

HIGH-RESOLUTION THERMAL GRAVIMETRIC ANALYSIS (HI-RES TGA) OF BAUXITES AND MUDS

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Abstract

High-Resolution Thermal Gravimetric Analysis was applied to a suite of bauxites and their muds to quantify gibbsite, boehmite, and goethite. A dynamic heating rate is applied to improve resolution of overlapping decompositions within a reasonable measurement time. The weight losses measured as LOI's/LOM's are related to the amounts of phases decomposing/transforming at specific temperature ranges.

The LOI's at three temperature ranges were used for phase quantification: 180-275°C is associated with gibbsite decomposition/dehydroxylation to boehmite and chi-alumina; 275-380°C is associated with goethite decomposition to hematite; and 410-580°C with dehydration of boehmite. The method performance was validated against certified reference bauxites and two other independent techniques, Differential Scanning Calorimetry and Powder-X-ray Diffractometry (XRD) with Rietveld refinement.

Investigation on decomposition reactions of gibbsite by TGA-XRD showed that at 275°C gibbsite is not completely dehydroxylated and decomposes to boehmite and chi-alumina. Therefore, 3 moles of H₂O cannot be used to relate the weight loss to gibbsite. A weighted average of 2.5 moles of H₂O loss for the two transitions was calculated.

Accuracy of Hi-Res TGA for gibbsite quantification was validated against reference bauxites within 1% error. Results for bauxite suite correlate well with Rietveld-generated values with an average difference of 1.1% gibbsitic alumina. An average difference of 0.3% boehmite was observed between Hi-Res TGA and DSC results. An average difference of 1% goethite was observed between Hi-Res TGA and XRD- Rietveld-generated results.

1. Introduction

The GEOMET Program aims to gain a better understanding of the mineralogy of the bauxite materials and relate this to processability which will minimise if not eliminate variability in bauxite feed for better resource management in the long run. As part of the GEOMET project, XRD-TOPAS is being developed and applied as a mineralogical quantification tool. TOPAS is a graphics based profile analysis program built around a general nonlinear least-squares fitting system (TOPAS User Manual).

Thermal analyses by TGA and DSC of bauxites and muds are techniques already applied in Worsley control and research laboratories. In the process of developing TOPAS for quantitative XRD of bauxites and muds, the thermal techniques were revisited for improvement to modify the existing methods for more reliable and more reproducible results. In this study,

- thermal analyses by Hi-Res TGA was applied to a suite of GEOMET bauxites, muds from mild-leached bauxites, and muds/residues to quantify gibbsite, boehmite, and goethite.
- method validation was done using certified reference bauxites and muds.
- the quantitative results were compared to TOPAS and DSC measurements.
- a better understanding of the transformations of the relevant phases in the samples was achieved by coupling the TGA technique with powder X-ray diffractometry.
- a mild caustic leach of bauxite was done prior to measurement of boehmite and goethite contents and leaching process was validated.

High Resolution Thermal Gravimetric Analysis (Hi-Res TGA)

The Hi-Res™ Technique is a dynamic rate TGA. The heating rate of the sample material is dynamically and continuously modified in response to changes in the rate of decomposition of the sample. This dynamic heating leads to a maximized weight change resolution. Using the Hi-Res ramp segments, very high maximum heating rates are applied without overshooting the transition temperature. The heating/cooling rate of the furnace varies during the ramp in response to the derivative of weight change (%/minute). When a decomposition or transition is accompanied by a weight change (i.e., percent weight change/minute increases), the heating rate is decreased. During the run, when no decomposition or transition is detected, then the percent weight change/minute decreases so the heating rate increases. This dynamic variation of the heating rate improves resolution and at the same time provides practical analysis or measurement time. The resolution setting in the instrument is used to select the most useful band of percent/minute values for proportional heating control. The minimum heating rate is 0.001°C/minute to a maximum specified in the ramp segment.

2. Methodology

Samples and Reference Materials

Bauxite samples of varying lithologies were received from various mining sites. To validate the Hi-Res TGA method in terms of accuracy, a seven-phase synthetic mixture and certified reference bauxites and muds were measured. Table 1 gives the reference materials used in the study.

Table 1 Reference Bauxites for the Thermal Analyses

Standard Name	Description	Source
Synthetic Bauxite	seven phase synthetic mixture	International Union of Crystallography ⁽¹⁾
BXT-03	certified bauxite	Alcan (Certificate of Analysis)
BXT-04	certified bauxite	Alcan (Certificate of Analysis)
BXT-07	certified Brazilian bauxite	Alcan (Certificate of Analysis)
BXT-08	certified Indian bauxite	Alcan (Certificate of Analysis)

Samples were micronized to remove any bias that may be due to particle size when the TGA results are compared to TOPAS measurements which were obtained on micronized samples. The reference bauxites were also leached in mild caustic-alumina solution to assess the effectiveness of the leaching process.

Hi-Res TGA

For the Hi-Res TGA measurements, a TA Instrument High Resolution (Hi-ResTM) Thermogravimetric Analyzer TGAQ5000-0325 with an auto sampler accessory was used. Samples of approximately 20-30 mg were heated in platinum HT pans at constant and dynamic rates from ambient to 1000°C in nitrogen atmosphere (ultra high purity) with a sample purge of 25mL/min and balance purge of 10 mL/min. Several segments in developing the method were applied and the optimized method for gibbsite quantification is named **HRD50C ISO-4T**: High Resolution Dynamic Mode at 50°C/min, resolution set to 5 and an isothermal hold for 15 minutes at 4 different temperatures: 105°C, 400°C, 600°C, and 1000°C. The total run time was 124.35 min per sample.

