Impurities Control – From a Mine to a Plant

Stephan Beaulieu
Process and Environment Consultant
Aughinish Alumina Ltd., Askeaton, County Limerick, Ireland
Corresponding author: stephan.beaulieu@augh.com

Abstract

The Rusal Aughinish Alumina (AAL) refinery is located on Aughinish Island, on the southern shore of the Shannon Estuary 33 kilometres west of Limerick city in the South West of Ireland. The plant, which commenced operation in 1983, has a current production capability of 1 990 000 tons per annum. It sources bauxite predominantly from Guinea, Brazil and Guyana and uses the Bayer process to produce Alumina. The refinery functions with an accredited Safety Management System (ISRS), Environmental Management system (ISO14001), Quality Management System (ISO9001) and Energy Management system (ISO50001). The selection of plant design and technology for an alumina refinery is based on the physical and chemical composition of bauxite supply. For a chosen plant design and technology, production, costs and quality are optimised within boundaries specific to the refinery. However, changes to the chemical composition of the bauxite can require new technology to ensure critical impurities are controlled and avoid a loss in production capacity or a deterioration in product quality. This paper outlines the impact of a change in bauxite chemical composition on the control of impurities.

Keywords: Alumina refinery, bauxite, impurities.

1. Introduction

Aughinish was commissioned in 1983 at a design capacity of 800 000 tons per annum. The refinery design was based on high quality dry CBG bauxite (62%) and dry MRN (38%) bauxite: both bauxites had very high extractable alumina well above 50% with low level of organics in particular MRN with total organic carbon (TOC) three times lower than CBG. The refinery was designed by Alcan using the best technology available at the time: a Kaiser digestion, an Alcan precipitation and Alcoa calciners were installed. A single chain was built with enough available space to build another two chains: the refinery in 2017 is still operating on a single chain but the production capability has been increased to approximately 1 990 000 tons per annum. These design choices have introduced some operational mechanisms:

- The precipitation circuit is an oxalate-free circuit: the precipitation, classification, seed filtration and pumping systems can operate optimally only if the circuit is oxalate-free.
- The organics and impurities removal unit has a small removal capacity to manage low level of organics input. Bauxite with high organics input require a large removal unit commonly known as external causticisation.

The selection of plant design and technology for an alumina refinery is based on the physical and chemical composition of bauxite supply. Bauxite handling, method of extraction of the alumina content, mud circuit requirement and control of bauxite impurities are just a few critical aspects that have to be considered in the plant design. For a chosen plant design and technology, production, costs and quality are optimised within boundaries specific to the refinery.

The alumina content has an obvious impact on the capability and efficiency of a refinery: Figure 1 shows the alumina content reducing at Aughinish in recent years. As a result, additional bauxite is required to sustain production leading to higher level of impurities entering the refinery.

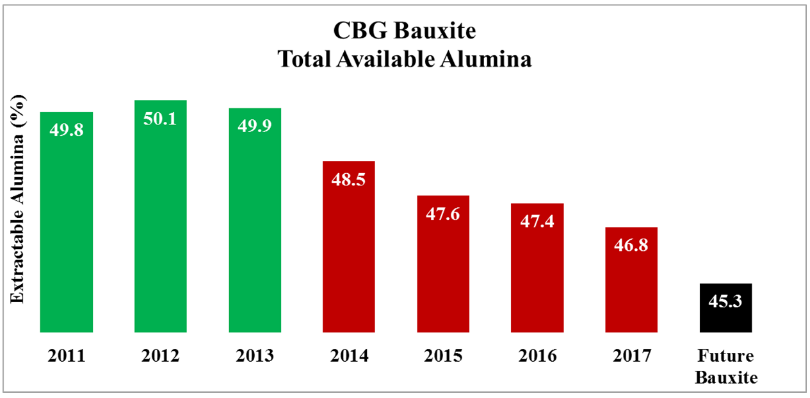

Figure 1. Reduction in extractable alumina in recent years.

