

## **Inaccuracies in Estimation of Bauxite Extractable and Mineralogical Constituents**

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### **Abstract**

It is necessary to know the complete mineralogy of bauxite to understand, interpret and predict correctly the outcome of mining, the plant digestion process as well as to know bauxite's commercial value. Over the years several methods have played a major role in the quantitative phase analysis of bauxite. The loss of mass on ignition (LOM) and elemental analysis of bauxite using modern instrumentation (XRF, ICP) yield excellent reproducibility and high productivity. However, the mineralogy required to evaluate the amount of recoverable alumina and other Bayer plant parameters has been much less readily accessible. Wet chemistry (WCh) is known to be slow, complex, expensive, occasionally erratic and delivers results of extraction but not of mineralogy. The X-ray diffraction analysis (XRD) requires a separate sample preparation stream. Interpretation of X-ray diffractograms is mainly influenced by amorphous phases and a poor limit of detection. The objective of this paper is to compare the performance of WCh, XRD and mathematical modeling (BauxQ software), using experimental data from several laboratories. The present state of analytical methodology for bauxite characterization is worrisome. The aluminium industry, which depends heavily on the conventional (WCh) and instrumental (XRD) data, often does not know the exact value of its principal raw material. Also, the industry should use mineralogical and not elemental composition to estimate bauxite's commercial value. Bauxite building blocks must be known and mass balance must be observed. The results demonstrate that mathematical modeling has distinct advantages for bauxite mineralogical quantification of various deposits, because it is the most consistent approach and provides an opportunity to significantly reduce operational costs. If the bauxite mineralogy is known, it is an easy step to calculate Bayer process parameters to obtain a better understanding of bauxite's economic value, leading to more efficient production control of a Bayer plant.

**Keywords:** bauxite mineralogy, methods of analysis, WCh, XRD, BauxQ.

### **1. Introduction**

Composition of bauxite deposits and aluminium bearing minerals, like any other mineral ores, can be described from many points of view. The geologist seeks to identify and quantify mineral phases or understand the qualities of the material which he knows from experience to be useful to alumina extraction. He wants to be able to measure the extent of a mineral deposit and perhaps attach to it an approximate monetary value. The process engineer wants to blend mined bauxite and to predict its behavior in a given alumina extraction process. He will also want to measure the efficiency of his plant against defined benchmarks. The analytical chemist seeks to characterize a series of samples using standard analytical techniques and to convert the results into data that the geologist and the process engineer can use. These various needs give rise to three different sets of descriptors:

- Elemental composition (oxides and LOM).
- Phase composition (gibbsite or tri-hydrate, boehmite or mono-hydrate, kaolinite, etc.).
- Extractive mineralogy (available alumina, reactive silica, etc.).

The commercial objective is to obtain fundamental information on mineralogical phase distribution in bauxite and to know the building blocks of the material. Bauxite mineralogical

composition is important and must be known to estimate its commercial value and to guide the process of its conversion to alumina. Several analytical methods are employed for this purpose. The cost, reliability, accuracy of determination and ease of use play an important role in the consideration of the best methods to use.

The main objective of this paper is to reflect on the present state of analytical methodology in bauxite quantitative phase (mineralogical) analysis. Another objective is to compare performance of WCh, XRD and mathematical modeling (BauxQ software), using recent experimental data from several laboratories.

## 2. Wet Chemistry (WCh)

Wet chemical procedures (WCh) involving laboratory bomb digestion were the first used for quantitative phase analysis of bauxite [1]. The bomb digestion analyses are performed under standardized conditions. Various terms may be employed to describe  $\text{Al}_2\text{O}_3$  determined during low-temperature (LT) digestion ( $\sim 140 - 150^\circ\text{C}$ ) with caustic, for example available alumina Av.  $\text{Al}_2\text{O}_3$ , ATH, or simply  $\text{Al}_{\text{LT}}$ . Silica extracted at low temperature is called Si(LT) or reactive silica ( $\text{R}_x\text{SiO}_2$ ) [2,3]. It is determined in a standard low temperature digestion as the amount of silica reacting with the liquor by passing first into the solution and then precipitating as an acid soluble alumino-silicate, called Bayer sodalite. As far as is known, it is mainly the kaolinite-type minerals that will dissolve under low temperature digestion conditions. Quartz will not dissolve, unless finely divided or poorly crystallized. Therefore, it is assumed that any silica not dissolving under these conditions represents quartz, plus other clay-type silicates rarely detected by XRD [4].

