TOWARDS A PRECISE AND ACCURATE METHOD TO DETERMINE BOEHMITE REVERSION

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Abstract

Bauxite containing boehmite and digested under low temperature conditions may cause boehmite reversion/precipitation, which may strongly affect recovery. This phenomenon is well known but poorly quantified, mainly due to a lack of adequate analytical methods. Boehmite reversion is often determined in plant laboratories by following total alumina in feed bauxite and in red mud. However, this is done with low accuracy since the boehmite phase is not directly observed. Over the last 30 years, some authors have proposed to analyse for boehmite in residue by different techniques including Differential Scanning Calorimetry (DSC). However, many questions have been raised regarding the proper value for the heat of dehydroxylation and about the possible difference of the heat of dehydroxylation between primary boehmite and reverted boehmite. In this study, results were obtained on red mud containing primary and reverted boehmite generated by the digestion of bauxite samples of different origins. The samples were digested in various laboratory conditions. The solids were analysed by wet chemistry, XRF, XRD and thermogravimetry, for which the signal is not dependent on the sample origins. The results obtained using these techniques, in addition to analyses done on leached samples, allowed us to differentiate and quantify many of the various phases present in the sample. Finally, using this new methodology, boehmite reversion may eventually be quantified with better accuracy.

Key words

Thermal analyses, thermogravimetry, red mud, boehmite, reversion, goethite

1 Introduction

Boehmite reversion/precipitation occurs in the Bayer process when boehmite crystallites remain in the pulp during digestion in low-temperature digestion plants. In these conditions, the boehmite crystallites may act as germs for boehmite precipitation, which is the thermodynamically stable form of alumina hydrate under low temperature digestion conditions. Recent works have demonstrated that the presence of germs is essential to this reaction, which explains why, in the absence of boehmite, there is no reversion [Skoufadis et al., 2003]. Once recrystallised, this newly formed boehmite follows red mud and causes productivity loss [Lepetit, 1986]. Since there is a loss of available gibbsite in this process, there is a need for more bauxite feed and, consequently, more caustic [Lamerant et al., 2002].

Boehmite reversion has been known for a long time and some factors that influence boehmite reversion have been identified. Among them, one could mention specific surface area of bauxite, morphology and size of boehmite crystallites, digestion temperature, digestion time, alumina-to-caustic ratio…[Authier-Martin et al., 2002; Lamerant et al., 2002; Gong et al., 2003]. Other factors such as goethite concentration in mud, residence time at solid/liquid separation, solids concentration, impurities [Lepetit, 1986] as well as vapour pressure in digesters [Gong et al. 2003], have also been mentioned. These numerous factors prove the complexity of boehmite reversion.

Variations in boehmite concentrations in red muds are nowadays often too small to be measured and may lead to significant underestimation of alumina losses for alumina producers. One of the first steps towards a control of this reversion phenomenon is a precise and accurate method to determine boehmite concentration in both red mud and bauxite. In red mud, the difficulty is enhanced by the amorphousness of many phases in the matrix that renders the analysis by X-ray diffraction (XRD) difficult. Spectroscopic techniques, other than XRD, such as Raman and infrared (FTIR) spectroscopies, have been evaluated for bauxite but there are no results published about

their uses for red mud analyses [Ruan et al., 2001]. Non-spectroscopic methods such as selective extraction by wet chemistry, Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC) [Authier-Martin et al., 2002; Ostap 1984, Du Toit 1970] have also been tested. Until now, many techniques have given us boehmite levels in red mud but there is no consistency from one technique to another and it is difficult to determine which one gives an acceptable indication of the reality.

It has been known for more than thirty years [Du Toit, 1970] that gibbsite and boehmite, which are thermally unstable minerals, could be quantified by measuring their behaviour as a function of temperature. By measuring the heat of dehydroxylation of a known amount of red mud, one could determine gibbsite content based on a previously elaborated calibration curve. However, these methods show results of questionable quality due to interference caused by the presence of goethite (FeOOH) and desilication products (DSP/sodalite). In addition, unpublished results obtained in our lab indicate that synthetic gibbsite and boehmite, which are often used as calibration standards, may have a heat of dehydroxylation different than that of primary gibbsite and boehmite. Furthermore, boehmite samples of different geographic origins, and thus of different crystallite size and purity, may have significant differences in their heat of dehydroxylation. Using DTA, Du Toit [1970] was able to demonstrate the impact of crystallite size on the peak shape as well as the difference in dehydroxylation temperature for reprecipitated minerals when compared to primary minerals.