For boehmite and goethite measurements in the leached bauxites (mud), the **HRD50CR5_ISO3T** was used. This method is almost the same method described above except that the final temperature was cut down to 650°C.

DSC Analysis

To validate the Hi-Res TGA Method for boehmite measurements, the results were compared to that of the DSC analyses done on a TA DSCQ2000 also equipped with an autosampler accessory.

Data Analysis

The TA Instrument Universal Analysis 2000 Version 4.5A software was used to analyse the thermogravimetric and differential scanning calorimetric data.

Leaching of Bauxite for Boehmite and Goethite Measurements

The boehmite in the bauxite samples were concentrated by removing gibbsite and kaolinite via a low temperature digest at 90°C in an alumina-caustic solution (A/C =0.16 to 0.18) for 3 hours and the washed and dried residues were analysed on the Hi-Res TGA for boehmite content.

Synthesis of Chi-Alumina

About 1.5 g of micronized Malakoff hydrate was dried in the oven at 105°C for 1 hour. The temperature was ramped at 10°C/min to 225°C and held at this temperature for 30 mins. The sample was removed from the furnace and allowed to cool. The temperature was again ramped from 200°C to 500°C at a rate of 5°C/min and held at the final temperature for 2 hours. The temperature was lowered to 105°C and the sample was removed from furnace and placed in a desiccator.

Powder X-ray Diffractometry

All powder X-ray diffraction patterns were obtained using a Bruker D8 X-Ray Diffractometer scanning from 5° to 70° 2-theta at a step of 0.050° with a step time of 4s.

3. Discussion

Decomposition Reactions

TGA provides a quantitative weight change associated with decomposition and volatilization of substance(s) present in the material. However, information about the identity of the decomposition products or specific off-gas substances is not available unless TGA is coupled with other analytical techniques. Knowing the identity of the decomposition products is essential in understanding the decomposition or phase transformation during thermal treatment. The nature of the decomposition products will give further confidence in the quantitative analysis derived from the sample weight loss.

A typical TGA thermogram or TGA plot for bauxite is shown in Figure 1. The first derivative ($\partial M / \partial T$) of the TGA curve with respect to temperature, **T**, i.e. the **DTG** curve, is also shown in the same plot. In order to utilize the weight loss in the TGA curve for quantification of analyte, the specific reaction that leads to a weight loss must be understood. Knowing the decomposition reactions makes the thermal technique powerful as a quantification tool.

The thermogram in Figure 1 shows three significant temperature ranges for a bauxite where the following decomposition or dehydroxylation reactions occur: These temperature ranges were obtained based on the thermograms of the bauxite samples used in the study.

Temperature range, **TI**, of 180-275°C – gibbsite

Temperature range, **TII**, of 275-380°C – goethite

Temperature range, **TIII**, of 410-580°C – boehmite and kaolinite.

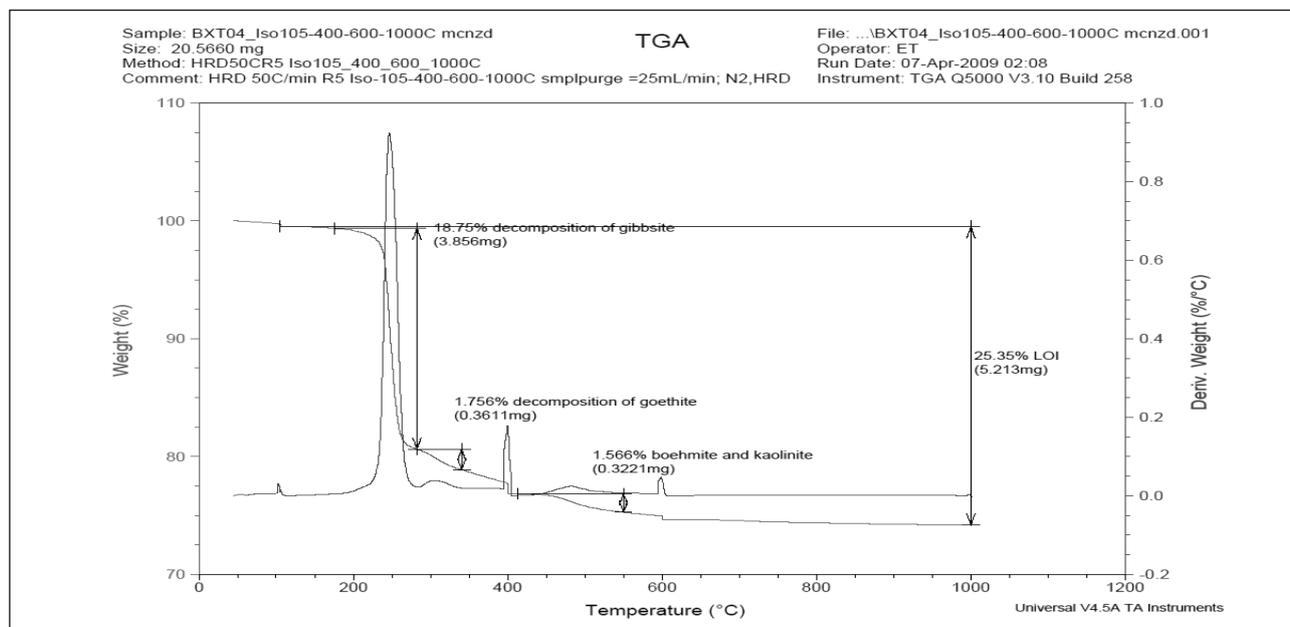


Figure 1. Typical Hi-Res TGA thermogram of a bauxite material showing the loss in mass of the sample in three successive steps during heating from 105°C to 1000°C in nitrogen atmosphere. The three significant weight losses are attributed to dehydroxylation/decomposition of gibbsite, goethite and boehmite and kaolinite.