In the laboratory high temperature (HT) digestion ( $\sim 225 - 270^\circ\text{C}$ ), not only gibbsite and boehmite are dissolved but also kaolinite, phosphates, some quartz, in addition to other minerals. It is assumed that additional parameters can be determined, for example Net Extractable Alumina =  $\text{Al}(\text{HT})$  and Total Available Alumina ( $\text{TEA} = \text{Al}(\text{HT}) - 0.85 \text{ R}_x\text{SiO}_2$ ), which is used to describe alumina in gibbsite and boehmite. TEA is also known by the name “total extractable alumina”. Sometimes corrections are made for silica dissolved from partial attack of quartz and other minerals. Hence, the TEA determination is less accurate than the determination of  $\text{Al}(\text{LT})$ , because it is based on several determinations, each with its own analytical error. As a result, the so-called MONO ( $\text{Al}_2\text{O}_3$  in boehmite) that is calculated by the difference between TEA and  $\text{Al}(\text{LT})$  is considered less accurate than boehmitic  $\text{Al}_2\text{O}_3$  ( $\text{b}.\text{Al}_2\text{O}_3$ ) determined by a direct method.

In general, there are five major problems associated with the WCh approach:

- the laboratory bomb digestion is carried out under different conditions from plant digestion
- the parameters of the bomb and plant digestion vary from one location to another; therefore, comparison of results is difficult or impossible
- concentration ranges of constituents determined by WCh are limited
- Bayer process control accuracy is limited by using the WCh data generally available
- the chemical analysis (bomb digestion) cannot accurately predict the mineral composition of bauxite most of the time.

Some bauxite is known to contain a very fine boehmite that partially dissolves at low temperature digestion conditions and contributes to  $\text{Al}(\text{LT})$  [5]. Such boehmite may act as seed for  $\text{Al}_2\text{O}_3$  already dissolved taking it out of the Bayer solution into the red mud, which reduces alumina recovery in the Bayer process. This phenomenon is known in the literature as boehmite reversion [6]. To avoid boehmite reversion or boehmite dissolution the digestion must be carried out within a limited and controlled A/C ratio ( $\text{Al}_2\text{O}_3/\text{Caustic}$  expressed as  $\text{Na}_2\text{CO}_3$ ). The required sample

mass may also need to be estimated using the expected Al(LT) or Si(LT) concentrations. The phenomenon is well known but poorly quantified, mainly due to a lack of adequate analytical methodology.

In general, users believe that they employ WCh to predict bauxite mineralogy. However, WCh delivers results of extraction but not mineralogy. To obtain bauxite mineralogy, X-ray diffraction (XRD) and mathematical modeling methods are generally employed. Some mineral phases may also be determined by other methods, for example boehmite by TGA.

### **3. X-Ray Diffraction (XRD)**

Application of a profile refinement procedure established by H.M. Rietveld, allows calculation of X-ray powder patterns using crystallographic and theoretical diffraction principles [7]. Quantitative phase analysis by the Rietveld method uses all the intensity data in a diffraction pattern (represented by a digital file) rather than a few of the most intense reflections [8 – 12]. Rietveld X-ray diffraction analysis has been increasingly used in the aluminum industry since the beginning of the 1990s. The performance of the Rietveld methods depends a lot on the quality of the diffraction data, which necessitates very fine sample grinding, and precise data collection. In contrast to the traditional XRD calibration, the Rietveld method helps perform quantitative analysis of bauxite without the need of reference materials.

Compared with WCh, X-ray diffraction (XRD) offers speed and much lower cost of analysis but is less accurate. A major shortcoming of XRD in general is the limit of detection for certain minerals due to low X-ray power. The limit of detection (LOD) of phase constituents is relatively high [13]. Even gibbsite, which is at high concentrations in lateritic bauxites but at low concentrations in karstic bauxites, is affected. Kaolinite usually cannot be analyzed if its content is below 1.0 %. Among the major sources of errors which affect all XRD methods, crystallinity and solid solutions [14, 15] are the most serious ones, as well as extreme preferred orientation in the case of gibbsite. The problem of bauxite amorphous content has a profound effect on quantification of selected phases using Rietveld-XRD methods and X-ray tube diffractograms. Even application of synchrotron radiation cannot overcome sample amorphicity [16]. Simply, if a part of the bauxite matrix is X-ray amorphous, it does not contribute to a diffractogram. If several mineral contributions are missing on diffractogram simultaneously, they can be quantified as a group, but not individually. Bruker reported that the results of quantitative phase analysis may be seriously biased when  $\text{CuK}\alpha$  instead of  $\text{CoK}\alpha$  radiation is employed [17].

Use of the Rietveld method requires an excellent XRD background, and a sound understanding of geology and chemistry as related to bauxite analysis.

### **4. Mathematical Modeling**

Mathematic modeling allows automatic estimation of the mineralogical composition of commercial bauxite [18,19]. In this work BauxQ ([www.bfsimulation.com](http://www.bfsimulation.com)) expert system, which evolved in the last 15 years was used. It is designed to predict the most probable (theoretical) bauxite mineralogy and in addition to gibbsite, boehmite, kaolinite, quartz, hematite, Al-goethite and anatase, the BauxQ software calculates concentrations of the remaining secondary phases in any kind of bauxite (gibbsitic and diasporic). The system employs the sample elemental (from XRF or ICP) and LOM concentrations as inputs. The success in output lies in the high accuracy and reliability of the input data [20]. The software integrates a user-friendly interface with a complex mathematical modeling platform. Unlike empirical fits of XRF data, BauxQ does not call for laboratory calibration [21], allows wide input composition ranges and is not limited to specific geological deposits. To predict the quantitative phase composition or mineralogy of bauxite, BauxQ requires the minimum input data, such as concentration of  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$  and LOM. For a more accurate estimate, the most frequently encountered minor oxide constituents are also needed, if meaningful. Assuming high quality elemental concentrations and

LOM data, the  $g.\text{Al}_2\text{O}_3$  (alumina in gibbsite) and  $k.\text{SiO}_2$  (silica in kaolinite) concentrations respectively, are the most probable (theoretical) concentrations estimated by BauxQ for a given set of input data. In the final BauxQ calculation stage, the digestion parameters module can also be used to compensate for systematic differences observed while comparing results with WCh.

