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Quantitative X-ray Diffraction (QXRD) analysis for revealing thermal transformations of red mud

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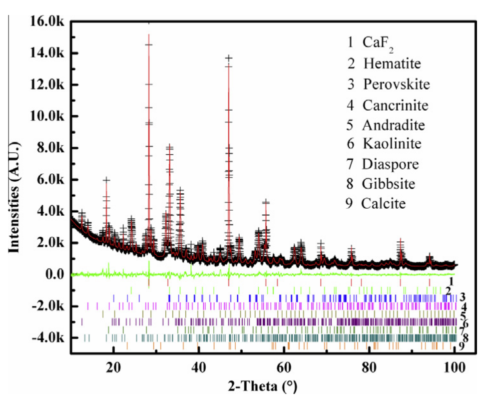
HIGHLIGHTS

- The phase quantification and transformation of the Pingguo red mud were analyzed.
- A new SFCA phase was first reported in the thermally-treated PRM samples.
- Two possible formation pathways for SFCA were proposed.
- Titanium enriches in the perovskite phase after treating PRM at 1200 °C.

GRAPHICAL ABSTRACT

The results of phase identification and quantification for the PRM samples. CaF_2 was used as an internal standard. Crosses indicate the observed data and are fitted with the calculated pattern. The bottom curve indicates the difference, and the vertical bars indicate the Bragg reflection positions of the corresponding phases.



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ABSTRACT

Red mud is a worldwide environmental problem, and many authorities are trying to find an economic solution for its beneficial application or/and safe disposal. Ceramic production is one of the potential waste-to-resource strategies for using red mud as a raw material. Before implementing such a strategy, an unambiguous understanding of the reaction behavior of red mud under thermal conditions is essential. In this study, the phase compositions and transformation processes were revealed for the Pingguo red mud (PRM) heat-treated at different sintering temperatures. Hematite, perovskite, andradite, cancrinite, kaolinite, diaspore, gibbsite and calcite phases were observed in the samples. However, unlike those red mud samples from the other regions, no TiO_2 (rutile or anatase) or quartz were observed. Titanium was found to exist mainly in perovskite and andradite while the iron mainly existed in hematite and andradite. A new silico-ferrite of calcium and aluminum (SFCA) phase was found in samples treated at temperatures above 1100 °C, and two possible formation pathways for SFCA were suggested. This is the first SFCA phase to be reported in thermally treated red mud, and this finding may turn PRM waste into a material resource for the iron-making industry. Titanium was found to be enriched in the perovskite phase after 1200 °C thermal treatment, and this observation indicated a potential strategy for

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the recovery of titanium from PRM. In addition to noting these various resource recovery opportunities, this is also the first study to quantitatively summarize the reaction details of PRM phase transformations at various temperatures.

1. Introduction

Red mud is the by-product of alumina production following extraction of the metal from bauxite ore via the Bayer process. The production of one ton of alumina generates approximately 0.3–2.5 tons of red mud, depending on the grade of bauxite (Pascual et al., 2009). At the Pingguo alumina refinery in China, one ton of alumina usually yields one ton of red mud. Every year, nearly 120 million tons of red mud are generated worldwide, and after 120 years of alumina extraction an estimated 2.7 billion tons of this by-product have accumulated (Power et al., 2011). Red mud is a hazardous material due to its high alkalinity. On October 4, 2010, an accident involving red mud in Ajka (Hungary) caused the deaths of 10 people and severe injury to more than 100 others due to alkaline solutions (Gelencsér et al., 2011). Moreover, red mud is thermally treated as an industrial waste in many alumina refineries and is classified as a dangerous waste by the Brazilian Standards Association (Rivas Mercury et al., 2010). Another concern is the ecological impact of red mud. The disaster in Hungary polluted about 40 km^2 of agricultural land and downstream rivers (Ruyters et al., 2011). The fine particles of red mud present a potential health risk to humans (Gelencsér et al., 2011) and the leachates from red mud storage areas may cause the pollution of groundwater (Liu et al., 2011).