When the thermograms for the reference bauxites were analysed for gibbsite content using 3 moles of water to account for the weight loss at a temperature range of 180-275°C, the calculated values are lower than the certified values. Table 2 summarizes the calculated %G. Al₂O₃ (% gibbsite expressed as % Al₂O₃) assuming it undergoes complete dehydroxylation/decomposition to Al₂O₃ as represented by Equation (1).



Table 2. Percent Gibbsitic Alumina in Reference Bauxites (Gibbsite Completely Dehydroxylated)

Sample	Gibbsite LOI bet 180-275 °C	%Gibbsite- 3 H ₂ O	%Gibbsitic Al ₂ O ₃ - 3 H ₂ O (LOI *1.888)	Reported Values [#] , %Gibbsitic Al ₂ O ₃
IUCr CPD Round Robin Synthetic Bauxite	15.80	45.6	29.8	35.9
BXT-03	22.23	64.2	41.9	50.9 ± 0.4
BXT-04	18.58	53.6	35.0	42.5 ± 0.4
BXT-07	17.62	50.9	33.2	39.7 ± 0.6
BXT-08	18.48	53.3	34.9	41.7 ± 0.4
Gibbsite Concentrate ^a	25.67	74.1	48.4	58.2
Malakoff Hydrate ^b	27.10	78.2	51.1	65.3

[#]The Alcan Certificates no longer quote percent gibbsitic alumina in their current certificates. Instead the %Al₂O₃ at low temperature digestion (2.5N NaOH, 150°C, A/C.0.41, 25 min) is reported. This value is assumed to be gibbsitic alumina. ^aNatural gibbsite concentrated from natural bauxite sample; ^bSynthetic gibbsite, 99.9% purity

These results suggest that at 275°C gibbsite is not completely dehydroxylated and therefore, the 3 moles of H₂O used in the conversion factor for the weight loss to quantify gibbsite under the given experimental conditions is not correct. This is not surprising since conflicting results of various studies on the thermal transformations of aluminium(oxy)hydroxide phases are attributed to differences in experimental techniques and conditions [2,3,4]. The reaction pathways as well as kinetics for the dehydration/dehydroxylation/decomposition of aluminium (oxy) hydroxides or alumina hydrates are affected by heating rate, particle size and water vapour pressure around the particle.

To investigate the reaction path of gibbsite for this experiment, several subsamples of Malakoff hydrate (gibbsite) were run on the Hi-Res TGA using the same heating rate and isothermal hold at 105°C in the HRD50C_ISO 4T method but the final temperature was held at 275°C. The TGA residues were collected and measured for qualitative analysis in the powder X-ray diffractometer. A synthetic chi-alumina was synthesized to aid in the analysis of the XRD pattern to establish the formation of chi-alumina during the thermal treatment to 275°C.

Figure 2 shows an XRD of the Hi-Res TGA residues of the Malakoff hydrate heated from 105°C to 275°C in the high –resolution dynamic mode, 50°C/min. The pattern confirms that the weight loss for the first temperature range of 180-275°C may be attributed to gibbsite dehydration/dehydroxylation to boehmite and chi-alumina.

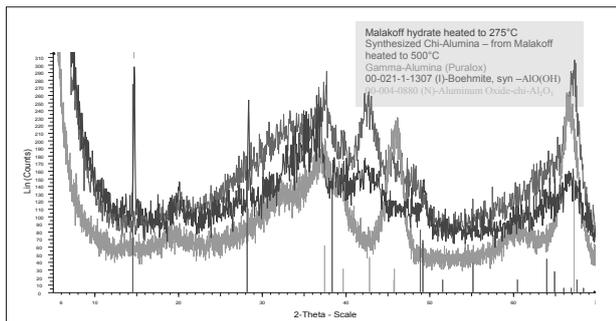
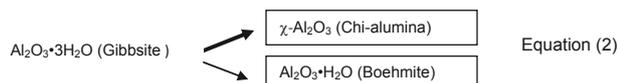


Figure 2. XRD Patterns confirming the formation of chi-alumina from roasted Malakoff hydrate (synthetic gibbsite).

Malakoff hydrate heated to 275°C formed both boehmite and chi-Al₂O₃. Malakoff hydrate heated to 500°C formed chi-Al₂O₃. XRD pattern of commercial gamma –Al₂O₃ (Puralox) is shown to distinguish it from the chi-alumina pattern.

