



Quantitative phase analysis of bauxites and their dissolution products



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ABSTRACT

Quantitative phase analysis for four bauxite samples sourced from different geological regions was conducted with Rietveld refinement of synchrotron sourced X-ray diffraction (XRD) data. Minor and trace phases were concentrated using (i) caustic leaching to selectively remove phases such as gibbsite, boehmite and kaolinite and (ii) dithionite–citrate–bicarbonate leaching to selectively remove the iron oxide phases such as goethite and hematite, and reanalysed. Bauxites are normally recognised as very difficult samples for quantitative phase analysis (QPA). The use of synchrotron XRD in this paper allowed characterisation with QPA, crystallite size determination and elemental substitution in some phases. Elemental composition analysis by X-ray fluorescence demonstrated close agreement with the diffraction data and allowed an estimate of the composition of the non-crystalline component of the bauxite samples. Other characterisation techniques used include thermogravimetric/differential scanning calorimetry to determine the phase transitions and mass loss, and transmission electron microscopy/energy dispersive spectroscopy to capture the morphology of the crystallites in the bauxite samples.

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1. Introduction

Bauxite ore, named after the French district of Les Baux where it was first discovered in 1821, is typically formed by the weathering of aluminium-bearing rocks. The relevant mineral constituents are the aluminium (oxy)hydroxides, gibbsite ($\gamma\text{-Al}(\text{OH})_3$), boehmite ($\gamma\text{-AlOOH}$) and diasporite ($\alpha\text{-AlOOH}$). In the Bayer process bauxite is digested in hot caustic solution, unwanted insoluble residues such as hematite are removed and the aluminium hydroxides precipitated and calcined to produce smelter grade (mostly gamma) alumina which is then electrolytically refined to produce aluminium.

The conditions required by the Bayer process are highly variable and depend on the type and abundance of the oxy-hydroxides and impurities in the ore. Gibbsitic bauxite is normally digested at around 150 °C while boehmitic and diasporic bauxites are processed at around 250 °C or higher (Burkin, 1987; Mal'ts, 1991; Smith, 2009). The type and amount of impurities are also important for process design and control. For instance, the reactivity and behaviour of the impurity mineral kaolinite varies with process temperature, it dissolves and re-precipitates as sodium aluminium silicate (desilication product, DSP) in predesilication consuming caustic soda from the liquor. Low silica content bauxites consume less soda during processing but can generate high silica concentrations in the pregnant liquor due to insufficient liquor desilication (Vergheze, 1988). Other impurities such as aluminous goethite, hematite or anatase, may be inert at low digestion temperature but may cause residue settling

and iron concentration control problems due to fine particle size, morphology and surface properties. At higher digestion temperatures, goethite dissolves and re-precipitates as hematite, usually a slow process that can be facilitated by the presence of hematite in the original bauxite (Basu, 1983; Li, 2001).

Lateritic bauxites (Bardossy and Aleva, 1990) mainly found in equatorial regions are formed by laterisation/weathering under intense wet and warm (tropical) or prolonged weathering conditions of silicate rocks, typically acidic rocks such as granite and gneiss, but also mafic and ultramafic rocks such as basalts and serpentines. Different parent rocks yield variations of quartz content and particle size as well as clays and other minerals, and significant variations can be observed in a single deposit, e.g. the kaolin group minerals can vary between kaolinite and halloysite while the crystallinity (or order) and thus reactivity of the kaolin minerals can also vary (Sadlier and Gilkes, 1976).

Karst bauxites (Bardossy, 1982) are also weathering products and occur above carbonate rocks such as limestone and dolomite. These bauxites have different mineralogical compositions, they are usually higher in boehmite and diasporite than the gibbsite rich laterite bauxites; the silicate minerals are dominated by kaolinite, but may also contain other minerals such as crandallite and chamosite, which are more difficult to process.

The main objective of this study was to determine the mineralogy of four typical bauxite samples using Rietveld quantitative phase analysis (QPA) by X-ray diffraction (XRD), allowing similarities and differences in the samples to be characterised. The QPA of synthetic bauxites is recognised as difficult due to the presence of multiple phases with associated peak overlaps, potential preferred orientation, and especially micro-absorption (Scarlett et al., 2002). The diffraction

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patterns are also complicated by phases with complex crystallite shapes including platy (e.g. kaolinite and hematite) and/or needle-like (e.g. goethite), peak broadening due to small crystallite size, strain or variable order (e.g. kaolinite) and lattice parameter shifts due to substitution (e.g. Al into goethite or hematite). Natural samples are also likely to have trace amounts of phases that will be detected but cannot be well modelled using laboratory based XRD data. The inability to model minor and trace phases well was also concluded to be a major problem in QPA of bauxites (Scarlett et al., 2002).

In the present work, selective leaching experiments were conducted to isolate and concentrate the minor and trace mineral(s) of interest allowing a better characterisation which could be used for improved quantification. Information gained from the analysis of these residues will contribute towards the development of a more comprehensive model for QPA of the original bauxite samples for future work. The quantitative phase analysis results were complemented with transmission electron microscopy to aid in the identification of unusual minerals in the bauxite samples.