The impact of bauxite on impurities in a refinery is often overlooked. The control of impurities is paramount to each alumina refinery and if not managed adequately the impurities would build up in the liquor as the liquor is recirculated continuously. Both inorganic and organic impurities can lead to serious plant problems if not controlled adequately such as:

- Deterioration in product quality due to product contamination, weak product and high level of fines in product caused by impurity interference with the crystallisation process.
- Reduction in process productivity; increase in costs caused by excessive fouling or scaling on key equipment such as heat exchangers, tanks and pipework.

Most of the impurities in the process liquor come from the bauxite and are modified through various chemical reactions occurring in the digestion process. Minor level of impurities are also coming from additives used in the process, oil and lubricants used for equipment, and return streams from the bauxite residue disposal area. Both inorganic and organic impurities require specific controls to ensure each impurity type remains in balance in the process liquor.

Mining operation has a significant role in providing both optimised chemical composition and low variability in the continuous bauxite supply as the capability of the refinery to control impurities cannot be adjusted. Changes to the chemical composition of bauxite can require new technology to ensure critical impurities are controlled and avoid a loss in production capacity or a deterioration in product quality.

The following sections will provide insight on the controls and limitations both at the mine and a refinery for the control of impurities. This paper focusses on a refinery designed for high purity blend of bauxites using Guinean bauxite as the main feed material. AlCircle website reported in March 2017 that Guinea is planning to increase bauxite production from 20 000 000 tons per annum in 2015 to 60 000 000 tons per annum by 2020 and move Guinea up the ranking in the top 3 producers of bauxite in the world with Australia and China [1].

2. Impurities Control – Starting at the mine

The production capability and operational stability at the refinery depends directly on a stable bauxite quality at an optimised quality level from the mine. In other words, the performance at the mine to deliver optimised bauxite quality parameters with little variability has a major impact on the performance at the refinery in terms of production, product quality and costs. The most critical operational aspects at the mine are:

- Usage of a robust mine planning strategy incorporating deposit characteristics from exploration and mining.
- Primary stripping procedure of the top soil and overburden one to two years in advance depending on the thickness of the vegetation and secondary stripping of mine area before mining [4].
- Good sampling system when mining is carried out with analytical results fed back into the mine plan model.
- Control blending at the mine using stockpile layers according to chemical and physical bauxite quality and control of blending at the ship loading stage with internationally recognised sampling standard and method.
- Provide adequate laboratory analytical capability with analytical methods established.

2.1 Deposit Characterisation and Mine Planning Strategy to Optimise Quality

A robust mining plan including deposit characterisation is required to ensure that the bauxite quality shipped to the refinery is optimised and variability kept to a minimum. The integration of the deposit characterisation from the exploration stage into the mining plan model is necessary as natural variability from the deposit has to be controlled to deliver steady quality supply in the short, medium and long term. Figures 2 – 4 show a typical deposit characterisation in Guinea with the level of variability between different sectors and depth at the mine [2]. Not only is the quality variable between mine blocks but it is also variable within the same block depending on the depth.

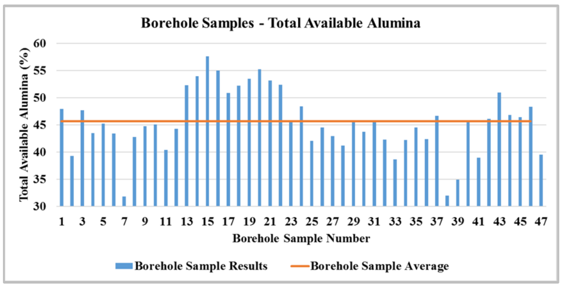

Figure 2. Borehole available alumina.

