

## IMPACT OF JAMAICAN BAUXITE MINERALOGY ON PLANT OPERATIONS

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### Abstract

Over the period 2003 to 2006 the bauxite feed to the Kirkvine refinery has undergone a dramatic change in composition with severe impact on plant performance. Surprisingly, the change in composition is not directly evident from the XRF analysis of the major elements, which showed that the total  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$  and LOI contents of the bauxite remained largely unchanged. A more detailed examination however, shows a remarkable change in  $\text{Al}_2\text{O}_3$  distribution over the various minerals, indicative of a substantial change in bauxite mineralogy. Over the same period significant changes in plant behaviour were experienced with respect to, notably alumina recovery, mud settling and liquor chemistry.

### Introduction

The Kirkvine refinery is a low temperature digestion plant located in the centre of Jamaica. It commenced operations in 1953 and is the oldest alumina refinery on the island. Over the period 2003 to 2006 the performance of the refinery came under intense pressure because of mounting difficulties in the mud circuit. The main direct causes were a gradually increasing mud factor and a gradual deterioration of the mud settling characteristics. The mud factor increased because the available alumina content in the bauxite decreased, from about 45% in early 2004 to about 42% by the middle of 2006, while at the same time the alumina recovery dropped by more than 6%. Plant production became constrained by the capacity of the mud circuit and the production rate decreased by 9%.

### Change in bauxite composition

The XRF based elemental composition of the bauxite does not reveal any clues about the underlying drastic change in the bauxite character (see Figure 1). The main constituents, total  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{SiO}_2$  and LOI, remained on their usual levels. The only change was an increase in  $\text{P}_2\text{O}_5$ , which doubled, from 0.6 to 1.2%. However, below that surface a different picture emerges when the mineralogy is examined, e.g. on the basis of the alumina distribution over the various mineral phases (see Figure 2).

#### Available alumina

$\text{Al}_2\text{O}_3$  present as gibbsite dropped from 44.5% to 41%. The decrease in available alumina content was less, from 45% to 42%, because the crandallite content of the bauxite had increased. Crandallite,  $\text{CaAl}_3(\text{PO}_4)_2(\text{OH})_5 \cdot \text{H}_2\text{O}$ , readily dissolves in Bayer liquor and is the source of soluble phosphate in Kirkvine bauxite. Phosphate is removed from the liquor through reaction with calcium. The reaction requires considerable more calcium than the crandallite itself can deliver. The extra calcium can be supplied for this purpose in just about any form [1]. The reaction product, carbonate-apatite does not contain alumina, hence all

alumina in crandallite reports as available alumina. Nowadays 2.5% of the available alumina in Kirkvine bauxite is associated with crandallite. This is 1.1%  $\text{Al}_2\text{O}_3$  on dry bauxite basis.

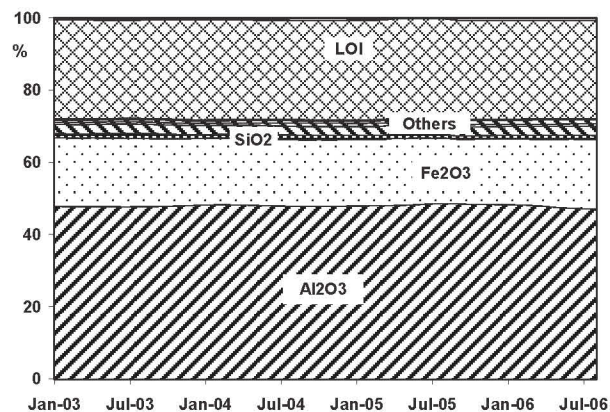


Figure 1. Elemental composition of Kirkvine bauxite feed.

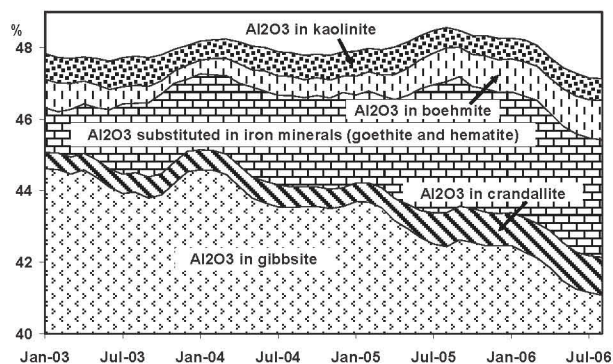


Figure 2. Alumina distribution in Kirkvine bauxite feed.

