Lab Report XRD 80

Accuracy in quantitative X-ray mineralogy - Part 2:
Aluminous goethite mixed-crystal in bauxite and iron ore

X-ray diffraction (XRD) is a method for determining the mineralogy of ore. The combination of fast detectors integrated in the XRD intruments with TOPAS quantitative phase analysis (QPA) allows standard-less analysis within minutes. The typical accuracy of QPA for well crystalline samples can be better 1 wt-%. This is proved by comparing the bulk chemical composition calculated from the concentration of the minerals and their stoichiometry to chemical analysis.

The report shows how variable Al/Fe stoichiometry can be handled in TOPAS. This helps the minerals industry to identify severe recovery losses in bauxite and iron ore processing.

Why X-ray diffraction in mining

Quantitative phase analysis is frequently applied to the study of geologic materials in research and service laboratories, but also in quality control of mining operations. Understanding the properties of ore (minerals from which metals are extracted) and gangue (deleterious minerals that need to be separated from the ore) is of tremendous economic importance for the process mineralogy. The reason for this is simple. Physical properties that determine the processability of the material such as hardness, solubility, magnetism, or density are directly related to the crystal structure of the minerals and not to their chemical composition. Therefore, those properties directly influence beneficiation conditions such as the method of separation (gravity, magnetic washing or dissolution).

Recovery estimates in mining operations are typically based on chemical grade-estimates. Severe recovery losses may occur if the element of interested is located in one of the gangue minerals that is removed, or not accessible during processing of the ore. For example several bauxite deposits in Brazil contain the iron mineral goethite, which may host up to 30 % aluminum instead of iron. This share of aluminum is not accessible during alumina production. To give an estimate on the economic order of those losses let's assume an annual production of 5 Mio tons just for the Itamaratí and Miraí mines in 2010. The equivalent to 1% improvement in recovery would amount to 35 Mio US-$ per year.

How to assess accuracy

QPA using the Rietveld method and X-ray diffraction data is one of the few direct methods for obtaining the relative or absolute phase abundances of crystalline and non-crystalline (amorphous or nano-crystalline) components in a mixture. A frequently asked question is: "How accurate is this method?".

Accuracy is considered as closeness of the analytical result to the true value. The accuracy of the QPA result may be evaluated by comparing to traditional chemical analysis. The XRD based chemical analysis of a multi-phase mixture follows from the phase abundances and the known stoichiometry of the crystalline phases. This method requires the composition of the crystalline phases to be well defined.

Site occupancies and site multiplicities of the crystal structure determine the mass of the unit cell of the mineral. In that sense the mass and the volume of the unit cell are equivalent to a calibration coefficient in quantitative analysis and the crystal structure represents a restraint or hard constraint. The precise knowledge of all crystal structures is therefore crucial for high accuracy quantification.

Different kinds of atoms may mix at the same position of the crystal structure. Standard crystal structure refinement of a single phase by the Rietveld method can determine site occupancy parameters. This is a challange in QPA because only limited measurement time is available in process control. This limits the scan range. Such short ranges may typically not permit independent site occupancy refinement but allow TOPAS QPA, however.

The use of geometric or chemical restraints may stabilize the refinement and help in achieving high accuracy QPA of mixed crystals. This report describes how to apply constraints in the TOPAS software. Both methods are applied to bauxite from Brazil, which may show high levels of aluminium to iron substitution in some minerals, e.g. goethite (Gt, FeOOH).

Bauxite BXMG- 3

Diffraction data of reference bauxite BXMG 3 was collected using a D4 ENDEAVOR diffractometer using Cobalt radiation in order to minimize micro-absorption. The diffraction data as well as chemical analysis were provided by CETEM, Rio de Janeiro, Brazil. CETEM characterized a whole suite of reference bauxites from Brazil within a round robin analysis (http://www.cetem.gov.br/mrc/ing/available_crms.htm). More detailed XRD results are discussed elsewhere [4].

The typical TOPAS QPA is shown in Figure 1. The major phases are gibbsite (Gb, $Al(OH)_3$), goethite (Gt, FeOOH) and hematite (Hem, Fe_2O_3). Gibbsite shows a bimodal size distribution, which was considered by refining two phases having different crystallite size parameters. Furthermore, small amounts of rutile and anatase (Rt, Ana: TiO_2), quartz (Qtz, SiO_2), and kaolinite (Kln, $Al_2Si_2O_5(OH)_4$) were detected and refined as well.

The phase abundances for the minerals with chemical formula as given in the above paragraph are reported in columne "nominal" in table 1. The bulk elemental composition (Table 2) was derived from the individual phase compositions according to the stoichiometry of the minerals. It is compared to the respective reference values from the CETEM certificate.

