# BX05 - Phase Estimation of Bauxite by Thermogravimetric Analysis

**Vinod Kumar Verma[1], Midde Rama Satyanarayana[2] and Kumari Amrita[3]**
1. Senior Manager (R&D)
2. Senior Manager (R&D)
3. Senior Manager (R&D)
National Aluminum Company Limited, Koraput, India
Corresponding author: vinod.verma@nalcoindia.co.in

## Abstract

The research activity deals with thermal analysis of bauxites for the identification and analysis of alumina-bearing minerals. The amount of tri-hydrate alumina, also known as gibbsite ($Al_2O_3 \times 3H_2O$), in bauxite is a crucial quality indicator for the Bayer alumina process. Classical methods for estimating it take a lot of time, so an effort has been made to develop a correlation between thermogravimetry analysis and bauxite phase quantification by XRD. The study attempts to find the gibbsite content of bauxite quickly and accurately with the help of thermogravimetric analysis.

**Keywords:** Bayer Process, Bauxite, TG/DTA, Thermal behavior, XRD.

## 1. Introduction

Bauxite, the primary source of aluminum metal, holds significant importance as it is the second most abundant metal on Earth. Comprising mainly of gibbsite, diaspore, and boehmite, with gibbsite being the dominant mineral, bauxite also contains other minerals such as goethite, hematite, rutile, quartz, kaolinite, halloysite, limonite, and residual silicates [1]. In the Bayer process, with low temperature digestion for alumina extraction, the gibbsitic form of aluminum hydroxide dissolves while most of the other minerals remain undigested. Notably, kaolinite experiences substantial dissolution in sodium aluminate liquors, leading to the formation of a desilication product, whereas the dissolution of quartz is insignificant.

Considering the impact of these minerals and their chemical-mineralogical characteristics on process control, it becomes crucial to determine the proportions of gibbsite and kaolinite in the bauxite feed. The overall process control directly or indirectly relies on their content. Panchpatmali bauxite deposits, used by Nalco alumina refinery for alumina production, are rich in gibbsite with a certain amount of kaolinite association. Nalco employs atmospheric pressure digestion with an operating temperature of approximately 106 °C.

Traditionally, estimating the trihydrate alumina content in bauxite involves a bomb digestion system, which entails numerous steps including digestion, filtration, and XRF analysis, making the process time-consuming and tedious. Challenges arise when a large number of samples need to be processed within a given timeframe to meet the process requirements. Although XRD analysis offers a quicker alternative, reliable results necessitate the use of refinement techniques for each sample.

In light of these considerations, there is a need to explore alternative methods that offer both speed and accuracy in analysis. Such methods would enable the completion of the targeted number of samples within the desired timeframe while maintaining reliable and dependable results.

## 2. Sample preparation

The bauxite samples used in this study were collected from plant feed bauxite samples, ensuring that they represent the actual material used in the alumina production process. In order to capture variations in mineralogy, additional boulders were also collected directly from the bauxite pile. Prior to analysis, the samples underwent a standardized preparation procedure. They were first dried at a temperature of 105 °C to remove any moisture and ensure consistent conditions for analysis. Subsequently, the dried samples were carefully grounded to achieve homogeneity, ensuring that the mineral composition is evenly distributed throughout the sample. This sample preparation process aimed to provide accurate and representative specimens for subsequent analysis and characterization.

## 3. Equipment details

### 3.1 X-Ray Diffractometer

Phase analysis of the bauxite samples was conducted using the X'Pert$^3$ Powder XRD model by Malvern Panalytical. In this study, copper radiation was employed as the X-ray source, operating at a tension of 45 kV and a current of 40 mA. To accurately quantify the phases present in the bauxite samples, a Rietveld refinement method was employed. Rietveld refinement is a widely used technique in X-ray diffraction analysis that utilizes mathematical modeling and least-squares fitting to determine the crystallographic structure and phase composition of a sample. By comparing the observed diffraction pattern with a calculated pattern generated from known crystal structures, the relative abundances of different phases in the bauxite samples can be determined. The combination of the X'Pert$^3$ Powder XRD instrument and Rietveld refinement technique enabled precise phase analysis and quantification, allowing for a detailed understanding of the mineralogical composition of the bauxite samples.

