APPLICATION OF THERMOGRAVIMETRIC ANALYSIS FOR ESTIMATION OF TRI-HYDRATE ALUMINA IN CENTRAL INDIAN BAUXITES - AN ALTERNATIVE FOR CLASSICAL TECHNIQUES

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Abstract

Tri-hydrate alumina or gibbsite ($Al_2O_3.3H_2O$) content in bauxite is a fundamental quality parameter in the Bayer alumina process using low temperature digestion. Classical techniques available for its estimation are time consuming and prone to standard and non-standard sources of error. Extensive studies on analysis of samples from Central Indian bauxite sources using thermogravimetry over varied temperature ranges and comparison with that of the data obtained from classical techniques, have revealed that loss of molecular water at different temperatures in thermo-gravimetry provides a meaningful tool to correlate with tri-hydrate alumina content by applying relevant correction factors derived from the experimental data at different concentrations of tri-hydrate alumina. The studies also have found that the thermo-gravimetric analysis can be used as a very fast and dependable technique with higher levels of accuracy over classical methods and is free from other interferences. The accuracy levels of the method developed were checked using reference standards.

Introduction

Central Indian bauxite sources contain three principal hydrates of aluminium, i.e., gibbsite or trihydrate alumina ($Al_2O_3.3H_2O$ or $Al(OH)_3$)), boehmite and diaspore or monohydrate alumina ($Al_2O_3.H_2O$ or $AlOOH$) with gibbsite often being the predominant mineral. The other major minerals are alumino-goethite, hematite, kaolinite, anatase, rutile and quartz. Alumina extraction using low temperature digestion in the Bayer process results in dissolution of the gibbsitic form of aluminium hydroxide where other iron and titania minerals remain undigested. Kaolinite ($Al_4[Si_4O_{10}](OH)_8$) shows significant dissolution in sodium aluminate liquors, subsequently forming a desilication product, whereas the effect on quartz is less significant. All the minerals present in the bauxite, and their chemical-mineralogical characteristics, will have some influence either on process control, or on the methods of estimation of primary pararmeters.

Determination of the trihydrate alumina content in feed bauxite is of paramount importance, as the total process control is directly or indirectly affected by its proportion in the bauxite and also the accuracy levels in its estimation. Vedanta Aluminium Ltd., at Lanjigarh is presently using varied sources of bauxites for production of alumina and a Central Indian source is one of them. Determination of the chemical and mineralogical composition of these sources with acceptable limits of accuracy, and with the necessary speed, is of pivotal importance to facilitate required blending and homogenising so as to feed a uniform quality of bauxite to the plant.

Trihydrate alumina content in bauxite is generally estimated by a bomb digestion system in the plants of the alumina industry using the Bayer process. Though this analytical method provides the required levels of accuracy, the large number of steps involved in the process, starting from digestion, filtration and titration to complete one analysis, becomes tedious and time consuming. If there are a large number of samples to be processed within a stipulated time to meet the process requirement, completion of the targeted number of samples in time is a challenge. This necessitates looking into quick alternative methods with equal levels of accuracy and dependability.

Since the above conditions are always prevalent at Vedanta, alternative instrumental techniques which are very fast, with competitive levels of accuracy to wet chemical analysis, particularly thermal decomposition techniques, have been tried. This is a reasonable approach as the thermal techniques to study the dehydration and dehydroxylation behaviours of bauxites have been widely documented [1]. It is well known that thermal decomposition of aluminium minerals in bauxite is a factor of time and temperature. Dehydroxylation of gibbsite occurs in the temperature range of 260-380 °C with peak losses at 320-340 °C.

