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Digestion of Boehmitic Bauxites: Problems, Challenges and Opportunities

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Abstract

This paper reviews selected aspects of high temperature bauxite digestion (HT > 250 °C). HT digestion is usually carried out owing to the presence of significant amounts of boehmite or diaspore (> 5 % Al_2O_3). Gibbsite is almost completely dissolved during digestion, and HT Digestion further removes the majority of the boehmite, with ultrafine natural boehmite particles (< 2 micron) dissolving first. If not removed these fine particles will act as seed surface area and promote auto-precipitation. Hot, high ratio (A/C) liquor in digesters, flash tanks and in thickeners can create the perfect conditions for boehmite seeding and growth. Coarse natural boehmite particles (> 10 microns) will constitute a lower exposed surface area and are unlikely to act as seed. Incomplete removal of boehmite will lead to an increase in g/L solids, and in-turn will increase the solids load to thickeners and washers. Over charging the bauxite to digestion would have a similar impact. Auto-precipitation will lead to a reduced extraction, and higher A/C targets (> 0.70) will become more difficult to achieve with boehmite precipitation occurring faster than boehmite dissolution. For some bauxites a higher activity in the mud fraction may impact on the performance of security filtration. To minimise alumina losses the target liquor ratios may need to be lowered to prevent: auto-precipitation, reduced filter performance, and white side scale losses. In the treatment of boehmitic bauxites to achieve high target ratios, ideally requires: 1) fine milled bauxite, 2) optimal bauxite charge, 3) short residence times in digestion, 4) rapid settling in thickeners and washers, and 5) addition of liquor stabilizers to minimise any security filtration related issues. Alternatively, the sweetening process can be implemented and is guaranteed to raise the A/C ratio of the final liquor. High alumina extractions are achieved during the primary digestion event. The second stage injection of bauxite raises the A/C ratio and lowers the "free" caustic concentration and the iron-content of the liquor.

Keywords: Boehmite, Sweetening, Digestion, Auto-precipitation, Scale.

1. Introduction

Gibbsite dissolves rapidly at low temperatures. However, when bauxites contain boehmite or diaspore the digestion behavior is thermodynamically and kinetically very different, and requires elevated digestion temperatures (>250°C) and caustic concentrations to deliver an appropriate A/C ratio. Incomplete digestion, with boehmite losses to the residue of > 5 mass% Al_2O_3, would be significant, unless bauxite costs are exceptionally low. The extra costs associated with mining, transportation, milling, digestion, clarification and mud disposal often justify the extra Al_2O_3 recovery.

The feed to the Ma'aden refinery contains > 25 % boehmitic alumina and has HT extractable alumina concentrations ranging from 40 to 55 %. The boehmite is generally coarse grained, whereas other bauxites such as in Weipa and Guinea are very different in that they are likely to contain considerable amounts of ultrafine boehmite within a gibbsitic matrix [1].

2. Bauxite Particle Size

The simple shrinking core particle model [2] infers that the particle size of bauxite is important for rapidly achieving a higher A/C ratio. This is important when considering kinetic and thermodynamic aspects of boehmite and diaspore digestion. The gibbsite and boehmite solubility curves (Table 1) suggest that if alumina particles are infinitely small (< 1 micron) and in equilibrium with the liquor, the solubility trajectory will follow the solubility curve with increasing digestion temperatures. However, as the A/C ratio increases the kinetics of particle dissolution will decrease owing to a lowering in Free Caustic (FC) and the start of boehmite precipitation. For coarser particles (> 10 microns) at increased A/C ratio there will be slower dissolution, also boehmite dissolution will start competing with boehmite precipitation at the higher A/C ratios. The boehmite solubility curve at higher ratios and at high temperatures (> 270 °C) begins to plateau and becomes more uncertain mainly because the boehmite cannot equilibrate fast enough with the liquor phase. Longer holding times may promote a higher rate of boehmite growth, and remove increased alumina concentrations from the liquor.

Tube digesters are designed for high digestion temperatures and short residence times. One of the advantages of a tube reactor is that the slurry undergoes turbulent “plug-flow” as the slurry moves through the tube circuit. In a unit slurry volume, the coarse and fine particles will both have the same residence time. This overcomes some of the issues related to differences in particle residence times as experienced in agitated tank digesters. Such a short residence time and plug flow may also prevent boehmite nucleation and growth. The liquor volumes, as they flow in the pipes, are kept separate and there is no chance of mixing with older liquor slurry volumes which may be enriched in boehmite seed.

