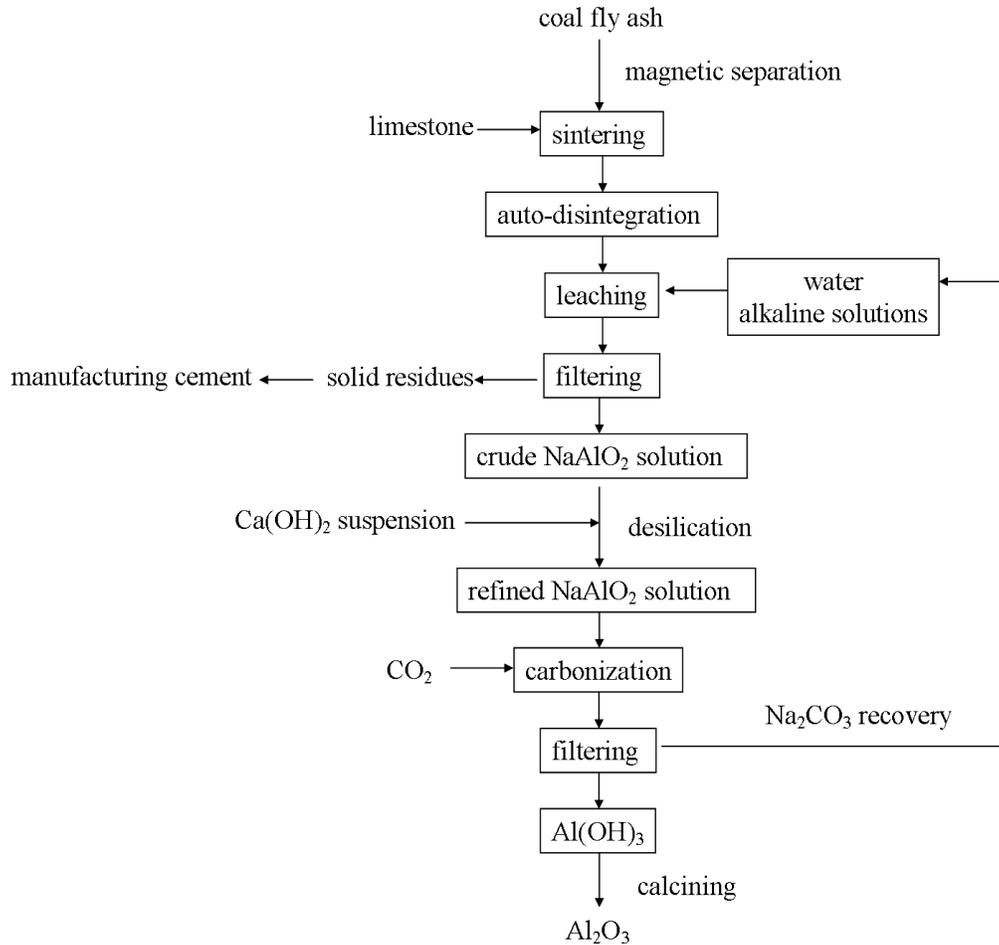


Fig. 2 Schematic diagram of lime sinter process

(2) Lime-soda sinter process

The first lime-soda sinter process was developed by Kayser in 1902 to separate alumina from silica [40]. The reaction of the mixture of lime and soda with fly ash is known to produce soluble sodium aluminate and insoluble calcium silicate. At high temperatures (generally 1100~1400 °C), the formation of other compounds is unavoidable, depending upon the fly ash type and sintering conditions. As in the lime sinter process, the sintered product is leached with water, caustic soda or sodium carbonate solution. The dissolution of small amounts of silica during leaching is unavoidable. Therefore, the lime-soda sinter process also includes a step for purification

of the pregnant solution. The resulting slurry is filtered, and the liquor is treated with Ca(OH)_2 suspensions to precipitate any dissolved silica at high temperature and pressure, which is then decomposed as in the Bayer process or is treated with CO_2 to precipitate hydrated alumina. The Al(OH)_3 is separated and can be converted to alumina by calcining. When operated in conjunction with the Bayer process, it is called the combination process. Padilla and Sohn [41] studied the main variables in the sintering step and the kinetics of sodium aluminate formation during sintering. The major sinters were identified as sodium aluminate and β -dicalcium silicate. Alumina recovery of about 80% was obtained at optimal conditions. The schematic diagram of the lime-soda sinter process is illustrated in Fig. 3.