A new avenue that was left unexplored up to recently is thermogravimetry analysis (TGA). Unlike DSC and spectroscopic approaches, TGA is a primary method that does not stand on the quality of a calibration curve. The water loss due to dehydroxylation could happen at lower temperature, on a larger range of temperature and at a different rate between different primary or reprecipitated boehmite. Even in these conditions, this measurement is still accurate. The progress in this analytical field has been enormous in the recent years. Among the improvements brought to TGA, one could mention the higher precision balances, the presence of auto-samplers that increase the productivity and the software developments that allow data treatments that were laborious until now. TGA has seldom been applied to red mud. A study found in the literature was about determination of

Table 1: Elemental composition of bauxite samples A and B by x-ray fluorescence

Bauxite	XRF (%)							LOM (%) ± 0.1
	Al_2O_3 ± 0.6	Fe_2O_3 ± 0.2	SiO_2 ± 0.06	TiO_2 ± 0.06	CaO ± 0.02	Na_2O ± 0.01	Others ± 0.08	
A	50.9	17.8	1.56	1.87	0.04	0.04	0.45	27.0
B	54.2	12.8	1.49	3.39	0.01	0.03	0.50	27.4

iron phases in red mud by following oxidation reactions of a reduced sample [Piga et al., 1995]. In the ceramic industry, Sglavo et al. [2000] have well characterised the thermal behaviour and dehydroxylation species as a function of temperature, but there was no attempt to quantify each of these phases. There was another study related to TGA for red mud that focussed on the dehydration process occurring at low temperature [Alp and Goral, 2003]. This study has demonstrated that dehydration is completed only at 229°C. Finally, a study has revealed the major effect of pressure upon peak resolution [Papp et al., 1977]. The authors have shown that resolution on DSC and TGA curves is much better at low pressure (10^{-5} Torr).

Alcan Arvida R&D Centre recently bought a high-sensitivity thermogravimetric analyser to replace its previous 15-year-old instrument. Using this instrument, it has rapidly been proven that boehmite, and other hydroxylated phases contained in red mud, may be analysed with a better precision than achieved in the past. This observation has led to a research program to eventually produce a mass balance of the phases present in red mud. In this paper, the early and very encouraging developments under this program will be exposed. Results for boehmite in red mud samples obtained under two conditions, one case where there is no boehmite reversion and another case where boehmite reversion has occurred during digestion, will be presented. Finally, a tentative mass balance of the different phases present in red mud samples, obtained under these two conditions and originating from bauxite samples from two different origins, will be discussed.

2   Experimental methods

2.1   Red mud generation

In this paper, two different bauxite samples, labelled A and B, were chosen. Table 1 presents their elemental composition. One of the main differences between these bauxite samples is that sample A is a trihydrate bauxite whilst sample B is a high-monohydrate bauxite.

To generate the corresponding red mud samples, bauxites A and B were digested in pure caustic into pressurised vessels (Parr model 4715 CN, USA). Before digestion, the bauxites were dried at 105°C for 16 hours, ground to less than 150 µm (100 mesh) and divided into the required fractions in order to produce representative sub-samples of the whole sample. Digestion parameters were carefully controlled to avoid (e.g. red mud samples A1 and B1) or to favour boehmite reversion (e.g. red mud samples A2 and B2). Vessels were placed in an Alcan rotary heater (ALEXX, STAS-Unigec, Canada) and heated at 150°C. Vessels were cooled under running water. All slurries were then quantitatively recovered with water and centrifuged. Solids (red muds) were recovered and washed a few times with a KCl solution to avoid soda contamination from caustic solution. Finally, the red mud samples were dried overnight in a laboratory oven, weighed and ground to less than 150 µm and stored in a dessicator. A gravimetric mud factor (MF) was calculated.

