Bauxite residue (red mud) is a solid waste produced in the process of alumina extraction from bauxite. More than 70 million tons of bauxite residue is generated annually. Presently, it is stored on land or in the ocean near alumina refineries. However, its high alkalinity is a potential pollution to water, land and air of close proximity. Meanwhile high costs are associated with the large area of land needed for storage of the residue. China is amongst the major producers of alumina in the world. There are some differences between the residues from China and other countries due to differences in ore type and production processes. Significant achievements in treatment and utilization of bauxite residues have been obtained in China in the last decade. In this paper, the properties of bauxite residues generated in China are analyzed and significant aspects to treat and utilize residues from the sintering process and the Bayer process are introduced (e.g., storage, preparation of building materials, application in environmental materials, and recovery of valuable elements). Problems associated with the commercial application of these research achievements are considered.

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1. Introduction

Alumina is an important basic raw material for national economic development, and the alumina industry has developed rapidly in the recent ten years in China. However, the production of alumina can also lead to serious environmental problems. The bauxite residue (red mud) is the main by-product generated in alumina production. To store bauxite residues on the land or in the ocean is widely applied all over the world at present. Its high alkalinity is harmful to water, land and air of the surrounding area. Potential problems of the disposal include leaching of alkaline solution from the containing barrier, and leaking of bauxite residue slurry due to damage of pipelines or failure of retaining dams. High costs and the large areas of land are also associated with the building of bauxite residues dams. The treatment and utilization of high volume red mud waste has been a major challenge for the alumina industry. China is paying greater attention to the treatment of bauxite residues. Indeed several achievements on red mud treatment have been made in China, e.g., storage and reclamation, production of construction materials, preparation of new materials for environmental protection, recovery valuable elements. A systematical study of the properties of bauxite residues generated in China is conducted. The current status and future trend of bauxite residues utilization in China also are introduced in this paper.

2. Production and characteristics of bauxite residues in China

2.1. Bauxite resources in China

2.1.1. Reserves and production of bauxite

Bauxite is a naturally occurring heterogeneous material. It is composed of one or more aluminum hydroxide minerals, including primarily gibbsite \([\text{Al}(\text{OH})_3]\), boehmite \([\text{γ-AlO(OH)}]\) and diaspore \([\text{α-AlO(OH)}]\). There are also other compounds in bauxite such as hematite \([\text{Fe}_2\text{O}_3]\), goethite \([\text{FeO(OH)}]\), quartz \([\text{SiO}_2]\), rutile/anatase \([\text{TiO}_2]\), kaolinite \([\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4]\) and other impurities in minor or trace amounts (MII, 2009).

Bauxite resources are estimated to be 55 to 75 billion tons, located in Africa (33%), Oceania (24%), South America and Caribbean (22%), Asia (15%), and elsewhere (6%) (USGS, 2009). Fig. 1 presents the reserves and reserve base of bauxite in some major producing countries in 2008. China has taken the sixth place with 2.3 billion tons of reserve base among the bauxite production countries (USGS, 2009, 1980). Fig. 2 shows the estimated worldwide bauxite production and the relative proportion of the various main producers in 2008. Australia was the top producer of bauxite with almost 1/3 of the world share. And China is the second producer with 32 million tons of bauxite (USGS, 2009).

2.1.2. Distribution and characteristics of bauxite in China

A number of large economic bauxite deposits have been discovered in the past five decades in many areas throughout China. And 98% of the proven reserves are distributed in 6 provinces, i.e., Guizhou, Shanxi, Henan, Guangxi, Yunnan, and Shandong (Fig. 3). Most bauxite deposits in China were formed during the Carboniferous and Permian period. China has the largest reserve of diaspore bauxite in the world, while there are few gibbistic ores. However, Mesozoic ores have been reported to be of poor quality (Yang, 1989).

Table 1 shows the main composition of bauxite samples from different sources in China. Diaspore is the major type of bauxite in China. And the mass ratio of \(\text{Al}_2\text{O}_3\) to \(\text{SiO}_2\) (A/S) in diaspore is much lower than that in boehmite or gibbsite. The contents of iron (hematite, and goethite) in Chinese bauxite samples (excluding those obtained from Guangxi province) are much lower compared with that from Australia and Indonesia.

2.2. Alumina production processes and yield in China

Bauxite is conventionally classified in accordance with its intended commercial applications such as abrasive, cement, chemical, metallurgical, and refractory. Of the total quantity of bauxite mined, approximately 85% is converted to alumina \((\text{Al}_2\text{O}_3)\) for the production of aluminum metal, and 10% is used for non-metal purposes including various forms of specialty alumina, with the remaining 5% being applied for non-metallurgical bauxite applications. Therefore, the bulk of bauxite production is used as a feed for the manufacture of alumina via the Bayer process or the sintering process. The majority of alumina with the highest purity is used to produce aluminum metal by Hall-Héroult process (USGS, 2001).

2.2.1. Production processes of alumina

Selected subsidiary companies of Aluminum Corporation of China and their production processes are listed in Table 2.

Practically most of alumina produced commercially by bauxite is obtained via a process patented by Karl Josef Bayer in 1888. In the Bayer process, the aluminium-bearing minerals in bauxite – gibbsite, boehmite and diaspore – are selectively extracted from the insoluble components (mostly oxides) by dissolving them in a solution of sodium hydroxide \((\text{NaOH})\) at elevated temperature and pressure,
followed by separation of the resulting sodium aluminate (NaAlO₂) solution and selective precipitation of the aluminum as aluminum hydroxide (Al(OH)₃).