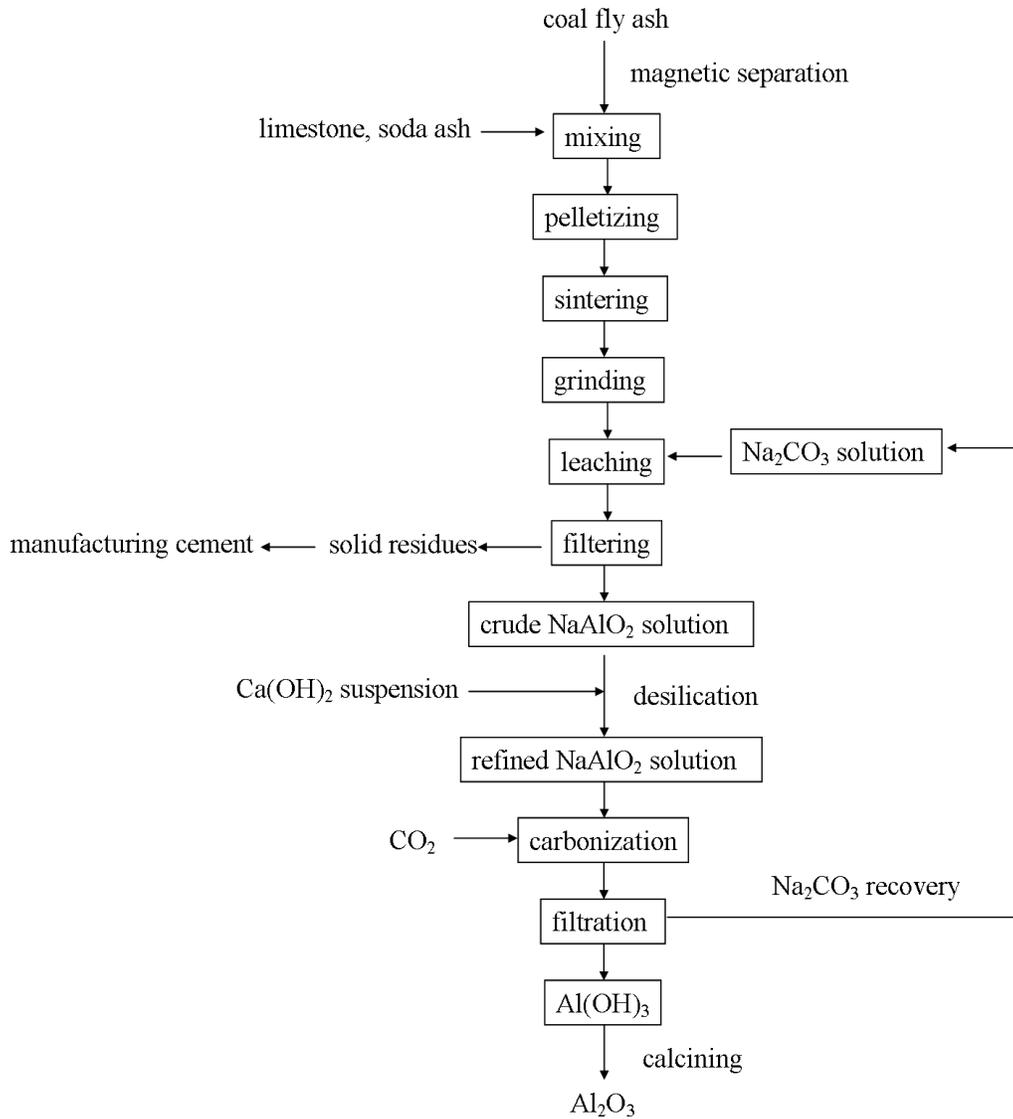


Fig. 3 Schematic diagram of lime-soda sinter process [40]

(3) Predesilication and lime-soda sinter combination process

The lime and lime-soda sinter processes were developed long ago; however, they are still in the early stages of commercialization. Problems are encountered when the process is used in industry because of the massive lime usage as well as the high energy cost. Besides, a considerable amount of calcium silicate residues are generated, but not utilized in an effective way except by producing cement. It has been roughly calculated that 7~10

tonnes of calcium silicate residues will be generated in recovering 1 tonne of alumina product. The problem results from the substantial silica content, which contributes to a large consumption of lime. Therefore, it is strictly required that the $\text{Al}_2\text{O}_3/\text{SiO}_2$ mass ratio of the fly ash be about 2 for the lime-soda sintering process. However, when the ratio of fly ash is in the range of 0.8~1.0, enriching aluminum content by removing silicon seems to be a good choice.

Except for mullite and crystalline quartz, amorphous and reactive silica is also present in the fly ash, the proportion of which accounts for 30~60 wt.%. Thus, pre-desilication followed by a sintering process was developed to reduce the silica content and the consumption of sintering mediums. In addition, the desilicated silicon could be reused as silica white and calcium silicate. Wang et al. [43] extracted alumina by pre-desilication of fly ash, lime-soda sinter, water dissolution and carbonation processes. The desilication rate reached 40% and the $\text{Al}_2\text{O}_3/\text{SiO}_2$ molar ratio of fly ash increased after pre-desilication. The extraction rate of alumina from the sinter reached as high as 91%. Bai et al. [44] recovered alumina from desilicated fly ash by lime-soda sinter process. The recovery rate reached 90% at the optimal conditions. Bai et al. [45] enriched aluminum in fly ash by alkali desilication and carbonation to transform amorphous silicon dioxide into an amorphous nano-particles product.

(4) Calsinter process

The Calsinter process was developed at the U.S. Oak Ridge National Laboratory. In this process, coal fly ash is blended and sintered with gypsum and limestone at a temperature of about 1000~1200 °C. The sinter is then leached with dilute acid. Waste solids are removed by filtration, and metal values are recovered from the filtrate. The

schematic diagram of this process is displayed in Fig. 4. In 1976, Goodboy [46] reported on the study of alumina extraction from coal waste and clays mixed with limestone and calcium sulfate. Alumina extraction of 90% was achieved by sintering at 1200 °C for 15 min. Seeley et al. [47] used the Calsinter process to recover alumina and determine the distribution coefficients for Fe^{3+} and 16 other metal ions in the liquid-liquid extraction system. The results showed that this process could effectively remove more than 95% of the aluminum, along with significant amounts of several other metals, from fly ash.

