

BOEHMITE REVERSION: PREDICTIVE TEST AND CRITICAL PARAMETERS FOR BAUXITES FROM DIFFERENT GEOGRAPHICAL ORIGINS

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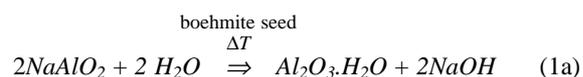
Abstract

Under low temperature Bayer conditions, boehmite present in bauxite is not dissolved and may promote the precipitation of dissolved alumina as re-precipitated boehmite on natural boehmite seed. This paper will describe a laboratory test developed to characterize and classify bauxites in their respective propensity to promote boehmite reversion. Using such analytical tools as differential scanning calorimetry and transmission electron microscopy, we can quantitatively measure the alumina losses linked with boehmite reversion and infer which boehmite characteristics are most prone to promote this reaction. Results obtained for bauxites of widely different origins will be presented and we will show, with a few selected examples, how these laboratory results relate to actual plant data. The test limitations will also be discussed.

1. Introduction

Aluminum-producing companies rely on the Bayer process for the production of smelter-grade alumina utilizing, to do so, the bulk of bauxites mined worldwide. Alumina is considered a commodity product on the market and, for this reason, cost reduction is critical in this industry. One of the cost factors that has an impact on the efficiency of the process and that the Bayer plants are aiming to control is alumina losses. To do so, it is essential to have a basic understanding of the forces driving the chemical reactions affecting alumina losses and occurring throughout the Bayer process. There can be several sources of alumina losses, to name only two, premature gibbsite precipitation and boehmite reversion [Authier-Martin et al., 2001]. This paper deals exclusively with boehmite reversion.

The main caustic-soluble alumina-bearing minerals present in tropical bauxites are gibbsite (also referred to as trihydrate or hydrate, $\gamma\text{-Al}(\text{OH})_3$ or $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) and boehmite (also referred to as monohydrate, $\gamma\text{-AlOOH}$ or $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$) [Wefers & Misra, 1987]. Boehmite is not attacked by caustic under low-temperature digestion conditions. However, since boehmite has roughly half the apparent solubility of gibbsite in hot caustic solutions, alumina trihydrate will precipitate from solution as boehmite on any boehmite seed present in the bauxite, under the digestion and mud separation conditions prevailing in a low temperature process (Equation 1a or 1b). This precipitated boehmite, termed boehmite reversion, represents a process alumina loss and boehmite reversion can be a significant problem when processing some bauxites [Ostap, 1984].



or more correctly



In the literature, very few authors have dealt directly with boehmite reversion [Ostap, 1984; Du Toit, 1970 & Lamerant & Perret, 2002]. In other cases, boehmite reversion is inferred to from the total alumina or gibbsite losses [Lepetit, 1986; Suss et al., 1992, Harato et al., 1982]. Also,

few others have assessed the extent of boehmite reversion at different stages such as predesilication, digestion and decantation [Lepetit, 1986; Harato et al., 1982]. Moreover, test conditions to study boehmite reversion in a laboratory set-up are often used to match, as closely as possible, actual operation parameters of the plant for which the tests are performed. Plant liquor is often used. Consequently, plant conditions and plant liquors being rarely identical from plant to plant and even from test to test, it complicates the comparison of results over a long period of time. Finally, it cannot help distinguish the bauxite impact from the process effect. For these reasons, a standard predictive test was needed as a better long term fundamental option.

This paper reports our findings on which boehmite characteristic is more prone to promote boehmite reversion for bauxites of widely different origins under a standard predictive test using DSC, XRD and TEM to characterize natural and precipitated boehmite. A few selected examples will also show how these laboratory results relate to actual plant data.

2. Boehmite analysis

At Alcan, boehmite levels were traditionally determined by wet chemical methods in a four-step procedure:

- i. High temperature caustic digestion in a pressure vessel under standard conditions approaching the Bayer process;
- ii. Dissolved alumina determination by titrimetry ($\text{Al}_{\text{G+B}}$);
- iii. Low temperature caustic digestion in a pressure vessel under standard conditions approaching the Bayer process;
- iv. Dissolved alumina determination by titrimetry (Al_{G}).