#### Aluminous goethite

The iron substitution for alumina is usually much greater in the goethite lattice than in the hematite lattice. This is also the case in Kirkvine bauxite. In the absence of sufficient data before February 2005, no differentiation has been made in Figure 2 between alumina in goethite and alumina in hematite.

The alumina content in iron minerals has increased significantly, from 1.2% to 3.6%, which clearly underlines the sharp increase in goethite content of the bauxite. At the same time the colour of the bauxite mined changed from reddish to yellowish, an observation which Jamaican alumina producers generally regard as bad news.

The term used hereafter for the alumina in iron minerals is "goethitic alumina", although strictly speaking this includes a modest amount of alumina in hematite.

Relationship with P<sub>2</sub>O<sub>5</sub>

Total CaO in bauxite over the review period has typically been 0.6 – 0.7% except for an excursion between March 2004 and March 2005 when it was higher, with peak values just over 0.9%. Calcium is essentially present in two forms: calcite and crandallite. The distribution of CaO over these two minerals is shown in Figure 3.

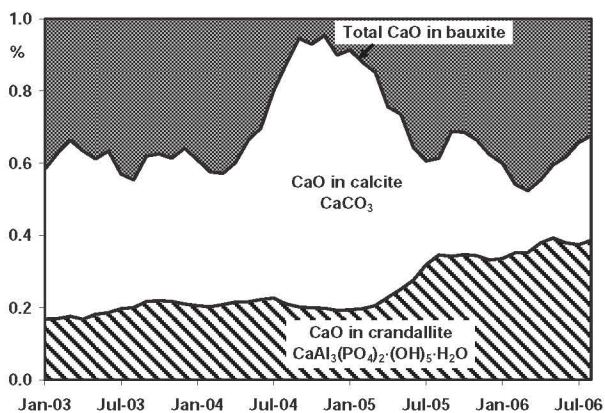


Figure 3. *Calcium distribution in Kirkvine bauxite feed.*

As already shown in Figure 2, the increase in crandallite coincides with the increase in alumina tied-up with iron minerals. This suggests a certain association between crandallite (soluble phosphate) and goethite. The correlation is not perfect, but definitely there (see Figure 4). This is in line with Grubbs [2] observation that yellow bauxites contain more P<sub>2</sub>O<sub>5</sub> than red bauxites.

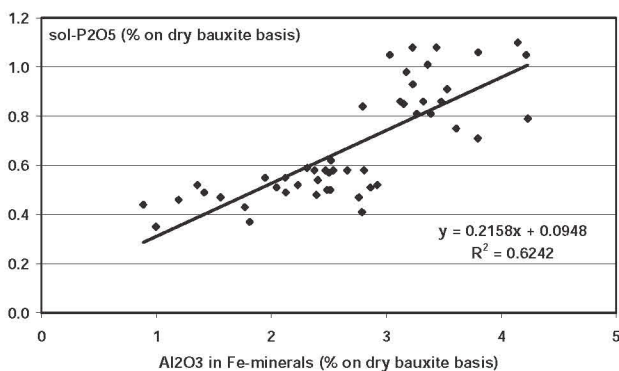


Figure 4. *Correlation between sol-P<sub>2</sub>O<sub>5</sub> and goethetic alumina.*

**Impact on Plant Operations**

The change in bauxite mineralogy has impacted on various aspects of refinery operation, namely on alumina and soda losses, liquor causticity and mud sedimentation characteristics. This paper focuses on the effects that have a predominant liquor chemistry flavour, namely the impact on alumina loss and the impact on liquor causticity.

**Impact on Alumina Loss**

The increase in alumina loss is broken down over the various categories in Figure 5. Gibbsite precipitation in the mud circuit, which increased from 3% to 5%, represents the largest loss. This is closely followed by boehmite reversion (according to the analytical methods applied), which showed the largest increase, from 1.5% to 4 – 4.5%.