Gibbsite:

\[ \text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O} + 2\text{OH}^- \rightarrow 2[\text{Al(OH)}_4]^- \]  

(1)

Boehmite and diaspore:

\[ \text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O} + 2\text{OH}^- + 2\text{H}_2\text{O} \rightarrow 2[\text{Al(OH)}_4]^- \]  

(2)

The actual processing conditions within the digester, such as the caustic concentration, leaching temperature and pressure, as well as the operating costs, are greatly influenced by the type of bauxite ore. Ores with high gibbsite content can be processed at about 140 °C. Processing of boehmite on the other hand requires 200–240 °C. Complete extraction from diasporic bauxite requires stronger caustic solutions, in addition to higher temperatures and pressures. In general, the reaction equilibria above move to the right with increases in caustic soda concentration and temperature. In practice this means that for deposits containing the more easily recovered gibbsite only, production costs are much lower than when boehmite or diaspore are present (IAI, 2009a; Liu et al., 2006; Lancashire, 2006). The Bayer process has been successfully applied in China for local gibsite and diaspore ore, as well as in more and more plants for imported gibsite bauxite from Indonesia, Australia, and Vietnam etc.

Over time, various modification to the standard Bayer process have been attempted to resolve the problem of high silica levels in some bauxite ores. Bauxite containing 8%–15% reactive silica may be processed by either a soda-sinter process that is used directly on the high-silica bauxite feed or by a combination Bayer-sinter process applied to bauxite processing plant red mud waste streams.

The largest numbers of modified processing plants in operation have been combination Bayer-sintering refineries where the high-silica bauxite is first subjected to a traditional Bayer caustic leach. The resulting red mud, containing sodium aluminum silicates is sintered with limestone and soda ash. Then the sintered mass is leached with water to recover alumina and soda. In Henan, Shanxi, and Guangxi, the combined process is widely used (Bi, 2006; Meyer, 2004; Yang 1993).

The sintering process is unique to China and Russia. The first alumina plant in China, Shandong Aluminum Co., is a classical example of the sintering process. In this process, the low-grade bauxite is sintered with limestone and soda ash at about 1200 °C in rotary sintering kilns to form sodium aluminate and calcium silicate. The major reactions in the sintering process were listed as follows.

\[ \text{Na}_2\text{CO}_3 + \text{Al}_2\text{O}_3 \rightarrow \text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 + \text{CO}_2 \uparrow \]  

(3)

\[ 2\text{CaO} + \text{SiO}_2 \rightarrow 2\text{CaO} \cdot \text{SiO}_2 \]  

(4)

\[ \text{Na}_2\text{CO}_3 + \text{Fe}_2\text{O}_3 \rightarrow \text{Na}_2\text{O} \cdot \text{Fe}_2\text{O}_3 + \text{CO}_2 \uparrow \]  

(5)

Fig. 2. Bauxite production and the relative proportion of main countries in 2008 (USGS, 2009).

Fig. 3. Distribution of bauxite in China.
2.3.2. Chemical and mineral compositions of bauxite residues

The sintering is followed by a water leach of the sinter residue and a carbon dioxide treatment of the resulting liquor to precipitate aluminum hydroxide. Additional desilication of the liquor is required, and this is achieved in a final autoclaving stage (Smirnov, 1996; Kogel et al., 2006). The flowsheet of the process is shown in Fig. 4.

2.2.2. Production of alumina

The production of alumina in the world has been increasing steadily in recent ten years. As Fig. 5 shows, the total output increased to 60.496 millions of metric tons in 2008 from 45.784 millions of metric tons in 1999 (IAI, 2009b), relating to a growth of 32.1%. Because a lot of private capital were invested in the alumina industry and many new plants were built during the last ten years, the production of alumina has expanded to 22.784 millions of metric tons in China, which is near six times greater than that in 1999 (IAI, 2009b), and the production capabilities are still enlarging now.

2.3. Production and main characteristics of bauxite residues

2.3.1. Output of bauxite residues

Usually, the production of 1 ton of alumina generates 0.6–2.5 tons of bauxite residues, depending upon the bauxite source and alumina extraction efficiencies (Yang, 2006; Kalkan, 2006). In China, there was over 30 million tons of bauxite residues produced in 2008, including more than 10 million tons generated from the Bayer process. Furthermore, the total storage of bauxite residues in China is over 100 million tons as of 2008.

Shandong Aluminium Co. was built in 1954 as a subsidiary company of Aluminum Corporation of China. More than 22 million tons of bauxite residues were produced in this plant from sinter process until the end of 1998. From this amount, only 6 million tons were utilized in cement processes. The remaining 16 million tons were disposed as well known bauxite residue hill. The hill covers an area of 700 m×800 m with an average height of 70 m (shown in Fig. 6) (Yang and Xiao, 2008).

2.3.2. Chemical and mineral compositions of bauxite residues

Due to different ore sources and production processes, the composition of bauxite residues varies greatly from each other (Li, 1998; Liu et al., 2007). The chemical composition of bauxite residue samples from the sintering process and the combined process in different regions are shown in Table 3. Moreover, Table 4 presents the chemical composition of bauxite residues from five different plants in China. From Table 3, the different bauxite residues from the sintering process and combined process have similar composition characteristics. The contents of CaO and SiO₂ in the residues from the sintering process and combined process are much higher than that from the Bayer process. The Fe₂O₃ in red mud of Chinese ore (excluding from Guangxi Province) are much lower than that from imported ore.