### 3.2 TG/DTA

For the determination of mass loss in the bauxite samples, a thermogravimetric analyzer (TGA) with model Exstar-6300, manufactured by M/s. Seiko Instrument Inc, now called Hitachi, was utilized in this study. The TGA instrument allows for the measurement of weight changes in a sample as a function of temperature.

To obtain the desired results, specific test conditions were employed. The analysis began at an initial temperature of 30 °C. The temperature was then ramped up at a rate of 10 °C per minute. Once the temperature reached 125 °C, it was held constant for a duration of 60 minutes. This step is included to get rid of any free moisture. Following this, the temperature was again ramped up at a rate of 10 °C per minute. The second hold temperature was set at 900 °C, and the sample was maintained at this temperature for 10 minutes.

During the TGA analysis, the weight loss of the bauxite samples within the temperature range of 220 to 350 °C was calculated. This particular range was chosen as it correlates with the temperature region where significant decomposition or phase transformations of gibbsite is expected to occur [2,3]. The weight loss data obtained from the TGA analysis was then compared and analyzed in conjunction with the gibbsitic content determined through XRD analysis. The weight loss in the temperature range of 450 to 700 °C was calculated and compared to kaolinite content.

## 4. Results and observations

The first weight loss peak was observed between 220 and 350 °C, indicating the decomposition or phase transformation of a mineral in the bauxite samples. To confirm that this weight loss peak correlates specifically to gibbsite, a portion of the sample was roasted in a muffle furnace at 400 °C for 8 hours. The purpose of the 8-hour heating was to ensure that the entire sample underwent the 400 °C temperature. The roasted sample was then analyzed using X-ray diffraction (XRD), and the absence of a gibbsite peak in the XRD pattern confirmed the assumption that the weight loss at 220-350 °C is indeed associated with the decomposition of gibbsite.