To obtain exclusively the alumina associated with gibbsite and boehmite in bauxite, the attack of quartz at high temperature and the associated loss of alumina needed to be accounted for. Boehmite content was then calculated from $(\text{Al}_{\text{G+B}}) - (\text{Al}_{\text{G}})$. Therefore, the quantification of boehmite reversion required several determinations since the feed material (bauxite) and the end-product (red mud) needed to be measured. The compounded error over these determinations, though quite acceptable for high boehmite

levels (well above 5% b. Al_2O_3), became statistically significant when dealing with low boehmite bauxites (<2% b. Al_2O_3), this error being roughly at 95% confidence level, just below 1%.

Since 1970, thermal analysis methods, traditionally used for thermodynamic applications, have slowly evolved into quantitative analytical tools [Du Toit, 1970]. Differential thermal analysis (DTA), or more recently differential scanning calorimetry (DSC), can be used to quantitatively measure gibbsite and boehmite in red muds [Wehrli & Kane, 1993]. This analytical procedure requires that the instrument be calibrated with primary standards such as pure synthetic gibbsite or boehmite doped at different levels in alumina. Theoretically, to quantify boehmite reversion, a direct method such as DTA or DSC would require two determinations, boehmite in bauxite and boehmite in red mud, with a compounded error roughly half the one experienced with wet chemical methods, that is around 0.5%. In practice, a sample pre-treatment is required in both cases to remove interfering species:

- for the bauxite sample, a low temperature caustic digestion under a controlled A/C ratio to remove gibbsite and kaolinite,
- for the red mud sample, a mild acid leach to remove the desilication products.

In the early 1980s, x-ray diffraction (XRD), a method of choice to identify mineralogical phases was extensively used to quantitatively measure gibbsite and boehmite in bauxites [Andrews & Crisp, 1980]. Over the years, the accuracy of this instrumental method was questioned on three grounds:

- effect of crystallinity on the quantitative assessment;
- limit of detection, estimated at > 0.5%, assuming high crystallinity;
- effect of amorphous phases in red muds on the quantitative assessment.

Our most recent development work has confirmed that DSC with sample pre-treatment is the most accurate and precise method for boehmite determination in boehmite reversion experiments. Therefore, this is the method on which all results reported below are based on. Moreover, whereas the boehmite peak in bauxite appears to be quite symmetrical, it was confirmed that boehmite reversion, i.e. re-crystallized boehmite, could be visually detected on thermograms of red muds through the appearance of a broad leading front on the natural boehmite peak, as already reported elsewhere [Du Toit, 1970].

3. Boehmite characterization

Boehmite reversion is driven, among other things, by a seeding effect of the natural boehmite present in the feed bauxite. The seeding effect is intrinsically related to the available specific surface area (SSA) of the boehmite crystals. Factors known to contribute to this SSA are: (i) boehmite content, (ii) boehmite crystallite size and (iii) crystallite dispersion [Authier-Martin et al., 2001 & Ostap, 1984]. It is then essential to determine, besides the boehmite content, the crystallite size and the morphology of the boehmite present in the bauxite. Boehmite crystallite size can be accurately determined by XRD [Smith et al., 1988]. Since boehmite size is typically well below 1 μm , morphology features and crystallite dispersion have to be assessed by Transmission Electron Microscopy (TEM) [Authier-Martin et al., 2001] — following an extensive sample pre-treatment to pre-concentrate the boehmite phase. TEM can also be used to visually detect boehmite reversion through the appearance of small crystallites on the natural boehmite crystals. However, the use of DSC for this last application is much more straightforward and has

been used throughout this work instead of TEM. Therefore, DSC, XRD and TEM have been used to measure and explain the results of our predictive test on several bauxites.

4. Standard predictive test for boehmite reversion

In the past, a standard indirect procedure developed in Alcan plants looked at two options when anticipating boehmite reversion during digestion tests:

- for small and large boehmite reversion trends, evaluate the increase in actual bauxite charge to reach a target ratio compared to the original calculated charge;
- for large boehmite reversion trends, calculate the difference between the target ratio and the actual ratio achieved for the calculated bauxite charge.

Both approaches were somewhat blind, with the first one requiring extensive laboratory work while the second option relied heavily on operator/method precision. Moreover, the digestion conditions used were specific to the plant operating conditions prevailing at the time of the test. Therefore, it complicated the comparison of results over a long period of time and did not really help distinguish, on the long run, the bauxite impact from the process effect.