Yang (2006) studied the main mineral phases in the bauxite residues from the sintering process (Table 5). In comparison, the phases in bauxite residues from the Bayer process were analyzed by X-ray diffraction (Fig. 7). The main composition of the bauxite residues from the sintering process is γ-2CaO·SiO₂, with the mass ratio being over 50%. However, major mineral compositions in Bayer process red mud include hematite (Fe₂O₃), nepernepheline (including natriodavyne, katoite etc.), gibbsite, quartz and other phases. This is consistent with the analysis of chemical compositions as stated above.

3. Storage of bauxite residues

The disposal of bauxite residues is a major problem in alumina plants throughout the world. Most of the bauxite residues produced in China are stored on land. A systematic effort has been carried out to improve upon present methods of disposal with the growing concern of environmental protection and land conservation (Agrawal et al., 2004). Major technologies for disposal include wet process, dry process, and a mixed storing process using both wet and dry processes (Qiao, 2004). Globally, dry stacking would be the current best practice for residue disposal.

In the wet process, the red mud is washed in a series of washing thickeners using large volumes of water. Although red mud is coagulated under normal processing conditions, polymeric flocculants are usually added to promote sedimentation of the solids in the washing and thickening stages. Generally, the solid content of the slurry from the last mud thickener is less than 50% by weight. Then the slurry is pumped to disposal in artificial tailings ponds or lakes where the solids settle out and the supernatant liquid is recycled. Red mud lakes have a clay seal at the bottom to contain the mud and prevent caustic leakage to ground water. This wet disposal practice of pumping large tonnages of the residue to pond in the form of dilute mud-sand slurries poses many technical, economical and environmental problems such as great volumes of material to handle and transport, high pumping energy and rapid wear in pipeline and pumps, slow rate of sedimentation and consolidation of fine mud leading to reduced life of lakes and slow rehabilitation, and potential leakage of caustic and alkaline water into underground water. This method is widely used in China for storing bauxite residues from the sintering process.

The dry stacking process involves pre-thickening the red mud to approximately 50% solid slurry and then depositing it in layers that are approximately 0.4–0.7 m thick. After initial drying the mud is turned by bulldozers which turn the dry top surface in and places the wet mud on the surface. This assists in the drying process and reduces dust emissions. Consecutive layers are then placed on top allowing the area to increase in height which subsequently reduces the over all residue footprint. This method has been working well in the Pingguo Aluminum Company in the Guangxi Province (Tian, 2008a). The operation and management are more complex in the dry process, as well as the initial investment for construction is greater. However, compared with the wet process, the dry process usually needs less farmland.

In the mixed process, the dried bauxite residues from the sintering process are used to build the dam and/or the primary base of the dam, while the bauxite residues from the Bayer process are stored in ponds or used for sub-dam construction. The advantages of these practices
are obvious. The bauxite residues from the sintering process have high shear yield strength and a low permeability coefficient thanks to the cementation reaction with water. So it is possible to build much higher dams with bauxite residues than with clay. It is also feasible to build sub-dams with dry bauxite residues from the Bayer process in the dry stack process. In this method, the requirements for clay are much less. Meanwhile, the bauxite residues generated from the Bayer process could be pumped to the dam directly without dewatering, which could make full use of the reservoir capacity without more operations. Environmental concerns has motivated the Bayer process industry in the west to increasing adopt processes to neutralize their red mud before disposal. A possible further advantage of this is that further utilization of the mud, particularly for environmental remediation, is made possible because the red mud is made more benign. Of course, the important objectives remain the same for disposal, i.e., 1) reduced mud volume, 2) reduced caustic content, 3) reduced environment impact, 4) improved reclamation potential, and 5) improved rehabilitation possibilities (Paramguru et al., 2005).

4. Reclamation of the storage yard

The disposal of bauxite residues upon the land is visually polluting and can be aesthetically damaging, while air pollution would occur from dust generated from dried areas of the disposal surface (Salopek and Strazisar, 1993; Li, 1998). The scouring of rainwater on the surface of the red mud dam is not considered as a potential problem for the physical safety of the dam. However, soluble compounds, such as sodium hydroxide, sodium carbonate, sodium bicarbonate etc., will leach into rainwater and pollute the land and rivers. As a result, the pollution from bauxite residues is enlarged.

The establishment of vegetation on the residues is useful for landscaping and pollution control on land. However, revegetation on residue storage areas was unsuccessful because of the high alkalinity and salinity, and poor nutrient contents of the fine residues (Wong and Ho, 1994a, 1993). The fine fraction of red mud is a major negative factor on the reclamation efforts (Wong and Ho, 1994b). And coarse fractions of the residue present fewer difficulties in establishing vegetation because of a higher hydraulic conductivity, which increases leaching and thereby reduces the salinity and alkalinity (Meecham and Bell, 1977). Furthermore, without drainage and reduction in pH, soluble levels of Al and Fe are high and therefore bring a risk to plant growth. In addition, the content of phosphorus compound is also limited in the high pH values soil (Barrow, 1982). Indeed, the deficiencies of the manganese micro-nutrients in sodium-rich substrates and in alkali bauxite residues have been reported (Gupta and Abrol, 1990, Wang and Ho, 1993; Gherardi and Rengel, 2001, 2003). Also, it should be noted that organic materials have been proven to be another extremely important factor for mud revegetation (Xenidis et al., 2005).

