Obtaining of Pigment-Quality Magnetite from Sintering Process Red Mud

A A Shoppert, I V Loginova and J A Napol'skikh

Metallurgy of non-ferrous metals, Ural Federal University, 17, Mira St., Yekaterinburg, 620002, Russia

E-mail: a.a.shoppert@urfu.ru

Abstract. The limited availability of high-quality bauxite and, at the same time, the formation of a considerable amount of harmful red mud (bauxite residue) causes to develop cost-effective technologies for bauxite processing. Selective separation of iron from red mud allows solving this problem and producing marketable products in the form of pigment-quality magnetite. In this context, the possibility of the pigment-quality magnetite obtaining by the interaction of freshly precipitated iron hydroxide (III) of the sintering process red mud with ferrous iron ions in an alkaline medium is studied. It was found that the optimal parameters of the process are: temperature = 90 °C; duration = 4 hours; a ratio of ferrous iron to stoichiometric quantity = 70 %. The yield of the magnetic concentrate under optimal conditions was 69.3 %, and the content of magnetite in concentrate was 47.7 %.

1. Introduction
The most important problem of the alumina industry is the limited availability of high-quality bauxite, so it is necessary to develop cost-effective technologies for processing alternative raw materials. Even though the sintering process or the combined method can hardly compete with the Bayer process due to high-energy costs, this technology is still the main method of low-quality raw materials processing. The obtaining of high quality products and the use of certain advantages of sintering can significantly reduce the cost of alumina.

Another problem is the formation of a considerable amount of red mud (bauxite residue). At the same time, the amount of residue becomes more substantial when the quality of bauxite deteriorates. Therefore, the solution to the problem of processing of aluminum-containing raw materials, including the extraction of useful components from man-made waste – red mud, has not received its logical conclusion.

Bauxite residue forms a kind of man-made deposits, the contents of which have been repeatedly proposed to be processed into building materials for the manufacture of raw and fine ceramics, such as tiles, floor tiles [1, 2], for the manufacture of bricks [3, 4], materials in road construction [5], components in the production of cement and its special brands [5, 6], pigments [7], coagulants for wastewater treatment [8–11], iron concentrate [13, 14], raw materials for the extraction of titanium [15], rare and rare earth metals [16–19].

Many of the developed technologies have not gone beyond laboratory and pilot tests, and as a result, millions of tons of red mud, which poses a threat to the environment and surrounding cities, are thrown into the red mud fields near alumina refinery every year.
To suggest one of the possible solutions to the specified problem, the possibility of selective separation of iron from red mud to produce marketable products in the form of pigment-quality magnetite, iron concentrate, and aluminosilicate residue with a high content of titanium was studied.

2. Experimental
All chemicals (except sinter) used in this study were of analytical grade. The Ural-aluminum-plant two-component bauxite-sintering product with composition presented in Table 1 served as the raw material for the experiments. Figure 1 shows an XRD pattern of the original sintering product.

| Component | Al₂O₃ | Fe₂O₃ | Na₂O | SO₃ | TiO₂ | CaO | MgO | SiO₂ |
|-----------|-------|-------|------|-----|------|-----|-----|------|
| Content, wt. % | 34.8  | 16.6  | 33.0 | 3.2 | 1.8  | 4.8 | 0.8 | 4.0  |

Table 1. Chemical composition of the bauxite-sintering product.

Studies were conducted on the chemical treatment of red mud, as a result of which, due to the reaction (1) in an alkaline medium, iron hydroxide obtained after the interaction of sodium ferrite with water by reaction (2) is converted into magnetite. The source of ferrous iron was FeSO₄ × 7H₂O.

\[
2\text{Fe(OH)}_3 + \text{Fe}^{2+} + 2\text{OH}^- = \text{Fe}_3\text{O}_4 + 2\text{H}_2\text{O} \quad (1)
\]

\[
\text{NaFeO}_2 + 2\text{H}_2\text{O} = \text{Fe(OH)}_3 + \text{NaOH} \quad (2)
\]

The reaction (1) was proposed in [20, 21] to obtain a pigment-quality magnetite from jarosite – a waste of zinc solutions purification, which also forms an amorphous ferric hydroxide in an alkaline medium.

