Impurities in Bayer Liquor: Learnings from the Ma'aden Alumina Refinery

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Abstract

This paper details some of the impurity issues commonly experienced at the Ma'aden Refinery. Elevated digestion temperatures (270 °C) release into the liquor a range of impurities that need to be monitored, modelled, managed and controlled. The main impurities discussed includes: sulphate (SO_4), carbonate (CO_3) and fluoride (F). De-Silication-Product (DSP) incorporates impurities SO_4>>CO_3>Cl, this does not include F. The high silica concentrations in the bauxite guarantee a very low SO_4 concentration in the liquor (< 1 g/L). When $CaCO_3$ is high in the bauxite, the CO_3 rapidly builds-up in the liquor. Fortunately lime injection at elevated temperatures promotes the transformation of DSP into cancrinite and incorporates CO_3 into its structure and controls concentrations in the liquor. CaO is present in the bauxite as $CaCO_3$ (< 2.5 %), additionally CaO (lime) is added to: 1/ settler, for liquor stability, 2/ during filter aid production, and 3/ digestion - injected at 270 °C. Tri-Calcium-Aluminate (TCA) and lesser amounts of Hydrogarnet (HG / Katoite) form during reaction of CaO with liquor and incorporates F into their lattice structure, this helps strip and remove F from the liquor. When there is insufficient $RSiO_2$ or CaO addition, the SO_4 and F respectively, can build-up in the liquor circuit. This condition will be amplified when a poor bauxite quality persists over a long period. In the Evaporation units, elevated impurity concentrations can occasionally give rise to excessive precipitation of NaF or fluoro-sulphate double salts. This deleterious scale formation in the heater tubes leads to process flow cuts and interferes with alumina production. The high impurity load drives the precipitation reactions through the 'common ion effect' and promotes the precipitation of the compound with the lowest solubility product.

Keywords: Boehmite, Fluoride, Cancrinite, DSP, Fluoride.

1. Introduction

In the planning of any bauxite mine or alumina refinery complex there is the requirement of "No Surprises" during the production phase. Implying that during evaluation and testwork everything has been considered both chemically and mineralogically, and there will be no serious unplanned impacts of impurities. In alumina refineries where liquors are continuously recycled low concentrations of impurities can incrementally build-up within the liquor phase and have a detrimental impact on operations. The causes may be through changes in bauxite composition (e.g. $RSiO_2$ grade, reduced CaO addition) or through operational changes, that may inadvertently change an impurity input or exit path [2, 3, 5]. Typically, a refinery is designed around a bauxite with a fixed compositional range representative of the future bauxite supply. The Ma'aden Alumina Refinery treats bauxite from the Al-Ba'itha Mine situated over 600km away. High alumina grades and high Reactive Silica ($RSiO_2$) contents characterize the bauxite.

The Bayer cycle requires steady state conditions, with constant flows, leading to consistent daily stability, these conditions will automatically lead to the delivery of high production and profitability. All continuous process steps need to work in harmony, with coordination and collaboration of operational centers. As process plants are usually operated at the highest practicable operating limits, any small destabilising event can interrupt the whole operation. High concentrations of impurities in liquor can easily lead to instability, notably in evaporation and precipitation where scaling and unwelcome crystallization can occur.

Impurities have two main impacts on the refinery, they can influence 1/ The liquor processability and operation efficiency (e.g. Precipitation Yield); and 2/ The SGA quality, which then goes on to influence the aluminium metal quality. Some of the impurity impacts on the aluminium cycle are reviewed in Table 1. The impurity chain leads directly back to the bauxite. To control these impurities, costs are often the lowest during mining operations where bauxite compositions can potentially be blended or controlled.

Table 1. Deleterious Impacts of Impurities on the aluminium production cycle.

Refinery Red Side	Refinery White Side	Smelting of SGA
Liquor viscosity	Precipitation yield. Can increase A/C ratio yet reduce yield	Conductivity impact
TC/TA, TS* TA-TC = Na_2CO_3 TS = TA + Impurities	Composition of SGA (Impurities in liquor can be easy transferred to hydrate)	SGA quality variability leads to operating issues (e.g. particle size)
Digestion / Extraction	Colour of SGA	Metal Product quality
Filtration Rate	Particle size distribution of SGA	Lower impurities the better
A/C target	Surface chemistry	Bath control and efficiency (e.g. Ca & P)
Requires constant monitoring	Crystal growth	Extra energy requirements
Lowers Free Caustic	Scale	Impurity build-up in the smelter bath
Settling Rate & Foaming	Viscosity impacts on settling rate in hydrate size classification	Metal product properties (hardness, ductility, reflectivity, brittleness etc)
Liquor density -incremental Impacts on milling, pumping and digestion	Lowers oxalate solubility and lowers maximum safe TC. Impacts on the achievable A/C. More oxalate can be held in liquors with higher TA.	Current inefficiencies.
Liquor boiling point elevation - Impact on heating	Apparent increase in alumina solubility (reduced yield).	Metal toxicity
Specific Heat Capacity	Refinery Odor (TOC)	

*TA = Total Alkalinity, TC = Total Caustic, TS = Total Soda,

2. Impurity Threshold Estimates

SGA and Aluminium metal customers demand stricter impurity concentrations and often they are prepared to pay extra for such premium products. For this reason, there is a focus on a wide range of impurities (g/L) and trace impurities (mg/L) in liquor, and include: V_2O_5, P_2O_5 and Ga_2O_3. Typical threshold concentrations in bauxite, liquor and SGA are given in Tables 2 to 4.

Precipitation of fluoride compounds in the evaporation stage is closely related to high TS (= presence of impurity) rather than high fluoride concentrations alone. Impurity impacts can originate from changes in the bauxite quality or from operational factors which may impact on an impurity input or exit path. Impurities can build-up in liquor and affect process efficiency, these can be incorporated in hydrate and ultimately affect metal quality.

In the Aluminium production chain attempts must be made to pass along a quality product from Mine to Refinery to Smelter to Customer. Collaboration can identify appropriate: strategies; practices and technologies to help reduce impurities. The cost implications and benefits for the removal of an impurity must be fully understood to assess whether it is financially justified and technologically possible. This requires communication between stakeholders and should enable appropriate and realistic thresholds to be established (Figure 3). This could be achieved through clear monitoring, and establishing Impurity and cost models to determine the quantitative impacts (US$) of individual elements on SGA and metal.

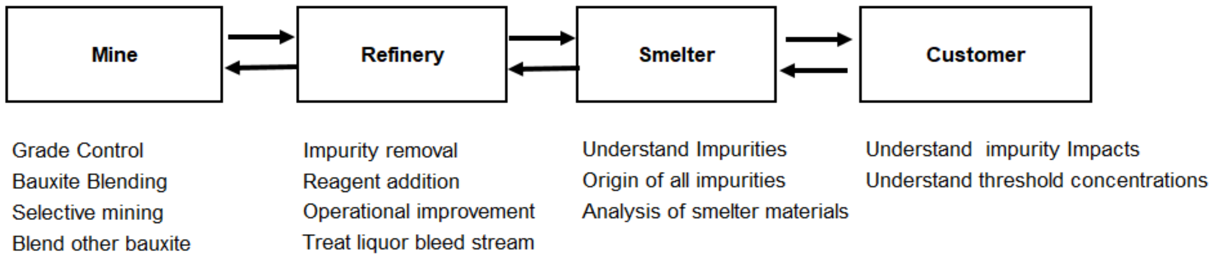

Figure 3. Stakeholder engagement for identification of impurity reduction opportunities.

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