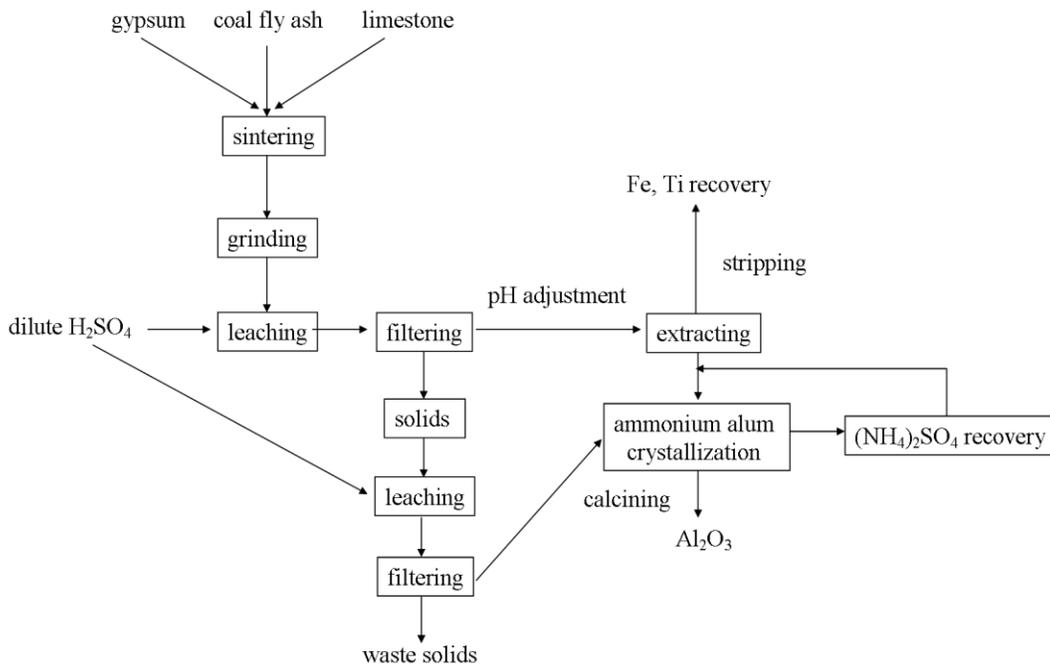


Fig. 4 Schematic diagram of Calsinter process [45]

(5) Other sinter processes

In addition to the lime and lime-soda sinter, other sinter processes such as salt-soda sinter, ammonium sulfate sinter and fluorides sinter are also reported. In the salt-soda sinter process, a $\text{NaCl-Na}_2\text{CO}_3$ mixture is sintered with fly ash, quenched in a water leach, and then leached in a dilute acid solution. In U.S. patent US 4254088 A [48], the

fly ash was first sintered with a mixture of NaCl and Na₂CO₃ at a temperature of 700~900 °C. The sinter was then leached with nitric or sulfuric acid, recovering 90~99% of the aluminum. Decarlo et al. [49] studied the effect of individual components of the salt-soda on the alumina recovery. The fly ash was sintered with NaCl and successively leached with Na₂CO₃ and HNO₃ solutions. The alumina recovery was a mere 27%. However, sintering fly ash with Na₂CO₃ gave an alumina recovery of 66%. Nehari et al. [50] described a process using CaCl₂ as a sintering medium. It consists of sintering fly ash with hydrated CaCl₂, leaching the sinter product with HCl and recovering alumina from the crystallized AlCl₃. Decarlo et al. [49] reported that sintering fly ash with CaCl₂-Na₂CO₃ and NaCl-CaCO₃, followed by leaching with H₂O and HNO₃ solutions, solubilized 78 and 74% of the alumina in fly ash, respectively. The leaching rate of fly ash using a CaCl₂-CaSO₄-NaCl sinter process and H₂SO₄ extraction was 30%. Tong et al. [51] sintered fly ash with KF and leached the sinter product with HCl. The leaching rate reached 96.92%. Alum is commonly synthesized as an intermediate material for the production of alumina from Al-containing nonbauxitic raw materials [52]. Park et al. [53] calcined fly ash with ammonium sulfate at 400 °C for 2 h to form NH₄Al(SO₄)₂. High purity alum was precipitated by the reaction of NH₄Al(SO₄)₂ and ammonia in water and then followed by crystallization.

II. Acid leach processes

(1) Direct acid leach (DAL)

Thorough separation of aluminum from silicon can be achieved by the DAL process. It usually uses sulfuric, hydrochloric and nitric acid to leach fly ash. However, the aluminium extraction by DAL at low acid concentration and ambient temperature is not

suitable for high recovery [54, 55]. An aqueous suspension of 20% (w/v) fly ash using 16 mol/L HNO₃ and 36 mol/L H₂SO₄ will dissolve no more than 10% of the total aluminum at ambient temperature over a period of 72 hrs. Greater amounts of aluminum are recovered by leaching under reflux conditions for extended periods of time; and even then no more than about half the aluminum is dissolved in the acid leachate [48]. Shemi et al. [56] employed a DAL process to extract aluminium. The sulphuric acid leaching yielded an extraction efficiency of 23.5%. Gudyanga et al. [57] investigated the feasibility of extracting aluminium from fly ash in acid and alkaline media. The results showed that in alkaline solution only aluminium was extracted, to yield 55% recovery, as compared with 29% recovery in an acid system. The apparent low recovery of aluminium in low acid concentration may be due to the co-dissolution of silica and the subsequent formation of an unfilterable silica gel [58]. It has been proposed that the glassy phase of fly ash dissolves rapidly and that the more stable quartz-mullite phase which remains dissolves more slowly. The schematic diagram of this process is exhibited in Fig. 5.