2.2   Red mud pre-treatments

Red mud samples were leached with sodium dithionite to eliminate goethite, which causes interference in TGA analysis. While stirring on a hot plate, red mud was added to a hot solution (75°C) of sodium citrate and sodium bicarbonate. Small portions of sodium dithionite were added while temperature was kept at 75°C, followed by one hour of stirring at the same temperature. After the dithionite leaching procedure, the slurry was quantitatively transferred with water into bottles and centrifuged. The solid fraction was recovered, washed with a KCl

solution and centrifuged. Then, it was carefully recovered and dried overnight at 85°C in a laboratory oven. The dried residue was weighed and a gravimetric mud factor (Dithionite MF) was determined.

The red mud was also pressure-digested at 150°C, at the proper alumina-to-caustic ratio to eliminate precipitated bayerite and/or undigested gibbsite. The contribution of the digested gibbsite/bayerite was minimal as confirmed by potentiometry analysis of the solution.

2.3   Chemical analyses

A wet chemical method was used to determine total extractable alumina (TEA) in red mud. In the first step, mud samples were leached with saturated SO_2 solution to eliminate desilication products (DSP/sodalite). Leached samples were then pressure-digested at 225°C in caustic solution (5 M NaOH) for 30 minutes. The pulp was recovered from the reactor and filtered. TEA content was directly determined using $CDTA/ZnSO_4$ titration for alumina determination on an aliquot portion of the filtrate.

X-ray fluorescence (XRF) analysis was carried out on a Philips PW 2400 series XRF spectrometer equipped with an Rh tube. Prior to analysis, all samples were fused with a flux and cast into a glass disk. The X-ray diffractometer (XRD) used in this study is a Siemens D5000 equipped with a cobalt source. Prior to analysis, red mud samples were ground to less than 44 µm (325 mesh) and pressed in a plastic sample holder.

The TGA/SDTA 851^e (Mettler-Toledo, USA) thermogravimetry analyser used in this study was equipped with a small low-temperature furnace. Prior to analysis, red mud samples were dried overnight at 105°C in a laboratory oven. About 20 to 30 mg of the dry red mud samples were placed into alumina crucibles. Samples were then heated from 30°C to 1100°C in a nitrogen atmosphere at a heating rate of 10°C/minute.

2.4   Interpretation of TGA results

Thermogravimetry analysis is a technique that consists in the weighing of a sample whilst this sample is submitted to a controlled temperature programme. Different phenomena could change the weight, which include the dehydration, the thermal decomposition and the reaction with a reactive gas. In the case of red mud samples, the dehydration or moisture removal is the first to occur. Then, dehydroxylation of gibbsite and/or bayerite, goethite, boehmite and other compounds will occur according to the following reactions:

$$2\ Al(OH)_3 + Heat \rightarrow Al_2O_3 + 3\ H_2O \qquad (1)$$
$$2\ FeOOH + Heat \rightarrow Fe_2O_3 + H_2O \qquad (2)$$
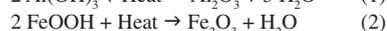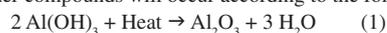$$2\ AlOOH + Heat \rightarrow Al_2O_3 + H_2O \qquad (3)$$

Figure 1 shows a typical TGA curve for a red mud sample. A first derivative could then be applied to the TGA curve to obtain what is called a DTG curve, which is simpler to interpret. However, the quantitative measurement is done on the TGA curve. Different inverted peaks can be observed on a DTG curve. These peaks represent thermal modification of the sample, mainly due to dehydroxylation in the case of red mud. It is generally recognised that, for a particular transition, the species crystallite size will set the temperature at which a signal is observed. As an example, for gibbsite, a loss of water at 250°C is characteristic of smaller crystals whereas a transition at 300°C is characteristic of larger crystals. As a consequence, a broad peak will be the characteristic of a large distribution of crystallite sizes. Many other reasons could also have an impact on the peak shapes. However, the crystallite size is certainly the factor that has the highest impact in the case of DTG of red mud.
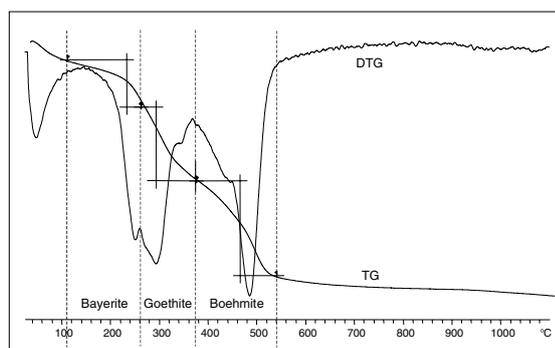
Figure 1: TGA and DTG curves for aluminium phases quantification in red mud. These thermograms were obtained under a nitrogen atmosphere at a heating rate of 10°C/min between 30 and 1100°C. The presence of bayerite is due to precipitation during handling of the solution.