In [20] it is shown that reaction (1) proceeds so quickly, that after 5–10 minutes the amount of ferrous ions in the solution remains less than 500 mg/l. However, to obtain a well-crystallized product, the authors carried out the process for 7 hours.

The method of our experiments was as follows. The sample of 100 g of the sintering product was leached in an aluminol treatment with a concentration of Na₂O₆ = 130 g/l and αₖ = 1.65 at 90 °C for 30 minutes. The
obtained pulp is then subjected to filtration, followed by washing of red mud. The red mud was repulped with 170 ml of distilled water and 40 ml of 25 % ammonium hydroxide or 70 ml of 25 % sodium hydroxide solutions, and an iron sulfate solution (60 g FeSO₄ × 7H₂O for 200 ml H₂O) was added. The resulted pulp was heated to the required temperature and kept for 4 hours.

After exposure, the resulting pulp was filtered, the red mud was washed and dried at 80 °C during the day. Further, the magnetic concentrate was recovered from the red mud by wet magnetic separation on a laboratory magnetic separator.

3. Results and Discussion

3.1. Influence of the type of sintering product

During the experiments, it was found (Figure 2) that the reaction (1) is less effective if the old sintering product was used.

This phenomenon is the most likely connected to the hydrolysis of sodium ferrite by the air water, resulting in the formation of iron hydroxide (III), which by the time of interaction with the bivalent iron will not be as active as the newly deposited. Therefore, in order to obtain the high yield of magnetite by reaction (1), it is necessary to use as fresh sintering product as possible.

![Figure 2](image)

Figure 2. The influence of the type of sintering product on the yields of the magnetic concentrate and the red mud.

3.2. Influence of temperature

Further, the effect of temperature on the formation of magnetite was studied.

In figure 3 the results of experiments at different temperatures of magnetite formation in alkaline medium in the presence of iron (II) sulfate are shown.

![Figure 3](image)

Figure 3. Effect of process temperature on the magnetic concentrate yield.
It is obvious that the temperature increase helps to enhance reaction (1) velocity. Therefore, the optimum temperature of 90 °C was chosen.

3.3. Influence of iron (II) sulfate amount

In figure 4 the influence of ratio of ferrous iron to stoichiometric quantity required for the reaction (1) on the yields of the magnetic concentrate and the red mud is shown.

Excess of iron sulfate leads to an increased yield of red mud and a relatively low yield of the magnetic concentrate, although the degree of reaction (1) is greater in this case.

In addition, as shown in figure 4, the greatest yield of the magnetic concentrate is achieved at 70% ratio of the amount of iron sulfate to stoichiometry, since the degree of reaction in this case is closest to the amount of added ferrous iron, thus the excess of the latter is undesirable, since it leads to an overspending of the reagents.

Incomplete conversion of iron (III) hydroxide to magnetite may be due to the "aging" of the raw material in contact with air, as sintering product was used in the study a few weeks after its receipt.

Therefore, the optimal ratio of the amount of iron (II) sulfate to the stoichiometric amount required for the reaction (1) is 70%.

When 70% ratio of the amount of iron (II) sulfate to the stoichiometric amount required for the reaction (1) was taken, the content of magnetite in the magnetic concentrate was 47.7% (figure 4), indicating insufficient recovery of iron in the concentrate and the need of finding another method of the magnetite separating from the resulting red mud.

4. Summary

The possibility of pigment-quality magnetite obtaining in the processing of bauxite-sintering product was studied.

The optimal parameters of the interaction of iron (III) hydroxide of the red mud with ferrous iron ions with the formation of magnetite in an alkaline medium, in our opinion, are:
temperature = 90 °C; duration = 4 hours; the ratio of bivalent iron to the stoichiometric amount according to reaction (1) = 70%; the method of addition of ferric sulfate = 4, also, the sintering product must be as fresh as possible.

The yield of the magnetic concentrate under the optimal conditions was 69.3%, and the content of magnetite in it was 47.7%. Therefore, it is necessary to study other ways of magnetite recovering from red mud. For example, the use of differences in the density of magnetite and other components.
of red mud in centrifugal gravity enrichment allowed to increase the content of magnetite to 97%, but the concentrate yield was only 11%.

Obtaining a better concentrate with a high yield according to the method proposed in the work will help to increase the complexity of bauxite processing with obtaining of cost-effective products.

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