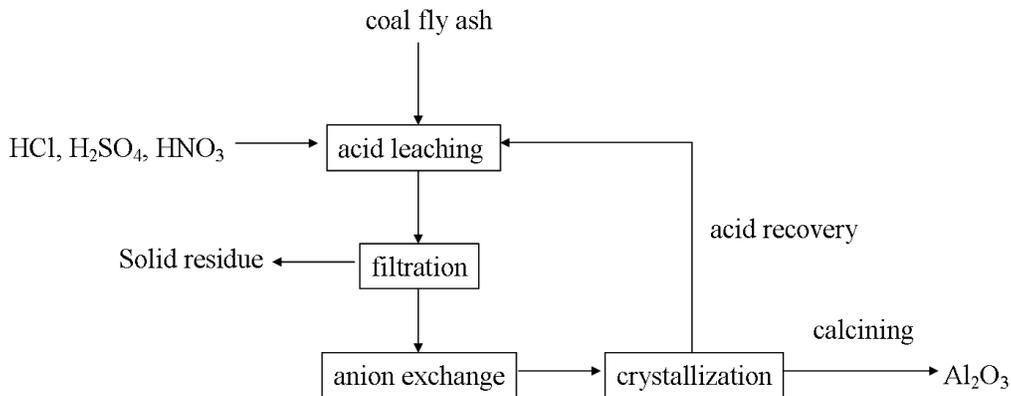


Fig. 5 Schematic diagram of DAL process [57]

(2) Enhanced acid leach

Various attempts have been made to improve aluminum extraction efficiency. Wu et al. [60] leached aluminum from fly ash by a pressure acid-leaching method. The optimum conditions were determined to be sulfuric acid concentration of 50% and reaction temperature of 180 °C for 4 h. Under optimum conditions, the extraction efficiency reached 82.4%. In comparison to conventional heating processes, microwave heating has inherent advantages in that it can be selective, controllable and efficient. The dissolution of both inorganic and organic materials by an acid can be accelerated due to the effective internal heating caused by microwaves. Gong [61] investigated microwave heat on alumina recovery in the acid leach process and found that the recovery reached above 75% at optimal conditions.

(3) Sinter-acid leach combination process

The industrial applications of acid leach processes have been limited due to their excessive use of acid and fluoride. This limitation can be lifted by calcining fly ash with concentrated sulfuric acid at high temperature. Liu et al. [62] and Bai et al. [63] extracted alumina using an acid sinter-leach combination process. The fly ash and concentrated sulfuric acid mixture was calcined to transform most of the aluminum into aluminum sulfate, which can be extracted by hot water. The rate of alumina recovery can reach 70~90 % with relative lower processing temperatures and less solid residue. Ji et al. [64] calcined fly ash with soda at 900 °C to yield soluble aluminates. The sinter was then leached with sulfuric acid to produce a solution containing aluminum. The extraction efficiency reached as high as above 98%. Matjie et al. [65] calcined fly ash with CaO at a temperature range of 1000~1200 °C. An aluminium extraction efficiency of 85% was

achieved when the sinter was leached with sulphuric acid using an acid concentration of 6.12 mol/L at 80 °C for 4 h.

III. HiChlor process

An alternative route for extracting aluminum and other metals is to chlorinate ash, a method investigated by Burnet et al. [66]. As a first step, the separation of a magnetic fraction of fly ash was conducted. However, this still left about one third of the iron, with the nonmagnetic fraction and about 10% of the total aluminum lost to the magnetic fraction. Moreover, in the chlorination step, the nonmagnetic fraction of fly ash was mixed with carbon and chlorinated in a fixed bed. To obtain aluminum metal, the recovered aluminum chloride can be decomposed electrolytically. The technology for this electrolysis step is commercially available. Interestingly, only 70% as much electrical energy is needed to obtain pure metal from aluminum chloride as from bauxite [67]. Mehrotra et al. [67] investigated the high-temperature chlorination of fly ash using a gas-fluidized bed reactor. With carbon and carbon monoxide present as reducing agents, about 25% of the alumina in ash could be chlorinated in 2 h at temperatures above 900 °C.

3. Alumina recovery status in China

At present, China is dependent mainly on imports for bauxite, the major source of aluminum. The total alumina demand was 33.86 million tonnes in 2009, while the domestic production of alumina was only 23.79 million tonnes. Imported alumina and bauxite amounts were 5.14 and 19.69 million tonnes, respectively. More than 40% of the bauxite has been supplied from imports in recent years, 90% of which are from Indonesia and Australia.

The feasibility of alumina recovery from fly ash mainly depends on its alumina content. Usually fly ash with alumina content of more than 30% can be considered feasible for the recovery of alumina. The average alumina content of the fly ash produced in China is found to range from 20 to 35%, as determined by analyzing the fly ash produced by the large scale thermal power stations [68]. However, the ash produced in southern Inner Mongolia, northern Shanxi and the Shaanxi province of China are characterized by its high aluminum content. The alumina content is in the range of 40~45% and in some cases it could reach as high as approximately 50%. The high alumina content of fly ash could meet the demand of the Bayer process for alumina production and makes it a potential substitute for bauxite [69, 70]. The proven coal reserves with high content of aluminium in the Junggar basin, Daqing Shan mountain, and Zhuozi Shan mountain in Inner Mongolia is about 50 billion tonnes. It is expected that 15 billion tonnes of coal fly ash will be generated and 5 billion tonnes of alumina recovered, which is equivalent to 12 billion tonnes of bauxite and 3.2 times the proven bauxite resources in China.