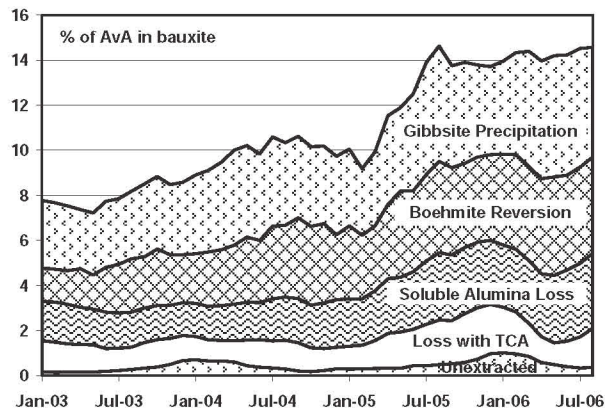


Figure 5. *Alumina losses per category.*

Gibbsite precipitation losses

The possible reasons for the rise in gibbsite precipitation losses in the mud circuit that are to be considered include:

1. Increased supersaturation;
2. Reduced stabilizing effect from calcium;
3. Increased unextracted gibbsite in the mud;
4. Increased presence of other seed material in the mud;
5. Increased mud factor.

1. Supersaturation

The increase in losses could not be explained on the basis of supersaturation, as can be seen in Figure 6. The digestion A/C ratio had been reduced considerably since the end of 2005, but the losses stayed at a high level.

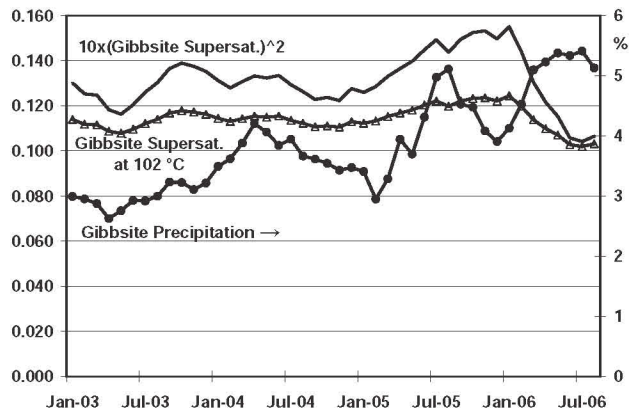


Figure 6. *Gibbsite losses with mud and supersaturation.*

2. Liquor stability, soluble calcium and phosphorus control

It is a generally accepted fact that soluble calcium has a stabilizing effect on pregnant liquors [3]. Phosphorus in liquor is thought to interfere with this process, because it readily reacts with the calcium in liquor to form carbonate-apatite [1]. Hence, a

lack of control over phosphorus could lead to unstable liquors in the mud circuit. The  $P_2O_5$  concentration in liquor is considered to be acceptable when it is less than 0.2 g/L. This level has not been exceeded at Kirkvane since the second half of 2003. Figure 7 shows that  $P_2O_5$  in liquor was higher in 2003 than in more recent times, marked by excessive gibbsite precipitation losses. Furthermore, the lime charge for phosphorus control has not been below a safe internal target, thus, phosphorus control does not offer an explanation.

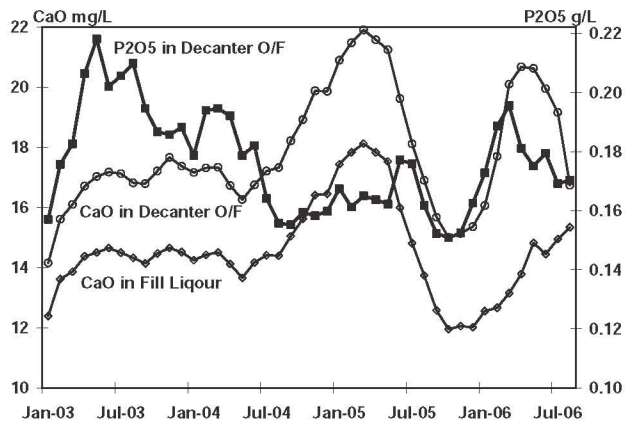


Figure 7. CaO in liquor and  $P_2O_5$  in liquor.