The established general decomposition pattern of gibbsite, $Al_2O_3.3H_2O$ is as below:

$$Al_2O_3. \, 3H_2O \longrightarrow Al_2O_3 \cdot x \, H_2O \text{ (as residual hydroxide)} + y \, H_2O\uparrow$$
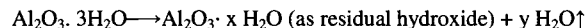
Using thermogravimetry, this property of losing hydroxyls as water molecules at elevated temperatures from the gibbsite mineral present in the bauxite, and converting the weight loss into an equivalent alumina content, is accomplished. The values obtained are then compared and equated with the data previously generated using classical techniques of analysis for the same samples. From the proportions of released and residual hydroxides lost as water molecules, a relationship is established at a particular temperature by comparing the thermal decomposition data with wet chemical data and by applying a correction factor if required.

Materials and Methods

1. Bauxite sample collection and preparation
   Bauxite samples were collected from the mines of M/s. CR Mittal from Central Indian region. A total of 29 samples have been collected and prepared using Indian Standard [2]. Apart from the mine samples, a total of 10 international reference standards of bauxite have been used for comparison.

2. Chemical analysis of bauxite

LOI of the sample is determined by subjecting 1 g of sample to 1000 °C for one hour and from the weight difference between before and after heating [3]. The major elements; alumina, silica, ferric oxide and titania in bauxite samples are also determined using the respective Indian standard test methods of [4-7]. Reactive silica in bauxite is obtained by deducting the percentage of nonreactive silica from the percentage of total silica [8].

3. Trihydrate alumina determination using wet chemical techniques

Using an M/s. Intronics bomb digester, a known quantity (1.3 $\pm$ 0.0001g and 0.65 $\pm$ 0.0001g) of bauxite are heated under pressure, in a solution of sodium hydroxide (165g/l as Na_2CO_3) respectively at 145 °C and 240 °C for gibbsite and boehmite; the insoluble matter is separated by filtration. Alumina present in the filtrate is given by titrating the equivalent of the hydroxide ions (OH⁻) released by fluorine in a chelating solution containing sodium gluconate [9]. Mass percentage of Al_2O_3 is calculated as gibbsite for the solution at 145 °C and as gibbsite and boehmite combined at 240 °C. The difference in the values between the two determinations is expressed as boehmite.

4. Trihydrate alumina determination using thermogravimetry

A thermogravimetric analyser, model TGA-701 of M/s. Leco Corporation is used for the determination of loss of mass in bauxite.

Step Name	Unit	Moisture	355 °C LOI
Covers	-	No	No
Start Temp	°C	25	107
End Temp	°C	107	355
Ramp Rate	°C/Min.	10	20
Ramp Time	Min.	00:08	00:12
Hold Time	Min.	00:20	00:20
Total Time	Min.	00:28	00:32
Max Time	Min.	00:00	00:00
Atmosphere	-	None	None
Flow Rate	ml/Min.	Off	Off
Comparator	%	0.1	0.1
Final weight	-	at constancy	at constancy

Table 1. Test conditions for bauxite observed during thermogravimetric analysis

A number of samples are analyzed using different instrumental conditions in the range from 100 to 420 °C to arrive at the most common and nearest temperature where the wet chemical values are comparable with the scanned data derived by applying the necessary correction factors. These are calculated on the basis of a combination of released and unreleased (bound hydroxyls) water molecules from the bauxite. The instrumental settings followed for the final analysis of bauxite samples are detailed in Table 1.

Since the percent loss of mass corresponds to the water molecules associated with trihydrate alumina in bauxite, the weight of trihydrate as alumina is calculated as below:

$$\text{Moisture \%} = \frac{(\text{Initial Mass-Moisture Mass})*100}{\text{Initial Mass}}$$

$$355\,°C\ LOI\ \% = \frac{(\text{Moisture Mass-355}\,°C\ LOI\ Mass)*100}{\text{Moisture Mass}}$$

$$THA\ \%\ at\ 355\,°C = \frac{(\text{Moisture Mass-355}\,°C\ LOI\ Mass)*100*1.889*1.06}{\text{Moisture Mass}}$$

Molecular ratio of Al_2O_3 : H_2O = 1.889
Factor for residual hydroxide fraction of $3H_2O$ = 1.06