The greatest advantages of BauxQ are: (i) ease of use; (ii) no operator's involvement in the process; (iii) the reliability of the mineralogical information; (iv) potential to simplify analytical laboratory (no WCh or XRD); and (v) very low cost of analysis.

## 5. Mineralogy, Wet Chemistry and XRD

Mineralogy of a bauxite sample is one (just like the sample elemental composition is unique) but the WCh degree of phase dissolution may be different for each deposit and for each set of digestion conditions. Because these parameters frequently differ among laboratories, the direct inter-laboratory comparison of digestion results is very difficult, if not impossible. The analysts often say that the digestion method of bauxite is "specific" to either laboratory or Bayer plant. Comparison has always been between theoretical calculations such as alumina hydrate recovery from the estimated phases under specific Bayer digestion conditions and those found under laboratory digestions.

Initial comparison of WCh data and other methods (XRD, microscopy, or BauxQ) may result in certain differences [22 – 26]. For example,  $k.\text{SiO}_2$  determined by XRD or BauxQ and reactive silica ( $\text{RxSiO}_2$ ) determined by WCh may differ to a specific degree mainly because quartz of fine crystallinity usually dissolves even under low temperature (LT) digestion conditions and contributes to  $\text{RxSiO}_2$ . The kaolinite mineral does not fully contribute to the diffractogram if it happens to be X-ray amorphous. Then, the XRD quantification gives different result from WCh. Similarly,  $g.\text{Al}_2\text{O}_3$  may be lower or higher than  $\text{Al(LT)}$  determined by WCh depending on behavior of boehmite and secondary minerals during digestion. Some bauxite is known to contain boehmite that partially dissolves under low temperature digestion conditions and contributes to  $\text{Al(LT)}$ . Boehmite at low content tends to be very fine and poorly crystallized. It very often contributes to X-ray amorphous content on diffractogram. The secondary minerals, for example wavellite, crandallite or lithiophorite (particularly important in Jamaica bauxite) may also partially dissolve.

Any major deviation from correlation between the methods is, most of the time, due to analytical error.

## 6. Experimental

Over the last several years very many sets of data came the author's way, and a few are selected for this article. The first group of data comparison involves results obtained in a mine laboratory.

Comparison between  $g.\text{Al}_2\text{O}_3$  (BauxQ) and  $\text{Av}.\text{Al}_2\text{O}_3$  in Figure 1 demonstrates, that there is no bias. The standard error of  $\pm 3.6\%$  obtained in the correlation is perhaps on the higher side but reflects the situation in the production laboratories. Some  $\text{Av}.\text{Al}_2\text{O}_3$  concentrations are impossible, because they are higher than the corresponding  $\text{Al(HT)}$  concentrations that were also determined for all samples. In Figure 2 the divergence between MONO and  $b.\text{Al}_2\text{O}_3$  (BauxQ) increases with decreasing  $b.\text{Al}_2\text{O}_3$  concentration. Certain contributions to the divergence also come from illite, which is taken care of in BauxQ estimates.

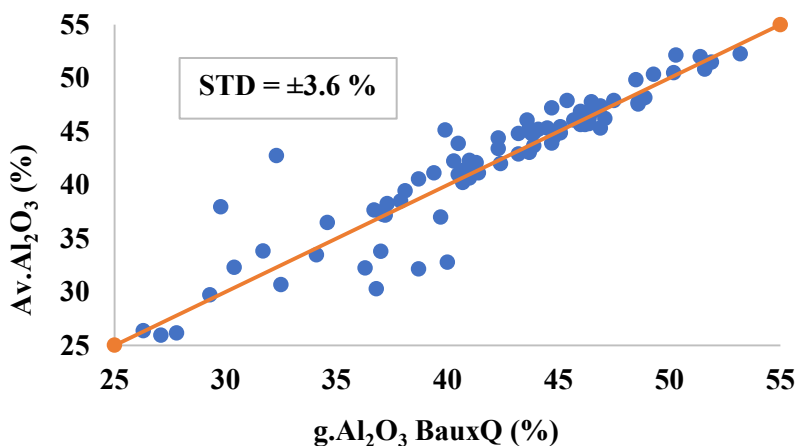


Figure 1. Laboratory I. Comparison between g.Al<sub>2</sub>O<sub>3</sub> (BauxQ) and Av.Al<sub>2</sub>O<sub>3</sub>.

