

APPROACHES TO THE PROCESSING OF JAMAICAN BAUXITE WITH HIGH GOETHITE CONTENT

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Abstract

Jamaican bauxite deposits can broadly be classified into two types, catchment and hillside, depending on their form and topographic setting. The major iron phase in catchment deposits is hematite, while in hillside deposits this is aluminous goethite. The difference in topographical setting between the catchment and hillside deposits has affected their degree of weathering, hence the degree by which the bauxite deposits have undergone secondary surficial alteration under the influence of ground water and humic acids. The dissolution and re-precipitation mechanism of surficial alteration has caused the original hematite and goethite in hillside bauxites to be transformed into aluminous goethite. Studies as well as plant experience have shown that aluminous goethite rich bauxites present several processing challenges especially under low temperature digestion conditions. This paper examines the major processing challenges and available approaches for their resolution. This is particularly important since the aluminous goethite rich bauxites become increasingly abundant in plant feeds as stocks of hematite rich deposits are getting depleted.

Geology

Geologically, Jamaican bauxite is considered to be 'young'. It is uncompacted and soil-like in nature, with deposits filling sinkholes or depressions in a karst limestone topography (Strahl¹, 1971; Grubbs et al.², 1980). The deposits are broadly classified into two types: catchment and hillside, depending on their typical characteristics that result from their topographic setting. The deposits consist primarily of gibbsite and iron oxides, with minor to trace amounts of boehmite, kaolinite, anatase and phosphate minerals (Grubbs et al.², 1980). Nordstrandite, a polymorph of gibbsite, has also been identified in Jamaican bauxite deposits (Davis³, 1973; Davis and Hill⁴, 1974; Davis⁵, 1976; Authier-Martin et al.⁶, 2001) and is typically associated with bauxites of relatively high kaolinite content (Davis and Hill⁴, 1974; Davis⁵, 1976).

The major iron phase in catchment deposits is hematite, which accounts for the red colour. Goethite present in these deposits shows a low substitution of aluminium within the goethite structure. Alumino-goethite is the dominant iron phase found in hillside deposits and accounts for the yellow colour. These differences stem from a lesser degree of weathering to which catchment deposits have been subjected to than hillside deposits. Weathering is characterised by a dissolution and re-precipitation

mechanism brought about by the passing through of rain water and therein dissolved humic acids (Grubbs et al.², 1980). In hillside deposits this has led to substantial transformation of hematite and goethite into poorly crystalline, highly aluminous goethite. Catchment deposits contain more syngenetic (primary) goethite, while in the hillside deposits more epigenetic (secondary) goethite is present. Hillside bauxites also show the increased presence of several minor and trace components, particularly P, Cr and Zn (Greenaway et al.⁷, 2013).

Substitution of aluminium into goethite in Jamaican bauxites has been recorded to be as high as 20 mol% (Wallen-Bryan⁸, 1998), while the maximum known substitution of aluminium in goethite is 33 mol% (Schulze⁹, 1984). Aluminium substitutes into the hematite structure to far lesser extent than into the goethite structure, with the maximum known substitution as high as 16 mol% recorded for Western Australian Darling Range bauxites (Anand et al.¹⁰, 1991). However, for Jamaican bauxites, there has been no substitution in hematite found for the samples studied.

Goethite compared to hematite in Jamaican bauxite has a smaller particle size and, by virtue of aluminium substitution, is also considerably less dense. This difference increases with increasing degree of substitution. While the density of pure goethite is 4.2 and that of hematite 5.26, a typical density of aluminous goethite is 3.2 (Ostap¹¹, 1983).

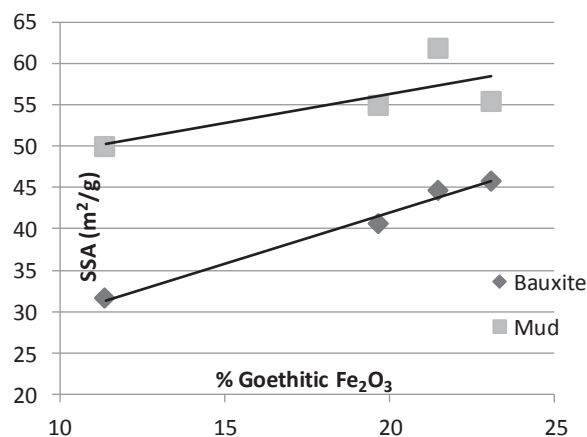


Figure 1. Relationship between specific surface area (SSA) and aluminous goethite content of bauxite and its corresponding mud.

