Research Article

Thermal Analysis in the Alumina Industry. Part I: Measurements, Observations, and Instrumentation

1. Abstract

In the work presented here, examples of the thermal analysis of bauxites for the recognition and analysis of both aluminous bearing minerals and other minerals which are presented. In addition to this, samples obtained from Bayer process production facilities were studied by the techniques of DTA, DSC, TG (TGA) and DTG for both product and by-product (red mud). Throughout the manuscript, a great deal of information is included regarding the thermal analysis instrumentation and its use for such mineral mixtures which may have special requirements for achieving good results. Particular interest is given to the operator choices while using DSC, DTA, and TGA/DTG for the analysis of samples with overlapping transitions. The liberation and elimination of water vapor arising from the dehydroxylation of selected components in product alumina, red mud by-product and bauxite raw material are also discussed. This paper will present the DTA, DSC, TGA and DTG analysis of two Jamaican bauxite ores, a bauxite specimen from northern Australia (Weipa), a Western Australia (Darling Range) bauxite ore, a red mud specimen and a product alumina from the Bayer Process.

2. Keywords
Alumina; Bauxite Clay; Bayer Process; Red Mud; Thermal Analysis; DSC; DTA; DTG; TGA

3. Introduction

This study addresses a range of usage of the thermal analysis techniques of Differential Thermal Analysis (DTA), Differential Scanning Calorimetry (DSC), Thermogravimetry (TG or TGA), and Derivative Thermogravimetry (DTG) in the production of alumina from bauxite ores. These thermal methodologies, along with X-Ray Diffraction spectroscopy (XRD), play a major role in the laboratory activities associate with the both the production and quality assurance of the final product aluminas (Al₂O₃).

Alumina (Al₂O₃) is an important inorganic material which finds a wide variety of uses in the chemical, metallurgical, and ceramics industries. The major source of alumina is from bauxite, a non-plastic claylike material used in the production of both aluminum metal and aluminum oxide. Australia is presently the largest producer of bauxite [1] followed by China, Russia, Canada, and India as the next largest producers of this important natural product. Some of these uses include use as an adsorbent, abrasives, catalysts and for the preparation of fused alumina bodies and glazes. Alcoa presently operates a bauxite processing plant, near Benton, Arkansas (USA) which produces a high strength proppant for use in the hydraulic fracking procedure in oil and gas wells. Lastly, it should be mentioned that bauxite
is presently the main source of the metal gallium (symbol: Ga, atomic number: 31). Gallium is extracted from the aqueous sodium hydroxide solution used in the Bayer process [2].

Bauxite ores are composed of a mixture of minerals. The aluminous constituent of bauxite ores may be either gibbsite $\text{Al(OH)}_3$, boehmite, $\gamma$- AlO(OH), and/or diaspor, $\alpha$- AlO(OH). The Al(OH)$_3$ found in lateritic bauxites are almost exclusively gibbsite. These minerals may occur individually or as mixtures of these components. In the alumina industry, gibbsite is often referred to as “trihydrate” with its formula written as $\text{Al}_2\text{O}_3\cdot3\text{H}_2\text{O}$ and boehmite is called “monohydrate” with the formula $\text{Al}_2\text{O}_3\cdot\text{H}_2\text{O}$. It should be stated however that these mineral components of bauxite ores are not hydrates but are hydroxides as is evident by infrared spectroscopy [3-5]. This “trihydrate” form finds great use in that it is added to carpets to serve as a flame retardant. Other minerals often found in bauxite ores include kaolinite clay mineral ($\text{Al}_2\text{Si}_3\text{O}_10\cdot\text{H}_2\text{O}$), goethite ($\text{FeO(OH)}$), hematite ($\text{Fe}_3\text{O}_4$), anatase ($\text{TiO}_2$), magnetite ($\text{Fe}_3\text{O}_4$) and silica ($\text{SiO}_2$).

The thermal analysis of bauxite ores is, for the most part, based on the dehydroxylation of the gibbsite and boehmite which produces water vapor along with the product alumina. The gibbsite dehydroxylation is observed at a lower peak temperature (ca. 270°C) than the boehmite (ca. 500°C). The stoichiometries for these thermal decompositions are questionable in thermal analysis experiments due to incomplete dehydroxylation of the aluminous species. This less than stoichiometric behavior has historically been the problem with quantifying these aluminous components by the use of the thermal analysis techniques of Differential Thermal Analysis (DTA), thermogravimetric techniques of Thermogravimetry (TG or TGA) and Derivative Thermogravimetry (DTG). This problem has been recently addressed in this journal by a publication by Earnest et al. [6], when using the thermogravimetric methods of TGA and DTG. This recently published TG/DTG methodology was shown to give results for gibbsite that agree within one percent of that obtained by the commonly employed XRD technique.