To encourage and support the comprehensive utilization of coal fly ash, the National Development and Reform Commission (NDRC) of China issued a newly revised joint decree "Utilization of fly ash management approach" in February 2011. In March, the NDRC and relevant departments of the State Council amended the "Guidance Catalogue for Industrial Structure Adjustment (2005 edition)". Fly ash with a high content of aluminum was listed in the encouraged items in the "2011 edition." Under a series of encouraged and preferential policies issued by the state and local government, the recovery of alumina from fly ash is being aggressively undertaken. Consistent with the distribution

of high-alumina fly ash, the plants established are mainly in Inner Mongolia and Shanxi province (see Fig. 6). Detailed information on the projects is listed in Table 2.

Table 2 Plants performing alumina recovery from coal fly ash in China

Plant location	Company	Expected production capacity /million tonnes	Commissioning date	Recovery technologies
Etuoke banner, Erdos city	Inner-Mongolia Melic Sea Ordos Al Co. Ltd.	alumina 0.4	2013	Lime-sinter followed by low-temperature Bayer process
Tuoketuo county, Hohhot city	Inner Mongolia Datang International Recycling Resource Development Co. Ltd.	alumina 0.24, active calcium silicate 0.2	2012	Pre-desilication followed by lime-soda sinter
Tuoketuo county, Hohhot city	Inner Mongolia Datang International Recycling Resource Development Co. Ltd.	alumina 0.5, active calcium silicate 0.56, zeolite 4A 0.1	2015	Pre-desilication followed by lime-soda sinter
Zhungeer banner, Erdos city	Inner Mongolia Datang International Recycling Resource Development Co. Ltd.	alumina 0.5, active calcium silicate 0.469	2015	Pre-desilication followed by lime-soda sinter
Zhungeer banner, Erdos city.	Shenhua Group Co. Ltd.	alumina 1	2013	acid leach
Zhungeer banner, Erdos city	Inner Mongolia Kaiyuan Ecological Aluminum Co. Ltd.	first-phase project: alumina 0.4, Si-rich product 0.12, second-phase project: alumina 0.6, Si-rich product 0.18	2015 or later	ammonium sulfate sinter
Zhungeer banner, Erdos city	Huadian Inner Mongolia Energy Co. Ltd.	alumina 0.055	2013 or later	ammonium sulfate sinter
Etuoke banner, Erdos city	Inner Mongolia Erdos Electrical Metallurgical Co. Ltd.	alumina 1, silica white 0.51, sodium silicate 0.77	2015 or later	acid leach followed by Bayer process
Qingshuihe county, Hohhot city	Inner Mongolia Tongsheng Electric Power Co. Ltd.	alumina 1	2015 or later	activation followed by water leach

Zhungeer banner, Erdos city	Erdos	qianhengxing	first-phase project:	alumina	2013 or later	-
	Industrial Co. Ltd.		1.2			
Shuozhou city, Shanxi province	China Coal Industry Co. Ltd.	Pingshuo Coal	alumina 0.1, silica white 0.04		2013	predesilication followed by lime-soda sinter
Baicheng city, Jilin province	-		alumina 0.2, silica white 0.2		-	alkali sinter-acid leach



Fig. 6 Distribution of plants for alumina recovery from coal fly ash in China

The Inner-Mongolia Melic Sea Ordos Al Co., Ltd. was established in 2006. Research on alumina recovery from coal fly ash was initiated in 1998. The industrial production test was finished in August 2004, based on a series of mechanism studies, laboratory tests, pilot-scale tests, and small-scale industrial production tests. The project was approved by the NDRC of China in 2006 and the total capital invested has been about 1.6 billion yuan. The technology used for alumina recovery is lime sinter followed

by a low-temperature Bayer process, developed based on the Polish technology. The schematic diagram of this technology is displayed in Fig. 7.