Improved comminution practice is recommended to reduce the average particle size of bauxite. Sand size particles (> 150 µm) are most likely to be the slowest to dissolve and most likely to be the cause of any boehmite losses. The treatment of a finer sized bauxite should dissolve more completely and help reduce bauxite usage and help achieve an appropriate A/C ratio.

3. Liquor Stability

High liquor A/C ratios can lead to gibbsite or boehmite scale formation and promote auto-precipitation. Seeds of growing boehmite in hot saturated slurry or liquor contribute towards the removal of alumina from the liquor phase. This growth is most apparent during flashing of hot slurries. The resulting alumina then reports to the mud, which is then lost. High g/L solids in the slurry will promote boehmite growth and prevent achieving theoretical target ratios. Goethite in the mud has a significantly lower activity than boehmite, however it can be present in bauxite in higher concentrations and promote auto-precipitation and lead to increased alumina losses and bauxite usage. Even trace quantities of ultrafine boehmite can dramatically enhance boehmite growth and remove alumina from liquor and increase the mud load. Lime addition to digestion may help stabilize the liquor and prevent boehmite growth during flashing. Likewise the addition of lime slurry to the thickener is often practiced to reduce liquor instability and prevent auto-precipitation.

The amount of boehmite precipitation is governed by the amount of seed and the residence time (=holding time) of the slurry at temperature. It is likely that it is the number of nuclei or the boehmite surface area that is more important than the actual boehmite content. For this reason, coarse boehmite particles (> 10µm) are likely to have a lesser impact on slurry stability. Bauxite samples from different geographic regions of a deposit can have highly variable behavior in digestion and this may be explained by changes in boehmite particle size and content.

For the thickener overflow it is well established that the mud content and Ca content of liquors impact on their filtration and stability. Use of dextran based reagents can reduce - filtration scaling events, flow losses and maintenance costs [3, 4]. This is more apparent when operating at higher liquor ratios as precipitation can occur within the filter aid or filter cloth, which can then impact on filtration rates.