3 Results and discussion

3.1 *Red mud characterisation*

Table 2 presents the red mud elemental composition determined by X-ray fluorescence (XRF) as well as the mud factor obtained by gravimetry. The mud factor represents the ratio of the weight of dry red mud recovered over the initial weight of bauxite. The gravimetric mud factor values are very close to those obtained by XRF analysis based on the iron oxide content. XRF mud factors of 0.287, 0.336, 0.295 and 0.382 were obtained for samples A1, A2, B1 and B2 respectively. Mud factor could be used as a primary indicator of boehmite reversion. It increases when boehmite reversion occurs due to precipitation of additional boehmite crystals. Also, high red mud factor may be an indication of incomplete digestion – a hypothesis that must be validated by XRD or TGA analyses.

3.2 *Thermogravimetric analyses*

3.2.1 *Sample analyses*

Four red mud samples produced with the method described above were analysed by TGA. The four derived TGA curves (DTG) are presented in Figure 2. Between 20 and 150°C, the samples are losing water from moisture. Then, many peaks are present in the region between 200 and 350°C. These are due to bayerite around 250 and 290°C, to goethite around 300°C and 320°C, and to a minor unknown compound at 350°C. The presence of bayerite instead of gibbsite was confirmed by XRD. This mineralogical phase is present in red mud obtained from laboratory unstable Bayer solutions and is not present in industrial red mud samples. The unknown compound with a maximum decomposition rate at 350°C is present in small amounts and it is not a form of goethite as confirmed by various chemical attacks. Since it is present as a small shoulder on goethite peak, its contribution is unfortunately included in the goethite concentrations reported and slightly overestimates the goethite contribution.
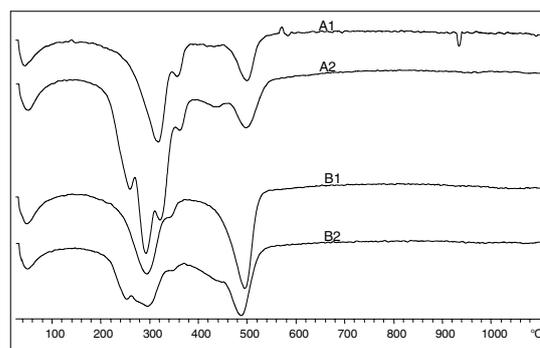

Figure 2: DTG analyses of red mud samples A1, A2, B1 and B2. These curves were obtained under a nitrogen atmosphere at a heating rate of 10°C/min between 30 and 1100°C.

The boehmite dehydroxylation region starts at around 450°C. The maximum rate of decomposition is around 500°C and varies with boehmite concentration as well as with sample origin. In samples from sources other than bauxite samples A and B, maximum decomposition rates as low as 440°C were observed. However, the maximum decomposition rate of boehmite occurs generally at 500°C. At 430°C, a distinct peak is observed for sample A2 and a shoulder is present for sample B2 around the same temperature. These peaks are due to boehmite dehydroxylation as revealed by XRD analyses but they are probably of a much smaller crystallite size than corresponding primary boehmite. They were not present in A1 and B1 samples and could probably be related to boehmite reversion, a finding that will be discussed in the following sections.

There is no peak between 600 and 1100°C. It is common to observe peaks in that region for plant red mud samples and in some laboratory tests. That region shows peaks, among others, related to calcium carbonate decomposition. However, on purpose, no lime was added during our laboratory tests.