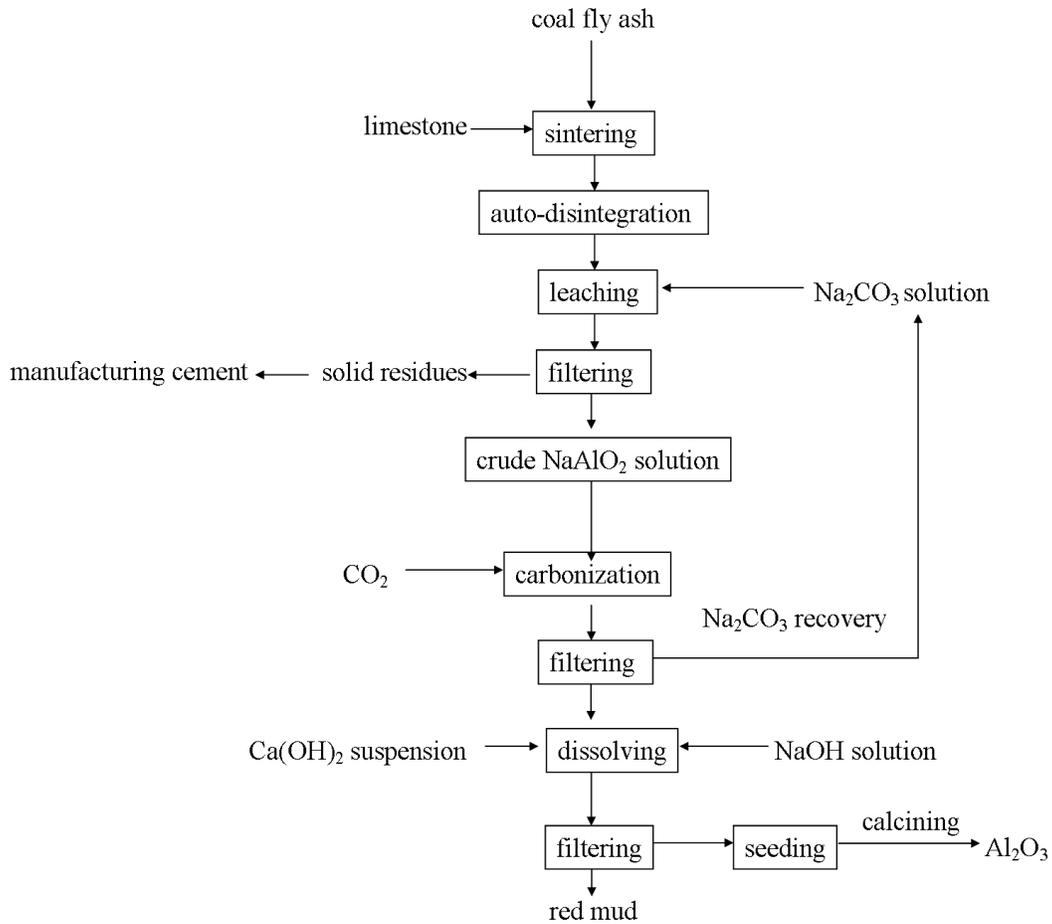


Fig. 7 Schematic diagram of lime sinter followed by Bayer process

The Inner Mongolia Datang International Recycling Resource Development Co., Ltd. was established in 2007. The research on alumina recovery was launched in 2004. The laboratory and industrial tests were accomplished in 2006 and 2008, respectively. The project in Tuoketuo Industrial Park is separated into three phases. Investment for the first and second phases of the project totaled 3.39 billion yuan and the project went into operation in 2012. The designed annual production capacity is 0.24 million tonnes of alumina and 0.2 million tonnes of active calcium silicate. The third phase of the project is

expected to produce 0.5 million tonnes of alumina and 0.56 million tonnes of active calcium silicate with invested capital of 13.3 billion yuan. Another project located in Erdos city is underway. The alumina recovery technology jointly developed by Tsinghua University is pre-desilication followed by a lime-soda sinter process. The fly ash is first desilicated removing ~40% of the total silica and doubling the $\text{Al}_2\text{O}_3/\text{SiO}_2$ mass ratio. The desilicated fly ash is then sintered with calcium carbide slag to extract aluminium. A solution rich in silicon is used to prepare active calcium silicate, which could be used as a filler in paper. The calcium silicates residue after neutralization and dehydration could be used as raw material to produce cement. The results showed that the alumina extraction rate could achieve ~90% and the obtained alumina meets the metallurgical grade standard. The schematic diagram of this technology is displayed in Fig. 8.

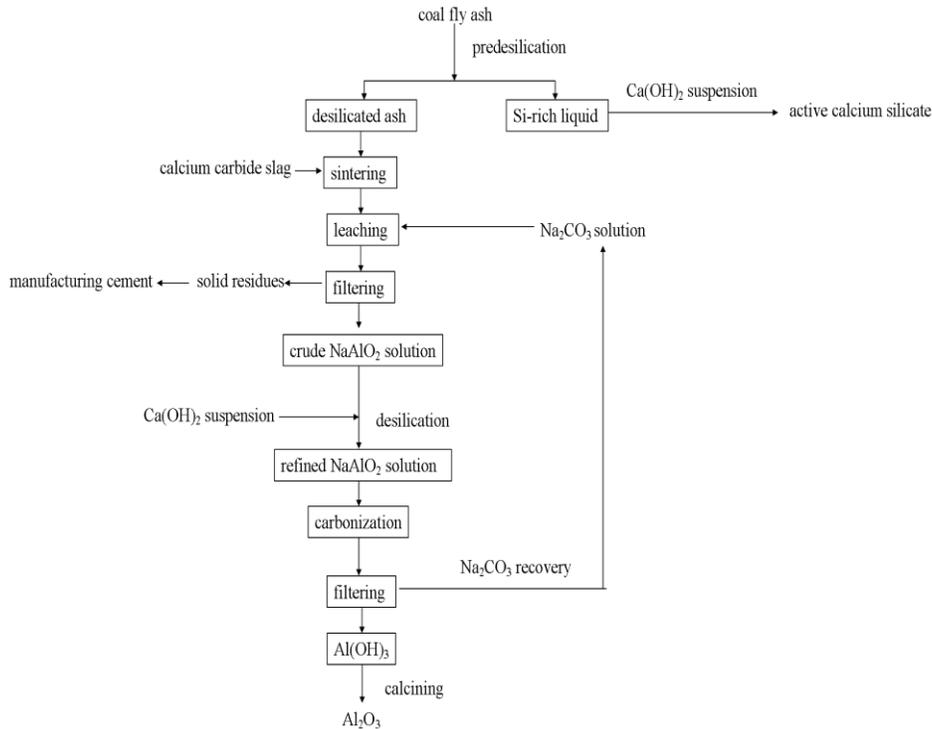


Fig. 8 Schematic diagram of pre-desilication followed by lime-soda sinter process

