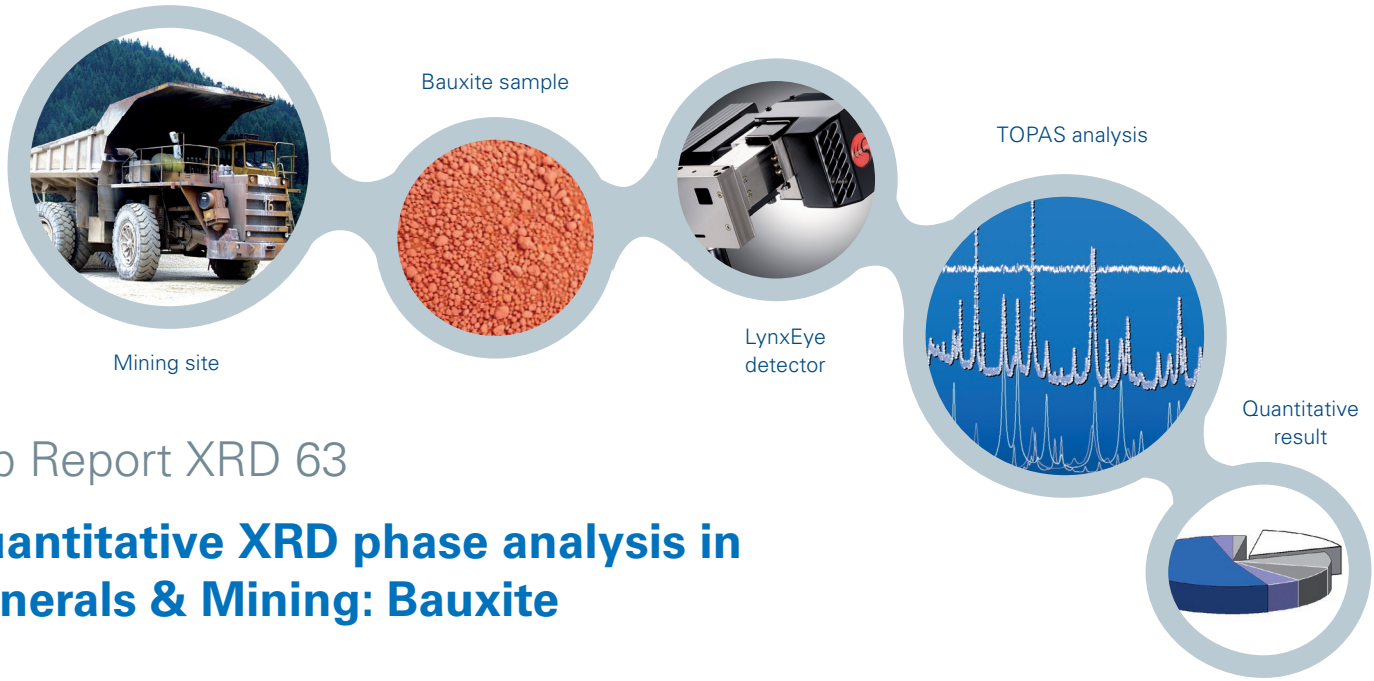

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Quantitative XRD phase analysis in Minerals & Mining: Bauxite

Abstract

TOPAS Rietveld analysis emerged as a routine tool in quantitative phase analysis of powder samples. XRD data measured rapidly with the LynxEye detector, the use of Co radiation and the TOPAS software allow for a fast and precise quantitative investigation of iron-bearing multi-phased samples. Here, the quantification of ten mineral phases in bauxite together with the determination of the crystallite sizes are demonstrated. Furthermore, the accuracy of the method is evaluated.

Why studying the phase content of bauxite?

Bauxite, named after its type locality Les Baux in the south of France, is mainly composed of hydrous aluminum oxides, iron and titanium oxides, quartz, and other silicate species. The name bauxite is used as a common synonym for hydrous clay rocks of different geological origin and composition.

Bauxite is the primary source for industrial aluminum production. Alumina (Al_2O_3) is prepared from raw bauxite by a hydrometallurgical process named after its inventor the 'Bayer process'. It involves high-pressure high-temperature leaching of bauxite with sodium hydroxide solution and the separation of the insoluble material (the so called red mud) to obtain a solution, which is seeded to precipitate aluminum hydroxide that, finally, is calcined to alumina. Afterwards, alumina is charged to electrolytic reduction cells for obtaining the pure aluminum metal.

Knowing the composition and mineralogy of bauxite deposits is essential for evaluating the 'processability' of the material. This characterization is needed for alumina producers in general and particularly for companies who want to develop bauxite deposits. Although the Bayer process is a mature technology there is always room for improvement. This is particularly true, since the world is running out of high quality (low silica) bauxite ore. "In-depth mineral characterisation of bauxites can point to the most effective processing options and can also be used to examine bauxite beneficiation techniques for improving the ore quality prior to processing"[1].