3.2.2 *Sample pre-treatment*

Peak attributions on TGA and DTG thermograms were done by some selective dissolution of mineralogical phases present in red mud samples. A first selective dissolution was carried out by digesting red mud samples at an appropriate alumina-to-caustic ratio. Under these conditions, a selective attack of bayerite is achieved while goethite and boehmite remain intact in the sample. The solid sample obtained is then analysed by thermogravimetry. An example of the thermogram obtained is presented in Figure 3. One could see that the small shoulder present in the untreated sample thermogram at temperatures lower than 300°C has disappeared. This suggests that the shoulder was due to bayerite. The bayerite removal was then confirmed by XRD.

Table 2: Elemental composition of four red mud samples by XRF. The results are expressed on a mud basis.

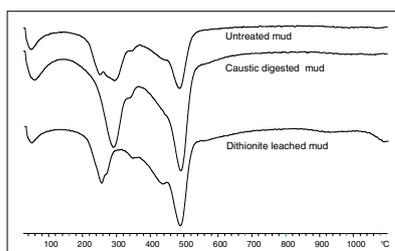| Red mud samples	XRF (%)							LOM (%) ± 0.1	Mud factor (gravimetric) ± 0.005
	Al_2O_3 ± 0.6	Fe_2O_3 ± 0.2	SiO_2 ± 0.06	TiO_2 ± 0.06	CaO ± 0.02	Na_2O ± 0.01	Others ± 0.08		
A1	15.9	62.0	3.88	6.24	0.14	1.43	2.05	8.3	0.284
A2	25.1	52.9	2.31	5.37	0.11	0.35	1.57	12.2	0.336
B1	28.3	43.4	3.74	11.1	0.03	1.08	2.02	10.2	0.295
B2	39.9	33.5	2.52	8.57	0.02	0.60	1.67	13.1	0.387

Figure 3 DTG analyses of red mud B2, which was: A) untreated, B) treated with a caustic digest at an appropriate alumina-to-caustic ratio, and C) treated with a sodium dithionite leaching method. These curves were obtained under a nitrogen atmosphere at a heating rate of 10°C/min between 30 and 1100°C

Selective goethite dissolution was then reached via a sodium dithionite leaching method. Afterwards, the solid sample was analysed by thermogravimetry. An example of the type of DTG thermogram obtained following this treatment is also presented in Figure 3. The peak with a maximum decomposition rate around 300°C on the untreated sample thermogram was removed and only the peak previously identified as bayerite remains. This confirms that this major peak at 300°C is related to goethite; in addition, the small non-identified peak at 350°C remains, confirming that it is not related to goethite, as mentioned above.

Goethite was determined quantitatively on the samples that were digested at a pre-selected alumina-to-caustic ratio. This ensures the complete removal of bayerite and leaves the goethite decomposition region free of this interference. Then, bayerite was calculated by difference between the untreated samples and the sample digested at a pre-selected ratio. This approach gave us the most reliable data for both bayerite and goethite. Determination of bayerite on the thermograms of samples treated with dithionite was also tried. However, even if the goethite removal is sufficient to do qualitative analyses, the presence of residual goethite, as demonstrated by XRD, was sufficient to cause a bias in the bayerite content.

For boehmite determination, the best results are obtained from the TGA curve of the sodium dithionite leached sample. This is due to a small overlap of the goethite in the region where boehmite starts its thermal dehydroxylation. The boehmite concentrations obtained via this methodology for the four samples are presented in Table 3. Boehmite is present at a concentration of 7.9% expressed as Al_2O_3 in sample A1, while the concentration reached 13.0% in sample A2. As mentioned above, a gravimetric mud factor was determined from the digestion that produced these red mud samples. Using this mud factor, the boehmite concentration may be expressed on a bauxite basis. On this basis, the boehmite concentration has doubled between the two experiments. The

same phenomenon has occurred in the red mud samples obtained from bauxite B. In that second case, boehmite concentrations up to 29.0% were observed in red mud.