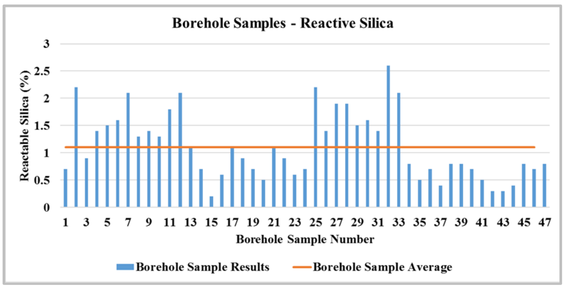

Figure 3. Borehole reactive silica.

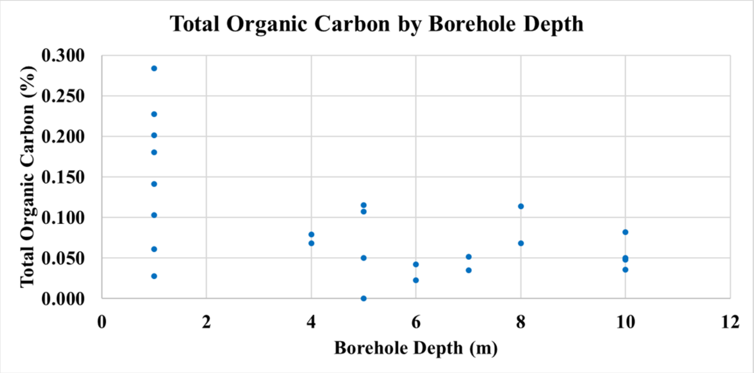

Figure 4. TOC by borehole depth.

The mining plan needs to define the bauxite product quality to be achieved from the deposit over the life of mine period. Some fundamental factors such as mining dilution, mining loss, weathering and season patterns will influence the production profile and hence should be incorporated into the mining plan. These factors are linked to the deposit characteristics, the mining method to be applied, in situ grades, strip ratio, and other technical or economic characteristics influencing the quality [3].

2.2 Stripping of the Overburden to Control Total Organic Carbon (TOC)

Bauxite mining methods vary according to the nature of the mineralised field bodies, but in most cases a strip or block of bauxite is exposed and surface-mined. The layer under the top soil is known as the “overburden”. On some surface deposits there is no overburden where on others, the bauxite may be covered by many metres of rock and clay. The overburden contains the highest level of organics and it varies depending on the amount of vegetation. The overburden must be removed well ahead of mining of the bauxite (Figure 5 shows bauxite block before and after primary stripping). Best practice for Guinean bauxite is to strip the overburden 1 to 2 years ahead of mining (primary stripping) with secondary stripping just before mining the bauxite [4]. The primary stripping process allows weathering of the top layer to take place so that rainwater can wash the top layer of bauxite and exposure to the sun reduces organic carbon. The secondary stripping removes the excess organic layer that might have built up between the primary stripping and the mining stage.

This preparation for mining ensures the lowest level of contamination by organics (TOC) in the bauxite. From an impurity point of view, organics control at the mine is critical to ensure supply of quality bauxite to the refinery: a low and stable level of TOC enables sustainability of production capability and operation stability in precipitation circuit.

Figure 4 shows TOC analysis for different depth without weathering of the top layer: not enough time was given for the rain and sun to weather the top layer of the bauxite and reduce TOC. The TOC within the first metre was variable with some very high level of organics. If this level of TOC contamination would supply the refinery without controlled blending, significant production losses would be incurred to maintain control in the precipitation circuit. These high levels of TOC can be eliminated at the mine by incorporating a stripping step in the overall mining plan. This is by far the most economical way of controlling organic impurities.

Figure 5. Typical photographs taken before and after stripping top soil and overburden.

2.3 Mining and Optimisation of Mining Plan

Mine planning is carried out based on exploration quality results, which are adjusted by the results obtained from sampling of the bauxite during the mining operation. In other words, this information is added to the mining plan to provide a more complete bauxite quality mapping and to ensure the bauxite is stockpiled according to physical and chemical bauxite quality.

2.4 Bauxite Blending Capability at the Mine and at the Port

Best practice is that each bauxite loader and trucks are fitted with GPS and transport of bauxite is monitored and controlled at all time. Based on the mining quality plan, each truck from the mine is unloaded to specific stockpiles to achieve optimum quality for each stockpile layer.