DIFFRAC^{plus} TOPAS quantitative Rietveld phase analysis

XRD is the most direct and accurate analytical method for determining the presence and the absolute amounts of minerals species in a sample. There are several advantages of Rietveld phase analysis over conventional methodes:

- Full pattern quantitative phase analysis applying the Rietveld method does generally not require time consuming calibration.
- Multi-phase samples are easily analyzed without being constrained by peak overlap.
- The adding of new phases found in qualitative XRD is straightforward.
- Additionally, crystallinity and crystallite size that influence the reactivity of the mineral components can simultaneously be derived from the peak profiles.

Fast and reliable Rietveld based quantitative analysis became routinely possible by combining fast modern computer technology and optimised mathematical algorithms with the fundamental parameters approach [2] in the DIFFRAC^{plus} TOPAS software.

Accuracy: the CPD round-robin data

Synthetic bauxite XRD data provided by the Commission on Powder Diffraction (CPD) of the IUCr were analysed using TOPAS. The result is shown in figure 1.

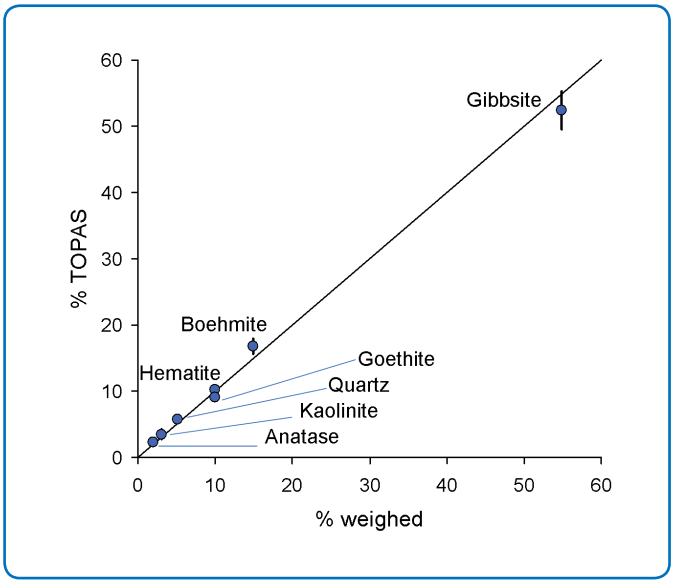

Fig. 1: Comparison of the TOPAS quantitative results with the expected values from weighing. The straight line (1:1 relation) corresponds to perfect agreement.

The excellent performance of TOPAS and the superior quality of the analysis directly follows from agreement of the calculated composition with the expected results (straight line). The differences between the TOPAS values and data from weighing are below 1 % for the minor phases. The largest deviations are 1.8 and 2.5 % for boehmite and gibbsite, respectively. This is most notable as the results of other participants of this round robin analysis show systematic deviations of 1 – 5 wt-% for the minor components and about 15 wt-% for gibbsite for the CPD data set, analysed here [3].

This means that TOPAS may partly compensate for deficiencies in the preparation of the powder sample by its advanced microabsorption, texture and peak shape abilities.

Bauxite from Turkey

Experiment

Samples from ETI Aluminium (Turkey) were analysed with a D8 ADVANCE diffractometer equipped with an automatic sample changer. Measurement details:

- Co *K*α-radiation, Fe *K*β-filter
- LynxEye detector
- 4° Soller collimators
- Counting time 0.5 sec/step, range 5 – 100°, step 0.02°, total measuring time per sample about 50 min.

Co- instead of Cu-radiation was chosen in order to prevent microabsorption caused by the Fe-bearing phases, which may seriously bias the results of a quantitative analysis (Tab. 1).

Tab. 1: Mass absorption coefficients in cm^2/g of selected compounds for Cu and Co *K*α-radiation.

Composition	Cu *K*α	Co *K*α
Fe_2O_3	224.1	44.5
FeO(OH)	202.3	41.5
AlO(OH)	27.2	42.4
$Al(OH)_3$	23.1	36.1
TiO_2	127.2	191.7
$CaCO_3$	69.8	105.4
SiO_2	33.6	52.2
$Al_2Si_2O_5(OH)_4$	28.9	45.1