The plot of sample weight loss over time as the heating rate was varied indicates two distinct inflections supporting the two decomposition reactions taking place in **TI**. The heating rate achieved when a transformation occurred at 186°C was 20°C/min and as temperature increased to 223°C, the heating rate dropped to 11°C/min all the way to 0.7°C/min. At 186°C gibbsite starts to decompose to boehmite and at 223°C gibbsite decomposes to chi-alumina. The investigations done on the Malakoff hydrate suggest that gibbsite under the running conditions of this experiment decomposes to boehmite and chi-alumina.

The decomposition pathway of gibbsite when heated to 275°C, which is the cut off temperature for the first weight loss in the TGA plot, is described by equation (2):



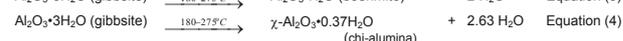
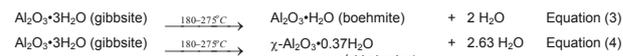
Hence, at **TI**, the 3 moles of water cannot be used to quantify the gibbsite based on the TGA plot.

Average Water Loss Associated with Gibbsite

Using Malakoff Hydrate (99.9% Gibbsite)

What portions of the gibbsite convert to boehmite and to that of a transition alumina? Based on the thermograms of micronised Malakoff hydrates, 14 % of gibbsite converted to boehmite. The boehmite content was calculated using the LOI in the **TIII** region of the thermogram with 2 moles of water loss per mole of gibbsite. These values were obtained assuming the chi-alumina does not lose appreciable mass in the same range

Taking the proportions of gibbsite decomposing to boehmite and chi-alumina, a weighted average of the water loss for the two transitions can then be used to quantify the gibbsite using the TGA thermograms. How to get this weighted average? The gibbsite to boehmite transition clearly shows 2 moles of water are lost per mole of gibbsite. The number of moles of water given off per mole of gibbsite decomposing to chi-alumina was determined from the LOI at 1000°C for a synthetic chi-alumina. The synthesized chi-alumina has 0.37 mole of water per mole of alumina and thus its formula is **Al₂O₃·0.37 H₂O**. Hence, the number of moles of water lost in the gibbsite to chi-alumina transition is 2.63. Equations (3) and (4) illustrate the water loss when gibbsite decomposes/dehydroxylates to boehmite and chi-alumina. The calculated weighted average moles of water loss per mole of gibbsite decomposing to boehmite and chi-alumina (equation 5) within **TI** is around **2.52 ± 0.03**.



$$\left(\frac{G_b}{100} \times 2 \right) + \left(\frac{G_\chi}{100} \times 2.63 \right) \quad \text{where } \begin{matrix} G_b = \text{gibbsite to boehmite} \\ G_\chi = \text{gibbsite to Chi-alumina} \end{matrix} \quad \text{Equation (5)}$$

The LOI in the **TIII** range was associated only with boehmite and any LOI due to chi-alumina in this range was assumed negligible. However, calculations done without assuming that the chi-alumina does not have an LOI at the range where boehmite is quantified showed almost the same factor with an average of **2.56 ± 0.02**.

Using Reference Bauxites

To further establish the 2.5 factor, the fractions of boehmite and chi-alumina were determined in the reference bauxites.

The fraction of gibbsite forming boehmite was determined by Hi-Res TGA of the bauxite and its corresponding mud. The bauxite had to be leached with mild alumina-caustic solution to accurately determine the amount of boehmite. To quantify boehmite in a bauxite sample by thermal analysis, gibbsite and kaolinite have to be removed because these phases interfere with the measurement. Gibbsite decomposes to boehmite and together with kaolinite have significant LOI or weight loss in the **TIII** range. The leaching liquor volume was large enough to prevent reprecipitation of silica as DSP (desilication product) which otherwise could also interfere with boehmite determination.

Two separate calculations were made to establish the average moles of water loss for the decomposition of gibbsite to boehmite and chi-alumina in bauxite samples. For the first set of calculations, the amount of boehmite in the mud (free of gibbsite and kaolinite) was measured by Hi-Res TGA. The total amount of boehmite (amount originally present + amount from decomposition of gibbsite) in the bauxite was also measured by Hi-Res TGA. By subtracting the amount of boehmite in the mud (which corresponds to the original boehmite content) from the total amount of boehmite, the amount of boehmite from gibbsite decomposition can be obtained and related back to amount of gibbsite converted to boehmite. The fractions of gibbsite decomposing to boehmite and chi-alumina are summarized in Table 3. The mean for the average moles of water loss for gibbsite is **2.54 ± 0.02**.

Table 3. Average Water Loss for Gibbsite Decomposition to Boehmite and Chi-Alumina at TI 180-275 oC.

Sample ID	%Boehmite in Bauxite (from Hi-Res TGA)	%Boehmite in Mud (from Hi-Res TGA of leached bauxite)	Fraction of G→B	Fraction of G→χ	H ₂ O loss G→B	H ₂ O loss G→c	Average H ₂ O loss for Gibbsite, moles
IUCr Round Robin	18.13	12.12	0.142	0.858	0.28	2.26	2.54
BXT 03	7.91	0.24	0.128	0.872	0.26	2.29	2.55
BXT 04	7.06	1.77	0.106	0.894	0.21	2.35	2.56
BXT 07	8.57	0.71	0.168	0.832	0.34	2.19	2.52
BXT 08	12.85	5.18	0.157	0.843	0.31	2.22	2.53

B = Boehmite; G = Gibbsite; G→B gibbsite to boehmite (assume 2 H₂O loss); G→χ gibbsite to chi-alumina (assume 2.63 H₂O loss)

%Boehmite in Bauxite = %Boehmite originally present + %Boehmite from G→B decomposition

%B in Mud = %Boehmite originally present

Note: %Boehmite in Bauxite was corrected for the weight loss due to kaolinite using the reactive silica (R_xSiO₂) numbers. The LOI due to kaolinite can be calculated from a R_xSiO₂ value as = 0.3 x R_xSiO₂ (using direct silica method) assuming that all reactive silica is due to kaolinite.