Additionally, specific stockpile should only be transferred from the mine to the port if the average bauxite quality complies with the forecast specifications.
Management of stockpiles at the port also needs to be fully monitored and controlled as far as the ship loading step. The bauxite loading stage is critical in the overall mining process particularly for the refinery: this is when the final blending of bauxite is done to deliver stable quality. The bauxite loading process must be accompanied by a fully automated sampling system using international standards and this system requires regular auditing to avoid introducing quality bias or quality drift.

A complete reconciliation should be made bi-annually between the mining plan from exploration (borehole) results, the mining results and the shipping results. This practice ensures that any gap found in the quality control is corrected in the mining plan model.

2.5 Laboratory Analytical Capability

An adequate laboratory capability is required to deliver consistent bauxite quality to a refinery [5]. Bias or drift in the analytical results could jeopardise the performance at the refinery. For example, if the reported TOC at the mine was 0.12% as per mine plan, but the actual TOC was 0.14%, this would result in severe reduction in production at the refinery unnecessarily. Any analysis bias on extractable alumina, TOC or reactive silica would have a significant impact on production and costs at the refinery.

The mine and port should have:

1. Competent laboratory personnel using established and approved methods with quality control and reference to standards.
2. Designated bauxite sample preparation area with moisture and size analysis.
3. Adequately equipped laboratories with purpose-designed equipment and instruments.
4. Laboratory lay out separating the sample preparation and analytical instrument areas.
5. A port facility with capability to produce a representative sample during the loading process of every ship and carry out analysis of physical properties and chemical composition. The ship loading sampling method should comply with internationally recognised standards. A sample for each ship would need to accompany the ship to the customer with certificate of analysis.

3. Control at the Refinery and its Limitations

3.1 Organic Impurities – Control at the Refinery

Organics contained in the bauxite are a mix of plant and animal derived products in various stages of decomposition. The bulk of organic matter is humic material – amorphous brown or black, hydrophilic acid, poly-disperse substances whose molecular weight ranges from several hundreds to tens of thousands. The brown or reddish colour of Bayer liquor is due to its organics content. [6].

The organics content in the bauxite is very much dependent on the bauxite origin but also on the mine strategy regarding timing and quality of stripping of the overburden and the blending of the top layer, which is richest in organics.

Organic carbon in tropical bauxites varies from 0.02% (Trombetas) to as high as 0.30 - 0.35% (Jamaica and Australia bauxites). MRN bauxite is known to contain a low level of TOC (0.04%) when compared to bauxite from Guinea (TOC of 0.13 – 0.15%); or with other bauxites which can contain TOC greater than 0.15% (see Table 1) [6].

Table 1. Total organic carbon in bauxite.

Bauxite	Total Organic Carbon (%)
Trombetas (MRN)	0.02 - 0.08
Guyana bauxite	0.15
Guinea bauxite	0.10 -0.14
Jamaica	0.28
Australia bauxite	0.20 - 0.30
Ghana bauxite	0.03 - 0.14

The organics are chemically modified in high temperature digestion and impact significantly on liquor productivity in many ways such as boiling point elevation, specific gravity or viscosity. In this paper, the focus is on sodium oxalate or simply “oxalate”, which is a critical impurity that builds up in the recirculating liquor within the refinery. The conversion rate from total organic carbon to oxalate is specific for each bauxite. Work from Steve Ostap shows that there are no general rules to be drawn as to how much of the organic carbon (see Table 2) in a bauxite would extract under a given set of digestion conditions or convert to oxalate or carbonate. This information must be experimentally derived [6].

Table 2. Conversion from organics to oxalate for different bauxite.