TOPAS quantitative phase analysis

Quantitative phase analysis (QPA) using the Rietveld [1] method was performed using the TOPAS [2] software. It is based on the calculation of the full powder pattern from crystal structure information. Therefore, it does not rely on calibration curves and also tube ageing does not need consideration.

Quantitative phase analysis in the TOPAS software is based on the method first described by Hill and Howard in 1987 [3]. This method is based on the assumption that (i) all phases in the specimen are identified, (ii) all phases are crystalline, and (iii) the crystal structures of all phases are known. The weight-% w_u of a phase u in a mixture of n phases is

$$w_u = S_u (ZMV)_u / \sum_{k=1}^{n} S_k (ZMV)_k$$

with S the scale factor of the Rietveld calculation, Z the number of formula units in the unit cell, M the mass of one formula unit, and V the unit cell volume. The factor (ZMV) is a phase specific scaling parameter that is solely defined by the usually well-known crystal structure of the mineral.
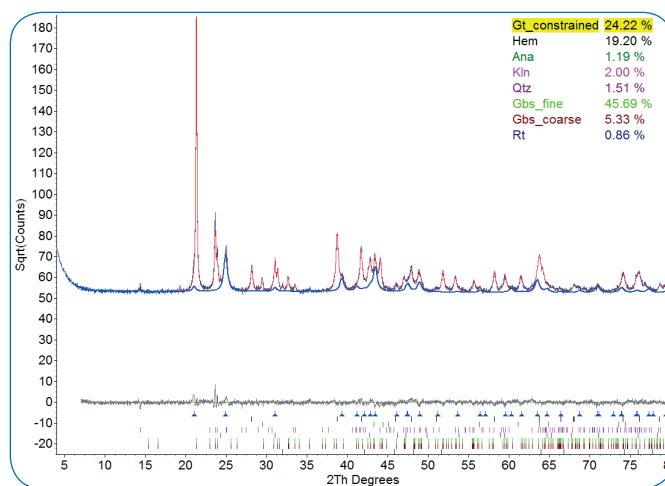

Figure 1: TOPAS QPA of bauxite certified reference material BXMG-3. The goethite contribution to the diffraction pattern is highlighted. Mineral names are abbreviated according to the IMA code of rock forming minerals.

Typically, results should agree within 1% or better. Table 2 shows almost 3% overestimation of iron and an underestimation of aluminum for the XRD data. This may point to the presence of some systematic error in the model. This is furthermore supported by unusual small unit cell parameters of goethite. The refined lattice parameter c of goethite is 2.9750(7) Å, thus indicating a highly substituted Al-goethite with the occupancy of Al at the Fe site of 0.28 (see Figure 2).

This finding is further supported by the independent refinement of the Fe site-occupancy in goethite (column "free" of Table 1) which gives 0.21. The underestimation of Fe is reduced from almost 3% to 1.5% (Table 2).

Lattice restraint

This section demonstrates how to couple the site occupancy to a lattice parameter. Lattice parameters are defined by the peak positions, which are usually much better resolved in the diffraction pattern, than the small intensity changes due to variations in concentration (scale factor) and site occupancies. This let us expect improved accuracy in QPA.

Figure 2 presents the variation of the lattice parameter c with the concentration of Al in goethite, FeOOH. The regression equation for the lattice parameter is used to define the
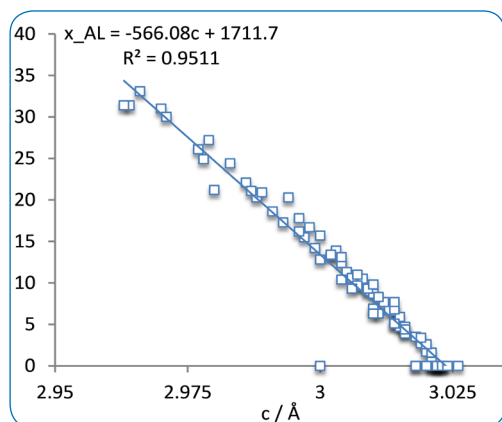
Figure 3: Example of a lattice restraint in TOPAS. It couples the Fe/Al site occupancy to the variation of the lattice parameter c in goethite, c_gt.

Figure 2: Variation of the goethite, (Fe/Al)OOH, lattice parameter c with the Al substitution in % [5].

occupancy of Al and Fe (Figure 3). The resulting phase and chemical compositions are shown in Tables 1 and 2 for column "latt_constr c". The Al fraction goes towards 0.27 with an overall improvement of the bias for element concentrations better 1%.