Various industrial wastes and low-cost chemicals are used as low-cost modifier to improve the possibility of revegetation on the cover of bauxite residues storage yards. The Pingguo Aluminum Co. did some study on the revegetation on the red mud. (CHALCO and BGRIMM, 2005). And the red mud from the Bayer process was modified with fluorogypsum and peat. Approximately, 8%-12.5% fluorogypsum (in weight) and some water were mixed with red mud, and the peat added into the mixture subsequently. The modified soil could be used to cover upon the surface of the red mud to encourage plant growth. Experiments showed that many kinds of plants grew well on this soil, such as vetiver grass, leucaena glauca and bermuda grass. The gypsum was used as a modification agent, because it could lower the solubility of...
Al, Na and Fe, and increase exchangeable Ca and Mg ions. In addition, gypsum could increase Mn and K (Courtney and Timpson, 2005).

Shandong Aluminum Co. also performed some studies concerning revegetation on the slope of the red mud hill. As reported, the cover rate of plants on the pilot area was above 85%. However, further monitoring of the plant performance and the transfer of elemental compositions ought to be carried out.

5. Preparation of construction materials from bauxite residues

The ban on the production and application of clay bricks was enacted by the Chinese government in 1999 in order to prevent damage to farmland (Ministry of Construction et al., 1999). The clay brick would be prohibited in all urban districts at the end of 2010 (NDRC, 2005). Non-fired bricks made from industrial waste are recognized as the main substitute. As a consequence, the construction and building materials industry becomes a major consumer of most industrial wastes (Reijnders, 2007).

5.1. Utilization of bauxite residues in cement production

As noted in Section 2.3.2, bauxite residues from the sintering process contain a great deal of $\beta$-2CaO·SiO$_2$, which is a common gelling agent in the production of building materials. Compared with bauxite residues from the Bayer process, it is much easier to use bauxite residues from the sintering process for cement and other construction materials production. It is worth noting that, the first cement plant in Shandong Aluminum Co. was built in 1965 to consume bauxite residues, and its cement production capability was increased to 1100 thousand tons annual in 1985. Several series of high quality Portland cements and oil well cements were produced with bauxite residues. Until 1998, more than 6 million tons of bauxite residues were consumed for cements production (Baidu, 2007).

Feng et al. (2007) explained the thermal activation mechanism of bauxite residues. The cement was prepared with the mixture of bauxite residue (50% in weight), several other solid wastes and a modifier. The production could achieve the standard of Portland 42.5 cement. Hence, the large-scale utilization of bauxite residues is feasible. However, it should be noted that the content of sodium in cement was limited in the newest standard of cement production (AQSIQ, 2007), which could potentially inhibit the utilization of bauxite residues in cement production.

5.2. Preparation of building materials from bauxite residues

5.2.1. Glass-ceramics

Traditionally, the glass-ceramics have been made from pure raw materials, and the products are expensive. Manufacturing glass or glass-ceramics with solid waste could recycle the waste and produce marketable products (Topping, 1976; Agarwal and Speyer, 1992). Red mud from the sintering process contains valuable mineral resources such as CaO, Al$_2$O$_3$, SiO$_2$, Fe$_2$O$_3$, and TiO$_2$. The chemical composition of red mud is quite suitable for producing glass-ceramics (Peng et al., 2005). In recent years, significant researches are carried out on producing glass and glass-ceramics with red mud (Romero and Rincon, 1999, 2000; Zhang and Yan, 2000; Bhat et al., 2002).

The CaO–SiO$_2$–Al$_2$O$_3$ glass-ceramic has been made from red mud and fly ash successfully (Yang et al., 2008a). The red mud from the sintering process is a CaO-rich slag. The fly ash is collected from electrostatic precipitator in the coal-combustion power plant as a solid waste. A crystalline phase system could be transformed from the parent glass after heat treatment, and the denser grain structure could be obtained by a suitable two-stage nucleation-crystallization process. The results showed that the total amount of these two wastes of red mud and fly ash was up to 85 wt.%, which means lower raw materials cost and greater environmental benefits.

5.2.2. Fired building materials

Considering the stabilization reaction of soluble sodium during sintering, fired bricks were prepared using the Bayer process bauxite

Table 3

<table>
<thead>
<tr>
<th>Compositions</th>
<th>Sintering process</th>
<th>Combined process</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Shandong</td>
<td>Guizhou</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>22.00</td>
<td>25.90</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>9.02</td>
<td>5.00</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>6.40</td>
<td>8.50</td>
</tr>
<tr>
<td>CaO</td>
<td>41.90</td>
<td>38.40</td>
</tr>
<tr>
<td>MgO</td>
<td>1.70</td>
<td>1.50</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>2.80</td>
<td>3.10</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0.30</td>
<td>0.20</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>3.20</td>
<td>4.40</td>
</tr>
<tr>
<td>LOI</td>
<td>11.70</td>
<td>11.10</td>
</tr>
<tr>
<td>Total</td>
<td>99.02</td>
<td>98.10</td>
</tr>
</tbody>
</table>

Fig. 6. The bauxite residue hill in Shandong aluminum Company
residues (Wang et al., 2007). The optimum process parameters were obtained as follows: fineness of gangue 100 mesh, with 25% gangue in the weight, moldering pressure of 10–15 MPa, sintering temperature of 1000 °C and a holding time of 120 min. The fired bricks were able to meet the requirements of the quality standard for common fired bricks (AQSIQ, 2003). Also, an alkali dissolution test revealed that the value of pH did not vary significantly. The X-ray diffraction analysis showed that the alkali in the bauxite residue reacted and formed NaCaAlSiO₄. He and Jiang (2007, 2008) also performed some research on fired construction materials with bauxite residue generated from the Pingguo Aluminum Company.

