

## 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<sub>4</sub>), carbonate (CO<sub>3</sub>) and fluoride (F). De-Silication-Product (DSP) incorporates impurities SO<sub>4</sub>>>CO<sub>3</sub>>Cl, this does not include F. The high silica concentrations in the bauxite guarantee a very low SO<sub>4</sub> concentration in the liquor (< 1 g/L). When CaCO<sub>3</sub> is high in the bauxite, the CO<sub>3</sub> rapidly builds-up in the liquor. Fortunately lime injection at elevated temperatures promotes the transformation of DSP into cancrinite and incorporates CO<sub>3</sub> into its structure and controls concentrations in the liquor. CaO is present in the bauxite as CaCO<sub>3</sub> (< 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<sub>2</sub> or CaO addition, the SO<sub>4</sub> 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<sub>2</sub> 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<sub>2</sub>) 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 <sub>2</sub> CO <sub>3</sub> 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<sub>2</sub>O<sub>5</sub>, P<sub>2</sub>O<sub>5</sub> and Ga<sub>2</sub>O<sub>3</sub>. Typical threshold concentrations in bauxite, liquor and SGA are given in Tables 2 to 4.

**Table 2. Impurity threshold concentrations for bauxites.**

Species	Mode of occurrence in bauxite	Typical Values** %	%Released into liquor***
NaF	Clay, Fluorspar, Gibbsite, Apatite	< 0.1 to 0.3	90
NaCl	Gibbsite	< 0.01	90
P <sub>2</sub> O <sub>5</sub>	Apatite	0.2, can be > 3.0 %	85
Ga <sub>2</sub> O <sub>3</sub>	Gibbsite / Boehmite	0.008 (80ppm)	70
V <sub>2</sub> O <sub>5</sub>	Iron oxides	0.1	60
Na <sub>2</sub> SO <sub>4</sub>	Pyrite / CaSO <sub>4</sub> .2H <sub>2</sub> O / other	0.5	90
EOC*	Organics (in pores and as rootlet)	< 0.2	90

\*Extractable Organic Carbon, As carbon

\*\*Must consider the Bauxite Use factor for estimating impurity per tonne of Al<sub>2</sub>O<sub>3</sub>

\*\*\*Estimated values (bauxite specific). Need to determine Available NaF, Available Na<sub>2</sub>SO<sub>4</sub> etc

**Table 3. Impurity threshold concentrations for Bayer liquors.**

Species	Encapsulation / Removal	Target Conc. g/L	Max. Conc. g/L
NaF	TCA	< 3.0	15
NaCl	DSP	< 8.0	15
P <sub>2</sub> O <sub>5</sub>	Apatite*	0.15	0.25
Ga <sub>2</sub> O <sub>3</sub>	liquor	< 0.25 to 0.35	0.4
V <sub>2</sub> O <sub>5</sub>	TCA	< 0.20	0.3
Na <sub>2</sub> SO <sub>4</sub>	DSP	< 5.0	20.0
TOC	Liquor Mud Product	< 10	30.0

\*first CaO bearing compound to precipitate

**Table 4. Impurity threshold concentrations for SGA product.**

Species	Target Conc. g/L	Max. Conc. ppm
NaF	Below detection	
NaCl	Below detection	
P <sub>2</sub> O <sub>5</sub>	0.0001	0.0004
*Ga <sub>2</sub> O <sub>3</sub>	< 0.01	0.0160
V <sub>2</sub> O <sub>5</sub>	< 0.0002	< 0.0003
Na <sub>2</sub> SO <sub>4</sub>	< 0.0003	
**Carbon	Below detection	

\*Ga<sub>2</sub>O<sub>3</sub> = Gallium = Ga (only in aluminium smelting is Gallium measured as the metal phase (ppm))

\*\*Trace amounts of C have the potential to discolor the product (removal requires O<sub>2</sub> injection into liquor)

Daily the refinery laboratory analyses many liquor samples. Upper concentration threshold values are set, and used to assess whether daily liquor compositions are above what is acceptable. Danger levels would require immediate operational changes and increased monitoring. During daily routine operations, Process teams are required to respond to Quality Alerts sent out by the laboratory and should investigate such changes, especially within evaporation where fluoro-sulphate scale can easily precipitate. For refineries with a high impurity load CO<sub>3</sub>, F, Cl and SO<sub>4</sub> are monitored and managed.