In the general direct procedure we then elected to use, as a standard predictive test, conditions typical of current Alcan Bayer plants, fed with Jamaican bauxite, since historical data had already been collected using very similar conditions. In this predictive test, a synthetic liquor of a composition approaching again the Jamaican plant conditions was used. Therefore, the test conditions depicted in Figure 1 can be labelled as those of a standard Jamaican boehmite reversion test and can be summarized as follows :

- i. ground bauxite is pre-desilicated and digested under the given specific tests conditions;
- ii. resulting enriched liquor is held at settler temperature for a given period of time;
- iii. boehmite level in the resulting red mud is compared to the level originally found in the feed bauxite as measured in both cases by DSC.

These conditions were then applied to any bauxite source or mix tested. The advantages of this procedure are three-fold:

- i. a direct determination of boehmite in feed material and end product;
- ii. a single test based on the calculated bauxite charge, whether or not the final target ratio is reached;
- iii. a standard procedure used for any bauxite tested.

5. Results and discussions

5.1 Initial tests

In our initial series of tests, five bauxites from three geographical origins, with different boehmite contents ranging from <<1% to 8% b. Al_2O_3 and with widely different boehmite crystallite sizes and morphologies were selected. Table 1 shows the general characteristics of the test bauxites.

Table 2 presents the extent of boehmite reversion and gibbsite losses calculated after digestion for the 5 test bauxites when these bauxites were submitted to the standard predictive test described in Figure 1. Under the standard conditions tested, it clearly appears that we are dealing with three different classes of bauxites:

- two bauxites with barely detectable reversion/loss (Group I): one bauxite with no detectable boehmite and one standard metal grade bauxite;
- two bauxites with some gibbsite losses but different boehmite reversion (Group II);
- one bauxite with extensive reversion/loss (Group III).

So far, the predictive test has shown that it was:

- reproducible over a wide range of boehmite characteristics (precision <0.2% on boehmite determination);
- selective, since it clearly sets apart the propensity of different bauxites for boehmite reversion;
- accurate, since it reproduced the extent of boehmite reversion observed historically during different pilot plant or full plant trials for the test bauxites.

5.2 Applications to current bauxite feeds

Having succeeded in showing that the predictive test we selected was reliable, we extended its application to current bauxite feeds in an attempt to:

- predict the extent of boehmite reversion for different day-to-day plant feeds;
- predict the extent of boehmite reversion for specific bauxites used in mixed feeds;
- correlate our findings with plant data.

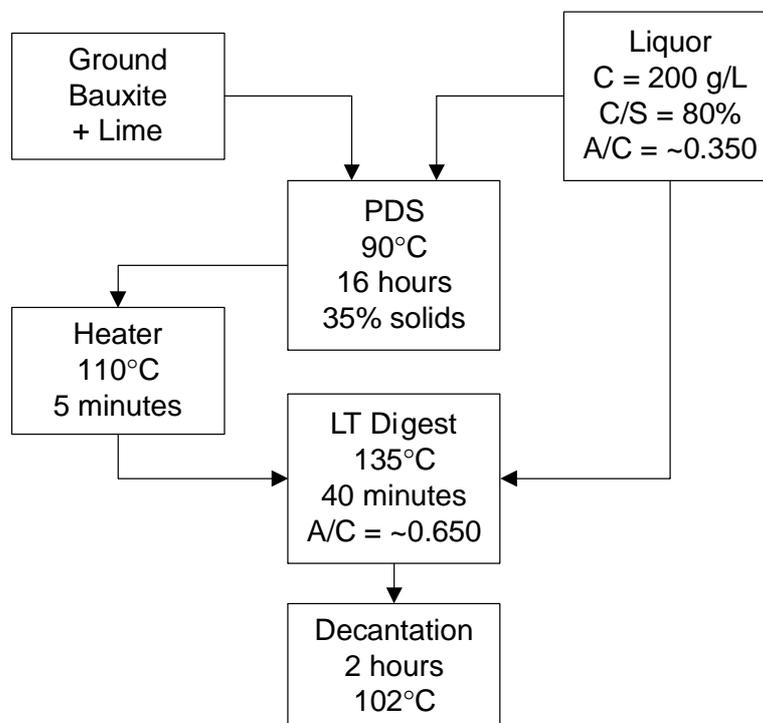


Figure 1 — Standard predictive test for boehmite reversion
 PDS = Pre-desilication, C = Caustic (g/L Na₂CO₃), C/S = Causticity, LT = Low Temperature

Table 1 — Descriptive features of the initial bauxites tested

Bauxite type	Boehmite content in bauxite (% b.Al ₂ O ₃) ¹	Boehmite crystallite size (L _c , Å) ²	Key morphology features ³
Brazil	Not detected	—	—
Jamaica-1	0.4	357	Uniform crystallite size, finely dispersed and discrete crystallites
Jamaica-2	2.5	550	Uniform crystallite size, stacked rods
Jamaica-3	3.5	528	Uniform crystallite size, finely dispersed and discrete crystallites
Africa-1a	8.0	644	Broad crystallite size distribution, coarse, blocky well crystallized boehmite

¹ as determined by DSC and confirmed by BQUANT™ [Kimmerle et al., 1997]

² as determined by XRD

³ as determined by T.E.M.