Note: Mud is assumed to be free of gibbsite and kaolinite. This was confirmed by XRD.

The second calculation uses an independent approach using the LOI's at 1000°C for the bauxite and its generated mud after the leach. This approach does not depend on knowing the exact formula of chi-alumina formed from the gibbsite transformation.

Using Delta LOI of Reference Bauxites

Using the same Hi-Res TGA thermograms for the reference bauxites and their corresponding muds from the mild alumina-caustic leach, the results were analysed in terms of LOI at 1000°C. The LOI's or weight losses in the TGA curves used in the calculations assume that the decomposition reactions evolve only water. The advantage of using the LOI's at 1000°C is that the gibbsite is fully dehydroxylated at this temperature as shown in Equation (1) and therefore, there is no uncertainty in the 3 moles of water loss per mole of gibbsite. (The use of the LOI at 1000°C for the Malakoff hydrate giving 99.9% gibbsite using the factor of 3 H₂O confirmed this as well.)

The LOI's at 1000°C or labelled as LOI* for the bauxites and muds were determined and the difference in the LOI* is the LOI of gibbsite and termed as Delta LOI*.

For a given bauxite, significant LOI at 1000°C (LOI*) is associated with the dehydroxylation/decomposition of the major phases such as gibbsite, goethite, kaolinite, and boehmite as shown in Equation (6).

$$LOI^*_{Bx} = LOI_{gibbsite} + LOI_{goethite} + LOI_{boehmite} + LOI_{kaolinite} + LOI_{organic\ C} \quad \text{Equation (6)}$$

For a mud generated by the leaching process, which removes gibbsite, kaolinite, and organic carbon, its LOI at 1000°C would be a summation of the LOI's of the remaining major phases such as goethite and boehmite as represented in Equation (7). The LOI* of the mud must be corrected for the corresponding LOI* of the bauxite by multiplying it with the mud factor, MF.

$$LOI^*_{Mud} = LOI_{goethite} + LOI_{boehmite} \quad \text{Equation (7)}$$

Re-arranging Equations (6) and (7) and assuming that the boehmite and goethite contents are the same (as well as their LOI*'s) gives Equation (8).

$$LOI_{gibbsite} = LOI^*_{Bx} - LOI^*_{Mud} (MF) - LOI_{kaolinite} - LOI_{organic\ C} \quad \text{Equation (8)}$$

The LOI due to kaolinite is obtained by multiplying the measured reactive silica by a factor of 0.3 assuming that all reactive silica is due to kaolinite. The LOI due to decomposition of any source of organic carbon is estimated by multiplying the TOC value by 2. The LOI_{gibbsite} is called the Delta LOI*. The % gibbsite associated with this Delta LOI* is calculated by using 3 moles H₂O for every mole gibbsite fully dehydroxylated at 1000°C. The LOI due to gibbsite decomposition in the TI range was also determined in the same TGA plot of the bauxite. Recall that in the TI range, the amount of water loss depends on the decomposition pathway taken by gibbsite. In the same bauxite, the gibbsite content should not change whether you base it on its fully dehydroxylated form at 1000°C or base it on its decomposition products at 275°C in the TGA run. Hence

$$\text{Amount of Gibbsite based on LOI}_{TI\ range} = \text{Amount of Gibbsite based on Delta LOI}^*$$

$$LOI_{TI\ range} \times \frac{156.007\text{g/moleGibbsite}}{\text{mole of H}_2\text{O in TI range}} = \text{Delta LOI}^* \times \frac{156.007\text{g/moleGibbsite}}{3\text{ mole of H}_2\text{O}}$$

$$\text{mole of H}_2\text{O in TI range} = \frac{LOI_{TI\ range}}{\text{Delta LOI}^*} \times 3$$

The second set of calculations again shows that a factor of 2.50 ± .01 can be used to quantify the gibbsite in the bauxite based on a Hi-Res TGA thermogram within the TI range. Results in Table 4 also show an independent method of determining the %gibbsite in bauxite using the corresponding LOI's at 1000°C of the bauxite and its mud (from leached bauxite).

Table 4. Average Water Loss for Gibbsite Decomposition to Boehmite and Chi-Alumina at TI 180-275°C using Delta LOI's at 1000°C for the Reference Bauxites and Corresponding Muds.