The fact that particle size of goethite tends to be smaller than that of hematite is demonstrated in Figure 1, which shows that the specific surface area of bauxite and of the resulting mud increases with increasing percentage of iron minerals being goethite. One of the implications concerns mud rheology, with viscosity and yield stress increasing with increasing percentage of goethite. Not only particle size, via specific surface area, impacts on slurry viscosity, but also the density of aluminous goethite being lower than that of hematite contributes. The lower density in itself is reason for a higher slurry viscosity when comparing a goethite rich slurry with a hematite rich slurry on the basis of equal solids concentrations in weight percentage. This is because the viscosity of a slurry increases with the volume fraction that the particles occupy in the slurry, as is known since Einstein's¹² publication on Brownian movement in 1906.

Major effects of aluminous goethite

Effect on mud settling and handling

The iron oxides are chemically not altered during processing of bauxite in a low temperature Bayer plant. The iron oxides form the major fraction of the bauxite residue material that needs to be separated from the pregnant process liquor. Studies highlighting the relative differences in separation amenability between red and yellow bauxite residues have generally shown that red bauxite residue has much better sedimentation characteristics, owing to its larger particle size and higher density. As a logical consequence of the mud characteristic described, overall settling performance was found to improve with increased hematite to goethite ratio and with the inverse of specific surface area of the residue material (Strahl¹, 1971; Grubbs et al.², 1980). Exceptions to these general trends are apparent in the literature where such anomalies were thought to be related to the presence of very fine or amorphous phases (Li and Rutherford¹³, 1996; Wallen-Bryan⁸, 1998; Gomes et al.¹⁴, 2005). Work done by Kirwan et al.¹⁵ (2009), using Mössbauer spectroscopy on a limited set of Jamaican bauxite samples, was unable to confirm the presence of any iron phases other than hematite and goethite.

In many Jamaican plants the processing of the residue in the mud circuit is the rate limiting factor in the production cycle. In fact these plants are sometimes jokingly described as mud plants because of the emphasis on managing the production of mud rather than that of alumina.

With the advent of modern flocculants, in particular of the hydroxamate type, it became possible to settle bauxite residues with their iron content being exclusively aluminous goethite at acceptable rates, also under liquor decanter conditions. Furthermore, the high molecular weight polyacrylate flocculants now available from all the major suppliers are capable of settling these residues at even faster rates, however with poor overflow clarities. By combining both polyacrylate and hydroxamate – co-dosing – the best attributes of both types of flocculant are utilised. This has been demonstrated not only in the laboratory, but also in plant trials.

For example, in Kirkvine laboratory tests were conducted in which muds from bauxites from two locations with 18% iron, but with little or no measurable hematite content, were checked for their settling characteristics. These bauxites were digested under typical plant digestion conditions. The resulting muds were

allowed to settle using various flocculants under liquor decanter conditions. In addition, the settled muds were repulped and then settled under first washer conditions. Both muds settled at acceptable settling rates under both process conditions. Settling under liquor decanter conditions was satisfactory with hydroxamate as well as with polyacrylate flocculants. The difference between these two types of flocculant was the supernatant liquor clarity, which for polyacrylates, at 300 mg/L, was poor, while hydroxamate gave <90 mg/L.

Also tests were done using Ewarton bauxites. This time bauxites with various goethite contents relative to the total iron content (expressed as a percentage goethite) were subjected to settling tests and only hydroxamate flocculants were used. The results of the tests are shown in Figure 2(a). Again the settling rates were acceptable. Interestingly, there were no great differences in settling rate as a function of the percentage of goethite in the mud.