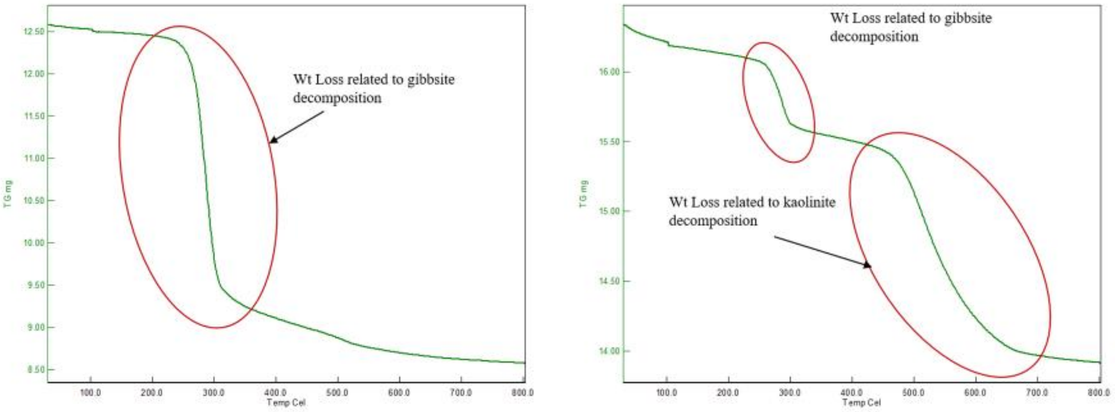

**Figure 1. TG graph of bauxite, high gibbsite bauxite on left and high silica bauxite at right.**

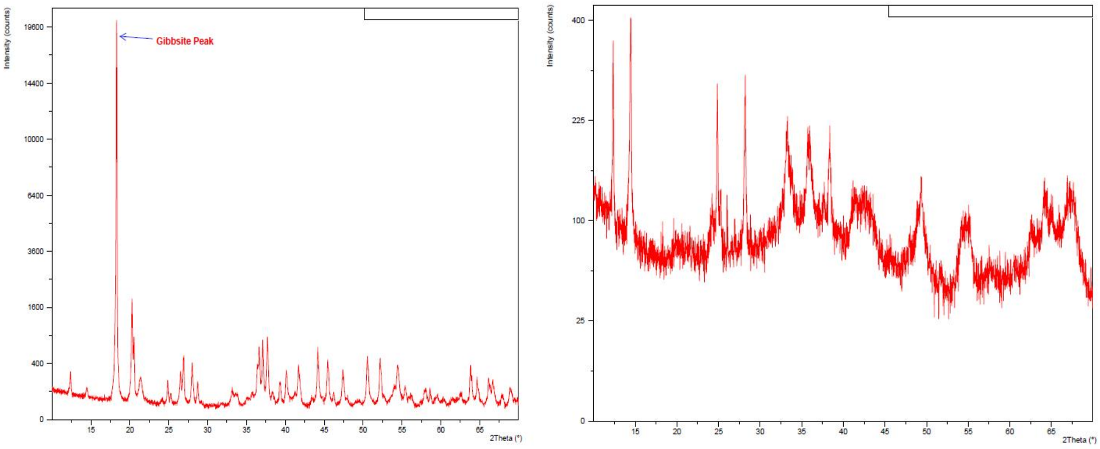

**Figure 2. XRD pattern of gibbsitic bauxite, as is bauxite on left and 400 °C roasted sample at right. Prominent gibbsite peak at 18 °2Theta is not visible in roasted sample.**

The second weight loss appeared at a higher temperature range of 450 to 700 °C, which was reported to correlate with the kaolinite content in the bauxite samples [4]. To validate this assumption, another portion of the sample was roasted at 700 °C for 8 hours, and XRD analysis was conducted. However, XRD analysis dose not confirm the hypothesis as it shows residual peak for kaolinite. Still the weight loss at 450-700 °C show a reliable correlation with the kaolinite content.

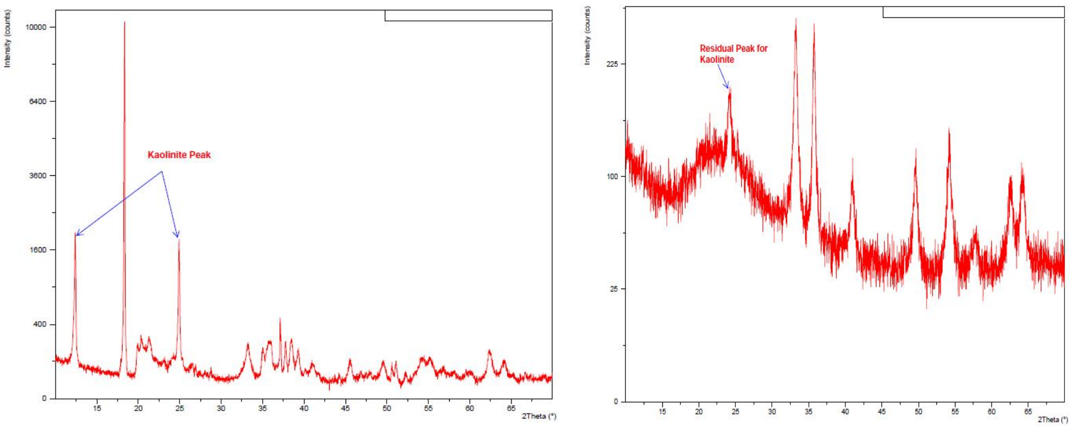

**Figure 3. XRD pattern of high kaolinite bauxite, as is bauxite on left and 700 °C roasted sample at right. One of the kaolinite peak at 25 °2Theta is still available in roasted sample.**

To further analyze the relationship between weight loss and gibbsite content, the weight loss percentage between 220 and 350 °C was plotted against the gibbsite content. The results showed a good correlation with an R-square value of 96 %. However, some data points deviated by 4–5 % from the correlation line, indicating possible factors influencing the weight loss other than gibbsite alone. Similar observations are made for weight loss between 450–700 °C and kaolinite content. However, kaolinite determination is not considered reliable because well spread data points could not be obtained and the data present in graph shows significant deviation from the trendline.