From a theoretical point of view, the CaO concentration in liquor is dependent on the type of calcium containing solid phase compounds present, that it tries to be in equilibrium with. The reaction of lime in Bayer liquor leads to a series of reactions whereby, in adherence to thermodynamic principles (Ostwald Rule of Stages [4]), the least stable compound is formed first, and again according to those principles the equilibrium CaO concentration in liquor is highest for this least stable solid compound. Rosenberg has identified hydrocalumite, a hemihydrate, as such intermediate reaction product in the reaction of lime to tricalcium aluminate and to calcium carbonate [5]. Similarly, in the absence of any of said lime products, but in the presence of  $P_2O_5$  in liquor, CaO in liquor tries to equilibrate with carbonate-apatite, one of the most stable calcium containing compounds, hence tending to drive CaO in liquor down. In turn, the concentrations of some other liquor species, notably fluorine, may influence the  $P_2O_5$  concentration, because of the tendency of these species to be incorporated in phosphorus precipitates [3].

Indeed, there is a general belief that high  $P_2O_5$  levels in liquor correspond with low CaO levels [3]. Figure 7 demonstrates that this not necessarily always applies. Although over the period July 2003 to July 2005 in broad terms CaO in liquor increased while  $P_2O_5$  in liquor decreased, the opposite is true outside this time period.

Common wisdom is the rule of thumb that CaO in liquor decreases when causticity (C/S) increases and this can be explained on the basis of a reaction mechanism involving hemihydrate [6]. Thus, the analysis would not be complete without considering causticity as a parameter in play. The plant situation lends itself well for testing this rule, because the change in liquor causticity was not insignificant. Figure 8 shows that, although during certain time periods the rule seems to apply, very

often this has not been the case. Fill liquor CaO increased from 12.0 to 15.3 mg/L over the period October 2005 to August 2006, while the causticity increased from 81.6 to 87.8%. At this causticity CaO in liquor was higher than in January 2004 when the causticity was 71.2%. It is recognized that other factors, such as the presence of certain organics in the liquor, play a role as well [7, 6].

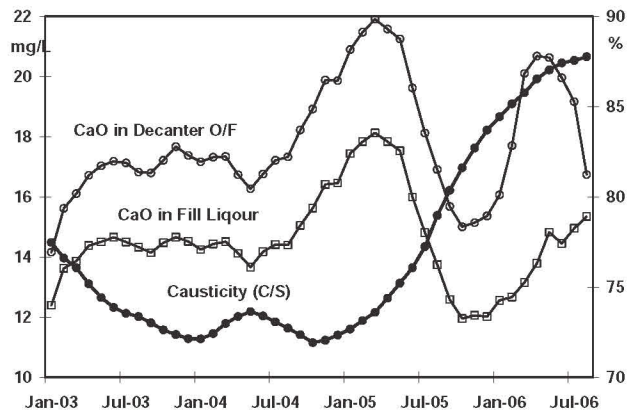


Figure 8. CaO in liquor and causticity.

As mentioned, the CaO concentration in liquor depends on the type of calcium containing solid phase compounds present, with the least stable compounds yielding the highest CaO levels. By nature, the least stable compounds also have the shortest life time. Figure 9 shows that the %calcite in the mud (largely originating from the bauxite feed) seems to have no obvious correlation with CaO in liquor, except during the period September 2004 to September 2005. Interestingly, during that time period the external causticiser was on-line, hence part of the calcite was freshly produced with its intermediate reaction product hydrocalumite in direct contact with mud wash liquor flowing up the mud wash trains. Furthermore, the gibbsite precipitation curve shows a pronounced dip in the referred period, which supports the general finding in the industry that the presence of causticiser sludge in mud reduces gibbsite precipitation in the mud circuit. Obviously, the dip around January 2006 must have a different reason, which is discussed hereafter.