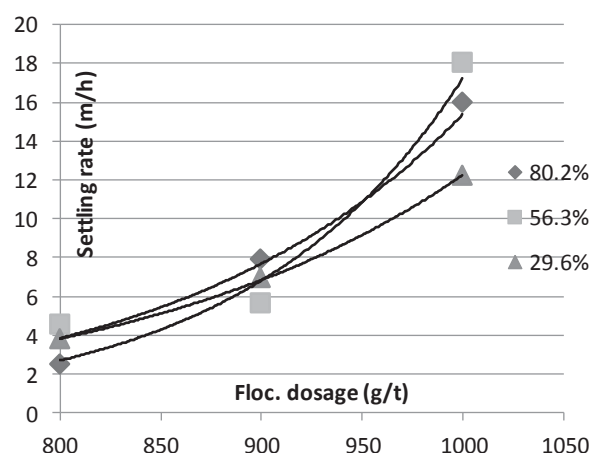


Figure 2(a). Settling rates, in metres per hour, of bauxite residues with various aluminous goethite contents, as a percentage of total iron, versus flocculant dosage, in grams per metric tonne of mud

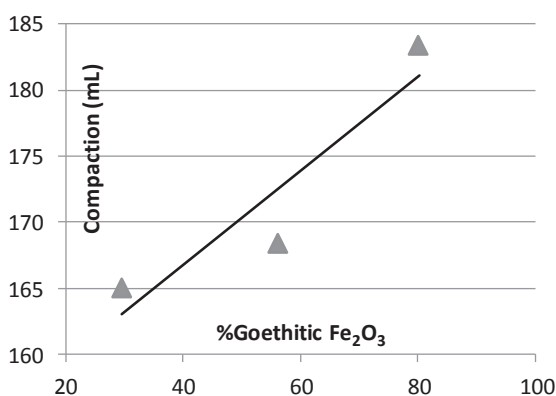


Figure 2(b). Volume, in cubic centimetre, occupied by mud residue after 30 minutes settling.

However, compaction decreased with increasing percentage of goethite, as shown in Figure 2(b), which depicts the volume occupied by the mud in the settling cylinder after 30 minutes of settling. Although part of the volume increase is the result of the

density of aluminous goethite being smaller than that of hematite (with approximately equal amounts of mud on a mass basis being generated), the largest contribution to the volume increase stems from a decrease in solids concentration on a volume/volume basis.

Despite this decrease in solids concentration the viscosity of the settled mud increased with increasing goethite content of the mud, at least for muds that have more than 50% of the iron minerals in the form of goethite (see Figure 3). This is because of the increased abundance of the finer goethite particles at the expense of the coarser hematite particles. Just as sands are known to lubricate mud, as long as their presence is not excessive (because then the opposite occurs: a sand bed is extremely viscous), also the coarser hematite particles lubricate the mud, thus their diminished presence increases viscosity.

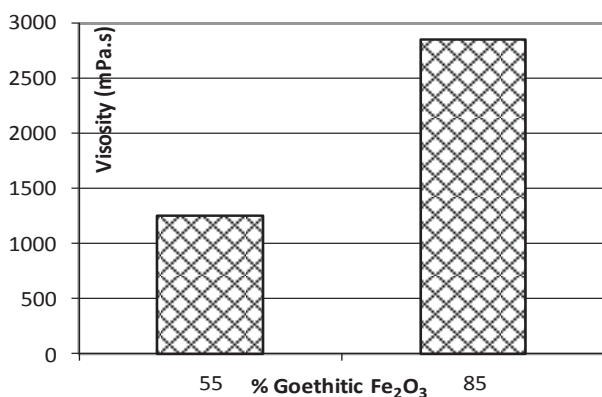


Figure 3. Comparative viscosity of two bauxites with different goethite content.