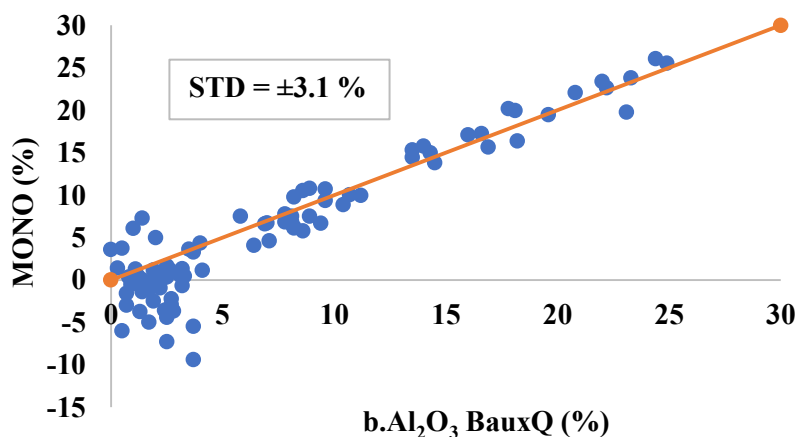
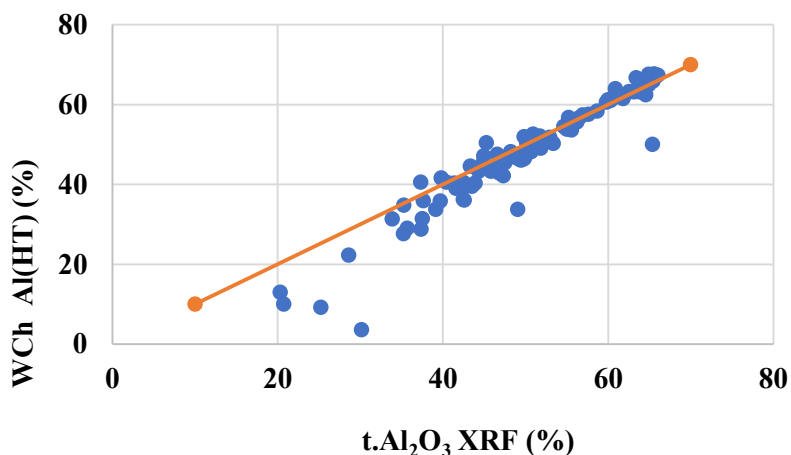


Figure 2. Laboratory I. Comparison of concentrations for Al<sub>2</sub>O<sub>3</sub> monohydrate.

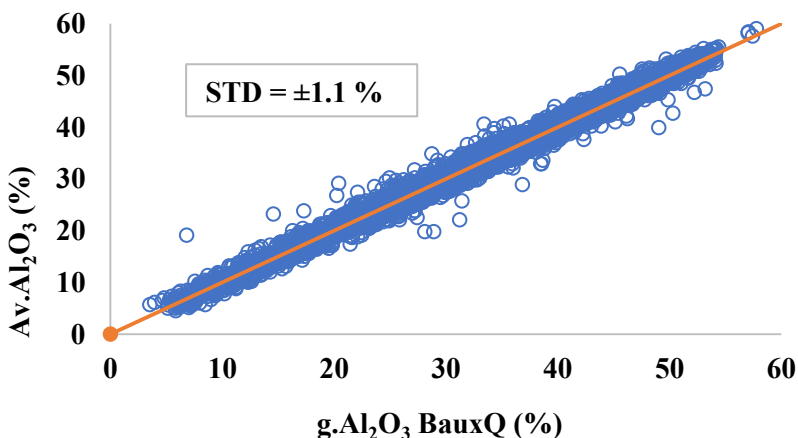
The overall standard error for the b.Al<sub>2</sub>O<sub>3</sub> (BauxQ) and MONO correlation is ±3.1 %. However, for the monohydrate concentrations above 4 % it is much lower. The problem with some outliers is that the formula for MONO calculation heavily depends on Al(HT), the concentration of which, for many samples, is just too low (Figure 3).

Figure 3 reveals yet another detail about the reliability of Al(HT) determinations. Illite and goethite should, at least partially, resist HT digestion conditions. For several samples in which illite does not even occur, the determined Al(HT) concentration is clearly impossible and constitutes gross analytical error. The error propagates and distorts calculation of MONO determined in the laboratory. With the total Al<sub>2</sub>O<sub>3</sub> (t.Al<sub>2</sub>O<sub>3</sub>) concentration decreasing, the HT digestion has increasing difficulty with extracting Al<sub>2</sub>O<sub>3</sub> from bauxite. This unavailable Al<sub>2</sub>O<sub>3</sub> ends up in the red mud and analytically contributes to the gap shown in Figure 3.