Released fraction of $3H_2O$	2.89	2.87	2.85	2.83	2.81	2.79	2.77
Unreleased fraction of $3\ H_2O$	0.11	0.13	0.15	0.17	0.19	0.21	0.23
% of unreleased $3\ H_2O$	3.67	4.33	5.0	5.67	6.33	7	7.67
% of released $3\ H_2O$	96.3	95.7	95	94.3	93.7	93	92.3
Molecular mass of released $3\ H_2O$	52.0	51.7	51.3	50.9	50.6	50.2	49.9
Factor for unreleased $3H_2O$	1.04	1.05	1.05	1.06	1.07	1.08	1.08

Table 2. Basis of gibbsite thermal dehydroxylation

The initial step in the thermal decomposition of gibbsite is the diffusion of protons and the reaction with hydroxyl ions to form water. From the comparative analysis of thermal decomposition data with wet chemical data of trihydrate, it is observed that there is a certain fraction of unreleased water molecules characteristic of either the source of bauxite or the concentration levels of trihydrate present in the bauxite. The factor for the unreleased fraction of water molecule is calculated with different combinations of released and unreleased proportions of three water molecules available with each alumina molecule for completion of the total quantity of water. Out of several combinations, as displayed in Table 2, a fraction of 0.17

unreleased molecules and its corresponding factor (1.06), is considered to be most appropriate for the calculation of actual trihydrate content, when compared with the values of trihydrate determined by classical techniques, for the Central Indian bauxite sources.

Results and discussion

The data obtained by conducting wet chemical analysis of the major elements and trihydrate alumina content in 29 samples collected from a bauxite source of Central India (M/s. CR Mittal) has been furnished in Table 4. Data on trihydrate alumina obtained from thermogravimetric analysis and boehmitic monohydrate data obtained from wet chemical techniques using a 240 °C bomb digestion of the same samples, is also furnished for comparison. The data on the other possible interfering parameters in wet chemical analysis, like reactive silica and boehmitic alumina, are also furnished in the table to study their effect

Interpretation of the above data reveals several interesting factors related to the thermogravimetric analysis and its application to the determination of trihydrate content in bauxites. Data on the wet chemical analysis of trihydrate alumina content is furnished in column 10 (ranging from 24.10 to 48.27%) and the respective values obtained by using thermogravimetric analysis are furnished in column 12 (ranging from 24.18 to 47.22%) in Table-3. Out of the total 29 samples analysed, only four samples are highlighted in the Table- 3 as showing a difference of $\geq$ 1% THA as under column 13, wherever the actual THA content is more than or equal to 45 % in the bauxite.

It is interesting to note that except the above four samples, all other samples have a THA of $\leq$ 40% and variation is < 1%. The data also indicates that as the THA content is increasing from 40% and above, the variation between the two methods is showing an increasing trend indicating that the factorial value needs to be corrected with increasing THA content. It is also clear from the table that the variation is very insignificant if THA value is < 35% as reflected in majority of the samples studied. These observations reveal that the thermogravimetric data obtained for bauxites having < 35% trihydrate alumina for the source studied can be a perfect match with the wet chemical data and it can be used as a direct alternative technique. Similarly, up to 45% THA content, the thermogravimetric method can be accepted with 1% variation. Above 45%, it is necessary to make corrections to the factor derived from the loss of mass.

The other advantages of thermogravimetric analysis over the classical techniques, is that the former facilitates multiple sample analysis i.e., up to 20 samples at a time resulting in higher throughput, whereas the later is confined to cumbersome time consuming individual analysis.

In the normal course, when wet chemical techniques are used for this analysis, parameters like boehmite and reactive silica effect the determination of trihydrate alumina. To verify this effect, the analysis of boehmite and reactive silica and other parameters were conducted and furnished in the table along with trihydrate data. Reactive silica ranged from 0.33 to 7.64% (column 9) and boehmite ranged from 0 to 33.52 (column 14) in the experimental samples. These parameters are not showing any significant influence on the respective values of trihydrate alumina determined by using thermogravimetry, confirming that the

method is free from such interferences. Other variables like heating rate, external pressure, water vapour pressure, sample particle size etc., do not have a significant influence on these determinations [10].