As was mentioned earlier, the removal of the aluminous material from bauxites is achieved commercially using the Bayer process. Seventy percent of the bauxite ores produced today proceed through the Bayer process. From this process one obtains what is often referred to as the “trihydrate” specimen, Al(OH)$_3$, and a by-product “red mud”. This study includes the results obtained for these materials as a result of studies performed by thermal analysis techniques of DTA, TGA, and DTG. The calcining of the Al(OH)$_3$ product to the dehydrated Al$_2$O$_3$ specimen is achieved by the use of high temperature (1000-1300 degrees Celsius) rotary kilns.

There have been at least 25 forms of alumina reported in the scientific chemical literature. Some of which probably do not exist. Of these, the alpha ($\alpha$) form is the most dense and most stable. The alpha form of alumina melts at about 2040°C with creeping and sintering beginning at ca. 1750°C [7]. It is the alpha form which is sought upon calcining the hydroxylated specie from the Bayer process.

4. Materials and Methodology

The Bayer process by-product, commonly referred to as “red mud”, and product alumina specimens used in this study were obtained from industrial sources in the alumina production business. These were located in Australia and Canada. X-Ray Diffraction (XRD) data were furnished for some of the specimens included in this work except the bauxite ores. Several bauxite standards (SRM standard reference materials) were also purchased from NIST (Washington, DC) for selected uses in this work. The NIST standard bauxite specimen had elemental analysis values as well as LOI (loss on ignition) values furnished as part of the standard certification. XRD results were also furnished for some of these but were not part of the certified values of the SRM standard. High purity nitrogen and air were purchased locally for use as purge gas in the thermal analysis instruments.

All thermal analysis experimental work was performed using 7 Series Perkin Elmer Instrumentation. This included a model DTA 7 Computerized Differential Thermal Analysis (DTA) System. This high temperature DTA was equipped with Pyris7 Software with allowed the original DTA data to be converted to Differential Scanning Calorimetric (DSC) form for energy of transition (enthalpy change) assignment if desired by the analyst. This instrument was calibrated for temperature accuracy (abscissa values) using ASTM standard (E-967) methodology [8]. These calibrations employed the use of high purity (99.99 %) metal standards of aluminum and gold. All DTA analyses with this instrument were obtained using dynamic nitrogen purge gas flow of 45 ml/min.

All thermogravimetric analyses were performed using a model TGA 7 Thermogravimetric Analyzer. This analyzer was used in conjunction with a Perkin Elmer Model TAC 7/DX Thermal Analysis Controller. This instrument employs an internal furnace as well as a large external furnace for use at high temperatures greater than 1025°C. All temperature values for the abscissa of the TGA thermal curves obtained with the internal furnace were obtained using a stainless steel covered chromel/alumel thermocouple located just beneath a small platinum sample pan. Temperature measurements made with the high temperature external furnace were made using a Pt(Pt,
10%Rh) thermocouple with the measuring junction placed near the TGA sample pan. In each case, the platinum sample pan was suspended vertically by a platinum wire connected to the microbalance. All analyses with the high temperature furnace were obtained using a dynamic purge gas flow of 50 ml/min of high purity nitrogen gas.

A Power Compensated DSC (Perkin Elmer DSC 7) was employed for use of smaller samples and high sensitivity applications. This instrument employs platinum resistance thermometers for temperature measurement and operates on a null balance principle of two microfurnaces which maintains the same temperature for both sample and reference pans in the DSC cell. Thus, the ordinate signal displayed by the calorimeter is the power (heat flow rate), in mWatts, required to maintain this equality in temperatures. This DSC 7 measuring cell employs a much smaller sample quantity than the DTA 7 instrument described above. The power compensated DSC 7 typically employs a purge gas flow of 20 ml/min but when studying analyte samples from which volatile matter is liberated the flow is more typically 30 ml/min. In the case of volatile matter evolution on heating of the analyte sample, this instrument requires a flow-through cover as the top sealing device of the analyzer cell. Thus, a “flow-through” cell cover was employed for all samples analyzed in this study with the DSC 7. When using this cover for the DSC cell, the purge gas and any volatile matter exits out of the top of the DSC cell rather than through a small orifice in the aluminum block (heat sink) surrounding the two Pt/Ir alloy cups of the measuring assembly. Temperature and heat flow rate (ordinate scale) calibration was achieved for this instrument using ASTM Standard (E-967 and E-968) methodologies [8,9].