### 3. Impurity Balance

For an alumina refinery it is important to identify the origin and quantity of the inputs and outputs of individual impurities. Most are derived from bauxite but may also originate from impurities in the Lime (e.g. F, CO<sub>3</sub> and SO<sub>4</sub>), Caustic soda (e.g. Cl) and rarely from Residue decanted water (e.g. Cl and CO<sub>3</sub>). It is suggested that the impurity balance is calculated as grams per tonne of Alumina produced. It is then easy to construct a simple block model and assess whether the

existing circuit will lead to a net accumulation or depletion. If the soluble impurity has no exit path it will inevitably build-up in the liquor and then may influence product quality. It is also necessary to avoid bauxite overcharging as it will increase the impurity input per tonne of alumina product.

Maximum precipitation yield will be highest when  $TC/TS = 1.0$  (i.e. no  $Na_2CO_3$  or other impurities). However, this value is usually unobtainable due to some impurities always being present in the liquor. Precipitation yield does dramatically drop-off through impurity interference during hydrate nucleation and growth. While most impurities are soluble, some impurities can come from ultrafine particulates which may migrate with the fluid phase through security filtration (Table 5). High precipitation yields can reduce selected impurity concentrations e.g. Ca, Ti, Fe from liquors. This is through a simple mass dilution effect.

#### 4. TCA and Fluoride Control

For a simple fluoride model, mass flows and elemental concentrations are required for the known exit paths and are illustrated in Figures 1 and 2. These also represent the impurity fluxes for most impurities unless there is a complication, such as when a soluble impurity combines to form a chemical complex (e.g. Fe with  $SO_4$  or an organic molecule). The liquor impurity concentrations eventually build-up in the liquor, and this represents an equilibrium or saturation state reflecting daily inputs and outputs. A factor can then easily be formulated to assess the ability of the refinery to remove NaF from the liquor.

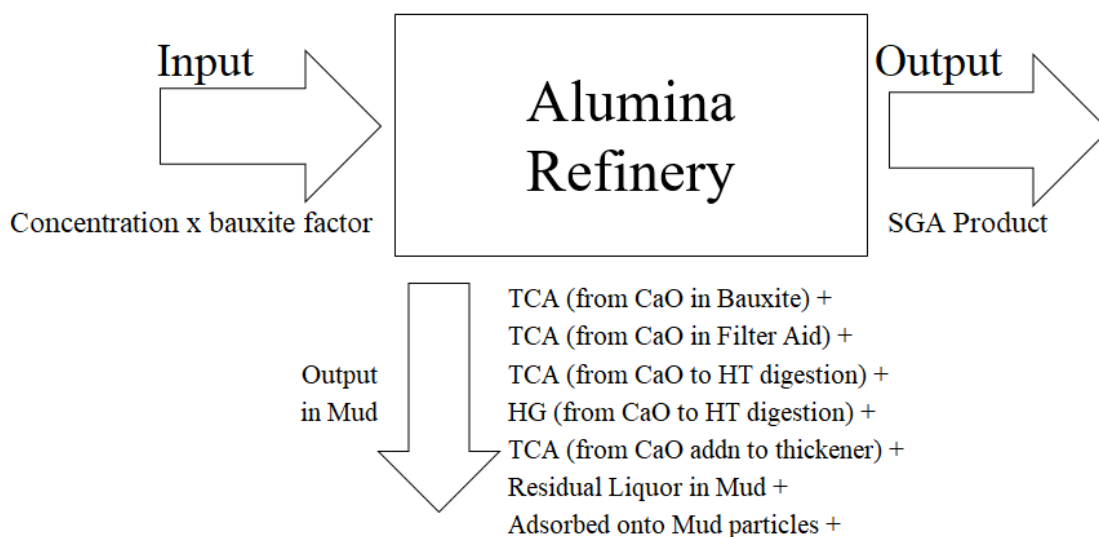


Figure 1. Inputs and exit paths for fluorides at the Ma'aden refinery.