Organic carbon (%)	Bauxite	Temperature Degree Celcius	As sodium oxalate
0.12	Guyana 59762	143	**5**
0.11	Guyana Comp.	143	**6**
0.076	Boké (Vaudreuil)	143	**5**
0.083	Boké 40598	143	**5**
0.14	Ewarton 79	135	**5**
0.14	Kirkvine 79	135	**5**
0.16	Kirkvine 81	135	**8**
0.071	Bintan 78	142	**8**
0.082	Seaba 78	127	**6**
0.096	Seaba 80	127	**3**
0.018	Trombetas 81	143	**5**
0.100	Muri	138	**2**
0.090	Boké 40599	250	10
0.22	Gove	142	**16**
0.21	Comalco 78	210	**34**
0.18	Comalco 80	210	**17**
0.24	Ducie Wenlock	150	**10**

The Aughinish refinery is designed to operate an oxalate-free precipitation circuit. This means that oxalate is always maintained in solution below its critical saturation point through the entire precipitation circuit including classification and the seed filtration systems. This is achieved by ensuring that the oxalate input and oxalate output are in balance.

If oxalate is not maintained in solution, oxalate co-precipitates with alumina trihydrate (gibbsite) in all areas of the precipitation circuit (Figure 8). Oxalate crystals tend to be needle-like (Figures 6 and 7) and cause various problems in a precipitation circuit:

- Increased nucleation of gibbsite fines in the circuit, which leads to weak alumina product and high in fines in the product.
- Oxalate causes both oxalate and gibbsite scales in pipework, tanks, overflow launders, precipitates on filter cloths and limit plant capability even at very low level of solid phase oxalate.

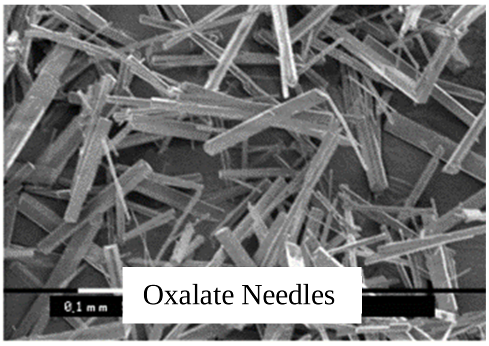

Figure 6. Oxalate needles.

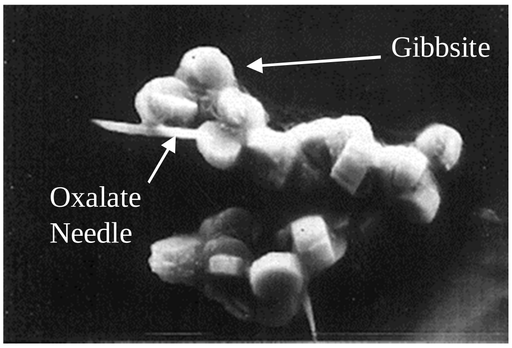

Figure 7. Gibbsite on oxalate needles.

Figure 8. Oxalate scale in pipework.

Oxalate is maintained in solution by adjusting precipitation parameters. The overall control is critical to precipitation stability and is monitored daily.

To maintain an oxalate balance in the process liquor, oxalate is removed from the liquor through a side process called “organics and impurities removal unit” where oxalate and other impurities are removed from the liquor (see Figure 9). The capacity of this oxalate removal unit has doubled over the years to enable production increases, but the removal capacity is still relatively small when compared to refineries designed for a high level of organics.

Figure 9. Aughinish refinery overview.

3.2 Inorganic Impurities – Control at the Refinery

Both CBG and MRN are low in impurities and the technology selected at the time it was installed, was chosen to deal with mainly carbonates, sulphates and chlorides at a low input level. The main digestion reactions are sufficient to remove the inorganic impurities such as sulphates, carbonates and chlorides and this paper does not cover other impurities such as phosphorus, zinc or others, which can be contained at higher levels in some bauxite in other parts of the world.