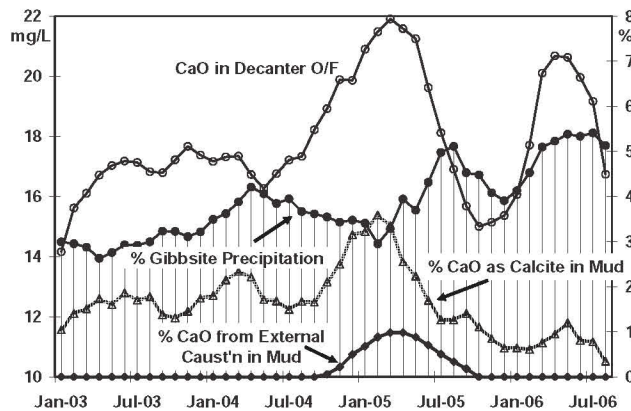


Figure 9. Effect of lime products on CaO in liquor and on liquor stability.

### 3. Unextracted gibbsite in the mud

The percentage of unextracted gibbsite in the mud, shown in Figure 5, is in fact from the available analysis ex the first digester. Already at that point the extraction is better than 99%. No correlation could be found between the gibbsite precipitation losses and the data for unextracted gibbsite.

### 4. Other seed material

The increase in gibbsite precipitation losses appears to coincide with the above mentioned increase in goethitic alumina and  $P_2O_5$  content of the bauxite, as Figure 10 demonstrates. The correlation with soluble phosphate, present in the mud as carbonate-apatite, is more pronounced than that with goethitic alumina over the time period since mid 2005. However, the goethite crystallite size reduced over that period from roughly 380 micron to roughly 320 micron, keeping goethite high on the list of suspects.

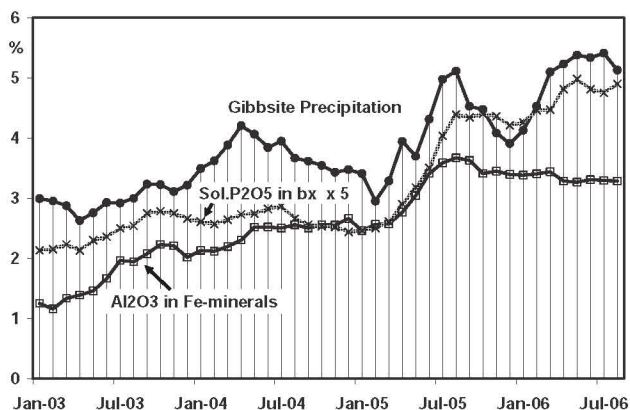


Figure 10. Gibbsite losses with mud and goethitic alumina and soluble phosphate in bauxite.

The question arises whether gibbsite precipitation is encouraged directly, through goethite and/or apatite acting as seed, or indirectly, through poorer settling characteristics leading to prolonged contact time between liquor and mud surface area, which acts as a substrate for gibbsite precipitation in general.

The seeding effect of minerals in mud on gibbsite precipitation has been previously investigated [8]. The studies showed that goethite and sodalite had a seed effect, but the effect of the latter was minor. A paper by Lepetit also highlights the seeding effect of goethite [9]. Laboratory testwork at Kirkvine confirmed that the gibbsite precipitation losses from a simulated 1<sup>st</sup> washer liquor at 85 °C were higher when the liquor was contacted with a mud with a high goethite content than when this took place with a mud with a lower goethite content. Overall, it can be concluded that the increase in goethite content in the bauxite feed can be held largely responsible for the increase in gibbsite precipitation in the mud circuit, through the seeding activity of the goethite.

Settling performance may have played a (secondary) role behind the dip in the gibbsite precipitation curve at the end of 2005, when a bauxite grade was processed with more favourable settling characteristics due to the higher hematite content (see Figure 11). The reduction in gibbsite losses was somewhat greater than expected on the basis of the reduction in bauxite goethite content alone.

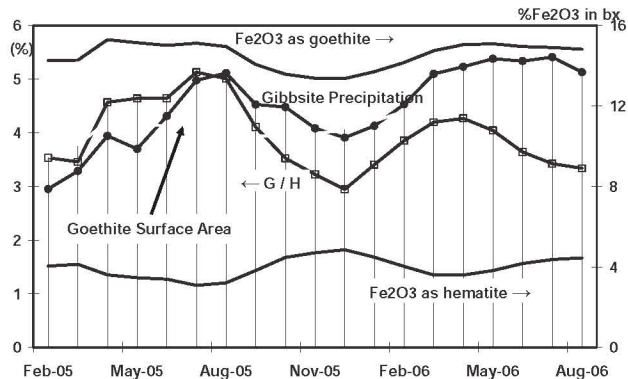


Figure 11. Gibbsite losses with mud around end of 2003.