3.2.3 DTG peak shapes and boehmite reversion

Figure 2 has shown the presence of a new boehmite peak on some DTG curves at the lower temperature end of the boehmite peak for the A2 red mud sample and the presence of a shoulder on the boehmite peak for the B2 red mud sample. In the literature [Authier et al., 2002], it is indicated that reverted boehmite presents smaller crystallite size. The presence of a new peak at lower temperature in conditions where boehmite reversion is known to occur suggests that these peaks are related to fine reprecipitated boehmite. The next step is to directly quantify this reverted boehmite from the low-temperature boehmite peak observed in the thermograms. This was tried and the results are presented in Table 4.

The values presented in Table 4 give indications that the low-temperature (LT) boehmite peak is related to boehmite reversion. The information presented in this table shows that reverted boehmite is generally characterised by small crystals, while the primary boehmite present in bauxite samples A and B is generally coarser. However, this difference is not distinctive enough to perform a direct quantitative analysis on these peaks individually. The best way to determine reverted boehmite remains calculation by difference from the total boehmite contents with and without reversion, A2–A1 and B2–B1.

3.3 Accuracy and precision

A mineralogical phase mass balance was performed on the four samples. Bayerite/gibbsite, boehmite and goethite were determined using TGA. Hematite was calculated from the difference between total Fe_2O_3 from XRF and the iron content in goethite from TGA. This calculation implied a hypothesis related to the aluminium substitution. Substitution between 0 and 30% were determined on bauxite from various sources. In this study, a mean value of 15% was taken. Careful washing of the red mud samples with KCl solution makes us believe that the total soda content in red mud is related to sodalite only. One of the unknowns is the sodalite formula. Based on Alcan knowledge, the following formula was used: $3(Na_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O)Na_2Al_2O_4$. $Al_2O_4^{2-}$ was used as the counter anion since there are no carbonate or anion impurities in the synthetic liquor used for these laboratory bauxite digestions carried out in this study. Quartz was calculated from total silica and silica present in the sodalite calculated previously from the sodium content. Finally, a contribution from the other oxides, including TiO_2, was added. The results of these calculations are presented in Table 5.

Table 3: Boehmite determination in red mud samples obtained from the sodium dithionite leached samples. Boehmite is determined by thermogravimetry between ~400°C and 550°C. Results presented on a red mud and bauxite basis.

Red mud samples	Boehmite (TGA) red mud basis (%, as Al_2O_3)	Boehmite (TGA), bauxite basis (%, as Al_2O_3)
A1	7.9	2.2
A2	13.0	4.4
B1	20.6	6.1
B2	29.0	11.2

Table 4: Boehmite concentrations from the low- and the high-temperature boehmite peaks on the thermograms obtained by TGA analyses for the four red mud samples (expressed as Al2O3 on a bauxite basis)

Red mud samples	Low temperature boehmite peak (%)	High temperature boehmite peak (%)	Total (%)
A1	0.6	1.6	2.2
A2	1.9	2.4	4.4
B1	0.0	6.1	6.1
B2	4.8	6.4	11.2

Table 5: Mass balance of the mineralogical phases present in the four red mud samples determined using TGA and XRF results

Mineralogical Phases	Red mud samples				Comments
	A1	A2	B1	B2	
Boehmite	9.4	15.5	24.6	34.8	TGA (dithionite leach mud)
Gibbsite/bayerite	0.4	11.5	1.4	6.2	TGA (caustic digestion mud)
Sodalite*	7.7	1.9	5.8	3.2	Na (XRF) / Na in sodalite
Quartz	1.8	1.8	2.1	1.6	Si total (XRF) – Si in sodalite
TiO2	6.3	5.8	11.3	8.7	XRF
Goethite	49.7	42.2	43.8	40.4	TGA (caustic digestion mud)
Hematite	22.4	19.2	8.4	1.1	Fe total (XRF) – Fe goethite
Minors	2.2	1.7	2.1	1.7	XRF
Total	99.8	99.6	99.5	97.8	

*Sodalite: $3(Na_2O \cdot Al_2O_3 \cdot 2\ SiO_2 \cdot 2H_2O)Na_2Al_2O_4$

Table 6: Accuracy and precision of TEA and TGA

Red mud samples	TGA (%)				TEA (%) ± 0.4	TEA –Bayerite (%, as Al2O3) ± 0.5
	Boehmite (as Al2O3) ±0.4	Bayerite (as Al2O3) ±0.07	Goethite (as Al2O3) ±0.1	Total (as Al2O3) ±0.4		
A1	7.9	0.27	4.4	12.6	9.9	9.6
A2	13.0	7.40	3.8	24.2	22.2	14.8
B1	20.6	0.90	3.9	25.4	23.6	22.7
B2	29.0	3.96	3.6	36.6	37.0	33.0