**Table 1. TGA and XRD analysis Data**

| Sample ID | % Wt Loss | | XRD Analysis | |
|---|---|---|---|---|
| | 220 to 350 °C | 450 to 700 °C | Gibbsite, % | Kaolinite, % |
| Bxt-1 | 19.03 | 3.25 | 60.24 | 3.56 |
| Bxt-2 | 18.07 | 3.80 | 54.79 | 5.88 |
| Bxt-3 | 17.30 | 3.88 | 49.71 | 10.39 |
| Bxt-4 | 10.12 | 3.83 | 32.91 | 7.47 |
| Bxt-5 | 11.25 | 4.27 | 34.70 | 9.65 |
| Bxt-6 | 14.10 | 4.12 | 43.13 | 9.35 |
| Bxt-7 | 15.15 | 4.15 | 45.21 | 11.98 |
| Bxt-8 | 16.38 | 3.86 | 48.26 | 10.71 |
| Bxt-9 | 16.98 | 3.83 | 48.86 | 9.77 |
| Bxt-10 | 15.93 | 4.46 | 46.73 | 13.91 |
| Bxt-11 | 18.04 | 3.39 | 54.46 | 6.10 |
| Bxt-12 | 17.87 | 3.32 | 55.70 | 5.72 |
| Bxt-13 | 18.46 | 3.68 | 56.64 | 7.80 |
| Bxt-14 | 17.90 | 3.50 | 53.54 | 6.99 |
| Bxt-15 | 18.25 | 3.71 | 56.33 | 8.52 |
| Bxt-16 | 18.76 | 3.50 | 58.72 | 5.57 |
| Bxt-17 | 16.90 | 3.63 | 53.61 | 7.58 |
| Bxt-18 | 3.48 | 9.52 | 19.54 | 46.30 |
| Bxt-19 | 19.60 | 3.50 | 58.19 | 5.46 |
| Bxt-20 | 19.53 | 3.64 | 59.72 | 6.61 |
| Bxt-21 | 25.58 | 4.12 | 79.86 | 4.49 |

**Table 2. Range of the main oxide constituents**

| Input Data | Composition Range (%) | |
|---|---|---|
| | **Low** | **High** |
| LOM 220-350 | 3.00 | 26.00 |
| LOM 450-700 | 3.00 | 10.00 |
| $Al_2O_3$ | 37.00 | 57.00 |
| $SiO_2$ | 1.5 | 27.5 |
| $Fe_2O_3$ | 9.50 | 27.00 |
| $TiO_2$ | 1.9 | 2.5 |

**Table 3 Detailed XRD analysis of selective samples**

| Gibbsite | Boehmite | Goethite | Hematite | Quartz | Kaolinite |
|---|---|---|---|---|---|
| 60.2 | 0.8 | 11.9 | 22.3 | 0.0 | 3.6 |
| 49.7 | 1.2 | 14.3 | 21.7 | 0.4 | 10.4 |
| 33.2 | 16.3 | 12.1 | 29.3 | 0.3 | 7.5 |
| 54.5 | 0.8 | 13.7 | 23.1 | 0.7 | 6.1 |
| 56.3 | 0.8 | 13.5 | 19.4 | 0.1 | 8.5 |
| 19.5 | 1.1 | 13.3 | 18.9 | 0.3 | 46.3 |
| 79.9 | 1.7 | 9.8 | 3.2 | 0.0 | 4.5 |

