Development of unsintered construction materials from red mud wastes produced in the sintering alumina process

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Abstract

A large quantity of red mud (RM) has been disposed to form hills from the Chinese sintering alumina process. These storage areas are generally bare of vegetation and subject to wind and water erosion, posing serious threats to the environment. Numerous sintered products made from RM have been developed, such as ceramics, burnt bricks, cements etc., however, such sintered products have seldom been applied because of the higher energy consumption and costs. Unsintered brick was developed from RM, cured at ambient conditions. The optimal proportions of RM brick are suggested as the following: 25–40% RM, 18–28% fly ash, 30–35% sand, 8–10% lime, 1–3% gypsum, and about 1% Portland cement. Samples of RM bricks with standard Chinese brick dimension were prepared. The results show that the RM brick product reaches the Chinese criterion of the 1st-class brick. Microstructure characteristics of the RM brick were investigated by XRD and SEM. C–S–H gel and ettringite are the main hydrated products, which might contribute to the strength of brick. No sintering, drying or grinding pre-treating process, and no emission of polluting gases are some of the benefits of such an unsintered product, and which may have a huge application in the market of construction materials.

Keywords: Red mud; Construction materials; Alumina production; Wastes reuse

1. Introduction

Alkaline red mud (RM) is a waste by-product from extracting alumina from bauxite with caustic soda in the Bayer process. Approximately 35–40% of bauxite ore is a waste material which is disposed as an alkaline RM slurry [1,2]. The solid phase occupies only 15–40% of the initial mud slurry volume. RM has a superfine particle-size distribution, large surface area, strong absorbing capacity of water, and long-term persistence of alkaline. Complicated washing-recovery of sodium, and dewatering-separation process, are expensive unavoidable parts in the alumina production. The disposal of RM waste costs the industry $3 per ton of alumina production [3].

In the last century, many countries (France, Great Britain, Jamaica, Japanese, Italy, USA) dumped RM slurry directly into the sea [4]. The effects of these deposits on the marine environment and marine organisms were found to be harmful, caused by the residual alkaline and fine particles’ suspension in the sea [4,5]. On the other hand, RM produced in non-coastal alumina plants are stored in confined impoundments, which can occupy huge areas of land. There are nearly 3 million tons of RM waste accumulated at an alumina plant in Turkey between 1973 and 1996 [1]. It is estimated that over 66 million tons of this waste is impounded annually in the world, with two million tons in India alone [6]. Shandong Aluminium Co. Ltd. (formerly called Shandong Aluminium Plant), one of the subsidiary companies of Aluminium Corporation of CHINA LIMITED, is the first aluminium plant in China, located in Zibo city. There has been more than 22 million tons of RM waste accumulated at Shandong Aluminium Plant since the plant was setup in 1954. The old landfill site of
RM occupies an area of 700×800 m, with an average height of over 70 m, and is nearly reaching the capacity limit (shown in Fig. 1). These storage areas are generally bare of vegetation and subject to wind and water erosion, posing serious threats to the environment, mainly due to its caustic nature [7]. Because of reddish-brown color and bare of any plants on the surface of RM landfill site, local people call it “RM hill”.

There are several researches on RM reuse, for example, being used as some fillers in PVC [8]; producing radiopaque materials [9], catalysts [10], and pigments [11]; for the recovery of some valuable elements [12–14]; and for the stabilization of clay liners [2]. Unfortunately, RM reuse techniques consume relatively small amounts of waste, compared to a huge quantity of RM discharged from the alumina production every year. Generally, 1–1.5 tons of RM is formed for the production of 1 t of alumina. Over the years, many attempts have been made to find a use for RM. However, effective reuse technologies have mostly not been put into practice, and no significant quantity of RM is actually being utilized anywhere in the world. Therefore, the storage and disposal of RM is a serious problem for all of the world’s alumina plants.

On the other hand, the construction and building industry is a major consumer of ‘virgin’ minerals that are chemically similar to most industrial wastes [15]. Many researchers have investigated the reuse of RM as construction and building materials, such as ceramics [16], cements [17], clay bricks [18], and glazes [1], produced by thermal or sintering processes. Unfortunately, it is necessary for such sintered products to introduce more dewatering, separating, drying, and sintering process, which leads to higher energy consumption and costs. Development of unsintered construction and building products from RM might solve the problem. Waghi reported silica bonded, unsintered ceramics produced from Bayer process waste [19]. However, drying the RM sample and vacuum impregnating the silica solution in the holes of the drying RM, is a necessary process, which also contributes to the higher costs. Jamaicam developed hydrated lime stabilization of RM from the Bayer process, but the strength of the product was found to be low unless limestone was added to about 40–80% [20].