### 5. Mud volume

The mud factor has increased by 28% over the review period while gibbsite precipitation losses increased by 86%. Consequently about 1/3<sup>rd</sup> of the increase losses can be attributed to more liquor having been in contact with the mud and 2/3<sup>rd</sup> to the increase in seed activity of the mud itself.

### Boehmite reversion losses

The investigation into the possible reasons for the sharp increase in boehmite reversion follows lines similar to those for the increase in gibbsite precipitation. Again no clues could be found in the areas of supersaturation (with boehmite) and lime chemistry. The obvious parameters to scrutinize are the boehmite content in bauxite and boehmite crystallite size. The relationship with these parameters is shown in Figure 12.

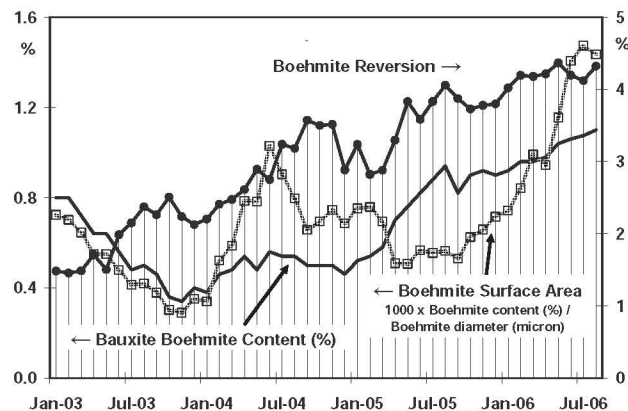
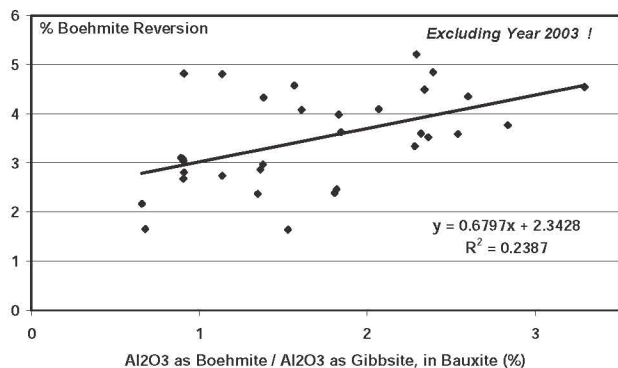


Figure 12. Boehmite reversion and boehmite in bauxite.

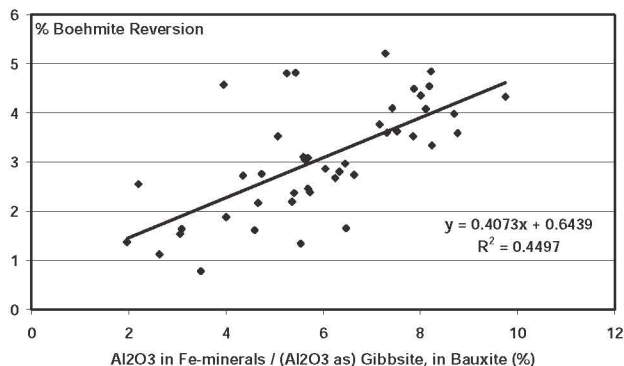
The boehmite reversion trend over the year 2003 is the opposite of what one would expect: Boehmite content decreased and crystallite size did not change, while boehmite reversion almost doubled. When the year 2003 is ignored, the trend is better in line with boehmite content, although not with boehmite crystallite size (or boehmite surface area, shown in the graph).



**Figure 13.** Boehmite reversion versus boehmite content in bauxite.

However, XY-plots do not provide convincing evidence that the boehmite content in the bauxite is the sole factor behind the increase in boehmite reversion, even with the year 2003 excluded, as shown in Figure 13.