Effect on liquor stability in the mud circuit

Apart from adversely impacting on process efficiency via compaction and mud viscosity, the goethite content of the mud adversely impacts on process efficiency in yet another way, namely via liquor stability. Aluminous goethite appears to be an effective seed for alumina reversion (Harato et al.¹⁶, 1982; Lepetit¹⁷, 1986; Powell et al.¹⁸, 2012). The impact of aluminous goethite on plant process chemistry and efficiency in the Jamaican context has been subject of a previous study (Lawson et al.¹⁹, 2008). Peter Smith (CSIRO) has developed a method for determining the propensity of a mud to evoke alumina precipitation. In this method the mud is suspended at 50 g/L in a liquor of standard composition and temperature, while the alumina loss is monitored over a 24 hour period through periodic sampling.

Summary of the effects of aluminous goethite on process

In the foregoing it has been highlighted that modern flocculants have made it possible to settle high aluminous goethite residues with acceptable settling rates and overflow clarities, also under liquor decanter conditions. The remaining negative effects of aluminous goethite that have to be dealt with are:

- reduced compaction of thickener underflows;
- increased viscosity of thickener underflows;
- increased alumina reversion in the mud circuit because of the aluminous goethite seeding effect.

Remaining Jamaican bauxite reserves more goethite rich

Since the early days of exploration it was recognised that the mineralogy of Jamaican bauxite and its implications for the Bayer process stand out as being special. Since the 1950s there have been many publications detailing the effects of Jamaican bauxite species on the Bayer process. In 1984 Douglas et al.²⁰, saw the need to develop a classification system for Jamaican bauxites based on boehmite contents and goethite relative to hematite contents. This, was felt, would provide the basis for broad resource development planning including the allocation of bauxite reserves to specific Bayer plants with the aim of optimising process efficiency. Three distinct types were identified: Jamaica-1 (boehmite <3.0%), Jamaica-2 (boehmite >3.0% and 30% to 80% of the iron mineral as goethite) and Jamaica-3 (boehmite >3.0% and >90% of the iron mineral as goethite). Note that no specific classification is mentioned for the goethite contents not covered by these three types.

Low temperature Bayer refineries were built to exploit the Jamaica-1 type bauxite deposits. Since the reserves of this type of bauxite are steadily decreasing and have been subject to high-grading with respect to low goethite contents, it has become necessary to find ways of using these refineries for processing the remaining high goethite containing Jamaica-1 type bauxite and the other types of Jamaican bauxite still present. This paper discusses the possible approaches considered for meeting this objective.

Approaches in dealing with aluminous goethite in bauxite

There are three possible approaches for dealing with the issue of aluminous goethite in bauxite:

1. Exclude aluminous goethite from the process feed;
2. Modify the process to accommodate the presence of aluminous goethite;
3. Recover process losses, inflicted by aluminous goethite, at the end of the circuit.

Excluding aluminous goethite from the process

The two methods of interest are:

- a. Selective mining/blending;
- b. Thermal transformation of goethite to hematite in a pre-treatment step.

a) Selective mining/blending

Selective mining by excluding goethite from the bauxite feed has already been extensively practised and is not sustainable because ultimately only goethitic bauxite with little or no hematite will be left. A more sustainable approach is blending. This option, however, has practical limits as to the cost effectiveness of sourcing suitable blending material.

b) Pre-treatment

Thermal pre-treatment of bauxite is not unknown and has been tried even in the early days of the Bayer process. Usually part conversion of gibbsite to boehmite was suffered. While examining bauxite roasting as a method for reducing the input of organic carbon from bauxite into Bayer liquor, Rijkeboer²¹ (1993) found that under particular conditions (including a roasting temperature of approximately 500°C) aluminous goethite in bauxite can be thermally transformed to hematite without losing low temperature extractability of the (original) gibbsite and even obtaining a slight

Table I. Digestion conditions.