Most of the Chinese bauxite ore has composite properties of low Al₂O₃/SiO₂ (A/S) (average 5–6), so alumina production is not the Bayer process, but a sintering process, in which the mixture of bauxite is firstly sintered at a temperature of about 1200 °C before extracting alumina from the sintered mixture of bauxite with caustic soda. Thus, the major crystalline phase of RM waste in the sintering process is β-2CaO·SiO₂, the same major crystalline phase of ordinary Portland cement. However, the major constituents of RM waste in Bayer process are hematite (Fe₂O₃), boehmite (γ-AlOOH), quartz(SiO₂), sodalite (Na₄Al₃Si₃O₁₂Cl) and gypsum (CaSO₄·2H₂O) and gibbsite (Al(OH)₃) [21]. Therefore, the strength of the unsintered product from sintering process RM is much stronger than that of the unsintered product from Bayer process RM. This presents the feasibility of manufacturing of an unsintered product from RM produced from the sintering alumina process.

In this paper, development of unsintered brick has been studied from RM produced by Shandong Aluminium Plant. Such unsintered brick product has lower cost and higher strength, and therefore has a large potential application market, and may provide an effective consumption method of RM in Shandong Aluminium Plant. Such brick products could assist in RM wastes management for other Chinese sintering alumina production plants, such as those located in Shanxi, Henan, Guizhou.

2. Materials and methods

2.1. Raw materials

2.1.1. Red mud

RM waste was obtained from the first RM landfill site in Shandong Aluminium Plant. There was found to be two typical kinds of RD. One has a water content of 45 wt%, and has been stored at the top of RD storage site for a short period time (less than 1 year), and is called fresher RM. The other has a water content of 38 wt%, and has been stored at the bottom of RD storage site for a long period time (over 10 years), and is referred to as elder RM. The chemical compositions of the two types of RM are shown in Table 1; XRD patterns are shown in Fig. 2. As shown in the XRD patterns, activated minerals, C₃A and C₂S, were the major crystals found in fresher RM. However, these major crystals transferred into CaCO₃ in elder RM because of the effects of carbonation in the atmosphere. This mineral transformation was quite consistent with the increase of loss on ignition (LOI) from fresher RM to elder RM, shown in Table 1. In order to maintain a suitable moisture content of the mixture, both fresher RM and elder RM are used in a ratio of 1:1.

2.1.2. Fly ash

Fly ash (FA) was collected from the electrostatic precipitator of the coal-combustion electric subsidiary plant in Shandong Aluminium Plant. Dry fly ash was used in the production of bricks.
2.1.3. Sand

Properties of unsintered bricks are greatly affected by the particle size distribution of sand, as an aggregate. Coarse-grained sand was used, and the sieve analysis of sand was evaluated as per Chinese standard of construction sand (GB/T14684-2001). The particle size distribution of sand is shown in Table 2.

2.1.4. Lime

Quicklime is a by-product of production of CO₂ gas in the calcination of limestone in the alumina plant. Quicklime powder passing through a sieve size of 0.5 mm was used. The chemical composition of lime is also shown in Table 1.

2.1.5. Gypsum

Gypsum powder passing through a sieve size of 0.5 mm was used. The major crystalline phase of natural gypsum is CaSO₄·2H₂O. The chemical composition of lime is also shown in Table 1.

2.1.6. Portland cement

Ordinary 425 Portland cement (PC) was used in experimental work.

2.2. Preparation of brick specimens

To enhance the activities of RM, fly ash, and sand, composite activators such as lime, gypsum, and Portland cement were investigated. Five groups of experimental plans were carried out in order to determine the optimal ratio of RM to fly ash, the optimal proportion of sand,
the effects of lime, gypsum, and Portland cement, respectively. The results are shown in Table 3.