Table 5 shows that the mineralogical species add up between 97.8 and 99.8%. Based on the authors' experience, this is a very good mass balance for red muds. It must be admitted that these red mud samples were obtained under highly controlled conditions with no lime addition and using a synthetic solution, hence helpfully limiting the complexity of the system. However, a mass balance so close to 100%, suggests that individual determinations must be accurate. Based on these findings, we estimated that the accuracy of the boehmite content is good enough to draw conclusions from these values.

On the other hand, the goethite and hematite concentrations still remain uncertain. Further investigations using quantitative XRD to determine hematite content in red mud samples need to be carried out. Goethite should not have been attacked by the digestion conditions used to produce red mud samples. This means that the difference in concentration between samples 1 and 2 should be related only to the mud factor and, unfortunately, this is not the case. Since the proportion of water in goethite is small, minor errors on the loss of mass may produce large errors on goethite content. In addition, a proportion of 15% of the iron site in goethite was considered to be aluminium substituted. The proposed amount of substitution is acceptable but was not determined on these samples.

So far, wet chemical approach has been Alcan's standard method for boehmite content evaluation. It involves the digestion of the red mud at high caustic and high temperature in order to digest all the extractable alumina (TEA for total extractable alumina). However, this method could not give the boehmite content directly. Therefore, a DSC or a TGA analysis has to be performed in order to determine the presence and the level of gibbsite/bayerite. If present, the gibbsite/bayerite contribution was subtracted from the TEA value. In Table 6, a comparison between values obtained from TEA analyses and from TGA analyses is shown. In terms of accuracy for the total extractable

alumina, the two methods give absolute values within ± 2%. However, it is worth keeping in mind that TGA directly gives boehmite instead of making assumptions related to the mineralogical phases really present in the sample, as does the wet chemical approach.

In terms of precision, the error (expressed as two standard deviations) is 0.4 for both boehmite values (TGA and wet chemistry). When a correction is made to TEA for taking into account the bayerite/gibbsite content, this increases the accuracy but decreases the precision because it adds another error factor to the errors already related to this analysis. Even if the TGA method does not improve the precision, it allows a better understanding of the meaning of wet chemical TEA.

4 Conclusion and future work

In this paper, a new approach to determine boehmite phase in red mud samples was presented. A mineralogical phase mass balance that closed between 98 and 100 % was obtained. This indicates a very good agreement of the different methodology implied and gives credibility for the accuracy of the TGA measurement. TGA is a universal technique that determines concentrations of gibbsite/bayerite and boehmite as well as goethite. The method developed confirms that red mud samples produced from each bauxite sample contain variable concentrations of boehmite. In agreement with the TGA principles, the new reverted boehmite has smaller crystallites size. Although reverted boehmite and primary boehmite have different maximum degradation temperatures, this was not enough to completely discriminate them on the thermograms.

For accurate quantitative analyses of bayerite/gibbsite and boehmite, it is required to apply a sodium dithionite leach method to eliminate goethite. This makes the determination much longer but also more accurate. The previous standard method, which was a wet

chemical approach, gives the concentration of all extractable alumina species in one value called the Total Extractable Alumina (TEA). This method has never been validated by species determination with a specific methodology such as thermogravimetry. TEA accuracy could be questioned since it gives the sum of boehmite, gibbsite and aluminium-goethite. Both methods give similar precision, but the advantages of TGA over TEA make the former a promising approach. However, this method needs more validation before it is applied at a larger scale. The main reason is that the samples analysed so far were obtained from digestion in synthetic liquor without lime addition, which is different from real Bayer plant samples.

The results presented in this paper represent only a portion of a much larger project. The methodology presented is still in development and is currently being applied to bauxite of other origins. Then, it would be applied to plant red mud samples to see the impact of the various Bayer additives currently used.

Acknowledgement

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