Sample ID	LOI* Bx	LOI* Mud	Delta LOI* due to Gibbsite	%Gibbsite from Delta LOI*	%G ₂ Al ₂ O ₃ in Bx from Delta LOI*	LOI due to Gibbsite in TI range	Ratio of LOI G _{TI} to Delta LOI*	^Moles of Water Associated with LOI _{TI}
BXT-03	28.68	5.636	26.9	77.6	50.6	22.30	0.830	2.49
BXT-04	25.36	7.762	22.5	64.9	42.0	18.63	0.837	2.51
BXT-07	24.56	8.293	21.3	61.5	39.9	17.73	0.839	2.52
BXT-08	25.47	7.828	22.4	64.6	42.0	18.48	0.831	2.49

LOI* – loss on ignition at 1000 °C; Bx = Bauxite; G₂Al₂O₃ = Gibbsitic Alumina; TI range = 180-275°C

$$\wedge\text{Moles of H}_2\text{O associated with LOI at TI} = \text{mole of H}_2\text{O in TI range} = \frac{LOI_{TI\ range}}{\text{Delta LOI}^*} \times 3$$

Using now the average water loss for gibbsite, **2.5**, the TGA plots for the reference bauxites were re-analysed at **TI** range. Figure 3 shows a plot of the Hi-Res TGA results for % gibbsite expressed as Al_2O_3 using the factors 2.5 and 3 compared to the reported values of the certified bauxites. A very good correlation exists between the values obtained using the 2.5 factor and the reported values with less than 0.8 % error.

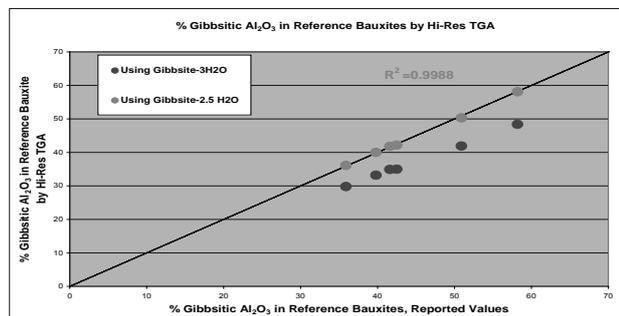


Figure 3. Correlation of % gibbsitic alumina measured by Hi-Res TGA using 3- and 2.5-moles of water loss per mole of gibbsite dehydroxylated/decomposed to the reported values of gibbsitic alumina values in the reference bauxites (micronized).

Effectiveness of Leaching Process

The effectiveness of the leaching process was assessed by calculating how much gibbsite was removed and comparing it to the initial amount present in the reference bauxites. The results in Table 5 suggest that the mild alumina-caustic leach is effective in removing the gibbsite, kaolinite, and organic carbon.

Table 5. %G. Al_2O_3 using Delta LOI Compared to Reported Values in the Reference Bauxites

Reference Bauxite	%G. Al_2O_3 in Bx from Delta LOI*	Reported %G. Al_2O_3 in Bx*
BXT-03	50.6	50.9 ± 0.4
BXT-04	42.0	42.5 ± 0.4
BXT-07	39.9	39.7 ± 0.6
BXT-08	42.0	41.7 ± 0.4

*The Alcan Certificates no longer quote percent gibbsitic alumina. Instead the % Al_2O_3 at low temperature digestion (2.5N NaOH, 150°C, A/C=0.41, 25 min) is reported. This value is assumed to be gibbsitic alumina.

Analysis of Bauxite Sample Suite for Gibbsite Content

The bauxite samples (micronized) were analysed for gibbsite content using the 2.5 factor (Figure 4). The same sample suite used in the XRD-TOPAS development was used to investigate the performance of Hi-Res TGA for gibbsite quantification using the weight loss for **TI** range from 180° to 275°C. The two independent methods quantified gibbsite in the various bauxites with an average difference between paired values of 1.1 % G. Al_2O_3 . Figure 4 also shows how lithology may affect the accuracy of gibbsite measurements. Greater deviations were observed among Hardcap and B-zone bauxites. Analyses of the gravel samples and composites show very good agreement with TOPAS numbers. At much higher concentrations of gibbsite, TOPAS is measuring low. Analyses of various bauxite samples with different mineralogies, lithologies, sources, particle sizes, and matrices will always be a challenge to the analyst. Some of the bauxites analysed in this study appear to have more complex compositions or mineralogies relative to the reference bauxites thereby contributing to a bias in the measurements. The two independent methods may be used to complement each other in understanding the complex compositions and behaviour of the GEOMET bauxites.

Hi-Res TGA can be a powerful technique for gibbsite quantification as validated by the use of reference bauxites and synthetic bauxite. The advantages of Hi-Res TGA for quantification of gibbsite in bauxite include: (a) small amount of sample required for analysis (10-40 mg); (b) reasonable analysis time (40-120 mins including the isothermal holds); (c) minimal sample preparation (well ground sample, powder form, could be micronized); and (d) good precision : less than 1.5 %RSD is achieved.

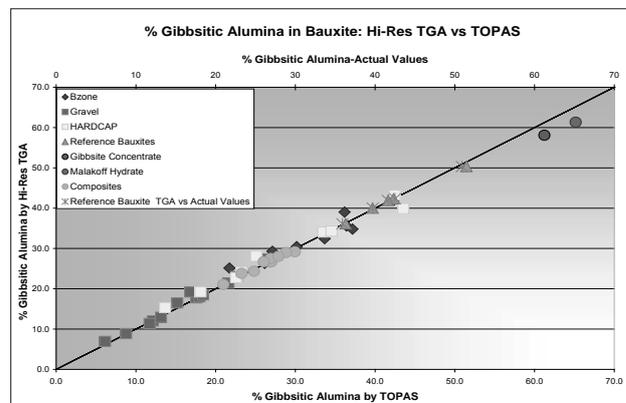
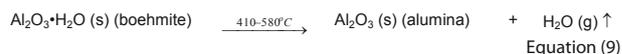