Specified proportions of mixtures were taken and mixed thoroughly. The water content in the mixture was controlled at approximately 15%, with the addition of a suitable amount of water in the mixing process. Bricks with dimensions of 120 mm · 115 mm · 53 mm, half the length of a 240 mm standard Chinese brick, were made by pressing in a hydraulic machine at a pressure of 20 MPa. Thereafter the bricks were unloaded from a steel mould and cured at ambient conditions. Bricks were tested for compressive strength after curing for 7 days and 28 days, and which were used to assess the initial strength and end strength of RM brick, respectively. Each strength was the average value of two parallel samples. The schematic for the preparation of RM bricks is shown in Fig. 3. During the ageing process of the mixture, the quicklime absorbed water and turned into hydrated lime. At the same time, the heat released from the hydrate reaction of quicklime was able to activate the following hydrate reaction of mixture.

<table>
<thead>
<tr>
<th>Mix designation</th>
<th>Proportions (wt%)</th>
<th>Compressive strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RM &amp; Fly ash &amp; Sand &amp; Lime &amp; Gypsum &amp; OPC</td>
<td>7 (days)</td>
<td>28 (days)</td>
</tr>
<tr>
<td>I-1</td>
<td>43</td>
<td>14</td>
</tr>
<tr>
<td>I-2</td>
<td>33</td>
<td>24</td>
</tr>
<tr>
<td>I-3</td>
<td>23</td>
<td>34</td>
</tr>
<tr>
<td>II-1</td>
<td>40</td>
<td>27</td>
</tr>
<tr>
<td>II-2</td>
<td>37</td>
<td>25</td>
</tr>
<tr>
<td>II-3</td>
<td>33</td>
<td>24</td>
</tr>
<tr>
<td>II-4</td>
<td>31</td>
<td>21</td>
</tr>
<tr>
<td>II-5</td>
<td>28</td>
<td>19</td>
</tr>
<tr>
<td>III-1</td>
<td>36</td>
<td>26</td>
</tr>
<tr>
<td>III-2</td>
<td>34.5</td>
<td>25</td>
</tr>
<tr>
<td>III-3</td>
<td>33</td>
<td>24</td>
</tr>
<tr>
<td>IV-1</td>
<td>35</td>
<td>25</td>
</tr>
<tr>
<td>IV-2</td>
<td>34</td>
<td>25</td>
</tr>
<tr>
<td>IV-3</td>
<td>33</td>
<td>24</td>
</tr>
<tr>
<td>IV-4</td>
<td>32</td>
<td>23</td>
</tr>
<tr>
<td>V-1</td>
<td>33</td>
<td>24</td>
</tr>
<tr>
<td>V-2</td>
<td>32</td>
<td>24</td>
</tr>
<tr>
<td>V-3</td>
<td>32</td>
<td>23</td>
</tr>
<tr>
<td>V-4</td>
<td>31</td>
<td>22</td>
</tr>
</tbody>
</table>

2.3. Preparation of RM bricks with the size of standard Chinese brick

Samples of RM brick with the proportions of V-2 were prepared in a steel mould of internal dimension 240 mm × 115 mm × 53 mm, the same as a standard Chinese brick. Two sets of specimens were prepared. The first set of 50 specimens was cured for 28 days, and then tested for properties, including compressive strength, flexural strength, bulk density, water absorption, resistance of freezing-thawing, radioactivity, coefficient of carbonation, and drying shrinkage. All of the tests were followed by Chinese test methods for wall bricks (GB/T 2542-2003). After the specimens were tested for compressive strength, broken specimens were used for investigation of microstructure characteristics. Broken specimens were immersed and saturated in anhydrate ethanol for 48 h in order to end the hydrate reaction, then dried at 40 °C for 48 h. A small section of dried sample was prepared for morphology analysis after coating with gold for SEM analysis (Sirion 200); and the crystalline phase was investigated by powder XRD technique (D/Max-RC). The
second set of 50 specimens were tested for long-term behavior of the strength, after being cured for 3 days, 7 days, 12 days, 20 days, 28 days, and 60 days.

3. Results and discussion

3.1. The effects of RM and fly ash on strength

In the first group of experiments, labeled I-1, I-2, I-3, I-4, effects of different ratio of RM to fly ash on strength were investigated, shown in Fig. 4 and Fig. 5. As shown in Fig. 4, compressive strength on the 7th day samples increased linearly with the increasing of RM content; compressive strength on the 28th day samples increased as RM content increased to 33%, but the compressive strength on the 28th day samples decreased as RM content increased above 20%.