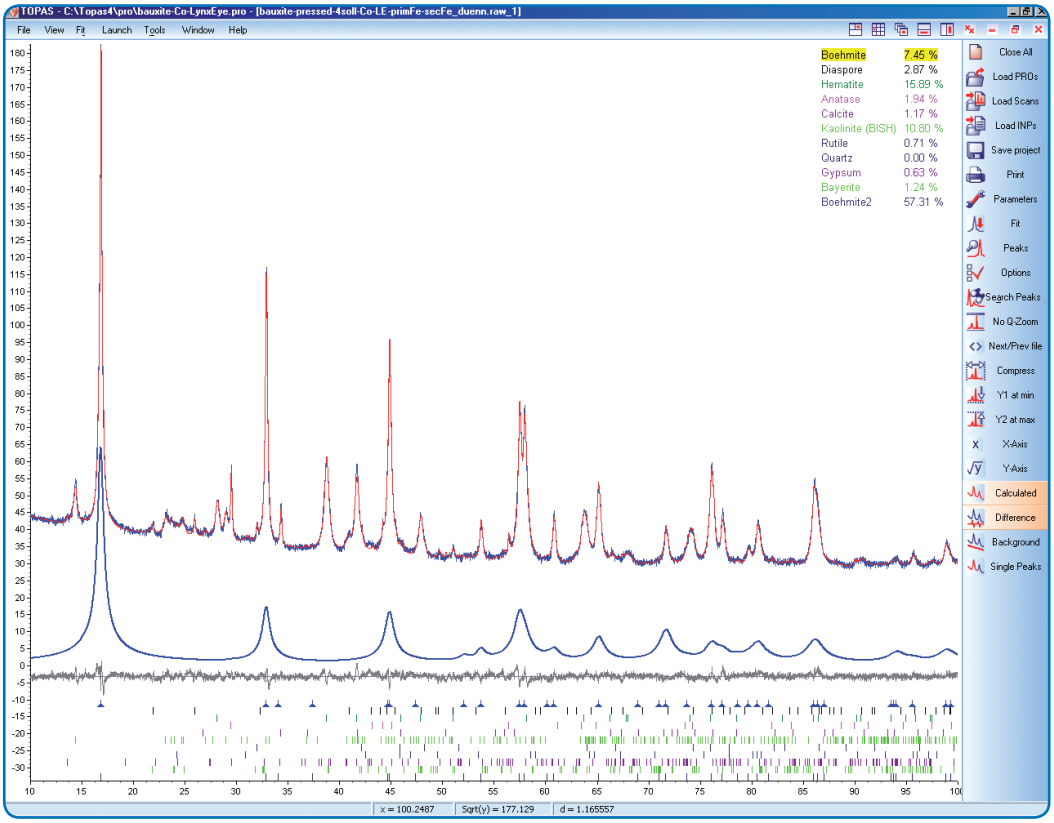

Fig. 2: Quantitative phase analysis of bauxite using TOPAS4. The intensity is given in sqrt(I) units, the fit converged to R_{wp}=4.1, GoF=1.6.

Results

Figure 2 shows the results of the quantitative analysis with TOPAS. In total, 11 phases were used in the analysis. For all minerals the scale factors and cell parameters were refined and the relative intensities of the Bragg reflections were calculated from the crystal structures. The instrument contribution to the peak shape of all phases was modelled by the fundamental parameters approach, while the individual contributions from each phase were taken into account by a single crystallite-size parameter per phase. Preferred orientation of kaolinite was corrected by 4th order spherical harmonics.

All phases quantified for the example shown in figure 2 are listed in table 2. Quartz was detected in other samples from that commodity and therefore included in the refinement. However, the sample analyzed here did not contain quartz (0 wt-%). Major phases are quantified with high precession (better 0.5 wt-%), minor phases below 1 % are also quantified.

The peak shape of the boehmite reflections indicated the presence of differently sized crystallites. Two independent boehmite phases with common cell parameters were therefore refined resulting in crystallite-size fractions of about 35 nm and 400 nm covering 11.5 and 88.5 % of boehmite, respectively.

Tab. 2: Quantitative TOPAS refinement results of bauxite from Turkey.

Phase name	Composition	Phase amount / wt-%	Crystallite size / nm
Anatase	TiO_2	1.9(1)	139(8)
Bayerite	AlO(OH)	1.2(1)	45(8)
Boehmite	AlO(OH)	7.4(7)	35(3)
		57.4(8)	401(35)
Calcite	$CaCO_3$	1.2(1)	155(22)
Diaspore	AlO(OH)	2.9(1)	58(12)
Gypsum	$CaSO_4 \cdot 2H_20$	0.6(1)	56(16)
Haematite	Fe_2O_3	15.9(3)	35(1)
Kaolinite	$Al_2Si_2O_5(OH)_4$	10.7(1)	30(1)
Rutile	TiO_2	0.7(1)	99(18)
Quartz	SiO_2	0.0	—

Conclusion

The use of Co-radiation and the LynxEye detector is the key to fast measurement of XRD data suitable for very accurate and precise Rietveld refinement of Fe-bearing samples. Convolution-based Rietveld profile fitting in combination with instrument function constraints allow complex phase mixtures to be quantified with TOPAS and to obtain additional microstructure information. Consequently, TOPAS permits the routine analysis of complex material from the Minerals and Mining industry that was all but impossible until now.

Keywords

XRD / quantitative phase analysis / TOPAS / Bauxite

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