Tian et al. (2008b) also explored acid proof fracturing proppants with the bauxite residue from the Pingguo Aluminum Company. The acid solubility of the samples was below 4.5% which met the Petroleum and Gas Industrial Standards of China (SY/T5108-2006). The acid solubility of the samples could be decreased effectively by adding barium carbonate to the raw materials because of the formation of monoclinic celsian (Ba₂Al₂Si₂O₈) after the sintering process. And the Ba₂Al₂Si₂O₈ can prevent other compositions of the proppants from being eroded by the acid. However, the addition of barium carbonate increased the cost of the production.

### Table 4
Chemical compositions of bauxite residues from the Bayer process in different plants in China (% w/w).

<table>
<thead>
<tr>
<th>Plants/or source</th>
<th>Chalco Shandong / Indonesia</th>
<th>Xinha Group / Australia</th>
<th>Pingguo / Guangxi</th>
<th>Coalinme / Henan</th>
<th>Chalco Guizhou / Guizhou¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>26.43</td>
<td>20.98</td>
<td>16.66</td>
<td>19.38</td>
<td>15.04</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>33.88</td>
<td>30.20</td>
<td>47.48</td>
<td>11.94</td>
<td>8.83</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>17.89</td>
<td>22.00</td>
<td>16.82</td>
<td>25.87</td>
<td>22.07</td>
</tr>
<tr>
<td>CaO</td>
<td>2.66</td>
<td>2.80</td>
<td>8.86</td>
<td>19.46</td>
<td>22.2</td>
</tr>
<tr>
<td>MgO</td>
<td>0.10</td>
<td>0.86</td>
<td>1.2</td>
<td>1.09</td>
<td>–</td>
</tr>
<tr>
<td>Na₂O</td>
<td>12.18</td>
<td>10.50</td>
<td>11.6</td>
<td>5.89</td>
<td>5.2</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.37</td>
<td>0.04</td>
<td>–</td>
<td>0.39</td>
<td>–</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.72</td>
<td>2.30</td>
<td>4.17</td>
<td>5.96</td>
<td>–</td>
</tr>
<tr>
<td>LOI</td>
<td>12.94</td>
<td>9.96</td>
<td>9.05</td>
<td>7.12</td>
<td>–</td>
</tr>
</tbody>
</table>

5.2.3. Non-fired building materials

Many researchers have been investigating the reuse of bauxite residues as construction and building materials, such as ceramics (Sglavo et al., 2000; Pontikes et al., 2007), cements (Singh et al., 1996), clay bricks (Kavas, 2006.), and glazes (Yalcın and Sevinc, 2000). Unfortunately, more dewatering, separating, drying and sintering processes are necessary for these sintered products. Consequently, higher energy consumption and costs will be associated. The unsintered construction and building products from bauxite residues might be more feasible (Yang and Xiao, 2008). The optimal proportions of the raw materials for the brick are often suggested to be the following (in weight): red mud 25–40%, fly ash 18–28%, sand 30–35%, lime 8–10%, gypsum 1–3%, and Portland cement 1%. A flow sheet for the production of unsintered bauxite residue bricks is shown in Fig. 8. The results showed that the brick reached the 1-st grade of Chinese standard for the brick. Analysis showed that C–S–H gel and ettringite are the main contributors to the strength of brick. Some other research similar to an investigation about aerated-concrete blocks was carried out by Wu et al. (2005).

Bauxite residues from the Henan province usually contain silicon and calcium with small quantities of iron. A kind of composite brick made from the Bayer process bauxite residue was produced depending on the combined solidifying performance of cement and lime-fly ash (Yang et al., 2008b). It should be noted that besides bauxite residue, several industrial solid wastes from industry were used in the brick, such as fly ash, boiler slag and carbide slag. The bricks were modeled under a pressure, and then cured with steam at a pressure of 0.8 MPa for 8 h. According to the test results from the Henan Province Building Materials Quality Supervision and Testing Stations, the quality of the product could reach the Chinese industrial standard for fly ash bricks (Building Materials Industry Bureau of China, 2001). Using this technology, a brick plant with production capability of 50 million bricks was built in Coalinme Aluminum (Sanmenxia) Co., Ltd.

It is important to point out the unique features of the alumina industry in China that make the residues rather unique in many of the operations. As mentioned above, the fact that the domestic sources of bauxite are mostly diasporic and contain high silica results in the use of the sinter process extensively. This also results in residues with properties similar to Portland cement which renders these more amenable to construction uses than the standard Bayer process residues.

### 6. Application in environmental materials

Besides high alkalinity, bauxite residues usually have a large specific surface area and a high ion-exchange capacity. Investigations have also been extended to develop bauxite residues as an adsorbent for removal of toxic heavy metals, metalloid ions and inorganic anions, as well as organic compounds.