In contrast, boehmite reversion plotted against goethitic alumina shows a much stronger correlation (see Figure 14). The nature of this correlation is not clear. A literature search did not reveal any mention of goethite as a possible seed, except for one paper where also activity constants were calculated [9]. In a more recent detailed study into critical parameters for boehmite reversion, goethite was not identified as one of them [10], neither in another recent study on boehmite reversion [11]. Therefore, it is unlikely that goethite is a seed for boehmite reversion. The correlation must have a different reason. Because of the apparent association of  $P_2O_5$  with goethite (see Figure 4), it is not surprising that boehmite reversion correlates rather strongly also with  $P_2O_5$  in bauxite. This moves the pointing finger to carbonate-apatite as the possible culprit, but no hard evidence or supporting information on this matter has been found either. Possibly part of what is being measured as boehmite reversion, via two different methods, is not boehmite reversion after all, but the consequence of alumina extraction from the goethite during (a) LT available alumina determination on the bauxite and (b) HT total extractable alumina determination on the mud. The subject of boehmite reversion is under investigation, including the analytical techniques underlying the quantification thereof.



**Figure 14.** Boehmite reversion versus goethitic alumina in bauxite.

Soluble alumina loss

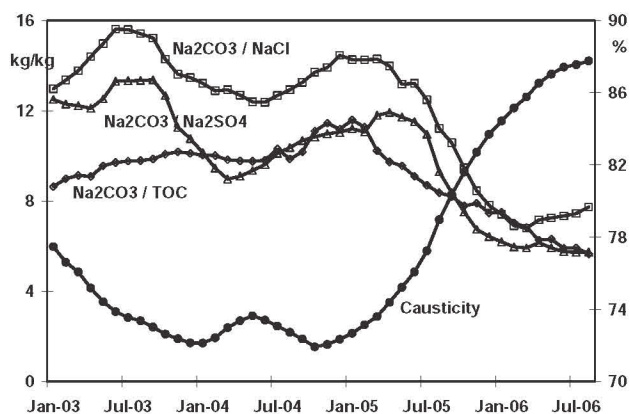
Soluble alumina loss, which more than doubled, increased not only directly because of the mud factor increase by 28%, but also indirectly because of the reduction in unit net wash (e.g. increased bauxite moisture input with increased bauxite factor) with common excursions into negative territory. Mud circuit underflow densities did not change much, thus had relatively minor contribution to the increase. Obviously, the above also applies to soluble soda loss.

Alumina loss with lime products

The losses with tricalcium aluminate increased until November 2005, because of the increased dosage of lime for phosphorus control with increasing levels of soluble  $P_2O_5$  in bauxite. The target dosage was in great excess of stoichiometric requirement, for process security reasons, with the excess largely turning into tricalcium aluminate, especially when the causticity had increased as well. Since November 2005 lime usage has been rationalized, while still sufficient control over  $P_2O_5$  is being maintained (see earlier section).

**Impact on Liquor Causticity**

The liquor causticity remarkably increased from about 72% in early 2005 to 88% by April 2006. The external causticiser had been on-line intermittently during the 1<sup>st</sup> and 2<sup>nd</sup> quarter of 2005, but the causticity continued to rise thereafter. The rise in causticity over and above external causticisation cannot be explained purely on the basis of the large liquor losses as a result of the increasing mud factor and hurricane impact in October 2005. The replenishment of the liquor losses with fresh caustic would have affected the sulphate and TOC concentrations in plant liquor in the same way as the carbonate concentration, but, as Figure 15 shows, the ratios of carbonate over sulphate and carbonate over TOC dropped significantly, suggesting that there must be another or additional reason for the increase in causticity. The fact that the causticity continued to be high without external causticisation is further support for this conclusion.