Due to the huge volume of red mud generated and its adverse effects on the environment and human health, many potential means of disposing or reclaiming it have been studied. Current storage practices at 17 representative alumina refineries worldwide include marine disposal, lagooning, sea disposal, "dry" stacking and dry cake disposal (Power et al., 2011). Some researchers have performed preliminary studies on reusing and recycling red mud. For example, Tsakiridis et al. (2004), Kogel et al. (2006) and Vangelatos et al. (2009) investigated the possibility of reusing it as a raw material for the cement industry. He et al. (2012) studied the incorporation of red mud with clay into ceramic bodies. Sglavo et al. (2000) reused red mud as a component for ceramic production and studied its influence on ceramic properties at various temperatures. Yang et al. (2008) investigated the feasibility of using it as a main component in glass ceramics and indicated that the loading contents of both red mud and fly ash can be up to 85 wt.%. Studies have also been conducted to explore its potential use as a coagulant, adsorbent or catalyst in applications of environmental treatments (Wang et al., 2008).

To investigate the use of red mud as an additive for the ceramic industry, it is essential to characterize its behavior under heat treatment. Papp et al. (1997) investigated the effects of atmospheric pressure on the thermo-analytical curves of Hungarian red mud. Their results indicated that different levels of pressure can assist in the separation of mineral phase signals in thermo-analytical curves. Alp and Goral (2003), Atasoy (2005, 2007), Pascual et al. (2009) and Palmer and Frost (2010) used thermogravimetry (TG) and differential thermal analysis (DTA) to study the thermal behavior of red mud samples between room temperature and 1400 °C. These experiments showed that different red muds had similar thermal behavior at temperatures below 700 °C, but their mineral phases decomposed and reacted differently at higher temperatures. Such results can be explained by the different chemical and mineralogical compositions of bauxite used and the different processes for extracting alumina. In addition to using TG and DTA, Sglavo et al. (2000) and Rivas Mercury et al. (2010) discussed the phase transformations of red mud at different temperatures. Using the Rietveld method for quantitative XRD, Rivas Mercury et al. (2010) quantified the amounts of crystalline and amorphous phases in a red mud sample and its product heated to 1250 °C.

As mentioned above, the thermal behavior of red mud depends largely on the chemical and phase compositions that are influenced by the bauxite source and extraction process. After many years of alumina exploitation at Guangxi Pingguo alumina refinery (China), a huge volume of PRM has accumulated behind a local dam. To understand the thermal behavior and phase transformation of such a high-silica and high-iron red mud (Yang et al., 1998) requires a detailed investigation, and such research is essential before undertaking any possible strategy for beneficial use. To the best of our knowledge, only two previous studies have been done concerning reuse of PRM. Lin (2004) characterized PRM and discussed its potential uses, and Tian et al. (2008) recovered PRM and refractory waste for acidproof fracturing proppants. To explore the potential for applying red mud in the ceramic industry, it is essential to obtain detailed information on the mineralogical composition and phase transformation of red mud during heat treatment.

The specific aim of this study was to document the thermal behavior of PRM and to quantify the changes of phase compositions after thermal treatments at 700–1250 °C. To facilitate a systematic understanding of PRM thermal behavior, thermogravimetry–differential scanning calorimetry (TG–DSC) and Quantitative X-ray Diffraction (QXRD) techniques with internal standards were used to further examine the reaction mechanisms of PRM at high temperatures. To evaluate the reliability of the quantitative results from XRD data, the weighted-profile factor (R_{wp}), R-patterns factor (R_p) and Goodness-of-fit (GOF), which can be expressed as Eqs. (1)–(3), are monitored. The smaller R_{wp} and R_p values indicate a better quality of fitting and an ideal GOF value is 1.

$$R_p = \frac{\sum |Y_{io} - Y_{ic}|}{\sum Y_{io}}, \tag{1}$$

$$R_{wp} = \left[\frac{\sum W_i (Y_{io} - Y_{ic})^2}{\sum W_i Y_{io}^2}\right]^{1/2}, \tag{2}$$

$$\mathrm{GOF} = \frac{\sum W_i (Y_{io} - Y_{ic})^2}{N - P} \tag{3}$$

Y_{io} is the observed intensity; Y_{ic} is the calculated intensity from the structure model; W_i is the weight assigned to each step intensity; N is the number of the observations; and P is the number of parameters.

2. Experimental details

The red mud samples used in this work were collected from the Guangxi Pingguo alumina refinery (China). The average particle size of the samples was 2.38 ± 0.6 μm. The chemical composition analysis of the PRM was performed using XRF spectroscopy (JEOL, JSX-3201Z).