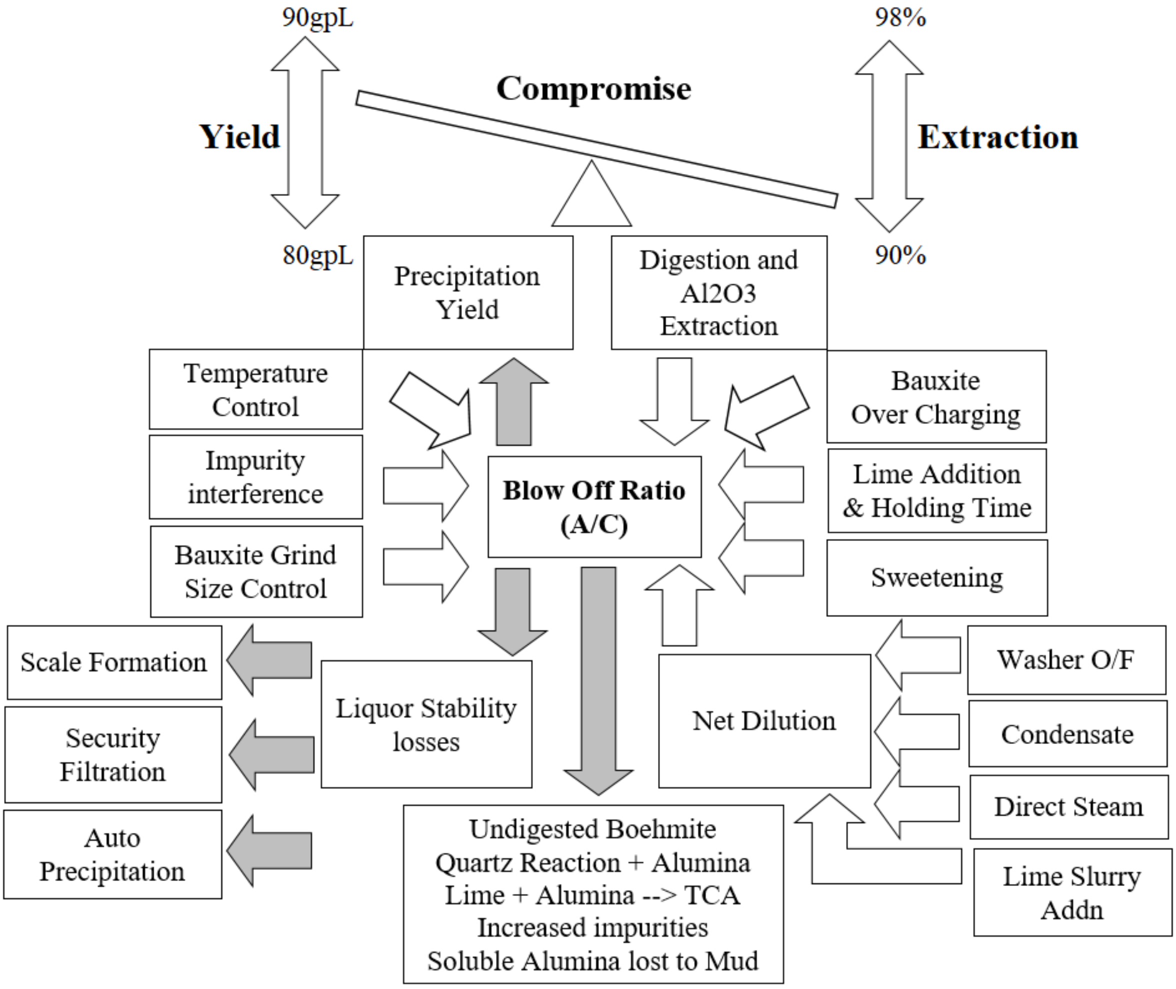
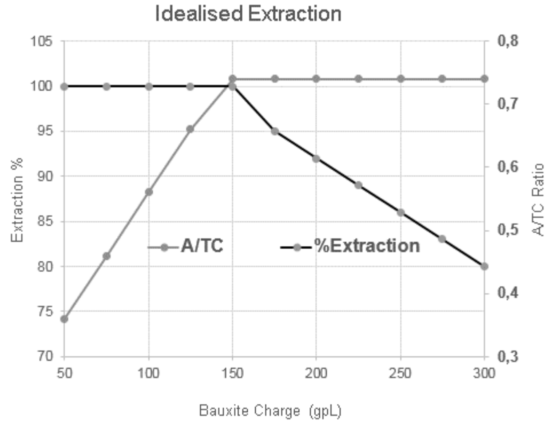


Figure 1. Blow-Off Ratio optimisation and control considerations.

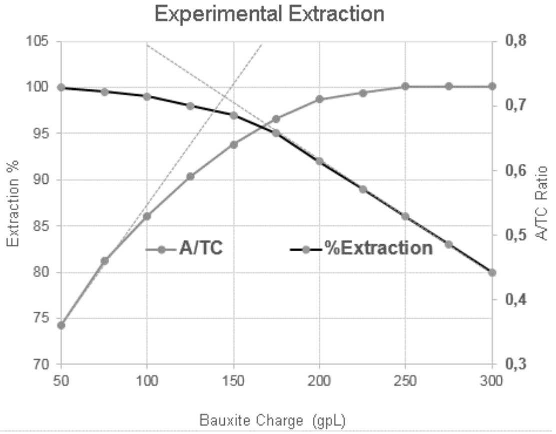
Table 1. Liquor ratio and alumina extraction during digestion.



Idealised digestion when there is no interference from boehmite or solids in the bauxite. Progressive ratio increase with a progressive bauxite charge. A/C ratio will increase until it hits a thermodynamic barrier, then it maintains a constant value which represents the solubility at a fixed temperature and Total Caustic (TC).

Reduced percentage extraction at higher bauxite charges is due to the system reaching the maximum alumina solubility. After this has been reached no extra alumina can be easily held in the liquor phase.

A bauxite overcharge situation essentially wastes bauxite. There is a need to hit a maximum ratio, and minimise bauxite addition. Otherwise bauxite consumption will rise unnecessarily.