	Atmospheric	Normal
Digestion temperature (°C)	108	135
Digestion time (minutes)	120	35
Digestion caustic (g/L eqNa ₂ CO ₃)	250	250
Digestion charge ratio (A/C)	0.600	0.650

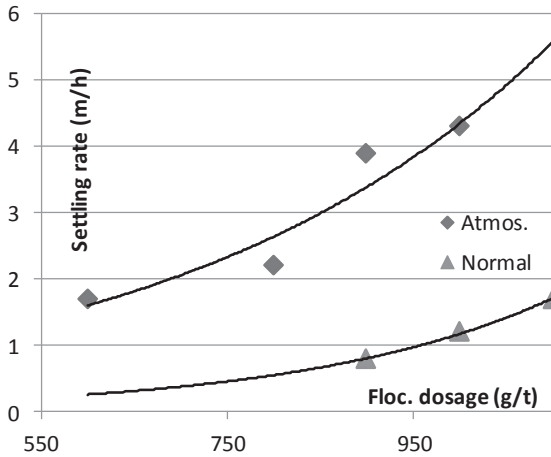


Figure 5(a). Comparative settling rates (metres per hour): Atmospheric vs. (normal) Low Temperature (135°C) digestion of bauxite with negligible hematite content. Flocculant dosage expressed in grams per metric tonne of mud.

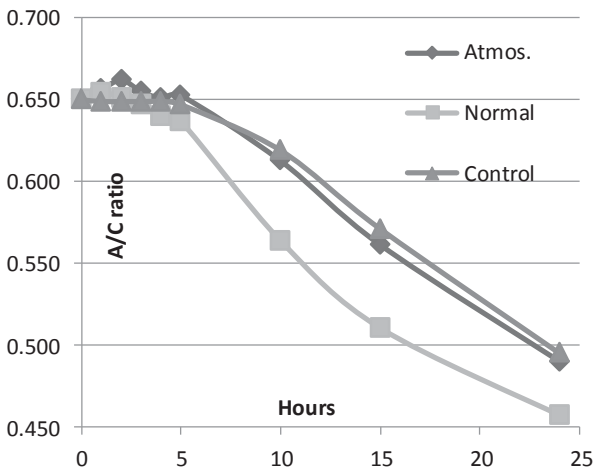


Figure 5(b). Alumina reversion tests done on muds from Atmospheric and (normal) Low Temperature (135°C) digestion. A/C ratio = alumina / caustic ratio in solution.

c) Chemical additives: reducing alumina reversion

Autoprecipitation, also called alumina reversion, can be moderated with chemical additives. It is known that soluble calcium in liquor tends to inhibit precipitation and that, as a further example regarding the effect of calcium, causticiser sludge reduces autoprecipitation in the mud circuit. It was found that the modest solubility and otherwise non-reactivity of natural calcite makes it an attractive autoprecipitation inhibitor (Raty et al.²⁵, 2004; Haverty et al.²⁶, 2005). This finding was put to test in a plant trial at Kirkvine. Locally won calcite was ground at the lime mills and added at 500 ppm per tonne mud to the first mud washing stage over a 15-day period. Autoprecipitation reduced indeed, being evidenced by a significant decrease in gibbsitic alumina content of the disposed mud with the increase of its CaO content, as demonstrated in Figure 6. The downside was a decrease in the causticity of the liquor in the mud circuit. Possibly this could have been avoided by applying the calcite further down the mud circuit, where the lower soda concentration makes calcium carbonate more stable, but then the calcite would not have addressed the largest source of autoprecipitation, being the first mud washing stage.

Other additives exist that reduce autoprecipitation, such as dextran. Some of these, such as polyols studied (Powell et al.¹⁸, 2012), are very effective, but are able to enter and be also effective in the precipitation circuit, where their effectiveness is not desired.

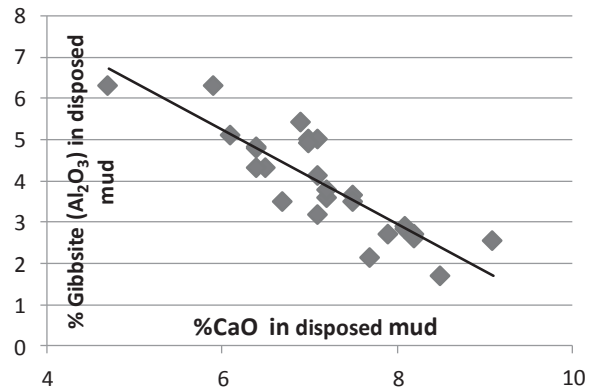


Figure 6. Relationship between gibbsite Al₂O₃ and CaO in disposed mud.

d) Chemical additives: applying rheology modifier

Depending on the quality of the bauxite feed, the production rate of a refinery may be mud flow constrained. For Windalco this was reason to investigate all factors that affect the flow rate of slurries, in particular that of red mud. Regarding mud slurry viscosity, correlations were established with percentage solids and with aluminous goethite content of the solids. The increasing effect of the latter on viscosity has been discussed in the foregoing. Figure 7(a) quantifies the effect of percent solids for deep thickened mud.