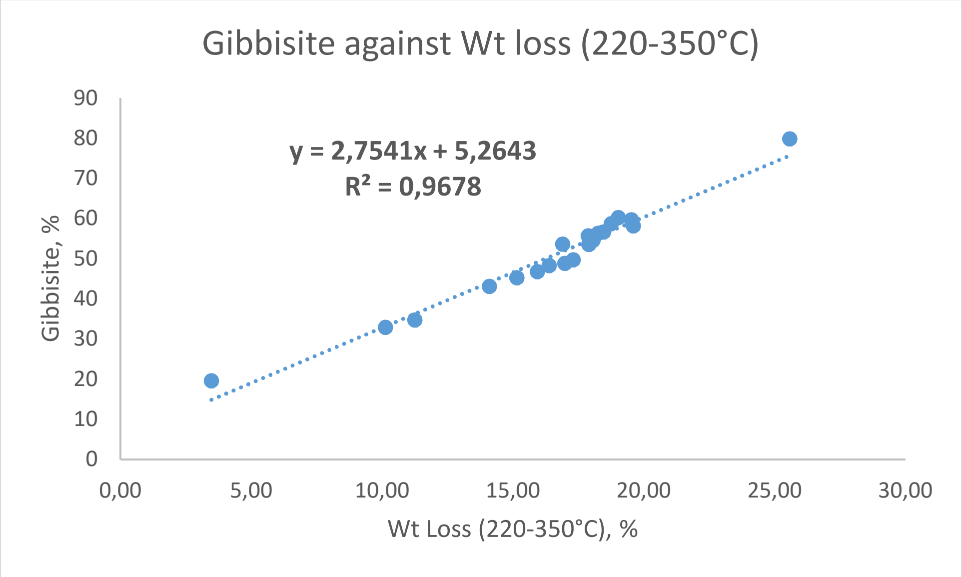

**Figure 3. Weight loss between 220 to 350 °C against gibbsite content bauxite.**

Based on the findings that gibbsite content is primarily obtained in the 200–350 °C range, it suggests that analysis of gibbsitic content could be conducted by heating the sample up to 400 °C only. This would reduce both the time and energy requirements for determining the gibbsite content in the bauxite samples, providing a more efficient and cost-effective approach.

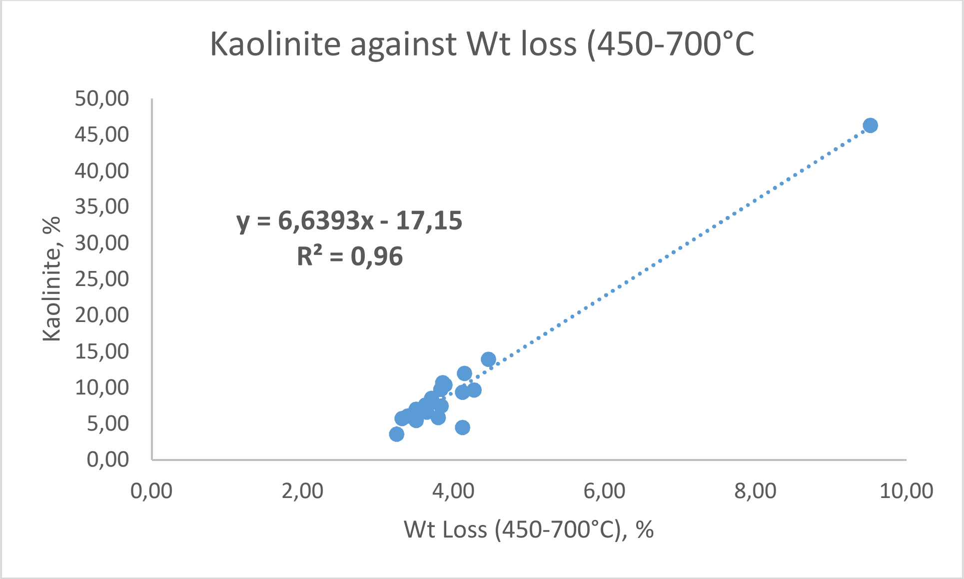

**Figure 4. Weight loss between 450 to 700 °C against kaolinite content bauxite.**

## 5. Conclusion

The study highlights the potential benefits of utilizing thermogravimetric analysis (TGA) as an alternative approach for quantifying gibbsite content in bauxite samples. The decomposition of aluminum goethite, along with potential contributions from other phases, within the 220–350 °C range underscores the complexity of the measurement. While acknowledging TGA's advantages, such as reduced sample size requirements and minimal reliance on specialized technicians, it is important to recognize the limitations of the method. Furthermore, the challenges of the XRD method posed by amorphous bauxite content and the restricted quantification of certain minerals emphasize the need for comprehensive investigations.

Further research is warranted to validate the applicability of TGA within operational plants and to refine its accuracy. While TGA offers a promising avenue, its utilization must be carefully considered alongside the limitations outlined. The study contributes to the advancement of mineralogical analysis techniques within the field of alumina production, providing insights into potential alternatives to traditional methods.

## 6. References

1. Earnest, Charles M. Thermal analysis in the alumina industry. Part 1: Measurements, Observations, and Instrumentation, *Advances in applied chemistry and biochemistry*, 2019 [1]: 40-54.
2. Ramana, Y.V. and Patnaik, Rajesh C. Application of thermogravimetric analysis for estimation of tri-hydrate alumina in central indian bauxites -an alternative for classical techniques, *Light Metals* 2011, 211–213.
3. Janković, Bojan et al. Thermal characterization and kinetic analysis of non-isothermal decomposition process of Bauxite red mud. Estimation of density distribution function of the apparent activation energy, *International Journal of Mineral Processing* 123 (2013) 46–59.
4. Deju, R. et al, Thermal characterization of kaolinitic clay. *Romanian Journal of Physics* 66, 904 (2021).