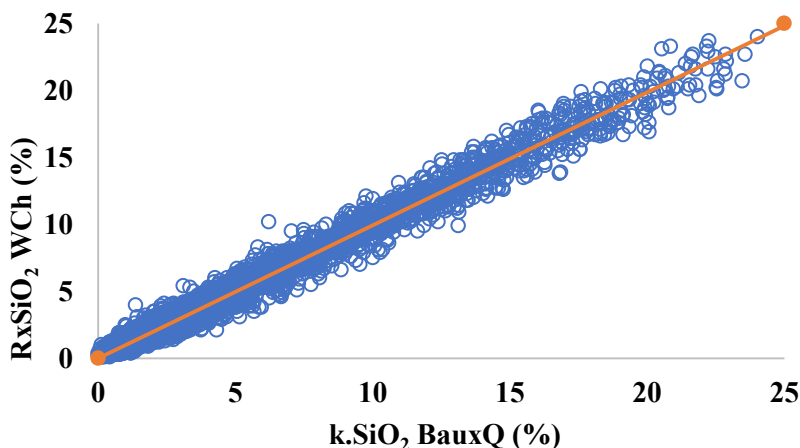
**Figure 3. Laboratory I. Comparison between t.Al<sub>2</sub>O<sub>3</sub> and the Sum of WCh determined Al<sub>2</sub>O<sub>3</sub>.**

The second group of results illustrate the analytical situation on the side of a commercial laboratory. The correlation shown in Figure 4 is for g.Al<sub>2</sub>O<sub>3</sub> and Av.Al<sub>2</sub>O<sub>3</sub> and involves a very large number of exploration samples. The standard error is ±1.1 % across the entire range and naturally reflects inaccuracy of all determinations, including several clear outliers. There is no bias and the overall quality of the results is good.



**Figure 4. Laboratory II. Correlation between g.Al<sub>2</sub>O<sub>3</sub> (BauxQ) and Av.Al<sub>2</sub>O<sub>3</sub> (WCh).**

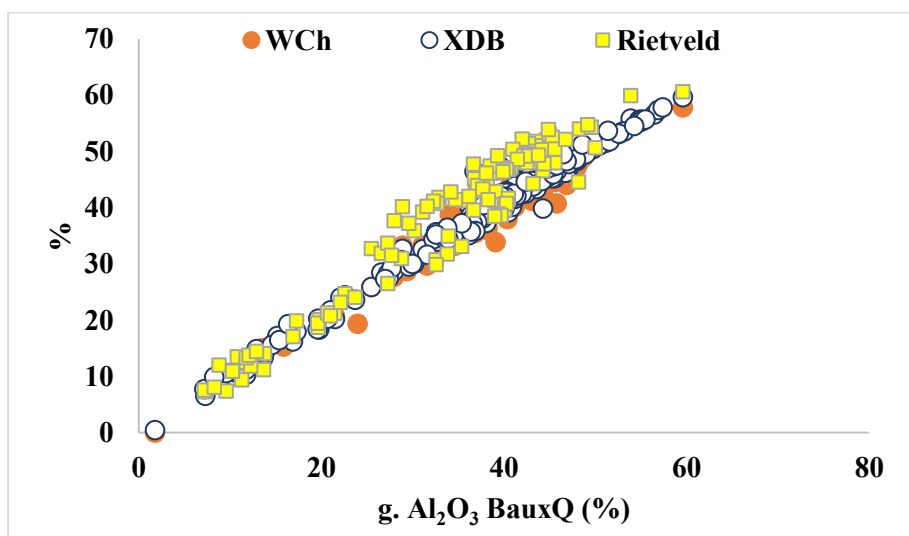
Figure 5 gives a correlation between RxSiO<sub>2</sub> determined by WCh and k.SiO<sub>2</sub> estimated using BauxQ. The correlation in Figure 5 covers the 0.4 – 24 % SiO<sub>2</sub> range. The 1 sigma standard deviation for the correlation at low SiO<sub>2</sub> (< 3 %) is approximately ±0.25 %. However, with increasing SiO<sub>2</sub> the standard error increases and is ±0.35 % across the 3 – 6 % range, and ±0.5 % for the 6 – 12 % range.



**Figure 5. Laboratory II. Correlation between k.SiO<sub>2</sub> (BauxQ) and RxSiO<sub>2</sub> (WCh).**

Usually with increasing SiO<sub>2</sub> concentration it becomes more and more difficult to obtain an impressive correlation. This is not because of mathematical modeling boundaries, but because of natural degradation of analytical accuracy of WCh determinations. Most WCh methods have the limit of applications set at 8 – 10 %, and it takes an unusual effort to extend the limit. Therefore, one cannot expect an impressive correlation for RxSiO<sub>2</sub> & k.SiO<sub>2</sub> when total SiO<sub>2</sub> exceeds 10 %.

In Figure 6 the BauxQ data for g.Al<sub>2</sub>O<sub>3</sub> is compared with WCh, XDB and Rietveld-XRD results. As Rietveld-XRD normalizes concentrations to 100 %, the amorphous content in same samples results in overestimation. The XDB data appears in excellent correlation with BauxQ as both share the mass balance principle.