As shown in Fig. 5, compressive strength on the 7th day samples decreased linearly with the increasing of fly ash content. However, there was non-linear relationship between compressive strength on the 28th day samples and fly ash content, since long-term curing time more than 28 days is needed with the increase in FA contents.

The results show that the influence of RD on compressive strength on the 7th day samples (initial strength) is stronger than the influence of fly ash. The possible reason for this is that RM contains many of the activated materials found in cement, such as C₃S, which can hydrate much more quickly than the activated materials in fly ash, such as SiO₂ and Al₂O₃. In general, the optimal RM content is 25–40%, and the optimal fly ash content is 18–28%.

3.2. The effects of sand aggregate on strength

In the second group of experiments, labeled II-1, II-2, II-3, II-4, and II-5, the effects of sand content on compressive strength were investigated, as shown in Fig. 6. It was found that compressive strength on the 7th day samples increased nearly linearly with the increasing of sand content; and the compressive strength on the 28th day samples achieved a maximum value when sand content was about 30%. Generally, optimal sand content is from 30% to 35%.

3.3. The effects of lime and gypsum on strength

In the third group of experiments, labeled III-1, III-2, and III-3, the influence of lime content on compressive

![Fig. 4. Effects of RM content on the compressive strength.](image)

![Fig. 5. Effects of fly ash content on the compressive strength.](image)

![Fig. 6. Influence of sand content on compressive strength.](image)

![Fig. 7. Influence of lime content on compressive strength.](image)
strength was investigated, as shown in Fig. 7. As presented, compressive strength both on the 7th day samples and 28th day samples increased with the increasing of lime content.

In the fourth group of experiments, labeled IV-1, IV-2, IV-3, and IV-4, the influence of gypsum content on compressive strength was investigated, presented in Fig. 8. As shown, compressive strength both on the 7th day samples and 28th day samples increased with the increasing of gypsum content, especially below 3%. In Chinese criterion of the 1st-class brick, compressive strength on the 28th day samples is over 15 MPa. Considering both strength and cost, optimal lime content is from 8% to 10%, and optimal gypsum content is from 1% to 3%.

3.4. The effects of PC on strength

In the fifth group of experiments, labeled V-1, V-2, V-3, and V-4, the influence of PC content on compressive strength was investigated, shown in Fig. 9. It was found that compressive strength increased as PC content increased from 0% to 1%, but the compressive strength values decreased as PC content increased above 1%. Normally the strength would increase with the increase of the content of PC. The reason of this repeated abnormal results would be investigated in the future. In general, the optimal Portland cement addition is about 1%.

3.5. Properties tests of RM bricks with dimensions of standard Chinese brick

The photographs of RM brick specimens are shown in Fig. 10. As shown in Fig. 10a, RM brick specimens with dimensions of 120 mm × 115 mm × 53 mm were prepared in five groups of experiments. As shown in Fig. 10b, RM bricks with dimensions 240 mm × 115 mm × 53 mm of standard Chinese brick were prepared, and their properties were determined. The Results of tests are summarized in Table 4. As shown in Table 4, all of the properties reached the Chinese criterion (JC 239-2001) of the 1st-class building brick. The bulk density of the RM brick is larger than a common burnt clay brick because the RM brick was prepared in a mould with high pressure, which is a shortcoming of such a product. However, it could be improved if the brick was prepared with inner hollows in the following research. Good resistance to freezing–thawing cycles shows that such a brick owns good durability in a humidity environment or cold climate. No sintering, drying or grinding pre-treating process, and no emission of SO$_2$ or CO$_2$ are some of advantages of such an unsintered RM brick, compared to ceramic products and burnt clay bricks. Claudia’s studies on the environmental compatibility on the reuse of Bayer RM gave encourage results: the treated RM generally showed a high metal trapping capacity and the release
at low pH was typically low [21]. In general, an unsintered RM brick may have a huge potential application in the market of construction materials.

Long-term studies of the strength of RM brick showed a much slower increase in the strength in the period beyond 28 days. This study lasted up to 60 days, as shown in Fig. 11. The result of a slower increase in the long-term strength shows the common characteristics of hydrate hardening of industrial wastes, compared to ordinary Portland cement.

### 3.6. Strength mechanism of RM bricks

The XRD pattern of RM brick cured for 28 days is shown in Fig. 12. As shown, the major mineral phases were quartz and calcite, and comprising of some C–S–H gel. C–S–H gel is the hydrated product of C_2S in RM and 1% ordinary PC, and C–S–H gel could also be formed from fly ash with the activation of lime. The formation of C–S–H gel from C_2S in RM and PC was show as Eq. (1). As the curing ages increases, pozzolanic reaction between fly ash and lime begins and hydration products are formed.