**Table 5. Inorganic impurity behaviour during precipitation.**

Impurity Type	Behaviour during precipitation	Comments
Soluble and Particulates (easily precipitated)	Early stage particulate solids removal. Also the co-precipitation of selected species almost complete in precipitation circuit.	May originate from fine mud particles – DSP, goethite or TCA. Fe – considered to be present as nano-particles Elemental concentrations in solids dependent on precipitation yield. For calculation use → Conc. % = Liquor conc. (mg/L) / PPT yield (g/L) x10 E.g. Fe, Ca, Zn, Cu, Ti, Mn, Mg, Nb, Be, Zr, REE
Soluble (proportionally precipitated)	Dependent on concentration in liquor. Incorporated into hydrate lattice during growth.	E.g. Ga – similar atomic size and valency to Al(III). (valency or cationic size effecting substitution). A lot of the other inorganic impurities will be captured on the crystal growth faces rather than getting incorporated into the structural lattice.
Soluble (partially precipitated)	Partial incorporation into hydrate through co-precipitation.	Builds-up in liquor owing to minimal losses to: - i/ product, ii/ lake and iii/ mud and iv/ condensate. When not removed in precipitation will return to liquor circuit and lead to an increased concentration if no other exit path available. There can also be some complexation with other species within the liquor. E.g. SO <sub>4</sub> , F, organics. Also, V and As. Silica is of this type and is not easily removed from liquor.
Soluble (not-easily precipitated)	Not readily co-precipitated or incorporated due to atomic size.	Ions are too large (E.g. Cl) or too small (E.g. Li) to be incorporated into hydrate structure. PO <sub>4</sub> behaviour comparable to Cl. TOC and CO <sub>3</sub> appears in this category

**Table 6. Formation of calcium compounds in Bayer liquors.**

Compound	Estimated Formula	Comments
TCA Family	$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot n\text{SiO}_2 \cdot (6-2n)\text{H}_2\text{O}$	Variable SiO <sub>2</sub> and water in structural end-members
Pure TCA6	$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ n = 0	Compound incorporates impurities (F + V)
Katoite Silication +	$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot 4\text{H}_2\text{O}$ n = 1	Incorporation of SiO <sub>2</sub> into structure + impurities (F + V). formed at >50 °C
HydroGrossular (High Temp.)	$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ n = 2	Incorporation of SiO <sub>2</sub> into structure + Fe → hydrogarnets (HG) >200 °C Unhydrated varieties unlikely to form in Bayer liquors at elevated temperatures
Calcite	CaCO <sub>3</sub>	Unlikely to form due to the compound being unstable in high TC/TA liquors.
Cancrinite	$6\text{NaAlSiO}_4 \cdot x\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ Where x = 2 to 6	Can also exist as the low Ca cancrinite variety and may be predominantly Na

During contact with spent liquor the CaO in the bauxite (as calcite) reacts to form TCA (Table 6) and will encapsulate F and any VO<sub>4</sub> and PO<sub>4</sub>. Likewise, during addition to the thickener and in Filter Aid production, the addition of lime to liquor forms TCA and incorporates soluble impurities. It has been quoted in the literature [2] that TCA can encapsulate up to 3 % NaF into its structure (w/w). Further quantification and validation needs to be pursued and impurity balance models improved upon. Injection of lime at elevated temperatures forms a high silicate TCA

compound (HG or Katoite). This may incorporate different amount of F than the low temperature TCA, however these compounds are also beneficial in that they help strip SiO<sub>2</sub> and partially incorporate soluble Fe into their structures.

The CO<sub>3</sub> input into the circuit is through CaCO<sub>3</sub> addition in the bauxite itself. Lime addition at elevated temperature (270 °C) can indirectly convert Na<sub>2</sub>CO<sub>3</sub> to NaOH and helps increase TC in the liquor, which in turn helps to increase boehmite extraction. A TCA-type compound is more stable under these conditions and will form in preference to CaCO<sub>3</sub>. At Ma'aden Cancrinite formation helps remove CO<sub>3</sub> and maintains a high TC/TA ratio (> 0.93). The addition of lime at elevated temperatures promotes the DSP to Cancrinite transformation which allows CO<sub>3</sub> to be incorporated into the structural lattice of the compound. Cancrinite would appear to have a greater ability to remove carbonate from the liquor than DSP/sodalite-type compounds and also benefits from soda savings.