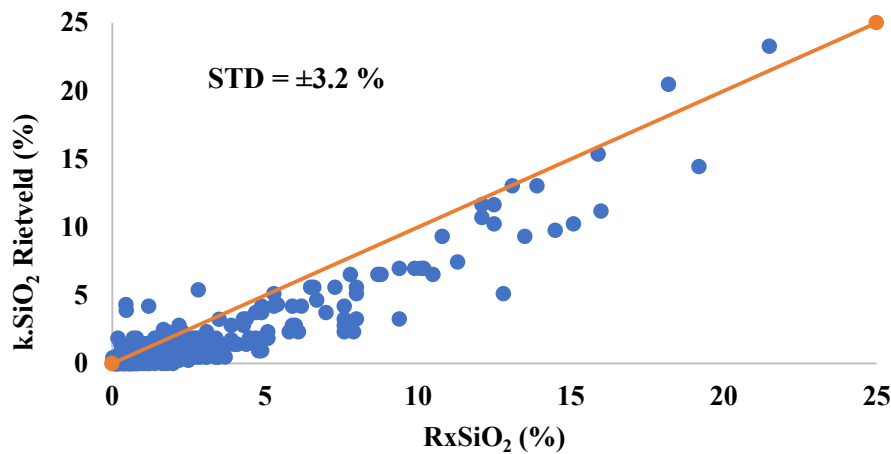


**Figure 6. Laboratory III. Correlation between g.Al<sub>2</sub>O<sub>3</sub> (BauxQ), XDB, Rietveld-XRD and Av.Al<sub>2</sub>O<sub>3</sub> (WCh).**

In Figure 7, WCh data is compared with Rietveld-XRD results obtained in the same commercial laboratory. Most points occur below the correlation line, which suggests partially X-ray amorphous kaolinite. Boehmite, Al-goethite and kaolinite are the most common phases underrepresented on diffractograms.

One would assume that results obtained from commercial laboratories (Figure 7) represent the quality benchmark, but it is not always the case. Some of these laboratories produce correct or

more realistic concentrations of bauxite constituents, some not. The results also reveal how difficult it is to handle the Rietveld-XRD task even for a commercial laboratory.



**Figure 7. Laboratory IV. Correlation Between RxSiO<sub>2</sub> (WCh) and k.SiO<sub>2</sub> (Rietveld).**

The standard error of any correlation corresponds to the combined uncertainty of XRF, LOM and WCh determinations taken into consideration in the calculations. Worth noticing is that many samples fall into the category of “identical” because their LOM & XRF composition is very, very close. Yet, their WCh concentrations may vary by quite an important margin. This suggests the WCh method’s precision.

Two of the simplest ways to check reliability of analytical data is mass balance calculations. First, if among the WCh data the Al(HT) concentrations are available, then a simple comparison between Al<sub>2</sub>O<sub>3</sub> (XRF) and Al<sub>2</sub>O<sub>3</sub> (WCh) can be made. The Al(HT) concentration, or RxSiO<sub>2</sub> must never be higher than Al<sub>2</sub>O<sub>3</sub> (XRF), or SiO<sub>2</sub> (XRF), respectively.

For additional verification one can use data from various sources and build a set of two equations:

$$\text{Diff Al}_2\text{O}_3 = \text{Al}_2\text{O}_3 (\text{XRF}) - \text{Av. Al}_2\text{O}_3 - \text{b. Al}_2\text{O}_3 - \text{RxAl}_2\text{O}_3 - \text{Al}_2\text{O}_3 (\text{Sec. Phas.}) - \text{go. Al}_2\text{O}_3 \quad (1)$$

$$\text{or Diff2 Al}_2\text{O}_3 = \text{Al}_2\text{O}_3 (\text{XRF}) - \text{Al}(\text{HT}) - \text{Al}_2\text{O}_3 (\text{Sec. Phas.}) - \text{go. Al}_2\text{O}_3 \quad (2)$$

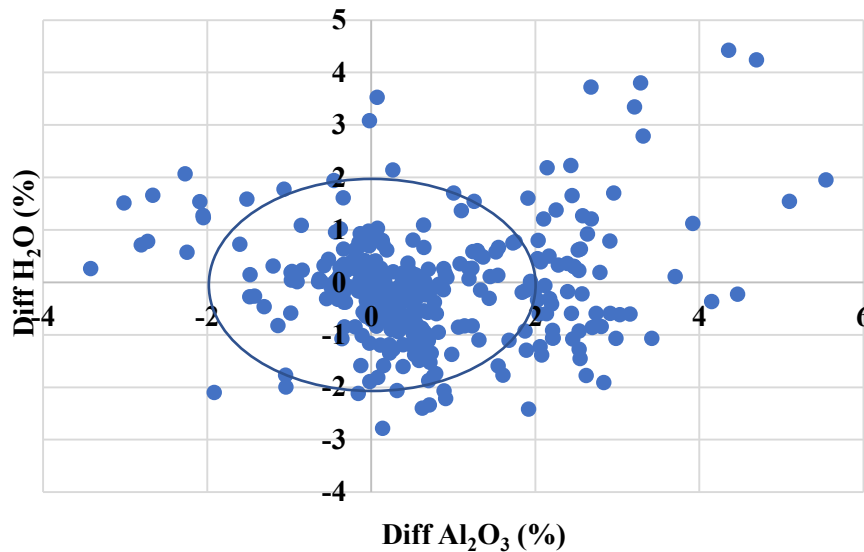
$$\text{and Diff H}_2\text{O} = \text{LOM1000} - \text{H}_2\text{O} (\text{Av. Al}_2\text{O}_3) - \text{RxH}_2\text{O} - \text{H}_2\text{O} (\text{Sec. Phas.}) - \text{b. H}_2\text{O} - \text{go. H}_2\text{O} \quad (3)$$