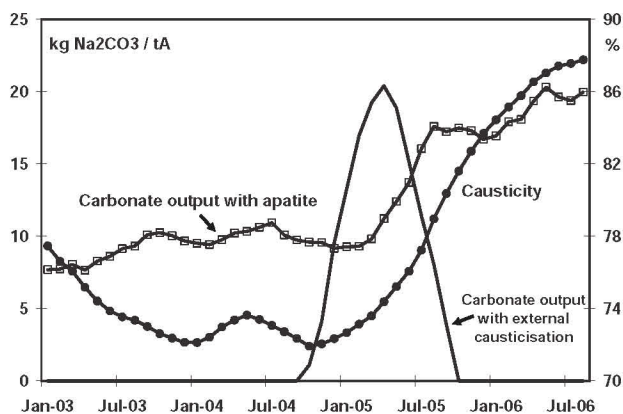
**Figure 15.** Change in liquor carbonate concentration relative to other liquor impurities concentrations.

The rise in causticity coincided with a sharp rise in soluble  $P_2O_5$  content of the bauxite as from March 2005 (see Figure 10). This is also shown in Figure 16, where the carbonate output with carbonate-apatite is depicted. The chemical composition of

carbonate-apatite is variable, e.g. in the carbonate to phosphate ratio, and can be described as follows:



Much credit goes to Ostap for his comprehensive research work that revealed how the composition is a function of liquor composition and digestion conditions [1]. In Figure 16 a conservative carbonate to phosphate ratio of 1 has been assumed, although in principle the ratio can be much higher.



**Figure 16.** Causticity and chemical blowdown of carbonate from process.

### Conclusion

The bauxite feed to the Kirkvine refinery underwent a significant change in mineral composition over the last few years, effecting production capacity and process efficiencies. The change particularly concerned an increase in the presence of aluminous goethite and soluble phosphate (crandallite). The consequences in the area of process chemistry have been discussed in this paper. Although many questions surrounding the process chemistry have been answered, certain important aspects are still not well understood and are subject of on-going study.

### Acknowledgement

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### References

1. S.Ostap; "Lime Reactions in the Bayer Process", Volume IV, Alcan International LTD, February 1988.
2. D.K.Grubbs, S.C.Ibby, J.K.Rodenburga and K.A.Wefers; "The Geology, Mineralogy and Clarification Properties of Red and Yellow Jamaican Bauxite", Jour. Geol. Soc. Jamaica, Proceedings of Bauxite Symposium, No. IV, June 23-36, 1980.
3. E.B.Teas and J.J.Kotte; "The effect of impurities on process efficiency and Methods for impurity control and removal", Jour. Geol. Soc. Jamaica, Proceedings of Bauxite Symposium, No. IV, June 23-36, 1980, 100-129.

4. R.A. van Santen; "The Ostwald step rule", Jour. Phys. Chem. 88 (24), 1984, 5768-5769.
5. J.H.N.Buttery, V.A.Patrick, S.P.Rosenberg, C.A.Heath and D.J.Wilson; "Thermodynamics of Hydrocalumite Formation in Causticisation", Light Metals, 2002.
6. S.P.Rosenberg, D.J.Wilson and C.A.Heath; "Some Aspects of Calcium Chemistry in the Bayer Process", Light Metals, 2001, 19-25.
7. B.I.Whittington; "The Chemistry of CaO and Ca(OH)<sub>2</sub> relating to the Bayer Process", Hydrometallurgy 43, 1996, 13-35.
8. T.Harato, T.Ishida and K.Yamada; "Autoprecipitation of Gibbsite and Boehmite", Light Metals, 1982, 37-50.
9. J.G.Lepetit; "Autoprecipitation in the Bayer Process", Light Metals, 1986, Vol. 2, 225-230.
10. M.Authier-Martin, R.Girard, G.Risto, D.Verville; "Boehmite Reversion: Predictive Test and Critical Parameters for Bauxites from Different Geographical Origins", Proc. Of the 6<sup>th</sup> International Alumina Workshop, 2002, 109-114.
11. J.M.Lamerant and Y.Perret; "Boehmite Reversion in a Double Digest Process on a Bauxite Containing Trihydrate and Monohydrate", Light Metals, 2002, 181-184.

12. J.C.Winch; "Lime Requirements for the Production of Alumina from Jamaican Bauxites", Jour. Geol. Soc. Jamaica, Bauxite/Alumina Symposium, 1971, 70-72.