Evaporation of liquors in a Bayer circuit leads to an increased TS (Total Soda) and promotes the crystallization of sparingly soluble salts and can lead to the scaling of pipework [2]. Simplistically the solubility product of a compound is exceeded and leads to precipitation of a fluoride containing compound. These crystalline solids include: – NaF, Na<sub>2</sub>SO<sub>4</sub>.NaF (kogarkoite) and NaF.Na<sub>2</sub>V<sub>2</sub>O<sub>5</sub>. Depending on the liquor matrix (= impurities) a whole range of compounds can form. When V<sub>2</sub>O<sub>5</sub> and SO<sub>4</sub> concentrations are low pure NaF can crystallize. For elevated sulfate concentrations, under extreme circumstances kogarkoite can even coprecipitate with hydrate [2], and interfere with its growth and morphology. It is the total concentrations of all impurities in the liquor that have a major impact on solid precipitation, rather than the fluoride concentrations alone. With increasing sodium ion concentration, the over-riding impact upon precipitation is the “common ion effect”.

Operational changes such as lime reduction or changes in the bauxite characteristics can result in problems even if NaF remains at the same concentration in the bauxite feed. Just as in oxalate control, in a refinery there is a need to operate within a suitable safety margin between the baseline level of the F and SO<sub>4</sub> concentrations. This helps avoid passing the kogarkoite solubility limit in the evaporator discharge [2]. To prevent salting-out of solids there is a need to limit the TC and TS targets during evaporation, alternatively targeting a reduction in the activity of one or more of the interfering element.