The Shenhua Group Co., Ltd. initiated this research in 2004 and has been working with Jilin University since 2006. The circular economic industry project, oriented toward recovering alumina from fly ash, was planned in 2010 and listed in the “National Science and Technology Pillar Program during the Twelfth Five-year Plan Period.” A pilot-scale plant recovering 4,000 tonnes of alumina with a recovery rate of 80% was constructed in August 2011. The first-phase demonstration project producing 1 million tonnes of alumina concluded on 25 August 2011 in Zhungeer Banner, Erdos City. The second and third phases of the project are expected to be completed at the end of 2020 and each phase is expected to produce 1 billion tonnes of alumina. The technology jointly developed by Jilin University and Guiyang Aluminium Magnesium Design & Research Institute Co., Ltd. is a one-step acid leaching, including dissolving fly ash in hydrochloric acid, filtering, evaporating, crystallizing and calcining. The obtained alumina meets the metallurgical grade standard. The schematic diagram of this technology is shown in Fig.

9.

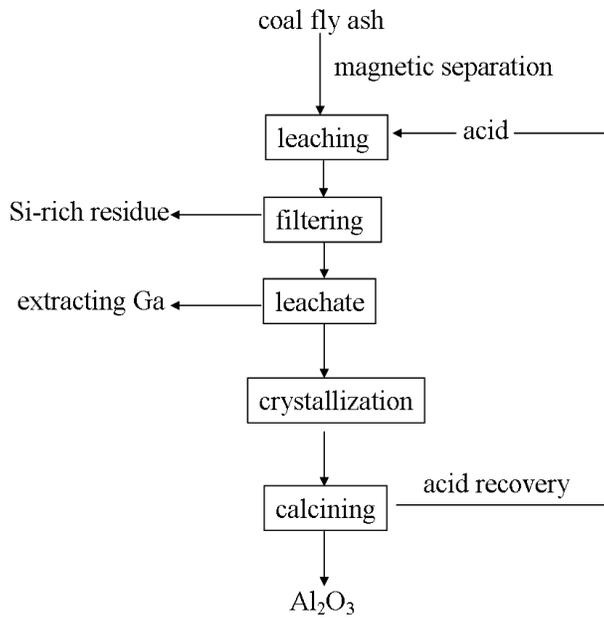


Fig. 9 Schematic diagram of one-step acid leach

The Pingshuo High-tech Research and Development Center was established by China Coal Pingshuo Coal Industry Co., Ltd. and the local government in early 2006. It cooperated with Northeastern University, Xi'an University of Architecture and Technology, and the Institute of Process Engineering, Chinese Academy of Sciences in an alumina recovery project, initiated in 2011 and expected to conclude in September 2013. Alumina production of 0.1 million tonnes, and silica white production of thousands of tonnes, are expected to be achieved. The technology used is similar to that used in the Inner Mongolia Datang International Recycling Resource Development Co. Ltd. The fly ash is first desilicated and the crude NaAlO_2 solution carbonized, to prepare the silica white. The desilicated residue is sintered with lime and soda to recover alumina.

The Inner Mongolia Kaiyuan Ecological Aluminum Co. Ltd. is a subsidiary of Beijing Century Harmony Technology Co., Ltd. It signed an agreement with Beijing SPC Environment Protection Technical Co., Ltd. in April 2012 and paid 1.58 million yuan for technology support, plant management and system debugging. The project was initiated in 2012 and is expected to conclude in 2015. It consists of two steps: the first-phase project is anticipated to produce 0.4 million tonnes of alumina and 0.12 million tonnes of Si-rich products with invested capital of 2.4 billion yuan; the second-phase project, 0.6 million tonnes of alumina and 0.18 million tonnes of Si-rich products, with invested capital of 3.6 billion yuan. The technology to be used is low-temperature ammonium sulfate sinter; the schematic diagram is displayed in Fig. 10.