Table 2 — Extent of boehmite reversion and gibbsite loss for different types and classes of bauxites

Bauxite type	Boehmite content in bauxite (% b.Al ₂ O ₃)	Extent of boehmite reversion after digestion (%)	Gibbsite loss due to boehmite reversion after digestion (%)	Bauxite classification
Brazil	Not detected	Not detected	Not detected	Group I
Jamaica-1	0.4	300	3	Group II
Jamaica-2	2.5	16	2	Group II
Jamaica-3	3.5	170	14	Group III
Africa-1a	8.0	< 1	<< 1	Group I

Table 3 summarized the reversion figures after digestion and decantation for seven additional bauxites.

Table 3 — Extent of boehmite reversion for different current bauxite feeds

Bauxite type	Boehmite content in bauxite (% b.Al ₂ O ₃)	Extent of boehmite reversion after digestion (%)	Extent of boehmite reversion after decantation (%)
Africa-2	0.6	Not detected	Not detected
Australia-1	0.9	Not detected	90
Australia-2a	1.9	—	110
Africa-1b	3.1	Not detected	Not detected
India-1a	5.0	Not detected	Not detected
India-1b	5.6	4	4
Australia-2b	8.9	—	50

India-1a (Group I bauxite) and India-1b (Group II bauxite) are two plant feeds that show different propensity for boehmite reversion, clearly indicating a bauxite effect. For a rather small difference in boehmite content, the two bauxite feeds behave quite differently in regards to boehmite reversion, a trend that was also observed in the plant but could not be attributed indiscriminately to the bauxite characteristics or the process conditions.

Australia-1, Africa-1b and Africa-2 are part of a plant mix that varies in composition. In this case, none of the feed bauxite seems to promote boehmite reversion until decantation. Only Australia-1a shows detectable reversion after decantation. The impact of Australia-1 in a bauxite mix was confirmed by plant data as shown in Figure 2. The increase of boehmite reversion in tail end muds is evident from the size of the leading front to the boehmite peak in these two thermograms as the amount of Australia-1 increases in the mix. This plant evidence, confirmed by limited but conclusive laboratory tests done with a similar mix, shows that boehmite reversion is not synergetically promoted or hampered by mixing different bauxites but follows a simple law of dilution.

Finally, by using bauxites from the same geographical origins with different boehmite levels, we were able to demonstrate that bauxites from the same origin show similar trends in boehmite reversion. Africa-1a (Table 2) and Africa-1b (Table 3) showed no detectable boehmite reversion, even though the boehmite content ranged from 3 to 8%. For Australia-2a and Australia-2b, which exhibit similar measurable trends, we can also observe a linear correlation in boehmite reversion when going from 2 to 9% b.Al₂O₃ in the feed bauxite.

5.3 Dominant boehmite characteristics ruling boehmite reversion

From the overall results presented in Tables 1 through 3, we then attempted to infer which boehmite characteristics are most prone to promote boehmite reversion. As already explained under Boehmite characterization, the extent of boehmite reversion is ultimately related to the boehmite seed activity or SSA, a bulk parameter linked to boehmite content, crystalline size and morphology.

It is clear, from Table 2, that boehmite content is not the overall ruling factor, a conclusion also confirmed by the additional data given in Table 3. As can be seen also from Table 4, crystalline size and morphology certainly appear to be more dominant factors but may both go towards:

- maximizing boehmite reversion (Jamaica-1),
- minimizing boehmite reversion (Africa-1a and Jamaica-2).

They can also be mutually exclusive and thus again ultimately reduce the extent of this reaction as in the case of Jamaica-3.