S. No.	Log No.	Sample Location	Fe₂O₃ (%)	TiO₂ (%)	SiO₂ (%)	Al₂O₃ (%)	LOI (%)	R-SiO₂ (%)	Wet THA (%)	THA (%) at 355°C	TGA-THA x1.06 (%)	Diff. (10-12)	Boehmite (%)
1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	6181	Pit-A/S1	31.04	4.81	3.60	38.65	20.61	3.26	33.47	31.72	33.63	-0.16	1.04
2	6182	Pit-E/S2	9.54	8.33	0.86	56.35	23.83	0.79	35.10	32.88	34.85	0.25	19.46
3	6183	Pit-D/S1	16.66	7.60	1.04	48.04	25.79	0.93	45.07	41.84	44.35	0.72	1.00
4	6184	Pit-C/S3	16.76	5.48	2.90	49.15	24.85	2.56	41.30	38.37	40.67	0.63	4.77
5	6185	Pit-C/S2	6.13	6.42	0.11	57.72	28.57	0.00	48.27	44.55	47.22	1.05	9.08
6	6186	Pit-A/S2	25.72	7.48	2.39	41.10	22.50	2.10	37.90	35.60	37.74	0.16	0.00
7	6187	Pit-C/S5	9.85	6.37	1.15	55.12	26.63	1.02	44.74	41.09	43.56	1.18	8.99
8	6188	Pit-D/S3	22.16	5.38	1.24	45.37	24.73	1.12	42.33	39.26	41.61	0.72	0.80
9	6189	Pit-C/S1	24.82	5.54	0.38	43.67	24.09	0.33	41.39	38.56	40.87	0.52	0.60
10	6190	Pit-D/S2	13.18	6.74	1.27	51.30	26.76	1.12	46.78	43.03	45.61	1.17	2.81
11	6191	Pit-E/S2	14.97	6.09	0.89	51.81	25.39	0.79	41.73	38.63	40.95	0.78	8.55
12	6192	Pit-E/S3	19.84	5.87	1.22	48.23	24.08	1.09	39.93	37.45	39.70	0.23	6.20
13	6193	Pit-C/S4	19.04	6.60	1.18	49.39	23.25	0.91	37.58	35.34	37.46	0.12	9.94
14	6194	Pit-1K/01	9.51	6.42	0.63	60.53	21.34	0.56	25.73	24.07	25.51	0.22	33.52
15	6195	Pit-1K/02	20.02	5.56	4.18	49.80	19.33	3.73	24.10	22.81	24.18	-0.08	21.24
16	6196	Pit-1K/03	16.30	5.57	2.30	54.81	20.09	2.05	24.60	23.10	24.49	0.11	27.11
17	6197	Pit-1K/04	15.20	5.86	1.93	56.38	19.84	1.72	25.23	24.17	25.62	-0.39	28.76
18	6198	Pit-1K/05	10.67	6.06	0.91	60.25	21.27	0.82	27.10	25.73	27.27	-0.17	31.87
19	9134	Pit-04	48.34	3.98	5.57	31.70	17.29	3.59	26.79	25.41	26.93	-0.14	0.00
20	9267	Pit-C	20.57	6.95	1.20	46.49	23.38	1.07	38.79	36.78	38.99	-0.20	5.10
21	9268	Pit-A/S5	14.92	7.84	1.12	49.13	25.53	1.00	42.44	40.69	43.13	-0.69	2.97
22	9269	Pit-E/S1	16.04	7.40	1.58	51.45	21.95	1.42	32.71	31.08	32.94	-0.23	16.32
23	9270	Pit-C/S2	7.30	6.37	0.84	56.02	28.31	0.75	47.62	43.80	46.43	1.19	4.67
24	9271	Pit-E/S2	18.53	7.09	1.43	48.95	22.77	1.28	35.27	33.42	35.43	-0.16	18.54
25	9272	Pit-A/S3	32.85	5.71	1.51	36.99	20.68	1.35	34.32	32.53	34.48	-0.16	0.00
26	9273	Pit-A/S4	16.97	6.14	0.54	48.32	26.20	0.49	43.92	41.96	44.48	-0.56	0.00
27	9274	Pit-A/S2	32.02	4.45	2.18	38.50	21.22	1.96	34.92	33.19	35.18	-0.26	0.00
28	9275	Pit-A/S1	12.42	7.14	1.05	50.12	27.54	0.93	46.69	44.60	47.28	-0.59	0.00
29	9276	Pit-A/S6	25.96	4.32	9.22	39.22	19.82	7.64	29.21	27.68	29.34	-0.13	1.20