Chemical restraint

A new TOPAS 5 feature is chemical restraints. Chemical restraints relate the occupancy parameters of the crystal structures to the known bulk chemistry of the sample. Figure 4 shows the example of the implementation for Fe and Al in goethite.

```
element_weight_percent FE+3 fe 0
restraint = (fe - (0.6994 35.3)); : 0
    ...
element_weight_percent AL+3 al 0
restraint = (al - (0.5293 37.9)); : 0
    ...
site s1 x !x1_gt 0.3539 y !y1_gt 0.25 z !z1_gt 0.4523
  occ FE+3 =1-xal; beq  0.4
  occ AL+3 =xal;    min =0; max =0.36; beq  0.4
```

Figure 4: Examples of TOPAS code for chemical restraints. They force the Fe/Al site occupancy parameter xal towards minimal difference between Fe and Al refined for the crystal structure and the bulk chemical analysis for Fe_2O_3 and Al_2O_3. The factors 0.6994 for Fe and 0.5293 for Al account for the transformation from oxide concentrations (reported in the certificate) to elemental concentrations used in TOPAS.

The QPA results for BXMG-3 bauxite are listed in columns "chem_constr" of Tables 1 and 2. Two cases are presented, for restrained elements Al, Fe and Al, Fe, Si, and Ti. The chemical restraints result in a slightly higher Al occupancy of 0.29/0.30. The agreement with chemical analysis is in the order of 0.5 %.

Table 1: BXMG-3 mineral concentrations from TOPAS refinement for different models of Fe/Al substitution in goethite (Gt). The lower line gives the Al fraction at the Fe site in goethite.

Phase Name	Phase concentration / Wt%				
	nominal	free	latt_constr c	chem_constr Al/Fe	chem_constr Al/Fe/Si/Ti
Gt_constrained	22.49	24.46	23.76	23.37	23.65
Hem	18.91	18.58	19.48	19.09	19.28
Ana	1.26	1.19	1.18	1.29	1.18
Kln	2.00	1.99	2.00	2.47	2.26
Qtz	1.66	1.62	1.50	1.59	1.50
Gbs_total	52.75	51.30	51.23	51.13	51.26
fine	47.26	45.97	46.10	45.75	45.89
coarse	5.49	5.33	5.13	5.38	5.37
Rt	0.95	0.86	0.86	1.06	0.87
mix Al/(Al+Fe)	0	0.21	0.27	0.29	0.30

Element	Element concentration calculated from TOPAS / %					
	Certificate	nominal	free	latt_constr c	chem_constr Al/Fe	chem_constr Al/Fe/Si/Ti
Al	20.06	18.67	19.91	20.35	20.51	20.65
Fe	24.69	27.52	26.12	25.66	25.02	25.13
Si	1.07	1.22	1.20	1.14	1.29	1.20
Ti	1.20	1.32	1.23	1.23	1.41	1.23
Bias: Certificate - TOPAS calculated concentrations						
Al		1.39	0.15	-0.29	-0.45	-0.59
Fe		-2.83	-1.43	-0.97	-0.33	-0.44
Si		-0.14	-0.13	-0.07	-0.22	-0.13
Ti		-0.12	-0.02	-0.02	-0.21	-0.02

Table 2: Element concentrations calculated from the phase concentrations obtained for the different models of Fe/Al site occupancy in goethite (see Tab 1). The lower part of the table shows the bias in the bulk elemental concentrations between the nominal mineral formulae and the different models of substitution.

Discussion

The quantitative mineralogy of CETEM certified reference bauxite BXMG-3 was determined using TOPAS refinement of XRD data. The method is considered accurate as the main chemistry figures derived from the XRD results agree well (better 1 wt%) with bulk chemical analysis from the certificates.

Knowledge on element partitioning into different minerals is obtained. This directly supports the process mineralogy in general. Gibbsite is identified as the main source of recoverable alumina in Brazilian bauxite, and both kaolinite and goethite account for the not-available alumina.

Lattice and site occupancy parameters are correlated in substitutional mixed crystals. The consideration of their ratio in TOPAS Rietveld quantification is possible via the built-in macro language and considerably improves the accuracy of the quantitative X-ray mineralogy results. The same level of accuracy is obtained using chemical restrains.

The particular example of Al-bearing goethite is of importance for the beneficiation of bauxite during alumina or refractories production. Another important application to be targeted with the restraints method is goethite-rich iron ore, which may also contain severe amounts of Al.

References

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[5] Data from ICDD PDF 4, Schwertmann, U. and Carlson, L. (1994) Soil Science Society of America Journal, 58, 256-261., Schulze, D.G. (1983) Clays and Clay Minerals, 32:1, 36-44.

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