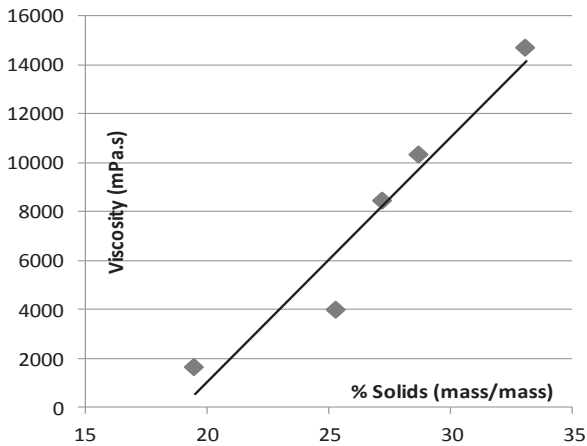


Figure 7(a). Relationship between the percent solids and viscosity for deep thickened mud.

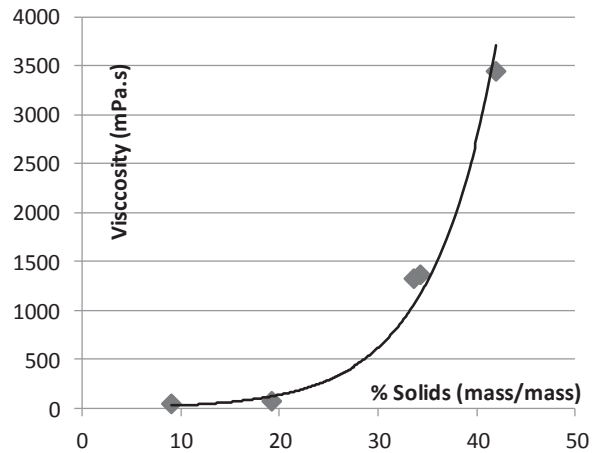


Figure 7(b). Relationship between the percent solids and viscosity for bauxite slurry.

In the case of bauxite slurry, Figure 7(b) shows the exponential increase of slurry viscosity with increasing percentage of solids after approximately 25% m/m. A further viscosity increasing factor, though not as significant as aluminous goethite content, is the flocculant dosage. This has been demonstrated by laboratory investigations to be dependent on type and molecular weight.

Rheology modifiers may help resolving slurry flow bottlenecks in a plant by reducing slurry viscosity. At the Kirkvine plant a rheology modifier was tried at the final stage of the mud circuit. This trial involved the addition of a rheology modifier at various dose rates. Figure 8 shows comparatively the yield stress of the mud at the disposal site for muds dosed with 10 g/tonne modifier and those with none. The effect of this change in mud rheology was a reduction in pump operating pressure and an increase in mud pumping capacity by 20% in solids mass flow.

Rheology modifiers may be used successfully not only on red mud slurries but also on bauxite slurries. Laboratory tests on

slurries of an aluminous goethite bauxite showed that a bauxite slurry leaving the ball mill with 57% solids to which a rheology modifier was added, gave the same viscosity as a normal bauxite slurry at 45% solids to which no rheology modifier was added. Since not only the weight percentage of solids increases, but also the slurry density increases, the combined effect is that for a given volumetric flow capacity of the ball mills the solids mass flow capacity potentially increases by roughly 40%. This is beneficial for systems where the mills are being applied more for the purpose of dispersing solids in the liquor than for grinding, since then only pump motor power in the milling system would need to be upgraded.