Table 3. Data on chemical composition and trihydrate alumina determined from wet chemical and thermogravimetric techniques on Central Indian bauxite samples.

Verification with international reference samples

To validate the above test data, a set of ten international reference bauxite samples with known trihydrate content have been analyzed under the same set of experimental conditions. The data of these samples with different combinations of released (2.89, 2.87, 2.85, 2.83, 2.81 and 2.79 H_2O) and respective unreleased (0.11, 0.13, 0.15, 0.17, 0.19, 0.21 and 0.23 H_2O) water have been tabulated in the Table-4. The data indicates that out of the ten, four standards namely; BXT 05, 06, 07 and 09 show a direct match with the reference value within a 1% limit of variation. By applying a factor of 1.06 derived from the release of 2.83 H_2O molecules, as established in the above experimental case of

Central Indian bauxite samples, five standards, i.e., BXT 02, 04, 08, 09 and 11 match with less than 1% variation. The other standards namely; BXT 01, and 03 show more than 1% variation between wet chemical and thermogravimetric determinations even after applying the factor. Since the mean value of THA is considered as the standard wet chemical reference and there is a chance of variation up to 1% in actual trihydrate value for an individual standard, these interpretations are considered as indicative but trends are close to the actual data observed for experimental samples.

Sample ID	THA mean value	THA% Ref Value	355°C (with out factor) THA%	Diff.	2.89 H₂O 1.038	Diff.	2.87 H₂O 1.045	Diff.	2.85 H₂O 1.053	Diff.	2.83 H₂O 1.06	Diff.	2.81 H₂O 1.068	Diff.	2.79 H₂O 1.075	Diff.
BXT 01	54.3	54.3 +/-0.5	49.28	-5.02	51.15	-3.15	51.5	-2.8	51.89	-2.41	52.24	-2.06	52.63	-1.67	52.98	-1.32
BXT 02	46.5	46.5 +/-0.7	43.23	-3.27	44.87	-1.63	45.18	-1.32	45.52	-0.98	45.82	-0.68	46.17	-0.33	46.47	-0.03
BXT 03	51	51.0 +/-0.4	45.86	-5.14	47.6	-3.4	47.92	-3.08	48.29	-2.71	48.61	-2.39	48.98	-2.02	49.3	-1.7
BXT 04	42.5	42.5 +/-0.4	40.42	-2.08	41.96	-0.54	42.24	-0.26	42.56	0.06	42.85	0.35	43.17	0.67	43.45	0.95
BXT 05	42.4	42.4 +/-0.6	42.99	0.59	44.62	2.22	44.92	2.52	45.27	2.87	45.57	3.17	45.91	3.51	46.21	3.81
BXT 06	45.5	45.5 +/-0.6	44.9	-0.6	46.61	1.11	46.92	1.42	47.28	1.78	47.59	2.09	47.95	2.45	48.27	2.77
BXT 07	39.7	39.7 +/-0.6	40.36	0.66	41.89	2.19	42.18	2.48	42.5	2.8	42.78	3.08	43.1	3.4	43.39	3.69
BXT 08	41.7	41.7 +/-0.4	39.08	-2.62	40.57	-1.13	40.84	-0.86	41.15	-0.55	41.42	-0.28	41.74	0.04	42.01	0.31
BXT 09	26.4	26.4 +/-1.0	25.67	-0.73	26.65	0.25	26.83	0.43	27.03	0.63	27.21	0.81	27.42	1.02	27.6	1.2
BXT 11	44.7	44.7 +/-0.9	42.58	-2.12	44.2	-0.5	44.5	-0.2	44.84	0.14	45.13	0.43	45.48	0.78	45.77	1.07