5. Results and Discussion

5.1. DTA and TGA/DTG studies of bauxite clay materials

As was pointed out in a previous discussion, the most common method for analyzing the content of the bauxite ore prior to use in the Bayer Process is X-Ray Diffraction Spectroscopy (XRD). It is a well-known fact, however, that both DTA and TGA/DTG thermal methods can provide valuable information about the composition of the mineral mixture known as bauxite clay. As was listed earlier, in a previous section, there are several non-aluminous mineral components that are often found in bauxite clays. It is the presence, or absence, of these minerals that determines the color of the bauxite specimen. The presence of these mineral components varies with the geographic location of the bauxite clay. Essentially all of these minerals with the exception of those of Titanium Oxide (TiO₂) found as anatase (or rutile) can be observed by the thermal method of DTA. However, neither TiO₂ nor SiO₂ can be observed by the thermogravimetric methods (TGA and DTG). This is because they do not exhibit loss of mass on heating to usual temperatures of thermal analysis procedures.

The most frequently used thermal analyses of bauxite ores is based on the dehydroxylation of the gibbsite and boehmite content. In studies employing Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC) these dehydroxylations are observed as distinguishable endothermic events (Figure 1). These DSC results were obtained for a Weipa bauxite specimen from northern Queensland, Australia, as well as a Jamaican bauxite specimen, using the same heating rate of 10 C/min and nitrogen purge atmosphere of 30 ml/min. As may be observed in the power-compensated DSC thermal curves given in figure 1, the gibbsite dehydroxylation is observed at a lower peak temperature (ca. 270°C) than the boehmite (ca. 500°C). These endothermic DSC peaks are displayed in a positive (upward direction) on the DSC Thermal Curve because of the ordinate scale being positive heat flow values (milliwatts) increasing in an ascending direction. This is the usual ordinate scale direction when using power-compensated DSC instrumentation. Since these decompositions of gibbsite and boehmite are associated with the evolution of water vapor, they are also observed as mass loss events in Thermogravimetry (TG or TGA) and Derivative Thermogravimetry (DTG). Figure 2 shows the TGA and DTG thermal curves for the same Jamaican bauxite (Jamaican #2) specimen which was analyzed by power-compensated DSC in figure 1. One will note the similarity of the DTG thermal curve to that of the DSC thermal curve given in figure 1. One can see by the intensity of the DSC thermal curves that both gibbsite and boehmite are present in these two particular ores. It has been reported that boehmite can be detected in samples of bauxite and red mud at low levels (0.05% and 0.20 %) using the thermal analysis technique of DTG [10].
Figure 1: Power Compensated DSC Thermal Curves for Australian (Weipa) and Jamaican (No. 2) Bauxite Ores.

Figure 2: TGA and DTG Thermal Curves for Jamaican No. 2 Bauxite Ore.
of the analyte mineral specimen. It can also be seen that the thermal curve for this Jamaican #1 bauxite in figure 3 shows little or no boehmite component when heating the sample at a rate of ten degrees per minute. It was reported to be present in approximately the 1.5 percent range from previous XRD analysis by the donor laboratory. This small boehmite content was both detectable and measurable by TGA/DTG methodology, however.

5.2. Quantification of aluminous components

5.2.1. Thermogravimetry: TGA and DTG methodology:
The quantification of both gibbsite and boehmite (or anatase) components in bauxites ores by thermal methods has been attempted, particularly in industrial settings, for many years. The thermogravimetric methods seem to be favored for this purpose but regardless of whether DTA (DSC) or TGA/DTG methodology is used, the problem which causes difficulty is the same. The dehydroxylation of these crystalline aluminous compounds does not, in most cases, exhibit complete stoichiometry. The author has discussed this extensively in a previous article in this journal [6] for the thermogravimetric methods of TGA/DTG. This problem was also recognized by Sanders in his quantitative efforts by DTG [10]. As a result of the study by Earnest et al., [6], a thermogravimetric method involving the use of an empirical gravimetric factor, G, rather than the theoretical gravimetric factor based on the balanced chemical equation, is recommended. This approach usually leads to results agreeing within one percent of those obtained by XRD for gibbsite. This will not be repeated here but is readily available to all [6].

![Figure 3: DTA Thermal Curves for Weipa and Jamaican No. 1 Bauxite Ores.](https://doi.org/10.33513/ACBC/1901-06)
more modern Thermogravimetric (TGA) methodology. One of the disadvantages of this type of instrument is that there is no DTG Thermal Curve equivalent to that associated with conventional TGA instruments. On the other hand, the LECO type analyzer allows for the choice of macro sample size as well as an auto sampler carousel if the analyst so desires (Figure 4).