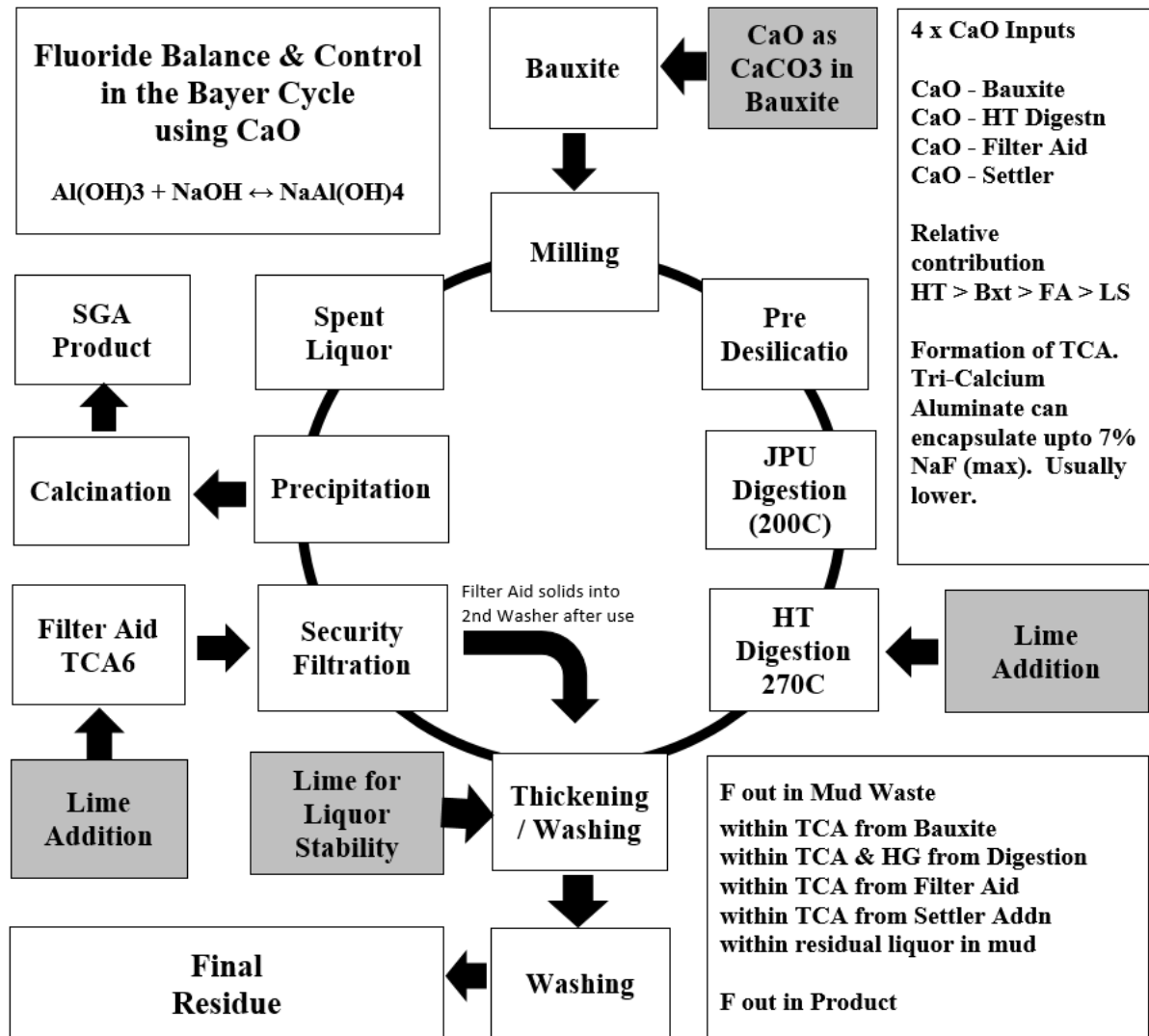


Figure 2. CaO addition and the exits paths for fluoride-bearing TCA compounds.

## 5. DSP and Sulphate Control

Kaolinite reacts with caustic to produce a DSP with a sodalite-type structure. Under Predesilication conditions (95 to 105 °C) the low temperature DSP can incorporate anionic molecules into its framework structure thereby stripping the liquor of selected impurities. This “capture” of impurities into the lattice is well established and contributes to impurity control. DSP incorporates impurities in the relative order  $SO_4 \gg CO_3 > Cl$ , it must be noted that F does not get bound into the lattice structure [3, 4]. The incorporation of  $SO_4$  will always take preference over all other impurities and fill structural sites prior to incorporation of carbonate and chloride. In the Ma’aden refinery as digestion temperatures are raised the DSP re-equilibrates and becomes more crystalline and the size and shape of the DSP cages are also likely to change. In the presence of calcia (from the bauxite) together with the addition of lime in HT digestion this promotes the formation of a cancrinite-type DSP.

**Table 7. Alumina refinery impurity inputs and outputs.**

Impurity	Inputs from bauxite	Outputs (removal process paths)
F	Apatite, CaF or Phyllosilicate minerals	CaO in bauxite → TCA Apatite or TCA (filter aid). Not incorporated into DSP Up to 7.3 % NaF has been reported in some TCA solids. Possibly a 20 % lime removal efficiency at equilibrium fluoride concentrations in liquor [2]. Soluble losses (and adsorbed) (< 0.1g /t Al <sub>2</sub> O <sub>3</sub> ) In SGA product (< 0.1g /t Al <sub>2</sub> O <sub>3</sub> ) High silica versions of TCA, (= Katoite = Hydrogarnet) [3CaOAl <sub>2</sub> (SiO <sub>4</sub> )(OH) <sub>8</sub> ], may not incorporate fluoride as efficiently as TCA (see Figure 2)
Cl	Apatite / Bauxite	Apatite & DSP
SO <sub>4</sub>	Sulphide or Gypsum. From acid cleaning of JPUs. Impurity in Lime.	DSP or Na <sub>2</sub> SO <sub>4</sub> . High concentrations of DSP can efficiently remove SO <sub>4</sub> . When DSP is low and SO <sub>4</sub> is high this can lead to the precipitation of double salts.
TOC	In bauxite and as rootlets. Originate from reagents	SGA Product (< 5 %), < 15 % in Mud, Through Liquor Burning, Thermal destruction.
PO <sub>4</sub>	Apatite Organic Reagents?	Apatite / TCA – through lime addition
CO <sub>3</sub>	Organics and CaCO <sub>3</sub> . Reaction of CO <sub>2</sub> in air with liquor / lake water. Reagent decomposition products.	Into DSP / cancrinite Cancrinite can incorporate CO <sub>3</sub> into its structure Cancrinites - Na <sub>6</sub> Ca <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> Al <sub>6</sub> Si <sub>6</sub> O <sub>24</sub> ·2H <sub>2</sub> O Formed during Lime injection and conversion of DSP to Cancrinite
V	Iron oxides	Iron oxides and in TCA and fluoro-vanadates
All soluble impurities		Removed in residual liquor and adsorbed onto particles within Mud* Proportion of elements exiting likely to be < 10–15%.