Figure 4. %Gibbsitic Al_2O_3 in GEOMET Bauxite Sample Suite by Hi-Res TGA and XRD-TOPAS

Determination of Boehmite by Thermal Analysis

The washed and dried muds were analysed for boehmite content by Hi-Res TGA using the HRD50CR5_ISO3T Method. The weight loss measured within the **TI** range of 410°C to 580°C is related to the amount of boehmite by Equation (9):



Since the boehmite values in the reference bauxites were no longer certified in the updated certificates of analysis, their boehmite content were measured using three independent methods. Results are summarised in Table 6. The Hi-ResTGA values agree quite well with the DSC measurements with an average deviation of about 0.4% but TGA values seem to be higher than that of the DSC except for BXT-08.

Table 6. Percent Boehmite in Reference Bauxites by Different Methods

Sample ID	% Boehmite in Bauxite			Reported Values (in Boehmitic Alumina) * expressed as % Boehmite
	TOPAS	TGA	DSC	
BXT-03	0.0	0.2	0.0	<0.5
BXT-04	1.8	1.8	1.5	3.8
BXT-07	0.1	0.3	0.1	0.0
BXT-08	7.1	5.0	5.8	6.6

* reported values(not certified) are based on differences between extractable alumina at high temperature digest at 225°C and low temperature digest at 150°C and represent upper limits for boehmite content

Since a certified reference material for boehmite was not available, the accuracy of the Hi-Res TGA Method for boehmite measurement was validated against a bauxite method control, BBC1, which was extensively analysed by two other independent techniques. Twenty-four subsamples of BBC1 were leached and analysed by Hi-Res TGA and DSC and three subsamples of BBC1 bauxite (unleached) were analysed by XRD-TOPAS. Table 7 shows the % boehmite in BBC1 determined by four different methods.

The DSC Method uses a standard calibration curve generated from Alcan boehmite standards and the DSC standard addition method involves “spiking” the sample with known amounts of standard boehmite. Thermal analyses were done on the muds generated from leaching the bauxite while XRD-TOPAS measurements were done on the respective bauxite.

A series of leached bauxite samples were analysed by Hi-Res TGA and DSC. Figure 5 shows a significant regression supports

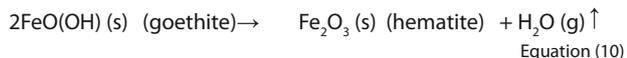
the presumed linear relationship between the two methods. At low boehmite concentrations, Hi-Res TGA gives higher values compared to that of DSC. As the signal-to-noise ratio improves in the DSC curve when the sample has > 1% boehmite, the values from the two methods give an average deviation of about 0.3% boehmite (N=75). Both methods have their sources of error but the advantage of Hi-Res TGA over DSC as a thermal analysis technique lies in the fact that analysis is not based on a calibration curve generated from standard solutions of the analyte.

Table 7. Percent Boehmite in BBC1 by Different Methods

Method	Sample Size, N	Sample Analysed	%Boehmite in Bx ± (SD)
Hi-Res TGA	23	Mud	1.6 ± 0.1
DSC –Standard Calibration	23	Mud	1.3 ± 0.2
DSC-Standard Addition	6	Mud	1.6 ± 0.1
XRD-TOPAS	3	Bauxite	1.6 ± 0.1
Average			1.5 ± 0.2

Determination of Goethite by Hi-Res TGA

Quantifying goethite in bauxite by Hi-Res TGA involves the LOI in the temperature range, TII 275-380°C. The measured weight loss is related to the decomposition of goethite as described by Equation (10):



The performance of the Hi-Res TGA Method for goethite in bauxites in terms of accuracy cannot be validated because of lack of reference material for goethite. The certified materials often report total iron oxides. Currently in the lab, goethite measurements in bauxites are generated by XRD-TOPAS, hence, results of goethite measurements by Hi-Res TGA are compared to that of XRD-TOPAS as shown in Figure 8. The figure below shows that leaching is necessary to have better measurement of goethite.

The LOI associated with goethite seems to be influenced by the LOI of gibbsite. Without leaching gibbsite, the LOI of goethite seems to be higher in the bauxite than in the mud resulting to positive bias in the goethite measurements. The goethite values calculated from TOPAS assume 20% aluminium substitution in the goethite structure. The different bauxites may have varying aluminium substitution which may account for the difference in the values obtained from the two methods. Previous studies showed that an increased aluminium substitution in goethite increases the weight loss due to dehydroxylation^[5]. The extent of substitution in the goethite structure used by TOPAS to quantify goethite may be a source of bias. In the same manner, the excess water present in natural goethite and aluminous goethite must also be determined to understand its degree of decomposition/ dehydroxylation.