It is then most revealing to compare the TEM micrographs presented in Figure 3 that illustrate even more clearly the above conclusions. Of particular interest is the case of Jamaica-2 (Figure 3a) versus Jamaica-1 (Figure 3b) where the combined effect of coarser, stacked rods to reduce seed activity (or SSA) can be better understood. These findings were also confirmed during the tests on current feed bauxites by looking also at the TEM micrographs. Figure 3c shows the typical boehmite morphology and crystallite size (coarse blocky well crystallized) of Africa-1a and Africa-1b, two Group I bauxites with no

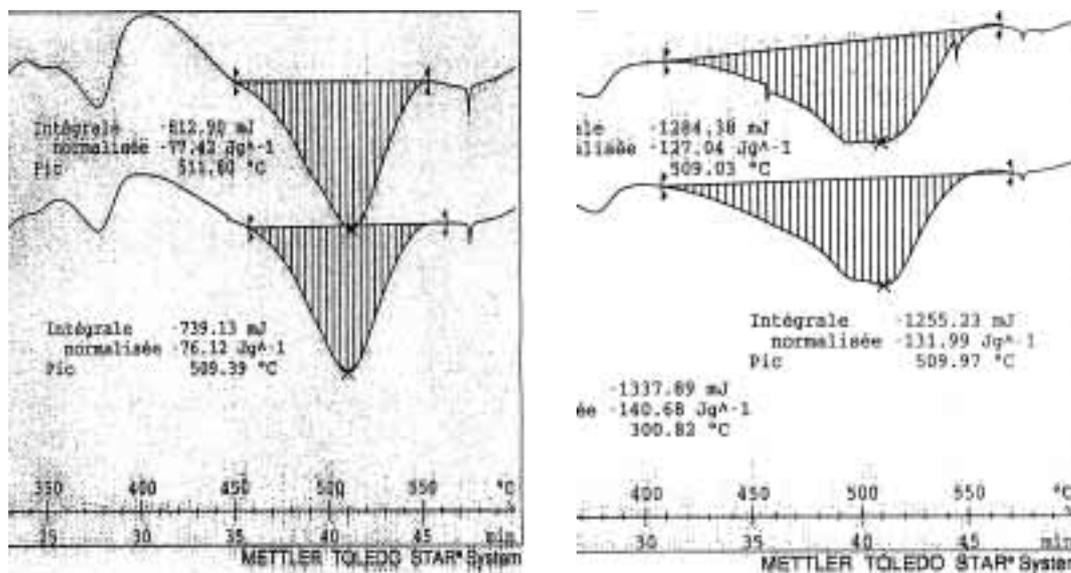


Figure 2 — Thermograms of tail end muds containing two different levels of bauxite Australia-1 in a bauxite mix (a) No Australia-1 in mix (b) Some Australia-1 in mix

detectable boehmite reversion. Figure 3d reveals typical morphology features of Australian bauxites, (dispersed discrete multi-size crystallites), bauxites with quite detectable levels of boehmite reversion.

Finally, under the predictive test described, it is also possible to state at which stage boehmite reversion is most likely to happen. In most cases, we found that the digestion stage is the critical step in the promotion of boehmite reversion, with little or no detectable reaction at decantation. However, in one case (Australia-1), boehmite reversion was only but extensively detectable at the decantation stage. On the other hand, for some Jamaican bauxites, it was found that, even though no detectable boehmite reversion could be found after predesilication, PDS may act as an activation step for the boehmite seed.

5.4 Test limitations

The proposed predictive test has very few limitations covering a wide range of conditions (from PDS to decantation) being applicable to a wide range of boehmite content (<<1%-10%) and accurately predicting the so-called bauxite effect. However, in order to obtain these results, it is critical that the boehmite analysis by DSC follows a systematic approach as described below:

- i. first, quantify the boehmite level in the bauxite feed and set preliminary boundaries for the boehmite peak integratio;
- ii. run the boehmite analysis by DSC for all the tests using bauxites from the same origin, with the above integration limits;

Table 4 — Correlation between boehmite content, crystallite size, morphology and boehmite reversion

Bauxite type	Boehmite in bauxite (% b.Al ₂ O ₃)	Boehmite L _c (Å)	Morphology	Boehmite reversion (%)
Jamaica-1	0.4	357	Finely dispersed discrete mono-size crystallites	300
Jamaica-2	2.5	550	Stacked rods	16
Jamaica-3	3.5	528	Finely dispersed discrete mono-size crystallites	170
Africa-1a	8.0	644	Blocky well crystallized multi-size crystallites	<<1