At Aughinish, the refinery relies on two process routes to control inorganic impurities: internal causticisation using milk of lime and desilication reactions both at low and high temperature:

Internal causticisation is carried out using milk of lime, which reacts in the digester at optimised conditions with the sodium carbonate present in the liquor. This reaction produces calcium carbonate and sodium hydroxide (Equation 1). The calcium carbonate reacts further with the anatase (TiO_2) in the bauxite to improve boehmite extraction at high temperature and form calcium titanate or perovskite ($CaTiO_3$) (Equation 2).

$$Ca(OH)_2 + Na_2CO_3 \rightarrow CaCO_3 + NaOH \qquad (1)$$

$$CaCO_3 + \text{Anatase } (TiO_2) \rightarrow \text{Perovskite } (CaTiO_3) \qquad (2)$$

Desilication process – Extensive work carried out by Peter Smith from The Commonwealth Scientific and Industrial Research Organisation (CSIRO) in this field has demonstrated some key removal mechanisms [7]. Kaolin in the bauxite (the majority of reactive silica) reacts with sulphates, carbonates and chlorides via the desilication process (see Figure 10). The kaolin reacts to form hydroxysodalite or sodalite at low temperature and cancrinite at high temperature. Both of these compounds have “cage like” structures (shown in Figure 11) that can trap various cations from the liquor such as sulphates, carbonates or chlorides [7]. The amount of impurities removed is proportional to the percentage of reactive silica in the bauxite as shown by the model developed by CSIRO (Figure 12) [7]. In other words, a minimum amount of reactive silica in the bauxite is required to maintain these impurities in balance.

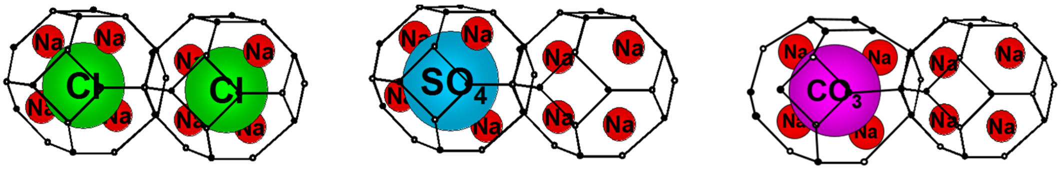

Figure 10. Carbonate, sulphate and chlorides trapped in cage structure.

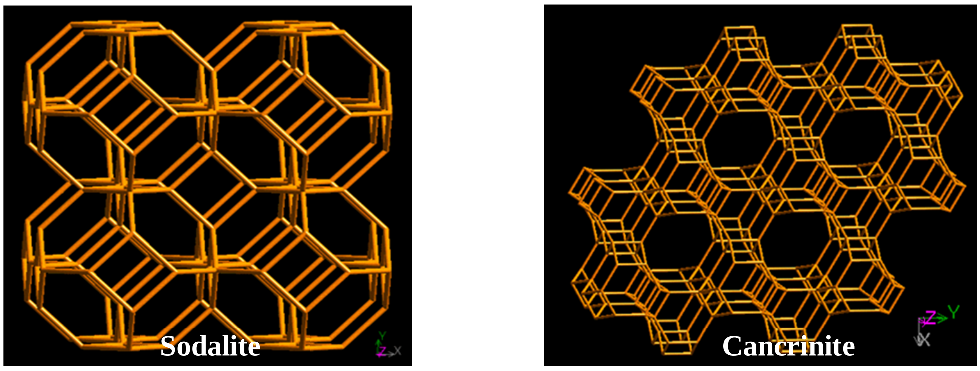

Figure 11. Structure of sodalite and cancrinite.