The results of the study [11] from the industrial lab in India were representative of 29 bauxite specimens from central India when analyzed with a LECO TGA-701 instrument. The analysts used the difference in total mass loss measured at 107°C (water loss) and the total mass loss reported by the instrument at 355°C. The total weight loss at 107°C was then subtracted from the total mass loss at 355°C. This assigned mass loss value, when adjusted with appropriate factoring, was used to calculate the percentage gibbsite (or “trihydrate”) component of the bauxite specimen. By using this technique with the analysis of a set of ten international bauxite reference samples (reference values assigned via wet methods) used in India. The authors report excellent agreement with the reference value provided the percentage gibbsite did not exceed 35% by mass. As the percentage of the “trihydrate” content of the bauxite increased to 45 percent gibbsite, the authors suggest that the gravimetric factoring, used in the calculation of results, be changed. No doubt that this is due to the corresponding decrease in the degree of dehydroxylation of the gibsite component as the amount of water liberated from higher percentages of gibsite (or “trihydrate”) increases. Although not stated in exactly the same terms, this observed trend is in accord with the tendencies reported by Earnest et al., [6].

5.2.2. Quantification using DSC and DTA methodologies:
The DTA/DSC method, for overcoming this less than stoichiometric behavior of the dehydroxylation of gibsite, can be approached in the same manner as that which is described in the article for the TG/DTG methodology. The DSC peak area, for a weighed quantity of bauxite of known gibbsite content (previous XRD assignment), is used to obtain an empirical calorimetric “K factor”. This “K factor”, having units of energy units ((Joules/gram) per % gibbsite), is then used to convert normalized endothermic peak areas to percentage gibbsite in the bauxite ore which was analyzed by DTA or DSC. This is described in table 1 where the calorimetric “K factor” is calculated from the mean energy value (J/g) of DTA/DSC results obtained from three NIST SRM Standards of known percentage gibbsite. Once the “K factor” was determined, for this particular instrument, it was used to assign the percentage gibbsite in a sample of Australian (Darling Range) Bauxite.

![Figure 4: TGA and DTG Thermal Curves for Australian Weipa Bauxite Ore.](image)
This procedure is similar, but different, to the “method of external standards” [11] which is frequently employed in some chromatographic and spectroscopic methods of analysis.

A. Determination of Calorimetric Factor, K

% Gibbsite = K (Normalized Peak area, J/g)

where, area (J/g) - Experimentally observed with DTA

% Gibbsite - XRD Data from NIST

\[
K = \frac{\text{area (J/g)}}{\% \text{Gibbsite}}
\]

Table 1: Assignment of Gibbsite Content for Australian Darling Range Specimen (NIST SRM 600) From DTA/DSC Results.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>% Gibbsite</th>
<th>Area (J/g)</th>
<th>K (J/g %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dominican</td>
<td>50</td>
<td>537.84</td>
<td>10.76</td>
</tr>
<tr>
<td>Jamaican</td>
<td>75</td>
<td>809.62</td>
<td>10.79</td>
</tr>
<tr>
<td>Arkansas</td>
<td>60</td>
<td>631.77</td>
<td>10.53</td>
</tr>
<tr>
<td>Average K</td>
<td></td>
<td></td>
<td>10.69 ± 0.11</td>
</tr>
</tbody>
</table>

B. Calculation of % Gibbsite for Australian Specimen

\[
\% \text{Gibbsite} = \frac{\Delta H_{\text{observed}}}{K_{\text{AV}}} = \frac{550.03 \text{ J/g}}{10.69 \text{ J/g %}} = 51.45\%
\]

The “DSC Thermal Curve” obtained for a 50.56 mg sample of the Western Australian bauxite (SRM 600) ore is shown in figure 5. The results and calculations are shown in table 1. One will note that a “sigmoid baseline” was employed in the area calculation of the gibbsite dehydroxylation endotherm of the bauxite in this case. This was employed due to the baseline shift observed for this endothermic transition in the thermal curve (Figure 5). One will observe that the results of the calculation for this bauxite specimen was a gibbsite content of 51.45%. This value is more than 4% (absolute) smaller than the value (56.18%) assigned for the same bauxite ore in the previous TGA/DTG study (6).