#### 6.1. Application in waste water treatment

Bauxite residues have been studied extensively for potential use as a low cost sorbent for the removal of metal ions (Brunori et al., 2005). Indeed the adsorbent exhibited high adsorption capability for cadmium after specific thermal or chemical treatment (Güçlü and Apak, 2000, 2003; Apak et al., 1998; Gupta and Sharma, 2002). Most researchers have investigated fine red mud powder as adsorbents for metal ions directly. Powdered red mud adsorbent has high specific adsorption area and other characteristics suitable for adsorption. However, the powdered red mud adsorbents are difficult to be regenerated and recycled after application. Zhu et al. (2007) prepared granular red mud ceramics and evaluated its potential use to remove cadmium ions from aqueous solutions as a low-cost adsorbent. The granular bauxite residue was made with Bayer red mud provided by the Shandong Aluminum Co., China. And the production processes of the absorbent are shown in Table 5. They found that the adsorption of cadmium ions on granular bauxite residue was spontaneous and feasible, and it could be indicated by the endothermic nature for cadmium adsorption. The cadmium-loaded granular adsorbents could be regenerated by pumping 0.1 mol/L hydrochloric acid through the adsorbed column.

Zhang et al. (2008a) found that the modified bauxite residue with FeCl₃ could be used for the removal of arsenate from water. Firstly, the bauxite residues were sieved, and the fine powder was added into water. Then the FeCl₃ solution was added into the mixture dropwise, and the resulting solution was aged and washed. The bauxite residue was then sieved again, and fine powders were used as the adsorbent for the experiments. Zhang et al. believed that the adsorption capacity was affected significantly by the pH of the solution. They also found that NO₃⁻ had little effect on the adsorption, while Ca²⁺ enhanced adsorption, and HCO₃⁻ decreased adsorption. The modified bauxite residue could be regenerated with NaOH solution.

#### Table 5
Mineral compositions of bauxite residue from the sintering process (Yang, 2006).

<table>
<thead>
<tr>
<th>Mineral composition</th>
<th>%, w/w</th>
</tr>
</thead>
<tbody>
<tr>
<td>j–2CaO·SiO₂</td>
<td>50–56</td>
</tr>
<tr>
<td>Limonite (Fe₂O₃·H₂O)</td>
<td>4–10</td>
</tr>
<tr>
<td>Calcite (CaCO₃)</td>
<td>2–12</td>
</tr>
<tr>
<td>Anorthite (3CaO·Al₂O₃·0.6SiO₂·4.9H₂O)</td>
<td>5–9</td>
</tr>
<tr>
<td>Sodium aluminosilicate (Na₂O·Al₂O₃·1.7SiO₂·2H₂O)</td>
<td>5–9</td>
</tr>
<tr>
<td>4CaO·Al₂O₃·Fe₂O₃</td>
<td>3–5</td>
</tr>
<tr>
<td>CaO·TiO₂</td>
<td>2–5</td>
</tr>
</tbody>
</table>
6.2. Soil remediation with bauxite residues

Heavy metal pollution of soil is an increasing problem all over the world. Heavy metals, unlike organic contaminants, are generally immutable, not degradable and persistent in soil (Adriano et al., 2004). Several studies have demonstrated the adverse effects of heavy metal contamination on the size, structure and functional diversity of soil microbial populations (Lombi et al., 2002; Akmal et al., 2005; Castaldi et al., 2005). It is a tendency to use industrial waste as additives to stabilize heavy metals to minimize the disturbance of contaminated soils (Garau et al., 2007).

Yi et al. studied the stabilities of heavy metals in solid with bauxite residues (2006). Two soil samples were collected from the Niujiaotang mining area, Guizhou Province, China. They were polluted by fly ash (sample I) and by waste water from a smelter (sample II), respectively. One of the red mud samples (noted as BRM) was collected from the Bayer process and the other (noted as CRM) from the combined process in the Aluminum Plant of Guizhou. The concentrations of free heavy metal ions in sample I increased after it was mixed with CRM, but decreased when BRM was added. The free ions concentrations of nickel and cadmium were found to vary greater when compared with copper and zinc ions. When BRM was added into sample II, the free concentrations of copper and zinc ions varied slightly, while the concentrations of free nickel and cadmium decreased noticeably when the addition ratio of BRM was 2.00% (in weight). Meanwhile, all experimental procedures were modeled by ECOSAT. The predicted and measured results were consistent except for zinc.

In the Guangdong Dabaoshan Mine, the soil was contaminated by acid sulfate, and the pH was 2.76 (Lin et al., 2003). Pot trials were carried out to investigate the effects of various soil treatments on the growth of

![Fig. 7. X-ray patterns of bauxite residues from the Bayer process (samples from Coalmine Aluminium Co. Ltd, Shandong Aluminium Company, Pingguo Aluminium Company and Xinya Group were marked from I to IV respectively.) 1, Natrodavyne (3NaAlSiO₄·Na₂CO₃); 2, Katoite (Ca₂.₉₃Al₁.₇₇Si₀·₆₄O₂.₅₆(OH)₉.₄₄); 3, Calcite (CaCO₃); 4, Gibbsite (Al(OH)₃); 5, Diaspore (Al₃(OH)₂); 6, Hematite (Fe₂O₃); 7, Nordstrandite (Al(OH)₃); 8, Cristobalite (SiO₂); 9, Quartz (SiO₂); 10, Sodium Hydroxide (NaOH); 11, hydrated Halloysite Al₂SiO₅(OH)₄·2H₂O; 12, Sodium Aluminum Silicate Hydrate (1.0Na₂O·Al₂O₃·1.68SiO₂·1.73H₂O).](image)

![Fig. 8. Flow diagram of bricks production made from sintering bauxite residue.](image)
vetiver grass (Vetiveria Zizanioides). Several kinds of sorbents and neutralization agents were used in this project, such as hydrated lime, red mud, biosolids, fertilizer and zeolite. The results showed that vetiver grass could grow well on the soil treated with red mud and hydrated lime. However, chemical fertilizer and zeolite powder were negative to the growth of the vetiver grass.