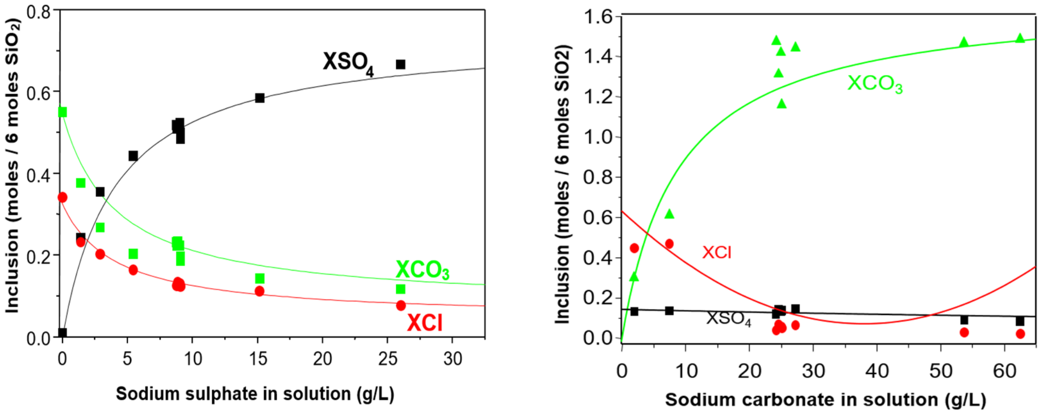

Figure 12. Impact of silica on impurities removal through desilication.

3.3 Impact of bauxite Quality on the Organic Impurities Balance

If the organics input into the refinery were to increase through an increase in TOC or a reduction in alumina content, then the organic impurities would build up in the liquor. This would result in the requirement to increase the organics removal capacity.

If the high temperature CBG bauxite consumed at AAL was to be replaced with other Guinean bauxite with lower extractable alumina and higher TOC, this would result in an additional bauxite input requirement for same production. The organics input would increase and the oxalate removal capacity would have to be increased to sustain production to match organics input. Figure 13 shows the impact of TOC and extractable alumina on oxalate input.

If MRN (TOC of 0.04%), AAL’s sweetening bauxite, was to be replaced by other Guinean type bauxite with higher TOC (e.g. 0.13%), the oxalate removal capacity would need to be increased. A major programme of investment would be required to support such an increase in organics and new technology would need to be implemented in the entire precipitation area, classification and seed filtration circuit to manage oxalate co-precipitation.

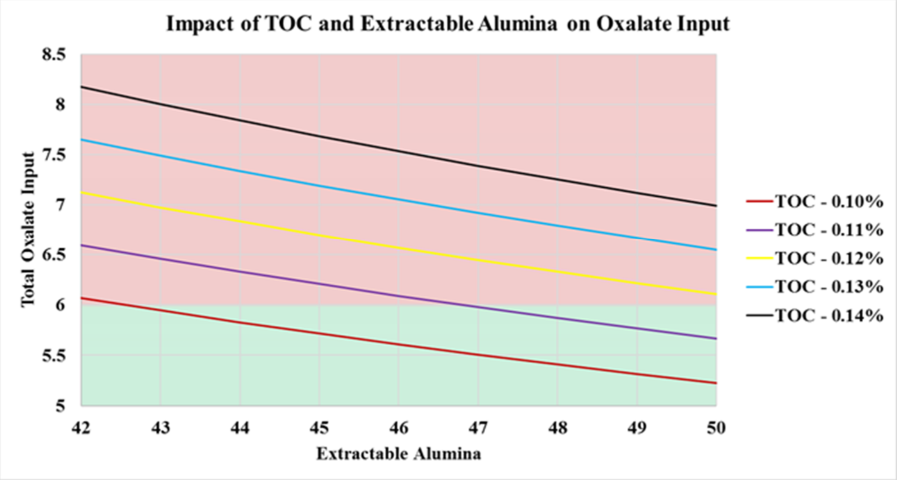

Figure 13. Bauxite quality and impact on oxalate input.

3.4 Impact of Bauxite Quality on the Inorganic Impurities Balance

A reduction of silica in the sweetening bauxite by using a low silica Guinean bauxite instead of MRN would more than double the carbonate removal requirement. As a result, the liquor productivity would reduce significantly.