Figure 5: DTA/DSC Thermal Curve with Calorimetric Peak Area Assignment for Australian Darling Range Bauxite Ore.
Consequently, a second bauxite ore (Jamaican #2) was chosen to be analyzed by DSC/DTA methodology and to be compared to that obtained thermogravimetrically by the use of an “empirical gravimetric factor, G”. Figure 5 shows the DSC thermal curve for a 40.28 mg sample of Jamaican #2 bauxite ore which was obtained at a heating rate of ten degrees Celsius per minute in an atmosphere of flowing nitrogen (40 cc/min). This DSC thermal curve was obtained by using the same computerized DTA instrument (Perkin Elmer DTA 7) as that used for establishing the “calorimetric factor K” employed in the analytical calculation in table 1. As is shown by the normalized peak area calculated in figure 6, by the instrument software, the Jamaican #2 bauxite required 639.94 Joules per gram for dehydroxylation of the gibbsite content of the bauxite ore. By dividing this value by the calorimetric factor (“K”) of 10.69 J/g/%gibsite, a gibbsite content of 59.86 % is obtained from the calculation. The TGA/DTG thermal curve for this Jamaican bauxite specimen was given earlier in figure 2 of this work. The amount of water liberated from the dehydroxylation of the gibbsite component of 19.0 was calculated from this TG thermal curve to be 19.02% by mass. Using the “empirical Gravimetric Factor” (G) of 3.06 %gibsite/% H2O from the previous study [6], a percentage gibbsite of 58.20% for the Jamaican #2 specimen was calculated. This is better agreement between the two thermal analysis techniques than the previous agreement obtained for the Australian Darling Range specimen. A number of possible reasons for this difference in results could be given but it is most probably due to either the variation of adsorbed water or changes in the “K” factor as larger amounts of water vapor are liberated with increasing gibbsite content and/or sample size. The sample sizes used in the two DSC (DTA) analyses differed by 16 milligrams. One must also remember that the “DSC” results used for these calculations were actually obtained with a High Temperature DTA instrument.

5.2.3. Thermal analysis of products from the Bayer process: The removal of the aluminous material is achieved commercially using the Bayer process. In the Bayer process crushed bauxite is digested with hot caustic soda solution under pressure. The aluminum hydroxide species dissolve to form a concentrated solution of sodium aluminate (NaAlO2) while the undesired impurity components (Fe2O3, FeO·OH, TiO2, and complex silicates) remain insoluble and may be separated by settling or filtering (or both). The red coloration is due to the large amount of iron minerals, hematite (Fe2O3) and goethite (FeO·OH)). This may be described by the following equation:

Bauxite Ore + NaOH (ag) → 2NaAlO2 (aq) + Red Mud (s)
After removal of the red mud, the sodium aluminate solution is seeded and $\text{Al(OH)}_3$ precipitates as colorless crystals.

$$2\text{NaAlO}_2 \text{(ag)} \rightarrow \text{Al(OH)}_3 \text{(s)} + 2\text{NaOH} \text{(ag)}$$

The thermal analysis techniques of DTA, TG, and DTG have also been used to characterize the “red mud” which is obtained as a by-product at the dissolution step. Figure 7 shows the TG and DTG thermal curves for the dehydroxylation of gibbsite, $\text{Al(OH)}_3$, as well as from the presence of crystalline goethite ($\text{FeO} \cdot \text{OH}$). A special problem exists in distinguishing the gibbsite dehydroxylation and the goethite dehydroxylation since almost complete overlapping of these DTG peaks occurs. The balanced equations for these are given below:

$$2\text{Al(OH)}_3 \text{(s)} \rightarrow \text{Al}_2\text{O}_3 \text{(s)} + 3\text{H}_2\text{O} \text{(g)}$$
$$2\text{FeO} \cdot \text{OH} \text{(s)} \rightarrow \text{Fe}_2\text{O}_3 \text{(s)} + \text{H}_2\text{O} \text{(g)}$$

One will note a partial separation of these two endothermic dehydroxylation events in the TGA/DTG thermal curve of figure 7. This observed partial separation is extremely rare when large sample specimens are employed in the thermal analyzer. In general, to achieve this type of distinction between the two events when using either DTG or DTA/DSC methodology, one must use small sample sizes and slow heating rates. This decrease in sample size and heating rate puts special demands on the ordinate sensitivity of the instrumentation used for the analysis. This is due to the decrease in peak amplitude with decreasing sample size and heating rate when using these techniques. Thus, many laboratories prefer the use of Differential Scanning Calorimeters (DSC’s) to conventional differential thermal analyzers. One of the limiting factors in DSC instrumentation is that the upper temperature limit is generally 600°C or 725°C depending on the manufacturer. However, in those laboratories where the primary interest is in gibbsite, goethite, and boehmite transitions, the operating temperature range of DSC is generally sufficient. However, sensitive DSC instrumentation, as a result of its nature, requires a smaller sample size. When analyzing geological, or mined samples in general, larger sample sizes are generally preferred to overcome the possible lack of homogeneity of the sample specimen being analyzed.