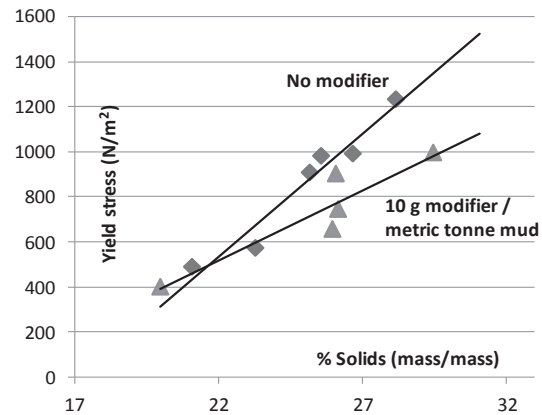


Figure 8. Yield stress of mud at disposal site with and without rheology modifier.

Compaction

As discussed earlier, an increased goethite content of the mud leads to a decreased compaction in thickener mud beds and hence to a reduced mud removal capacity. Kirkvine took several actions to mitigate this adverse effect on the mud circuit throughput at minimal cost. In addition to optimising normal operations, the thickener feedwells were redesigned using computational fluid dynamics software and the capacity of the underflow pumps was increased together with the installation of variable speed drives. With these upgrades the mud circuit capacity was increased from 2000 tonnes per day to 2350 tonnes per day.

Recovering process losses at the end of the circuit

The main process losses associated with elevated aluminous goethite in the mud are alumina and soda. Although soluble soda and alumina losses can always be reduced at the expense of capital investment in additional mud washing equipment and/or evaporation, the recovery of gibbsitic alumina from the mud poses a challenge. Since about 8 years a relatively simple digestion technology, the M2M technology, is in principle available for the recovery of gibbsite from decanter (settler) underflow (Den Hond et al.²⁷, 2007). This concerns residual gibbsite in the main digester discharge and extractable alumina (gibbsite, pseudo-boehmite) precipitated in the decanters. The reduction in gibbsite content of the mud is expected to reduce the seeding effect in the mud circuit, while the reduction in mud mass facilitates recovery of soluble soda and alumina losses and lifts a slurry flow bottleneck that may exist.

Conclusions

Aluminous goethite is prevalent in Jamaican bauxites. Since most of the refineries established on the island were designed to consume Jamaica-1 type bauxite there will be an increasing proportion left of the other two types of bauxite with time, as well as remaining Jamaica-1 type bauxite rich in aluminous goethite due to high grading. Processing the remaining bauxites on the island present challenges, among which is dealing with the aluminous goethite content of the bauxites. Although some of the approaches presented here are untried and would indeed require significant process changes (but with potentially significant benefits), there are sufficient other approaches of dealing with aluminous goethite that are less involved and have been tested to have potential or even have already been successfully put to practice.