The option to sustain production capability with 100% Guinean bauxite would require a major investment programme. The industry standard to increase carbonate removal capacity is with the installation of external causticisation (shown in Figure 14) [2]. Milk of lime is added to heated liquor stream from mud washing circuit in a reactor where lime reacts with carbonate in the liquor to form calcium carbonate and regenerate caustic (Equation 3). High lime consumption up to 45 tons per day would be required. Planning permission and a licence review would have to be undertaken.

$$CaOH_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaOH \qquad (3)$$

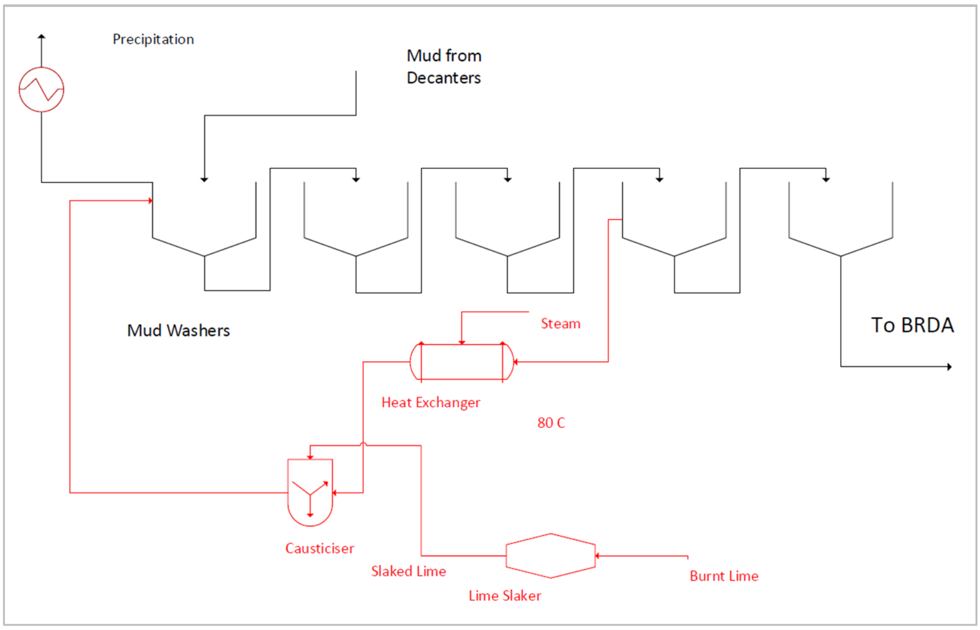

Figure 14. External causticisation.

5. Conclusions

The selection of plant design and technology for an alumina refinery is based on the physical and chemical composition of the bauxite supply: technology and equipment to control impurities play a critical part in the selection process. A bauxite quality change has to be thoroughly assessed and the bauxite quality must be compatible with the refinery technology.

The mine operation has a key role in controlling the overall bauxite quality and level of impurities, particularly its organics content. Optimised alumina, silica and TOC content with low variability in bauxite quality is critical to maintain production and performance in terms of product quality and costs.

A refinery such as Aughinish is highly optimised for its current bauxite blend and any increase in the level of impurities would require the appropriate technology modifications to overcome the change. This would necessitate a major programme of investment.

6. References

1. http://www.alcircle.com/bauxite/newscircle/general/detail/27336/top-five-bauxite-producing-countries-in-the-world , *Website AlCircle.com*, 25th March 2017.
2. Martin Fennell, Plant Capacity Report – Review of Bauxite Options, *AAL Internal report*, 2017.
3. Filip Orzechowski, Developing Bauxite Projects – Planning for Quality Product, *33rd International ICSOBA Conference*, 29 November – 1 December 2015.
4. CBG bauxite quality to Aughinish, *AAL Internal Report*, 29th August 2006.
5. Martin Fennell, Bauxite options review and laboratory requirement, *AAL Internal Report*, 2017.
6. Steve Ostap, Organics in the Bayer process, *AAL internal Bayer chemistry lecture series*, 1999.
7. Peter Smith, The processing of high silica bauxites — Review of existing and potential processes, *Elsevier*, 21st April 2009.