Table 4. Thermogravimetric data of international reference standard bauxite samples

These observations show that the trends noticed with Central Indian bauxite samples are mostly applicable to the international reference standards and vice versa, hence confirming that the observations for Central Indian case can also be applied for other sources within the defined ranges of trihydrate concentration. The observations also indicate that wide variations and deviations in case of BXT 01 and 03 standards are most likely due to the very high concentrations of trihydrate present, i.e., > 50 % and they may need to have a different correction factor, depending on the release of water molecules at that concentration of trihydrate. A similar effect is also observed in case of Central Indian sources with more than 45% trihydrate.

Conclusion

Thermogravimetric analysis based on the loss of mass of water molecules is found to be a very fast and alternative technique for assessing trihydrate alumina in comparison to classical methods of analysis which are tedious and time consuming.

The data obtained with some Central Indian bauxite sources showed very good agreement between the two methods. An excellent comparison is noticed up to 35% of trihydrate alumina in the bauxite and up to 45% it is comparable with acceptable limits of variation. Above 45%, the data needs appropriate correction based on the proportion of molecules of water released/unreleased.

The test data obtained is verified by comparison with that of international reference bauxite samples. Similar behavior and trends were observed, indicating validity of the experimental data. The results also show scope for adapting the technique for other sources.

References

1. Lodding E., 1969. The gibbsite dehydroxylation fork. Schwenker RF and Gran, PD (eds.), Thermal Analysis, Volume-2. Inorganic materials and Physical Chemistry. New York: Academic Press pp. 1239-1250.
2. Indian Standard: Methods of sampling bauxite (First Revision), IS: 1999-1987 Page 1-15.
3. Indian Standard: Methods of chemical analysis of bauxite, Part1- Determination of loss on ignition (First Revision) IS: 2000 (Part-1) – 1985, Page 1-5
4. Indian Standard: Methods of chemical analysis of bauxite, Part 2- Determination of silica (First Revision) IS: 2000 (Part-2) – 1985, Page 1-6.
5. Indian Standard: Methods of chemical analysis of bauxite, Part 3- Determination of alumina (First Revision) IS: 2000 (Part-3) – 1985, Page 1-6.
6. Indian Standard: Methods of chemical analysis of bauxite, Part 4- Determination of ferric oxide (First Revision) IS: 2000 (Part-4) – 1985, Page 1-6.
7. Indian Standard: Methods of chemical analysis of bauxite, Part 5- Determination of titania (First Revision) IS: 2000 (Part-5) – 1985, Page 1-5.
8. IBM Manual, 1979. Manual of procedures for chemical and instrumental analysis of ores, minerals and ore dressing products, Page 11-12, Issued by the Controller, Indian Bureau of Mines.
9. Ibrahima Sory Cisse and Jiwen Ge, 2010, Determination of bauxite's phases by the bomb digest method at Kamsar laboratory ISO 9002 (Guinea), Journal of American Science, 6 (6), 139-145, 2010.
10. Paulik F, Paulik J, Naumann R, Kohnke K and Petzold D, 1983. Mechanism and kinetics of the dehydration of hydrargillites, Part I & II. Thermochimica Acta, 64, 1-12