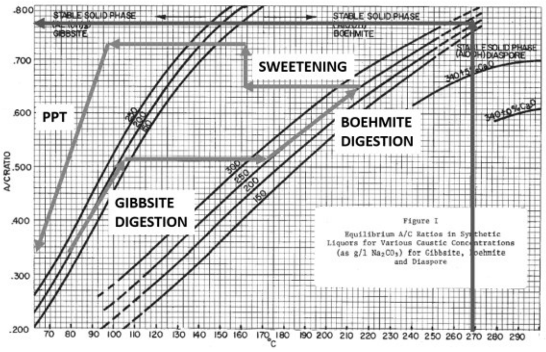


In refinery digestion data the A/C ratio will drop progressively with bauxite over charge owing to the impact of increased solids. With raised g/L solids nucleation will occur, even for boehmite depleted bauxites. Extended digestion holding times will promote autoprecipitation.

The use of Mannitol during lab testing can stabilize the liquor and prevent this boehmite auto-precipitation. The drop-in extraction is due wholly to auto-precipitation during cooling.

The diagram indicates that there is an extraction loss as the bauxite charge is increased. It is unlikely that the A/C ratio will reach the theoretical solubility of gibbsite or boehmite. A/C ratio are also likely to drop with increased charge during cooling. A simple boehmite activity test can be used to assess - the impact of boehmite-enriched mud fraction on liquor stability [5, 6].

Gibbsite and Boehmite solubility curves [7]



The Boehmite solubility curve suggests that a much higher digestion temperature is required to achieve the same A/C ratio as gibbsite.

During digestion when ultrafine gibbsite is slowly heated up, the change in A/C will follow the Gibbsite solubility curve. The A/C ratio will stop after depletion of gibbsite in the slurry. If only boehmite remains the only way the A/C can rise is through increasing the temperature and fine boehmite will start to dissolve and the ratio will move along the boehmite solubility curve. Digestion at high temperatures (>270°C) ceases as it will reach an equilibrium between dissolution and boehmite precipitation.

The digestion trajectory illustrates “Sweetening” with the later addition of a gibbsitic bauxite. Complete digestion occurs at low ratio, followed by injection of up to 20% gibbsitic bauxite into a flash tank (160 - 170°C). E.g. A/C is raised from 0.65 to 0.73.

4. Blow-Off Ratio Control

Alumina production at a Refinery is determined by the simple formula - Liquor Flow x Precipitation Yield. Increasing yield will impact on Refinery efficiency and this will help incrementally reduce unit production costs. Higher A/C ratios is an important target condition and can help maximise the yield.

Figure 1 reviews the complex interactions when targeting an A/C ratio. The actual digestion process is ultimately a compromise between 1) alumina extraction, and 2) precipitation yield. Digestion and alumina extraction is a function of temperature, caustic concentration, particle size and lime addition. Higher alumina extractions can be achieved when lower A/C ratios are targeted. However, when higher ratios are targeted increased alumina losses start to occur though unstable liquor compositions and slower particle dissolution. The maximum alumina concentration in the liquor is governed by the stability of the slurry on cooling and the subsequent stability of the liquor during solid/liquid separation. A marginally lower ratio may be targeted to counter the variability in bauxite quality and operational changes. Such lower ratios will almost certainly guarantee higher alumina extraction from the bauxite and deliver a more controlled g/L solids content.

Following flashing of the digestion slurry there will be a significant water loss (> 20 % evaporation) which super saturates the remaining liquor. This can lead to auto precipitation (Figure 2) and scaling in selected flash tanks. On cooling to ambient pressure, the BO slurry flow is increased in volume with addition of Washer Overflow and condensate. However, the mud content of the slurry (80 to 100 g/L) may have become significantly "active" owing to the presence of secondary boehmite that has grown during the flashing.