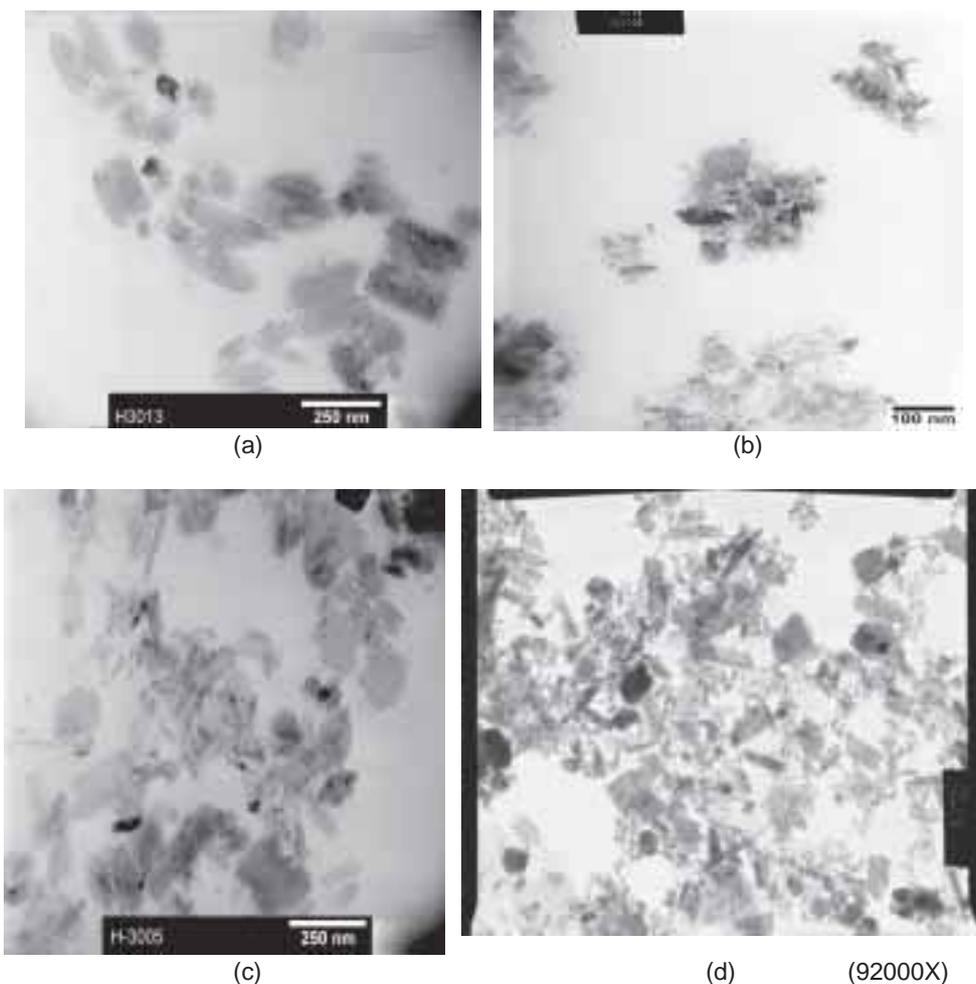


Figure 3 — T.E.M. micrographs showing different morphological features of four bauxites
 (a) Jamaica-2: Stacked rods
 (b) Jamaica-1: Finely dispersed discrete monosize crystallites
 (c) Typical Africa-1: Blocky well crystallized multi-size crystallites
 (d) Typical Australia Bauxite: dispersed discrete muti-size crystallites

- iii. fine tune the integration limits according to the red mud thermograms;
- iv. re-apply these new set limits to all the samples originating from the same bauxite family.

6. Conclusions

A selective, reproducible predictive test that can accurately predict the extent of boehmite reversion due to the bauxite effect has been described. The procedure is based on a simulation test that includes pre-desilication, digestion and decantation steps under one set of standard plant conditions. The critical boehmite determination is done by Differential Scanning Calorimetry, allowing accurate and precise boehmite quantification in the feed bauxite and the resulting red mud, as well as visual confirmation of boehmite reversion, once set limits of peak integration have been fixed.

The predictive test was applied to several bauxites to show the different propensities of various bauxites to promote boehmite reversion. These findings successfully

matched plant data and therefore helped those plants to refine their bauxite mix strategy.

The extent of boehmite reversion found by this predictive test was then related to bauxite features such as boehmite content, crystallite size and morphology. It was found that morphology and size are the predominant factors over boehmite content. However, it is still unknown why certain bauxites are more sensitive to pre-desilication and decantation than to digestion in the promotion of boehmite reversion.

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