It should be pointed out that there are two different types of
DSC instruments which are commercially available for use with such inorganic materials. These use very different measuring cells and are referred to a “Heat-Flux DSC” and “Power Compensated DSC”. When using the power compensated DSC instrument, it is recommended by the author that small sample sizes (10 mg or less) and “flow through” covers be employed for analysis of these “water liberating” types of analytical samples. A discussion of the use of the flow through cover is given in the Materials and Methodology Section given earlier in this manuscript.

Figure 7 shows the TGA and DTG thermal curves for a red mud specimen which was obtained from an industrial site after separation of a Jamaican bauxite ore. This specimen was previously assigned a residual gibbsite content of 5.4% by XRD. The thermal transitions of interest in red mud arise from the endothermic dehydroxylation of residual gibbsite, goethite, and boehmite. A special problem exists in distinguishing the gibbsite dehydroxylation event from the goethite dehydroxylation since almost complete overlapping of the two weight loss curves occurs. One will note a partial separation of the two transitions in the DTG thermal curves presented in the TGA/DTG expanded scale thermal curves given in figure 7. The higher temperature portion of this overlapped DTG peak is due to the goethite component of this red mud sample. These thermal curves were obtained using a small (8.54 mg) sample heated at 10 degrees Celsius per minute. The weight loss results for four different temperature ranges of the TGA thermal curve, using the DTG curve as a guide, are given in table 2. One will note that the total mass loss between 209°C and 344°C, due to the gaseous water liberated from the residual gibbsite and the goethite, is 4.84% of the original sample mass. This represents the sum of the percentage water lost from the dehydroxylation of both residual gibbsite and goethite as described by the chemical equations given above.

As will be seen in table 3, this total mass loss value for this dehydroxylation temperature range, as well as the fact that the gibbsite content was previously analyzed by XRD, can be used in a two-component equation to assign the percentage by mass of goethite in the red mud specimen. The equation in table 3 also employs gravimetric factors obtained by using the balanced equations for the dehydroxylation of both gibbsite and goethite components. As is shown by the calculation in table 3, the goethite component is assigned a value of 1.59% by mass in this particular red mud specimen.

### Red Mud (5.4% Gibbsite)

<table>
<thead>
<tr>
<th>We% Change</th>
<th>To</th>
<th>From</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.68</td>
<td>209.14</td>
<td>37.53</td>
</tr>
<tr>
<td>4.84</td>
<td>344.86</td>
<td>209.12</td>
</tr>
<tr>
<td>2.15</td>
<td>675.58</td>
<td>344.84</td>
</tr>
<tr>
<td>0.99</td>
<td>1023.46</td>
<td>675.58</td>
</tr>
</tbody>
</table>

**Table 2:** TGA Calculated Mass Losses at Different Temperature Intervals during Heating of “Red Mud” By-Product Shown in figure 7.

A. Data and information

1. Total water loss assigned from TGA/DTG curve in figure 7 for overlapped dehydroxylation 4.84% H₂O,
2. % Gibbsite in Red Mud Specimen from XRD 5.4% Gibbsite,
3. Balanced equations for dehydroxylation of Gibbsite and Goethite given in Section 5.2.3 of this paper.

B. Equation for total % H₂O as a summation of the H₂O liberated by dehydroxylation of each component using information from Part A above.

Total H₂O Liberated (% H₂O) = 5.4% Gibbsite (3 H₂O/ 2 Al(OH)₃) + X (H₂O/2 FeO·OH)
where X = % Goethite

C. Calculation of % Goethite (using equation in Part B above)

4.84 % H₂O = 5.4 (0.3456) + 1.014 X
X = 1.59% Goethite

**Table 3:** Calculation of Percentage Goethite in Red Mud Specimen Using Overlapped DTG Peaks in figure 7.
Figure 8 displays the power compensated DSC Thermal Curves obtained with the same “red mud” specimen that was used in the TGA/DTG experiment described above. The sample size (8.58 mg) was very nearly the same as was used in the TGA experiment given above. Knowing that resolution of overlapping thermal events is usually improved by decreasing the heating rate in such DSC experiments, the red mud specimen was studied at both 5.0 and 10.0 degrees per minute heating rates. One will quickly notice that the ordinate signal for the endothermic heat flow rate (mWatts) signal is decreased and a slight increase in resolution is gained by using the 5.0 degree per minute heating rate. With this in mind, the possibility of using even slower heating rates was dismissed since one would have to employ an increased sample mass to offset the decrease in ordinate signal accompanying the decrease in heating rate. Any quantitative efforts for assigning % gibbsite using the overlapping DSC thermal curves given in figure 8 should be based on the peak height, assigned at maximum ordinate value, at a particular heating rate. The “K” value obtained in units of normalized peak height values mWatts/% gibbsite could be applied to peak height response of an unknown in the same manner as described for peak area response in table 1. It is of utmost importance that such peak height comparisons be made at the same experimental heating rate.