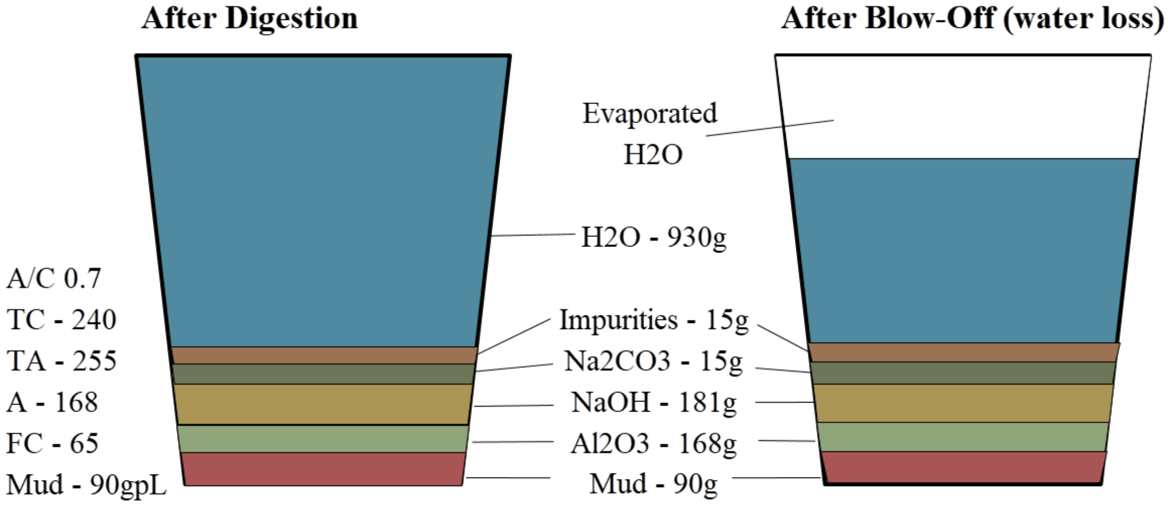


Figure 2. Blow-off liquor undergoing significant water loss after flashing.

5. Impact of Caustic Concentration

Refineries are operated to maximize A/C through use of an optimal Total Caustic (TC) as this is the best way to increase yield. The boehmite solubility curves in the Kotte diagram (Table 1) illustrates the impact of increased A/C with an increased TC. For increased TC conditions the chemical driving force can promote increased reaction rates.

When using higher free Caustic (FC) concentrations for increased extraction and improved yield this may be at the expense of caustic embrittlement of metal. Metal degradation is usually more apparent on metal used in high temperature plants and explains the importance of the material of construction in metal areas exposed to high concentrations of FC. On consideration of the calculation of FC (TC minus Al, see Table 2) it is apparent that spent liquors will contain lower alumina content than green liquors and will have a higher FC content. The FC is carefully monitored and controlled during digestion, evaporation and caustic cleaning, to minimize any caustic embrittlement related issues. The TC in plant liquors can also be limited through the impact of oxalate solubility (precipitation), with the solubility product decreasing at higher TA compositions. Fortunately in Ma'aden Bayer liquors, Organics are very low and this does not pose any restriction.

Table 2. Important Calculations.

Calculations	Formulae
Iron in Product (SGA)	Iron in Product (%) = Iron in Liquor (mg/L) / (Precipitation Yield (g/L) x 10). The iron in the solid sample is simply diluted with increased amounts of gibbsite precipitation. The presence of iron in SGA is an unwelcome impurity and is detrimental to the aluminium metal quality. Concentrations of Fe_2O_3 in product should ideally be well below 0.025 %.
Free Caustic in Liquor	Free Caustic = TC - ((Al_2O_3 (g/L) x 106 / 102) expressed in g/L as Na_2CO_3 (approximates FC = TC – Al)
Iron in Liquor (Bayer)	When converting mg/L in liquor to % Fe_2O_3 in solids use equation above to avoid confusion. The majority of iron in liquor (> 95 %) is removed during precipitation. (e.g. at 100 g/L Yield, 0.02 % Fe_2O_3 solids = 20 mg/L Fe_2O_3 in Liquor).
Calculation of experimental digestion TC (Total Caustic)	High reactive silica bauxites will consume a significant amount of caustic in PDS prior to digestion. This TC reduction must be accounted for in digestion experiments [8, 9]. Bauxite Charge = (TC x ΔRatio x 100) / (% TAA + (% $RSiO_2$ x (Na_2O/SiO_2) x Target Ratio) TC (= starting Caustic concentration) needs to be adjusted to deliver a Target Ratio using an appropriate Bauxite Charge. Na_2O/SiO_2 (mol/mol) for DSP containing no CaO ~ 0.66 – 0.69.
TC TA	Total Caustic (as Na_2CO_3) Total Alkalinity (as Na_2CO_3)

6. Scale Formation

Generally, scale precipitating at lower temperatures favour a gibbsite composition, while those from hotter liquors favor boehmite. The region in between the gibbsite and boehmite solubility curves demarcates the boehmite precipitation region. Also, the higher the A/C ratio and the lower the temperature the higher the risk of a scaling event. To minimise any flow losses during any scaling event (e.g. in thickeners or filters) the use of liquor stabilizers may be warranted. Protecting flow through the filters is important and limits must be carefully controlled and Specific Precipitation Rate and biscuit scale formation monitored. With a careful calibration study the onset of scale formation can be predicted and this is closely related to: liquor ratio, Time, calcia, mud g/L, impurity concentration and mud activity. Operating at lower ratios will lower rates of scale formation.