Acknowledgements

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References

1. Strahl E.O., "The mineralogy of Jamaican bauxite and its effect on Bayer process technology", *Journal of the Geological Society of Jamaica: Bauxite/Alumina Symposium*, 1971, (special issue), 62-69.
2. Grubbs D.K., Libby S.C., Rodenburg J.K. and Wefers K.A., "The geology, mineralogy and clarification properties of red and yellow Jamaican bauxites", *Journal of the Geological Society of Jamaica, Proceedings of Bauxite Symposium*, No. IV, 1980, 176-186.
3. Davis C.E., "The mineralogy of Jamaican bauxites", *Journal of the Geological Society of Jamaica, Proceedings of Bauxite Symposium*, No. II, 1973, 6-20.
4. Davis C.E and Hill V.G., "Occurrence of Nordstrandite and its possible significance in Jamaican bauxite", *Travaux, ICSOBA*, 1974, 61-70.
5. Davis C.E., "Recent advances in the understanding of the mineralogy of Jamaican bauxite", *Light Metals*, 1976, 185-200.
6. Authier-Martin M., Forte G., Ostap S. and See J., "The mineralogy of bauxite for producing smelter-grade alumina", *Journal of Minerals, Metals and Materials Society*, **53**, 2001, 36-40.
7. Greenaway A.M., Bucknor A.N., Henry K. and Coley M.D., "Identifying possible associations of minor and trace elements with major elements in Jamaican hillside and catchment bauxites using multivariate analysis tools", *Minerals Engineering*, **53**, 2013, 124-135.
8. Wallen-Bryan W., "Characterization of goethites in poor-settling Jamaican Bayer muds", *Light Metals*, 1998, 5-9.
9. Schulze D.G., "The influence of aluminium on iron oxides. VIII. Unit-cell dimensions of Al-substituted goethites and estimation of Al from them", *Clays and Clay Minerals*, **32**, 1984, 36-44.
10. Anand R.R., Gilkes R.J. and Roach G.I.D., "Geochemical and mineralogical characteristics of bauxites, Darling Range, Western Australia", *Applied Geochemistry*, **6**, 1991, 233-248.
11. Ostap S., "Effect of bauxite mineralogy on its processing characteristics", *Light Metals*, 1984, 651-751.
12. Einstein A., "Zur Theorie der Brownschen Bewegung", *Annalen der Physik*, **19**, 1906, 371-381.
13. Li L.Y. and Rutherford G.K., "Effect of bauxite properties on the settling of red mud", *International Journal of Mineral Processing*, **48**, 1996, 169-182.
14. Gomes, A.M.D., Vieira, M.B., Santos, N.A. and Alves, C.A., "Applied mineralogy studies: An important tool to understand the red mud sedimentation process", *Light Metals*, 2005, 43-46.
15. Kirwan L. J., Deeney F.A., Croke G.M. and Hodnett K., "Characterisation of various Jamaican bauxite ores by quantitative Rietveld X-ray powder diffraction and ⁵⁷Fe Mössbauer spectroscopy", *International Journal of Mineral Processing*, **91**, No. 1-2, April 2009, 14-18.
16. Harato T., Ishida Y., and Yamada K., "Autoprecipitation of Gibbsite and Boehmite", *Light Metals*, 1982, 37-50.
17. Lepetit J.G., "Autoprecipitation of alumina in the Bayer process", *Light Metals*, 1986, 225-230.
18. Powell K.A., Hodnett B. K. and Kirwan L.J., "The effect of additives on gibbsite auto-precipitation and bauxite residue flocculation when processing goethitic bauxites", *Travaux, Proceedings ICSOBA*, 2012, *Alumina Program, AA12*, 1-12.
19. Lawson D., Rijkeboer A., Andermann L.J., and Mooney A., "Impact of Jamaican Bauxite Mineralogy on Plant Operations", *Light Metals*, 2008, 113-118.
20. Douglas C.G.C., Hill V.G. and Lyew-Ayee P.A., "Mineralogy and Process Characteristics of Jamaican Bauxite", *Light Metals*, 1984, 349-369.
21. Rijkeboer A. and van der Meer A.P., "Bauxite Roasting – An Option to Reduce the Organics Input to Bayer plant Liquor", *Proceedings of the 3rd International Alumina Quality Workshop*, 1993, 254-269.
22. Hollitt M, Kisler J. and Raahauge B, "The Comalco Bauxite Activation Process", *Proceedings of 6th International Alumina Quality Workshop*, 2002, 115-122.

23. Brown N, "Some studies of the iron mineral transformations during high temperature digestion of Jamaican bauxite", *Light Metals*, 1974, 825-844.
24. Solymár K., Sajo I., Steiner J. and Zoldi J., "Characteristics and separability of red mud", *Light Metals*, 1992, 209-223.
25. Raty D. Stanton K.T, Hodnett B.K and Loan M., "Calcite in the Mud Washing Circuit of the Bayer Process: Experimental Solubility and Adsorption", *Light Metals*, 2004, 104 -108.
26. Haverty D., Raty M., Kenneth S.T., Hodnett B.K. and Loan M., "Influence of Calcium on Gibbsite Crystallisation: Calcium Incorporation Within a Gibbsite Crystal Lattice", *Proceedings of the 7th Alumina Quality Workshop*, 2005, 112-116.
27. Den Hond R., Hiralal I. and Rijkeboer A., "Alumina Yield in the Bayer Process, Past, Present and Prospects", *Light Metals*, 2007, 37-42.