Please remember that the low temperature portion (and peak maximum) of this overlapped peak is used for estimating the gibbsite or “trihydrate” content. It is the opinion of the author that the best thermal analysis approach to the assignment of goethite in such overlapping samples is achieved with Derivative Thermogravimetric (DTG) areas in a similar manner as that described by Sanders [10].

5.2.4. Thermal analysis of Aluminas: In the production of alumina, the monoclinic “trihydrate” from the Bayer Process is calcined in rotary kilns. During calcination water vapor is evolved from the dehydroxylation of the Al(OH)₃, and the aluminous material passes through several intermediate phases until the stable high temperature rhombohedral structure, Alpha (α) alumina, is formed. The amount of water evolved and the percentage of alumina that is transformed to the Alpha (α) alumina structure depends on both the temperature and length of time use for calcination. Despite the high temperatures (1200-1300°C) used in the rotary kilns, incomplete calcination may be observed by thermal analysis techniques. Gamma (γ) aluminas (Al₂O₃·nH₂O, where 0 > n < 0.6) are partially hydrated species which may exist up to ca. 600°C. Another crystalline form of aluminas is the high temperature δ group. The δ aluminas are nearly anhydrous and may be obtained from...
the Gamma (γ) alumina on heating between 900 and 1000°C [3]. It is easy to understand why LOI (loss on ignition) values are important to the alumina industry.

Figure 9 shows the TGA and DTG thermal curves for an incompletely calcined alumina specimen. One can easily follow the loss of sorbed water at temperatures up to the onset of a small amount of residual gibbsite trihydrate form above 240°C. It is this Derivative (DTG) response to the change in rate of mass loss that allows low level assignment of residual gibbsite in the calcined alumina product. The DTG response is enhanced by increased heating rates in obtaining the experimental TGA data. This is why the heating rate was increased to 20 degrees Celsius per minute for obtaining the thermogravimetric data given in figures 9 and 10. It is also useful to have a good smoothing algorithm, as a part of the TGA Data Handling software, for use with expanded ordinate axes in TGA/DTG thermal curves. However, one must be aware that smoothing of the TG (TGA) data decreases the resolution of overlapping peaks such as those observed in the DTG Curve of figure 7. Continued increase in the degree (or level) of smoothing can eventually turn such overlapped peaks into singular peak responses as well as, completely eliminate very small peaks such as that shown in the DTG Thermal Curve of figure 9.

In closing this discussion, the reader will be referred to the mass loss assignments for the TG thermal curve in figure 9. The first two weight loss regions for "Alumina Specimen A" are 37.36 to 241.75°C and 241.75 to 340°C. The first of these (lowest temperature range) is assigned as 2.61% "sorbed molecular water" and the second corresponds to the dehydroxylation of gibbsite (or the so called "trihydrate" form of alumina). Thus, the percentage water liberated for this dehydroxylation step is measured as 2.61% trihydrate component in the calcined "Alumina Specimen A" assuming that the trihydrate component experienced complete dehydroxylation. In this case, the % gibbsite remaining in the alumina specimen is calculated using a theoretical gravimetric factor of 2.89% gibbsite per % water vapor liberated in the dehydroxylation temperature region. The percentage of residual gibbsite in the alumina is increased in value if one expresses the results on a so called "dry weight" or "moisture free" basis. In this case, the sorbed molecular water (2.61%) is eliminated from the total mass of the alumina specimen that was analyzed by the TGA experiment and the % gibbsite (or trihydrate) is then recalculated. This conversion is discussed by the author in the previous article...
dealing with TGA of bauxites. In this case for the Alumina Specimen A, the 1.68% gibbsite is simply multiplied by the unitless factor \((100/(100-2.61)\) or 1.027). This gives a value of 1.73% gibbsite when expressed on a “dry weight” basis. It is a certainty that there are some who work in the alumina industry who may not agree with the analyte terminology used for the calculations presented above for “Alumina Specimen A”. The basis of the use of this terminology (i.e., “sorbed molecular water” and “crystalline trihydrate dehydroxylation”) is the observed temperature and mass loss profile (peak width) for these water releasing transitions in the TGA thermal curve for “Alumina Specimen A”.