Progressive growth of scale on the inside of a pipe which is being heated externally starts to incrementally impact on flow volume inside the pipe and on the thermal conductivity/heat transfer. For this reason, the build-up of scale has a negative impact and needs to be periodically removed by caustic, acid washing or mechanical removal. Titaniferous minerals, notably anatase and crystalline rutile may also react at higher temperatures and combine with calcia to form perovskite and several other possible compounds. The titaniferous mineral freudenbergite can start to grow at temperature >200°C. This scale is a cause of concern as it is exceptionally hard, and once an initial layer is formed will act as a growth medium and continues to grow. To date this compound has not been identified at Ma'aden owing to the innovative 2-stage digestion design that has been installed. Kassite and Perovskite have been identified as a scaling product at Ma'aden and so far, has been found to be relatively easy to remove.

7. Sweetening

When processing boehmitic bauxites high A/C ratios are often not achievable (i.e. > 0.7), the sweetening process is usually the best recommendation. This is an established process and its main function is to: - increase liquor A/C ratio; improve precipitation yield; remove the free caustic and lower the iron content in the final product (see Table 2). Ratio increases of 0.03 to 0.06 can be readily achieved and iron concentrations in SGA product dramatically lowered.

Following sweetening the final slurry solids contain BO solids from the primary digest, together with any undigested solids from the extra (10-20%) bauxite introduced into the hot BO slurry (~ 160 °C). In the second stage injection of slurry the sweetening removes gibbsite only, and natural boehmite (coarse and ultra-fine particles) will remain and will act as seed surface. Alumina losses from this later bauxite addition will come from the undigested natural boehmite and gibbsite/boehmite from any auto-precipitated alumina. Ideally a non-boehmitic bauxite should be chosen as the sweetening bauxite and this should ideally contain a high hematite content, and a low concentration of all impurities (EOC, SO_4, CO_3). While Amazonian bauxites are the most suitable, other gibbsitic bauxite types could equally be used.

8. Conclusion

An appreciation of high temperature digestion chemistry can help guide operations and help understand the complex interplay between mineral components and the caustic liquor. When target A/C ratios cannot be achieved it is required to identify the causes and identify the required steps to improve extraction and reduce alumina losses. The auto-precipitation of boehmite from slurries and liquors should never be underestimated as this phenomenon can lead to significant alumina losses. Those bauxites with a high percentage of ultra-fine boehmite will be susceptible to auto precipitation problems in a low temperature operation. Higher temperatures readily digest the fine boehmite particles and the impact of auto-precipitation can be partly reduced.

A trade-off between refinery production and alumina extraction must be considered when operating at optimal ratio. The complexity required to deliver a target A/C ratio must consider variations in bauxite grade and mineralogical variations. The equilibrium between boehmite dissolution and precipitation becomes the final controlling step for optimal A/C and explains the reason for not being able to achieve higher ratios. The process challenge then becomes what A/C can be realistically achieved. The position of the boehmite dissolution-precipitation equilibrium will be dependent on temperature, time, TC, slurry solids and liquor impurities.

Bauxite overcharging will increase bauxite usage and increase g/L solids further which will only increase processing costs. It is inevitable that high A/C ratio liquors will increase scaling in the white side and needs to be considered and controlled when higher ratios are targeted. Operating at lower ratios, owing to digestion limitations, partially avoids some of these scaling issues. However, targeting lower and safer operating conditions will lead to lower refinery production.

If higher target ratios are not delivered this is a lost opportunity and will lead to a reduced overall plant performance. Helping deliver the optimal target requires 1/ Finer bauxite particle sizes, 2/ Shorter digestion times, 3/ Rapid settling, and 4/ Potential use of reagents for process control. Alternatively, sweetening can be used to deliver increased A/C ratios, with increases of up to 0.03 to 0.06 units, this would also reduce the FC and guarantee a significantly reduction in the Iron in product simultaneously.

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