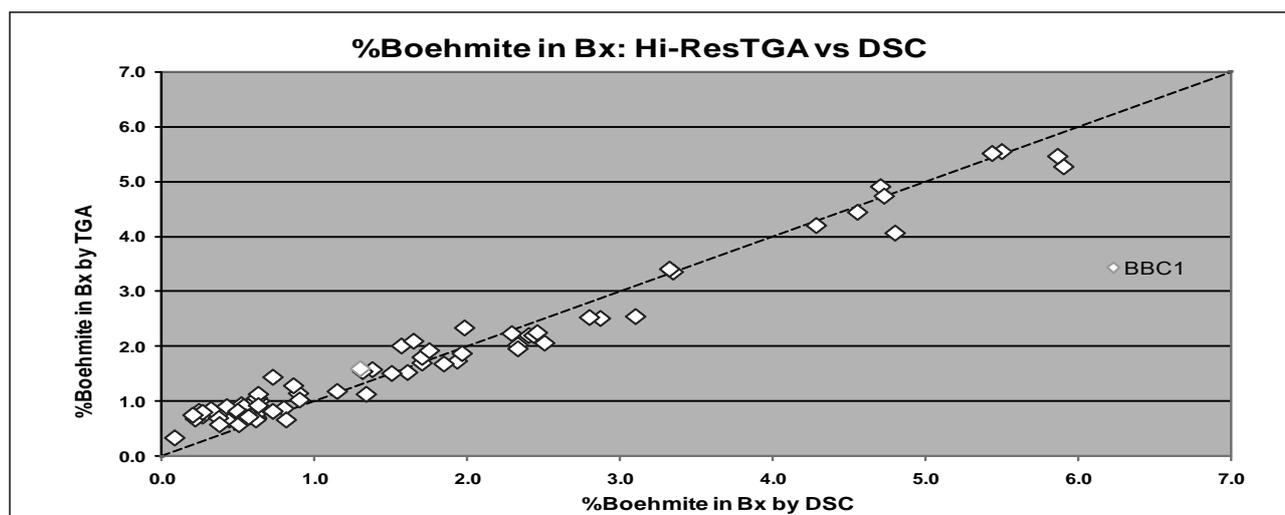


Figure 7. Comparison of % Boehmite in Bauxite by Hi-Res TGA and DSC.

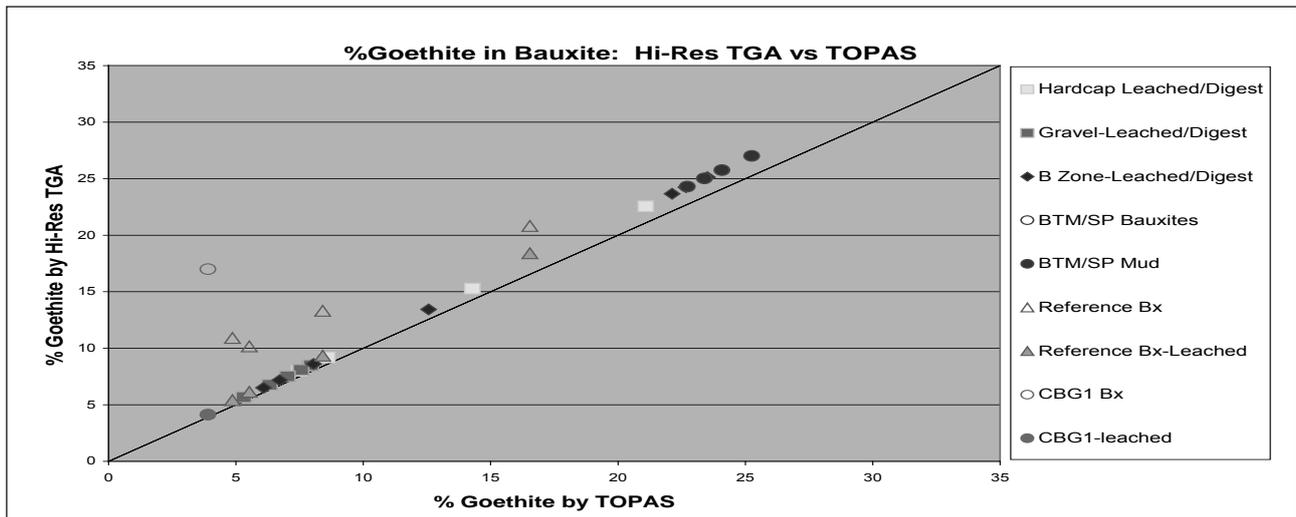


Figure 8. Comparison of % Goethite in Bauxite Measured by Hi-Res TGA and XRD-TOPAS Methods.

Conclusions and Recommendations

A method for gibbsite quantification in bauxites by High-Resolution TGA has been successfully developed. Under the experimental conditions used in the Hi-Res TGA runs, the loss of mass associated in the **TI** range (180 to 275°C) is attributed to gibbsite decomposition to boehmite and chi-alumina with an average number of moles of water loss of 2.5.

Accuracy of Hi-Res TGA Method for :

- gibbsite quantification was validated against reference bauxites within 1% error. The average difference between results of Hi-Res TGA and XRD-TOPAS for gibbsite in bauxite is 1.1 % G. Al₂O₃.
- boehmite was validated against another independent technique, DSC. An average difference of 0.3% boehmite was observed for more than 75 samples compared using the two thermal methods.

- goethite was validated by comparing the results with that of XRD-TOPAS. An average difference of 1% goethite was observed between the results of the two methods.
- A mild caustic leach is necessary to quantitatively measure boehmite and goethite by the thermal techniques.

Precision : A precision <2% RSD for gibbsite quantification in the sample bauxites by Hi-Res TGA was obtained. The precision of Hi-Res TGA for boehmite determination was validated by running the leach residues of 24 subsamples of BBC1. The average boehmite content is 1.6% with standard deviation of ± 0.1%.

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