6.3. Absorption and purification of acid waste gases with bauxite residues

Chen et al. (2007) studied the absorption and purification of the waste gas of SO2 with Bayer bauxites residue from the Guizhou Aluminum Plant of Chalco. They found that Bayer bauxite residue could be used as a desulfurizer because of its high alkali, large absorption capacity and simple production process. The content of SO2 in the outlet gas was below 150 mg/m3, and the absorption rate was over 95%. Followed by physical adsorption, chemical neutralization reactions played the main roles in the process of absorbing SO2. The desulfurization residues could be reused as raw materials in the production of cement.

Actually, the market requirements of these environmental protection materials are very small. However, it is beneficial to utilize bauxite residues as a low-cost raw material. And it is also meaningful in the view of environmental protection.

7. Recovery of valuable elements from bauxite residues

Due to the special coexisting state of aluminum with some other elements in bauxite, there are usually many valuable elements remaining in bauxite residues such as titanium, scandium, gallium, sodium, and iron. With the exhaustion of many natural resources, the extraction of the aforementioned elements from bauxite residues would be a highly useful research project.

7.1. Recovery of alumina and/or sodium from bauxite residues

The alumina plant II of the Shandong Alumina Co. produces alumina by the Bayer process with gibbsitic bauxite ore imported from Indonesia. Part of the bauxite residue from the Bayer process was recycled in the sintering process together with diaspore bauxite. During the process, alumina and sodium in the bauxite residue could be recovered effectively (Li, 2005; Ahmet and Mehmet, 2003). However, the addition of red mud with high content of iron should not be too much, because the ferric oxide could react with Al2O3, SiO2 or CaO in the sintering process, and produce insoluble substance, which is negative to the recovery of aluminum. As a result, most of Bayer process bauxite residue is pumped to disposal site in the alumina plant II of the Shandong Alumina Co.

There is about 15–25% Al2O3 and 5–12% Na2O remaining in common red mud generated from the Bayer process. Liu et al. (1997) did some work on recovery of aluminum and sodium. Firstly, they mixed bauxite residue with hydrated lime. Then the mixture was treated in a hydrothermal process. After calcination, 70% of Al2O3 and 90% of Na2O in the red mud were concentrated and recovered with soda solution. Sodium aluminate solution was pumped back to the Bayer process. The solid residues could be calcined for producing cement.

Zhou et al. (2008b) analyzed the thermodynamic data of the chemical reactions which were involved in the sintering process for alumina recovery from high-iron bauxite residue. They also investigated factors in the sintering process, such as sintering temperature and sintering duration time. The results showed that the formation of insoluble compound salts (Na2O·Al2O3·2SiO2, 4CaO·Al2O3·Fe2O3 etc.) would result in the decrease of alumina recovery in the sintering stage. Meanwhile, increasing the mass fraction of sodium ferrite (Na2O·Fe2O3) in the sintering process improved the recovery ratio of alumina from iron-rich the bauxite residue. According to experiments, the optimized conditions were as follows: 10%–12% of the mass fraction of sodium ferrite, approximately 1.0–1.2 M ratio of calcium oxide to ferric oxide, 1000–1050 °C sintering temperature, and 30–40 min sintering time. Under the optimal conditions, the recovery ratio of alumina could reach 85%–90%.

7.2. Recovery of iron from Bayer bauxite residues

The content of Fe2O3 in Bayer bauxite residues could reach 25–50% by weight. Generally, it is feasible to recover iron from bauxite residues.
7.2.1. Recycling iron ore with ore dressing technology

The separation of iron ore from solid waste can be achieved using a physical process. In order to decrease the burden of batch sintering and recycle the iron mineral, Li (2005) investigated the new iron ore dressing of bauxite residue. Firstly, the ore sand was separated from the bauxite residue by washing twice. The iron content in sand achieved was between 30%–40% (iron percentage varied depending on ore grade). Then the sand was ground. Thirdly, the iron ore was further concentrated from the ground sand. Compared with flotation, gravity dressing, and sintering magnetic dressing, the pulsatling high-grade magnetic dressing was believed to be the best method to concentrate the iron ore. According to the results, the grade of iron ore concentrate was about 56%, and the recovery rate was about 90%. Generally speaking, the flow was simple and was easily controlled. Using the similar method, ten production lines for iron recovery were built in Shandong Xinfu Aluminum-Electricity Group. The bauxite residue was separated into three parts, i.e., the iron ore, sand and fine mud, through the cyclone separator, the magnetic separator, the spiral chute and the shaking table sequentially. The total ferrum content in the concentrate was over 56%. The sand was used as a raw material in concrete bricks. The economic assessment showed that the process is profitable. However, the fine mud was pumped to the storage site without further utilization at present.

7.2.2. Recovery of iron with reduction roasting process

Mei et al. (1995, 1996a,b) did systemic experimental research and theoretical analysis on the recovery of iron from bauxite residue using the direct reduction roasting process. They discovered an efficient catalyst (noted as catalyst A) for the direct reduction roasting process to recover iron from bauxite residue. The impact of several parameters on recovery ratio and the quality of concentrated iron were analyzed, and the optimized conditions of the process were obtained as follows: mass ratio of bauxite residue: coal: catalyst A = 83.6: 13.9: 2.5, roasting at 1150 °C for 110 min. The positive impact of sodium on the process. In this process the leaching rate of TiO2 was found to be 96.57%.