Figure 10: TGA Thermal Curve of “Alumina Specimen A” with Calculated Mass Losses at Different Temperature Intervals during Heating.

6. Summary of Results and Conclusion

In the previous pages of this manuscript, several thermal analysis techniques were demonstrated for use in various stages of alumina production from bauxite ores. The study did not include in depth discussion of all possible applications and is therefore entitled …….“Part 1.” It is hoped that Part II will soon follow this paper and will include thermal methodologies for the recognition, and in some cases quantification, of the non-aluminous components of bauxite raw ores such as the iron bearing components (siderite, goethite, hematite, magnetite, etc.), clay mineral kaolinite, and quartz. Also, the use of high temperature TGA to assign LOI (Loss on Ignition) in dynamic air atmosphere for both bauxite ores and product aluminas will be included.

The studies presented here, however, demonstrate the use of DTA, DSC, TGA (TG) and DTG techniques for assessing the aluminous components of several bauxite ores. The results of these analyses often lead to the use or non-usage of the term “Good Bauxite”, a term which usually reflects only one meaning and that is “Commercial Value.” The quantification of gibbsite by the use of both DTA/DSC and TGA/DTG methodologies were demonstrated using the gibbsite dehydroxylation transition in both methods. Two separate bauxite ores which were analyzed by both DTA/DSC (calorimetric) and thermogravimetric, TGA/DTG, methods and were then compared for agreement between the two experimental quantitative results which
were obtained. The results for the Jamaican specimen agreed more closely (1.66% by mass) than the Western Australian (Darling Range) specimen which differed by more than 4.0% by mass (absolute). In each case, the thermogravimetric value is considered the more accurate. The major reason is that the DSC data was obtained using a high temperature DTA instrument. These high temperature DTA instruments are not known for high accuracy in calorimetric measurements.

The reported use, by an Indian aluminum company, of a somewhat different TGA instrument, which is sold by the Laboratory Equipment Company (LECO), for quantification of gibbsite in 29 samples of bauxite ores from Central India was discussed. The published data [11] showed trends very similar to those published in this journal by Earnest et al., [6] using conventional TGA equipment. Throughout the manuscript instrument choice, as well, as operator choices of heating rates and sample handling techniques are offered. TGA and DTG were shown to detect and estimate reasonably low level gibbsite and goethite in in by-product red mud samples. TGA can do similarly for boehmite content of Red Muds by-product of the Bayer Process.

The study of the “Red Mud” specimen from an alumina production site included TGA/DTG and DSC analyses. The use of a two component equation to describe the total water lost by overlapping dehydroxylation TGA/DTG thermal curves for gibbsite and boehmite was demonstrated. With the prior knowledge of the percentage gibbsite, and the balanced equation for the dehydroxylation of both overlapping species, the percentage goethite (by mass) of the red mud was assigned. The DSC study of the same red mud specimen also gave a great deal of advice involving types of DSC instrumentation and temperature ranges, sensitivity, purge gas elimination design for expelling volatiles from DSC analysis cells, sample size, etc. Software requirements such as smoothing algorithms, etc. were also given. It was demonstrated, by use of power compensated DSC, that the separation of overlapping peaks in thermal analysis can often be improved by the use of slower heating rates. The Red Mud specimen containing overlapping endothermic dehydroxylation peaks of gibbsite and goethite, was used as an example. This improved separation was shown to be done at the expense of the magnitude of the ordinant signal response (peak height). It was recommended that extreme caution be taken when power compensated DSC is used for studying analysis samples that lead to the liberation of volatile products. In this case, a flow-through cover and increased purge gas flow rate should be used. The power compensated DSC can be used with good calorimetric accuracy provided the samples do not exhibit decomposition transition during the heating run. This type of DSC is not used for many soils or geological samples as a result of the effect of the volatile matter which is liberated on heating in the measuring cell. For clays and minerals, high temperature instruments (DTA and TGA) are recommended for general thermal analytical use.

An example of an incompletely calcined alumina product from the Bayer Process ("Alumina Specimen A") was used to demonstrate the use of the DTG thermal curve to recognize and estimate low levels of residual monoclinic crystalline “trihydrate” in such calcined alumina products. The same analysis can be based on the dehydroxylation of the “trihydrate” component by DTA/DSC analysis. The enhancement of the DTG signal by increased heating rates was discussed along with the decrease in resolution, and possible elimination, of small peaks from the thermal curve as a result of excess smoothing of the TGA and DTG data.

References


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