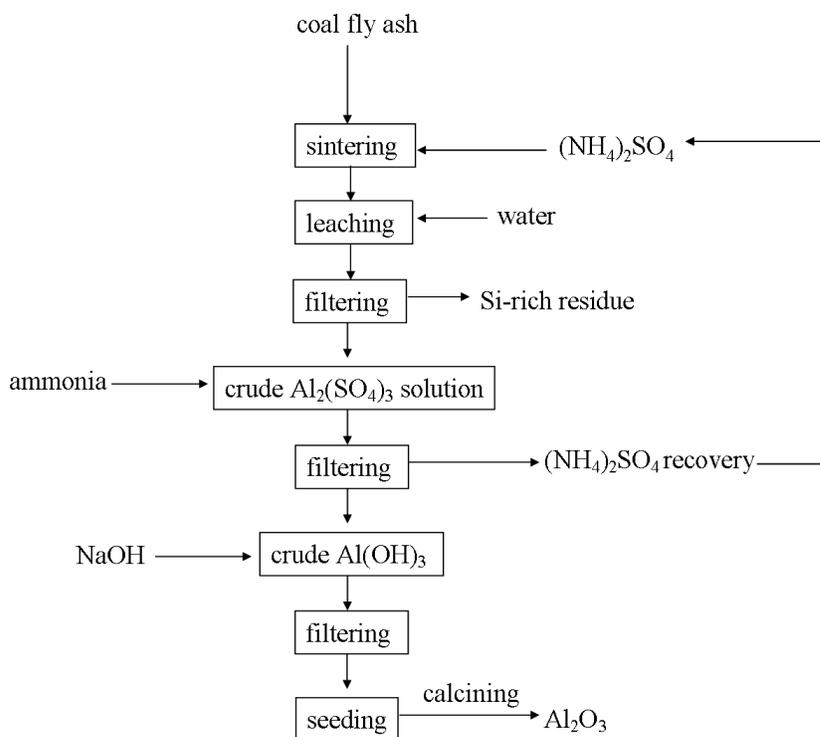


Fig. 10 Schematic diagram of ammonium sulfate sinter

The capital invested in the project in Inner Mongolia Erdos Electrical Metallurgical Co., Ltd. is 5.75 billion yuan, and it is designed primarily to produce 1 million tonnes of alumina at metallurgical grade, along with by-products such as silica white (0.51 million tonnes), sodium silicate (0.77 million tonnes) and zeolites (6.52 million tonnes). The selected technology is acid leach followed by the Bayer process.

Besides the companies listed in Table 1, other companies are also reported to be initiating this type of research. The Beijing Lucency Environ-tech Co., Ltd. (a subsidiary of the China Guodian Corporation) obtained a technology breakthrough in the decomposition and utilization technology of coal fly ash. In this laboratory test, fly ash was used to produce alumina, silica white and iron oxides with a high extraction rate.

4. Conclusions and future research

With the diminishing reserves of bauxite as well as the increasing demand for alumina, recovering alumina from fly ash has attracted extensive attentions. Such research has been seriously undertaken in China. A number of recovery methods have been developed since the pioneering work of Grzymek. However, there are some drawbacks to all these methods and most reported work to date has been at the laboratory scale. The acid leach processes can dissolve aluminium and other metals with silicon-rich residue as by-products. However, it requires acid-resistant and air-tight processing equipment, such as that used in the Shenhua Group Co., Ltd. plant, prepared from tantalum niobium alloy. In addition, alumina recovery and waste treatment can be quite complex. In the leaching process, a proportion of soluble impurities such as Fe, Ti and Mg contained in the ash are introduced into the pregnant solution, necessitating post-treatment to purify the aluminium; another drawback of the acid process includes the low extraction rate and the necessary cost of environmental protection. Most sinter processes are not related to the simultaneous extraction of alumina and silica. In addition, a generous amount of calcium silicate residues are generated, but not utilized in an effective way except by manufacturing cement. Predesilication and the lime-soda sinter combination process offer the advantages of simultaneously extracting silica and reducing the solid residues to some extent. Other problems, however, such as filtration and the washing of desilicated liquor, are also confronted in the industrial application of these processes. The cost of each tonne of alumina can be hundreds to a thousand yuan higher than that of alumina produced from bauxite using the traditional Bayer process. While fewer residues are produced in the lime-soda sinter process, as compared with the

lime sinter process, the energy cost is relatively high and the process is complex, problems that have restricted its large-scale application.

Fly ash utilization is expected to increase potential industrial synergy opportunities because of the growth of various applications that can use the by-products of recycled fly ash. However, most reported methods are still in the early stages of commercialization. Further studies are needed to turn this research into commercial reality. The following recommendations can be made based on this research:

1) Investigate the distribution of alumina-rich coal and its flow. Economies of scale can be realized in alumina recovery. The revised “Market Access Conditions for the Aluminum Industry” promulgated by the Ministry of Industry and Information Technology of China, requires that annual alumina production be no less than 500 thousand tonnes for each new plant, and that the company produce more materials or have different types of businesses that include several follow-on products, such as “coal-electricity-ash-alumina/silica/gallium-cement,” ash-cenospheres/alumina-aluminum alloy,” which could offer synergetic advantages.

2) Because the more recent technologies have their own disadvantages, there should be a greater emphasis on the development of new technology. We can use combinations of processes, such as pre-desilication followed by a lime-soda sinter process, sinter-acid leach combination process. It is also better to simultaneously recover more valuable materials, such as unburnt carbon, cenospheres, alumina, silica, gallium, titanium, etc. Additional work is needed to optimize the processing steps, particularly in the area of aluminum separation.

3) Long-term economic and environmental impact analysis, using life cycle

assessment, is needed. There is a scarcity of information on the environmental impacts of fly ash in the preparation of materials ^[9]. Likewise, economic evaluation of the applications would give greater weight to the research; currently economic data are sparse.

4) The distance between fly ash sources and recycling sites need to be taken into account. Generally, fly ash should be transported no more than 100 kms, and definitely not more than 200 kms; otherwise the production costs of recovery will be prohibitive. To promote the usage of fly ash, state and local governments should issue preferential policies that encourage its recycling, such as the preferential purchase of recycled fly ash products and reduction of the overall effective tax rate for the recycling companies.

Acknowledgements

We gratefully acknowledge financial support from Scientific Research Foundation of Hangzhou Dianzi University (Grant no. KYS205612029), Zhejiang Provincial Natural Science Foundation of China (Grant no. LQ13B070005) and Chinese National 863 High Technology (Grant no. 2007AA06Z128).

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