where: Sec. Phas. = secondary phases; go. Al<sub>2</sub>O<sub>3</sub> and go. H<sub>2</sub>O = Al<sub>2</sub>O<sub>3</sub> and H<sub>2</sub>O in goethite (hematite).

A graphical example is presented in Figure 8. Any point occurring far from the beginning of origins indicates a problem.

The case shown in Figure 8 (350 samples) is typical. The points found in the upper right quadrant indicate underestimation, whereas those in the lower left quadrant indicate overestimation of phase concentrations.

If the results quality is good, the points found in the upper left quadrant most likely suggest overestimation of gibbsite, or that also boehmite partially dissolves at low temperature digestion.



**Figure 8. Comparison of Mass Balances for  $\text{Al}_2\text{O}_3$  and LOM1000.**

Various reasons can be given to explain some of the major differences between conflicting results. From the mining point of view, it is essential that representative samples are produced so that the laboratory measurements are for the right material. In several cases, it is possible that questionable analyses came from questionable samples.

## 7. Discussion

Over the last few decades the wet chemical analysis (WCh) of bauxite has been recognized as the benchmark in bauxite characterization. The WCh analysis is destructive to the sample and extractive to its constituents, so that all bauxite constituents that can be soluble under the specific digestion conditions pass into the caustic liquor. Depending on the digestion conditions a series of extractive results may be obtained for the same sample. Obviously, the degree of extraction depends on the process conditions.

Wet chemical analysis of bauxite is not standardized. This is a major problem involving both the low and high temperature bauxite digestion, which is generally recognized by the industry. Even within the same company, various laboratories may employ different digestion conditions. Depending on historical development – the digestion equipment, sample mass, particle size distribution, digestion temperature, digestion time, caustic strength and A/C ratio vary. In addition, results may differ, even using the same set of parameters, due to the human factor. The analysts often say that the digestion method of bauxite is specific to either laboratory or Bayer plant. As a result, the industry does not speak the same language and data comparison is not always possible. Moreover, the concentration ranges for which the WCh methods apply are limited and often prevent obtaining data for exploration samples that fluctuate greatly in composition.

Some WCh standard methods do not even mention the expected precision, or accuracy of analysis. Accuracy cannot be determined because WCh is empirical and there is no independent reference method or certified reference material available to many laboratories. Regarding precision, the repeatability limit for Al(LT) is approximately  $\pm 0.5\%$ . At the 95 % confidence limit, the reproducibility is  $\pm 1.5\%$ . These numbers are for one specific sample and in common practice it is difficult to attain them.

Mathematical modeling represents the most promising solution under existing laboratory circumstances. The elemental composition data from XRF or ICP that is required to run the software such as BauxQ is obtained with high accuracy and precision and for most laboratories, the results compare favorably with one another. The same input data always produces the same output anywhere. BauxQ can even deal with overburden, clay floor and is independent of the exact geological nature of the deposit. Given its rapidity, it is particularly useful for estimating the potential of new deposits. Given its accuracy, it greatly facilitates mine exploitation control. Among the drawbacks, diasporite cannot be distinguished from boehmite and anatase from rutile. Also, ilmenite ( $\text{FeTiO}_3$ ) cannot be quantified, as the corresponding  $\text{Fe}_2\text{O}_3$  and  $\text{TiO}_2$  are assigned to hematite and anatase, respectively.

Without doubt, in bauxite exploration and Bayer process control we will see more and more modern instrumental methods that are faster, easy to use and accurate. Given the advent of the current computing potential and understanding of the bauxite field, one can clearly foresee that the reliance on chemical methods will be minimized in the future. Wet chemistry is too expensive, too complex and may be too erratic to apply to exploration or exploitation activity on a large scale that involves thousands of samples. The WCh methods require a large supply of chemicals as well as considerable space and manpower. Despite being costly and slow, WCh methods that involve bauxite caustic digestion remain the standard tool, especially to verify extraction efficiency, in process control and trade activities.