7.3. Recovery of rare earth elements from bauxite residues

Some rare earth metals such as scandium (60–120 g/t), gallium (60–80 g/t), and yttrium (60–150 g/t) are contained in the bauxite residues (Smirnov and Molchanova, 1997).

Zhang et al. performed systemic studies in the recovery of pigment, Sc2O3 and TiO2 by the acid leaching process (2003, 2005a,b; Zhang and Zhang, 2006). They found that Fe2O3, Al2O3, and Sc2O3 in bauxite residue were soluble in dilute hydrochloric solution, but the TiO2 component was soluble in sulphuric acid solution. Hence, a two-step acid leaching process was proposed. The first leaching process was completed using 6 mol/L HCl solution with the leaching rate of Sc2O3 being over 80% and the leaching rate of TiO2 at approximately 1%. Then the insoluble residue from the HCl leaching process was treated by the H2SO4 leaching process. In this process the leaching rate of TiO2 was found to be 96.57%.

Scandium could be transferred to the organic phase (consisting of 1% P507 and kerosene) from the HCl solution. After cleaning twice with 6 mol/L HCl and water, more than 90% Sc from the HCl solution transferred to organic phase. After reverse extraction by NaOH solution, the content of Sc2O3 in the product was about 66%. The purity of Sc2O3 in product could be improved to over 96%, if some impurities in the HCl solution (i.e., Fe3+, Al3+ and Zr) were removed. Fe3+ and Al3+ could be separated by adjusting pH with ammonia. TiO2 could be recovered from the H2SO4 solution by concentrating, hydrolyzing, washing and calcination.

Scandium could be selectively extracted from bauxite residue by activated carbon that is modified by tri-butyl phosphate (TBP) (Zhou et al., 2008b). The influences of adsorbent dosage, adsorption temperature, and time on capacity and selectivity of adsorption of scandium were examined. An optimum adsorbent dosage (6.25 g/L), adsorption temperature (308 K), and adsorption time (40 min) were obtained. A pseudo-second-order kinetics model was employed to describe the adsorption process of scandium.

Generally, it is not economic to exploit bauxite residues as raw materials to recovery one component exclusively due to the limited contents of valuable elements. Aluminum and iron are the main components of bauxite residues from the Bayer process. Typically, the aluminum exists in the residue as sodium silica slag and diaspore commonly. Consequently, the sintering or smelting process is necessary for the formation of Na2O·Al2O3, CaO·Al2O3 or 12CaO·7Al2O3. The reactions are shown as follows.

\[
\begin{align*}
\text{Na}_2\text{CO}_3 + \text{Al}_2\text{O}_3 & \rightarrow \text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 + \text{CO}_2 \uparrow \\
\text{CaO} + \text{Al}_2\text{O}_3 & \rightarrow \text{CaO} \cdot \text{Al}_2\text{O}_3 \\
12\text{CaO} + 7\text{Al}_2\text{O}_3 & \rightarrow 12\text{CaO} \cdot 7\text{Al}_2\text{O}_3 
\end{align*}
\]

Meanwhile, the high temperature process also is required to complete the deoxidation reaction of Fe2O3.

\[
\begin{align*}
\text{Fe}_2\text{O}_3 + 3\text{C} & \rightarrow 2\text{Fe} + 3\text{CO} \uparrow \\
\text{Fe}_2\text{O}_3 + 3\text{CO} & \rightarrow 2\text{Fe} + 3\text{CO}_2 \uparrow \\
3\text{Fe}_2\text{O}_3 + \text{C} & \rightarrow 2\text{Fe}_3\text{O}_4 + \text{CO} \uparrow 
\end{align*}
\]

If these two processes could be combined in one high temperature process, the energy consumption and associated costs would be greatly reduced. In this method, the sodium aluminate or calcium aluminate would be leached from the sinter, and then the iron could be collected with a magnetic separator from residue. Also, the residues could be used in building materials production directly or after extracting rare elements. Thus, it will be an economic method to realize zero waste of red mud.

8. Conclusion

Many efforts to utilize bauxite residues are being made in various fields in China. However, few of them are commercially applied. Reasons for this could be explained by the following.

(i) The characteristics of bauxite residues make it difficult to be treated and utilized. The residue is characterized by complex compositions, small grain size, and large specific area. The high water content and high alkalinity create more problems for disposal and reuse of the residue.

(ii) The problem of a large quantity of bauxite residues cannot be solved because of the limited consumption and incomplete utilization by existing technologies. And the markets for these
products should be considered seriously. Preparation of building materials with bauxite residues could consume waste with simple procedures, but the use of bauxite residues is usually limited by residual sodium and its radioactivity. Although some kinds of waterproof dope could decrease the impact of scumming, the cost of production would be much higher. It would be beneficial to utilize bauxite residues in the preparation of environmental protection materials. However, the market requirements of these productions are very small. A large amount of residues are generated after the recovery of valuable elements, Fe, Ti, Sc etc, and the treatment and utilization of these residues should be faced seriously.

(iii) The environmental and safety concerns are usually negative to the spread of new technologies. Some times, customers do not want to accept product which is made from waste. For example, many people worry about the radioactivity or the exudation of soluble alkali of bricks and glass-ceramics prepared with bauxite residues.

In summary, the treatment and utilization of bauxite residues is an urgent problem in China. Based on the processes and the compositions of red mud, two strategies may work. 1) Recovering elements (i.e., aluminum, sodium, iron etc.) from Bayer red mud, and then using the residues as raw materials for rare elements extraction or building materials production. 2) Preparing valuable materials, e.g., glass-ceramics, with red mud from the sintering process.

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