<table>
<thead>
<tr>
<th>Tests</th>
<th>Results</th>
<th>Criterion of the 1st-class brick</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compressive strength (MPa)</td>
<td>19.43</td>
<td>≥15</td>
</tr>
<tr>
<td>Flexural strength (MPa)</td>
<td>5.05</td>
<td>≥3.3</td>
</tr>
<tr>
<td>Bulk density (kg/m²)</td>
<td>1.62 × 10³</td>
<td>–</td>
</tr>
<tr>
<td>Water adsorption (%)</td>
<td>22.39</td>
<td>–</td>
</tr>
<tr>
<td>Compressive strength after 15 cycles of freezing-thawing from –20 to 20°C (MPa)</td>
<td>12.93</td>
<td>≥12</td>
</tr>
<tr>
<td>Weight loss after 15 cycles of freezing-thawing from –20 to 20°C (%)</td>
<td>0.35</td>
<td>≤12</td>
</tr>
<tr>
<td>Drying shrinking (mm/m)</td>
<td>0.63</td>
<td>≤0.65</td>
</tr>
<tr>
<td>Coefficient of carbonation (%)</td>
<td>0.86</td>
<td>≥0.8</td>
</tr>
<tr>
<td>Radioactivity parameter I ((\frac{\text{Ra}}{\text{C}}))</td>
<td>0.26</td>
<td>≤1</td>
</tr>
<tr>
<td>Radioactivity parameter II ((\frac{\text{ARa} + \text{ATh} + \text{AK}}{\text{C}}))</td>
<td>0.56</td>
<td>≤1</td>
</tr>
</tbody>
</table>

![Fig. 11. Relationship between compressive strength and days curing.](image1)

![Fig. 12. The XRD pattern of RM brick cured for 28 days.](image2)
shown as Eqs. (2) and (3). Ettringite is also a possible hydrated product of RM and fly ash with the activation of gypsum, shown as Eqs. (4) and (5). However, it was not identified by the XRD pattern since the intensity of ettringite is much lower, compared with that of quartz.

\[
\begin{align*}
2(2\text{CaO} \cdot \text{SiO}_2) + 4\text{H}_2\text{O} & \rightarrow 3\text{CaO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O} + \text{Ca(OH)}_2 \\
\times\text{Ca(OH)}_2 + \text{SiO}_2 + m\text{H}_2\text{O} & \rightarrow \times\text{CaO} \cdot \text{SiO}_2 \cdot n\text{H}_2\text{O} \\
3(\text{CaO} \cdot \text{Al}_2\text{O}_3) + 3\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + 32\text{H}_2\text{O} & \rightarrow 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O} + 2\text{Al(OH)}_3 \\
3(\text{CaO} \cdot 2\text{Al}_2\text{O}_3) + 3\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + 47\text{H}_2\text{O} & \rightarrow 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O} + 5\text{Al(OH)}_3
\end{align*}
\]

SEM images of RM bricks cured for 28 days are shown in Fig. 13a and b. As shown, a large quantity of ettringite with needle-like structures filled the interspaces of other particles, accompanied with some hydrated C–S–H gel. Results of SEM are again consistent with the results of XRD. It can be inferred that both ettringite and C–S–H gel might contribute to the strength of RM brick.

4. Conclusions

Many activated mineral phases such as \(\beta\)-C\(_2\)S and C\(_3\)A exist in RD, which shows the feasibility of unsintered brick products made from RM formed in the sintering alumina production process.

It is suggested from five groups of experiments that the optimal proportions of RM bricks are: 25–40%RM, 18–28% fly ash, 30–35% sand, 8–10% lime, 1–3% gypsum, and about 1% Portland cement.

The unsintered RM brick reaches the Chinese criterion of the 1st-class brick, and shows good durability in rigid climate conditions, and shows a slower increase in long-term strength. It can be inferred that both ettringite and C–S–H gel might contribute to the strength of the RM brick from results of XRD and SEM analysis.

Unsintered RM brick may have a good application in the market of the construction materials because of its lower energy consumption and costs in current processes, and may play an important role to eliminate the storage of the RD in China.

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