Contemporary instrumental tools have a limited chance of being widely accepted in situations where throughput counts due to their relatively low efficiency (XDB-Hungalu) [27] and when physical effects hamper accuracy (Rietveld). The Rietveld methods may be considered quantitative in determination of major phases, whereas secondary phases at low content cannot be quantified. Whilst the method may work suitably for some well crystallized bauxite [28], it will not work for an X-ray amorphous bauxite. In other words, one cannot expect a perfect answer from imperfect input data. In the final analysis stage, using a diffractogram combined with the mass balance analysis is very beneficial (available in the XDB-Hungalu). The evidence generally provided indicates that XRD is a tool of a high but limited potential, and certainly calls for caution when used alone (Rietveld methods) in the bauxite phase quantification. FTIR has never gained momentum in numerous countries, including Jamaica as an example, because the local bauxite matrix appears too complex for FTIR. Also, a need for a large number of reference materials required for a calibration process per deposit represents an overwhelming hurdle.

Table 1 gives a summary of the methods. They are compared in relative terms with respect to accuracy, speed, economy, usability and availability.

Three phenomena are increasingly calling for a commonly recognized standard or guideline, which would apply in all stages of the bauxite business. A continuous rise in the price of bauxite in the last decades caused a change in status of this commodity from ordinary to special. The time when bauxite traded at \$20 a ton is long gone. Also, the quality or grade of bauxite generally available to the industry has deteriorated markedly with time. Moreover, the market has become fragmented as the number of bauxite and alumina producers have increased, as has the annual bauxite consumption.

**Table 1. Methods of Phase Quantification.**

METHOD		Accuracy	Speed	Economy	Usability	Availability
<b>Wet Chemistry</b>	WCh	accurate <sup>(1)</sup>	very slow	expensive	difficult	decades
<b>Infrared Spectroscopy</b>	FTIR	Limited <sup>(1)</sup>	moderate	moderate	moderate	decades

<b>XRD Calibration</b>	XRD	Limited <sup>(1,2)</sup>	moderate	moderate	difficult	1950's
<b>XRD-Rietveld</b>	XRD	Limited <sup>(2)</sup>	moderate	moderate	difficult	1980's
<b>XDB</b>	XRF + TGA + XRD	accurate	slow	expensive	difficult	1990's
<b>Mathematical Modeling – BauxQ</b>	XRF + TGA	accurate	very fast	inexpensive	very easy	2000

(1) deposit specific, laboratory specific, determination ranges limited, strong human factor

(2) sensitive to sample X-ray amorphous content

For many decades, the commercial value of bauxite has been estimated using total Al<sub>2</sub>O<sub>3</sub> and total SiO<sub>2</sub> concentrations. This approach continues because seller and buyer well agree on the elemental composition, as opposed to the WCh digestion results. But as Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> occur in several minerals, using them alone yields erratic results. Decades ago when the average bauxite quality was much higher, this could have been tolerated. Over time, bauxite Al<sub>2</sub>O<sub>3</sub> content gradually decreased and that of SiO<sub>2</sub> increased. We may see high quartz or other minerals that not only change performance of the established methods, but heavily undermine the application of past commercial rules. Information on total SiO<sub>2</sub> is insufficient because kaolinite and quartz may contribute to it at different rate, which has major impact on process economy. For example, between RxSiO<sub>2</sub> = 3 % and 5 % the difference in caustic soda consumption is 50 kg/t Al<sub>2</sub>O<sub>3</sub>. In the case of an alumina plant of 1 mt/year capacity, the difference is 50,000 tons of caustic soda consumption per year. The corresponding cost is in the millions of USD per year. Very often, the analytical methodology used by a bauxite producer is different from that which a Bayer plant employs. Global confusion continues.

The present state of analytical methodology with respect to bauxite characterization is worrisome. A user becomes confused when he obtains results from two or more sources and methods. This will not stop the bauxite industry from operating but leaves a lot to be desired. The aluminum industry should do better to know the commercial value of its principal commodity and use mineralogical, not elemental composition, for its estimation. Bauxite building blocks must be known, and mass balance must be observed. If the bauxite mineralogy is known, it is just an easy step to calculate Bayer process parameters. Among them there are: available alumina, mud factor, chemical caustic consumption, lime consumption, or goethite/hematite ratio. Information on process parameters allows for a better understanding of a bauxite's economical value and a more effective control of a Bayer plant. Most refineries employ Bayer technology to process bauxite and they are tuned to a specific raw material. A major change in mineralogical characteristics of the raw material calls for revision of the refinery set up [29 – 31].

But if a commercial laboratory has difficulty providing reliable data, what can we expect from a typical plant production laboratory? Mathematical modeling constitutes an alternative and appears to have many advantages for bauxite mineralogical quantification of new and established deposits. It is the most consistent method and provides an opportunity to significantly lower operational costs by close to two orders of magnitude as compared with WCh. The required elemental and LOM data is generally available for almost all samples and is determined with acknowledged accuracy and precision. Industry laboratories would benefit from mathematical modeling tools for their internal quality control to avoid the release of impossible results.

This paper does not pretend to cover all methods used in the bauxite phase quantification. Primary methods, which do not require calibration standards were covered. Methods such as optical microscopy, thermal analysis or Infra-Red were deliberately omitted. Also, other major bauxite constituents, such as boehmite, hematite or goethite are not dealt with here. Obtaining a

quality correlation among different methods for these constituents is much more difficult than for gibbsite or kaolinite.

## 8. References

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