2. Experimental

2.1. Materials

The Australian bauxite is a lateritic bauxite sample with predominantly gibbsite and minor boehmite, with some kaolinite, hematite and quartz. The Northern European bauxite is of typical karstic topography consisting of dolomites/carbonates with around 30% clay. There is no gibbsite present but other minerals include boehmite, diaspor, hematite, goethite and a significant amount of chamosite. The Jamaican bauxite is an unusual example of karst bauxite consisting of gibbsite with a small amount of boehmite, some goethite and fine grained crandallite. The Vietnamese bauxite is an equatorial lateritic pristine bauxite, with a high degree of crystallinity. The mineralogy consists of gibbsite, goethite, kaolinite and a small amount of ilmenite. The Jamaican and Vietnamese bauxites are digested at low temperatures although the processing can be complicated by the presence of a small amount of boehmite, which can act as seed to cause the dissolved aluminium to re-precipitate later in the process (called reversion in the industry).

2.2. Initial sample preparation of bauxite samples

The as-received bauxite ores were split into 1 kg portions using a rotary-splitter and pulverised using a ring-mill for subsequent characterisation. In addition, the samples for quantitative phase analysis were wet-milled in a McCrone micronising mill for 2 min prior to data collection.

2.3. Quantitative XRD

The Rietveld method (Rietveld, 1967, 1969) is a pattern modelling procedure in which the set of intensities comprising the calculated pattern, determined according to an initial model, is fitted by non-linear least squares to the corresponding measured pattern. Structural parameters (atomic positions, thermal parameters, site occupancies and lattice parameters), pattern background function coefficients, scale factors for phase composition determination, preferred orientation, extinction, profile parameters (peak widths and shape), crystallite size and microstrain (through profile parameters) may be included in Rietveld analysis (Young, 1993). Least squares Rietveld refinement is designed to minimise the residual summed over the n points in the pattern at which the intensity is sampled (Rietveld, 1969).

$$R = \sum_{i=1}^n w_i (y_{io} - y_{ic})^2 \quad (1)$$

where y_{io} and y_{ic} are the observed and calculated intensity at the i th step, respectively, and w_i is the weight assigned to each observation which is normally set to the inverse of the counting error variance (σ_i^2) at the i th step. Numerous R factors are used in Rietveld refinements to measure the progress of the Rietveld refinement (Young and Wiles, 1982), with the most meaningful being the weighted profile R factor (R_{wp}) as the numerator in the expression is the quantity being minimised by least squares during refinement.

$$R_{wp} = \left[\frac{\sum w_i (y_{io} - y_{ic})^2}{\sum w_i y_{io}^2} \right]^{1/2} \quad (2)$$

Quantitative phase composition results are obtained when a known amount of internal standard is added to the polyphase mixture and the entire pattern is fitted using the Rietveld method. The concentration for a particular crystalline phase, W_k , is given by

$$W_k = \frac{W_s (ZMV)_k \cdot S_k}{(ZMV)_s \cdot S_s} \quad (3)$$

where W_s is the known wt.% of the internal standard in the mixture, S is the Rietveld scale factor, ZM is the unit-cell mass and V is the unit-cell volume. In this study, the amorphous level was not modelled but determined as the difference between the sum of the analysed weight fractions for all crystalline phases and 100% and may also refer to poorly ordered phase(s) and/or undetected phase(s) after Rietveld refinement.

XRD quantitative phase analyses of the bauxite samples were performed with an internal standard, CaF_2 (Sigma-Aldrich, ~90% crystalline material) in an 80:20 bauxite:CaF₂ weight ratio to determine the absolute phase quantification of the samples. The XRD data were collected at the Australian Synchrotron on the powder diffraction beamline (ASPD), 10-BM-1 with Debye–Scherrer geometry using a MYTHEN detector with a microstrip detector system comprised of 16 detector modules enabling simultaneous collection of X-rays and a short readout time (Schmitt et al., 2003; Wallwork, Kennedy and Wang, 2007). Each bauxite sample was packed into a 0.3 mm ID quartz capillary and datasets were collected for a period of up to 10 min. The capillaries were spun at 15 rpm during data collection. The spinner incorporated a motorised goniometer head with image capture and processing software that automatically aligns capillary eucentric positions reproducibly to $\pm 10 \mu\text{m}$. The sample capillary was rotated during data collection in order to obtain accurate diffraction peak intensities.

The other instrumental settings for the synchrotron are summarized in Table 1. The instrumental characterisations including accurate wavelength ($\approx 1.000 \text{ \AA}$), zero error and instrumental convolutions of this configuration were determined with NIST SRM 660b (LaB₆) diluted with diamond powder 1:9 by weight.

Crystalline phases in the XRD patterns were identified using Bruker® Diffrac^{plus} EVA v16 software to search the ICDD® Powder Diffraction File (PDF4+ 2010 edition). The crystal structures of the phases were extracted from the FIZ Karlsruhe Inorganic Crystal Structure Database (ICSD 2009/2) in the form of crystallographic information files (.cif). Bruker® (2008) TOPAS v4.2 was used to perform Rietveld quantitative analyses.

Table 1
Operating parameters of the powder diffraction patterns at the ASPD.

Parameter	Value
Radiation wavelength	0.999047 Å (approx. 12.396 keV)
Source	Bending magnet on a 3 GeV synchrotron
Detector	MYTHEN II microstrip detector
Monochromator	Si (111) flat crystal pair
Goniometer radii	761.2 mm
Source size	2 mm wide, 0.5 mm high
Take off angle	1.2 2θ°

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