\*Residual liquor in mud stream can be deliberately increased to deliver on the removal of soluble impurity targets. This practice is more typically carried out to reduce organic carbon concentrations. However, it has also been known for refineries to bleed Bayer liquor directly.

For a bauxite stockpile of known chemical composition an empirical “DSP” SO<sub>4</sub>, CO<sub>3</sub> and Cl removal factor can be devised. For liquors that are highly saturated in impurities it is likely that the DSP impurity removal process may not be able to cope with the very high impurity load. This factor will be refinery specific depending on the nature and quantity of the DSP and Cancrinite species and the impurities present in the bauxite. At Ma’aden very low sulphate concentrations are maintained in the liquor (<1g/L) through the ability of high concentrations of DSP to incorporate SO<sub>4</sub>. CO<sub>3</sub> introduced with the CaCO<sub>3</sub> in the bauxite constitutes a major impurity input and the cancrinite and DSP-type compounds enable the CO<sub>3</sub> to be incorporated into their structure and strip the liquor of CO<sub>3</sub> (Table 7).

## 6. Chloride and Gallium

Within the Ma’aden Bayer liquor significant quantities of chloride influences the efficiency of operations. Another example of an impurity is Ga which has an impact on metal product quality. While there are low concentrations of chlorides in the bauxite, it is mainly introduced into the liquor from the caustic supply. Diaphragm Cell caustic has typically 10 to 20 g/L NaCl, whereas

Membrane Cell caustic – is significantly lower (1 to 2 g of NaCl) and commands a higher unit cost.

Chloride concentrations are controlled by partial incorporation into the DSP/Cancrinite and an equilibrium concentration is built-up. NaCl has a high solubility in evaporated liquor and is not easily salted-out, whereas F, SO<sub>4</sub>, CO<sub>3</sub> and V are more easily removed from the liquor during evaporation owing to their incorporation into selected solid phases which have a lower solubility product.

Ga has a similar atomic size and valency to aluminium, and partially co-precipitates within the hydrate as it is easily substituted into the crystal structure. Newly introduced Ga from bauxite slowly bleeds out of the circuit with SGA, mud and residual liquor. Globally Bayer Liquors appear to reach an equilibrium or saturation concentration of around 0.25 to 0.35 g/L [5]. Ga is incorporated into the hydrate in concentrations that relate to the equilibrium elemental concentrations in the liquor. The TC and Al concentrations in the liquors will dictate the equilibria and the Ga/Al ratio in the products are likely to be reasonable constant. Vind et al, 2018, estimated a Ga removal of ~67 % to SGA and ~33 % to mud fraction.

## 7. Impurity Control Options

Mine grade control is the first possible area where impurities can be controlled and reduced. Mapping of the floor and roof of the bauxite horizon is the key for any successful grade control change. Refined borehole spacing and identification of the optimal stratigraphic horizon is required to control the impurity inputs into the aluminium metal cycle. TAA, Fe<sub>2</sub>O<sub>3</sub>, RSiO<sub>2</sub>, CaO, concentrations can be controlled in different pits and selected anomalies blended out. Some impurities are unavoidable owing to their low concentrations in the bauxite e.g. Ga, and their close association with gibbsite and boehmite. Selective mining can produce a higher alumina grade bauxite, but this may raise or lower the CaO in feed (= Calcite) which may then impact on the amount of TCA formed for F control. However, this is also detrimental in that it introduces CO<sub>3</sub> into the liquor. It is required to establish blending strategies to prevent large surges in impurities (F/SO<sub>4</sub>) and ensure at least 4 to 5 operating pits are simultaneously in production to create a consistent blend composition. Communication with the Mine on a regular basis together with the education of personnel on the importance of blending and impurity control is of paramount importance.

A basic understanding of the individual impurity will help identify how it can be extracted from Bayer liquor (see Table 8). Many options are available including: evaporation and precipitation from concentrated liquors. The cost for the removal of such impurities is often easily justified as this is considered a precipitation yield improvement enabler.

In the various processes water is removed, through evaporation or liquor chilling, crystalline solids are precipitated. High concentrations in liquors may require a continuous side-stream treatment process. In any salting-out evaporation process the viscous slurry will need to be filtered to remove a fine-grained precipitate. As TC is raised SO<sub>4</sub> is precipitated as a double salt below TC 300 g/L. Above a TC of 300 to 360 g/L the CO<sub>3</sub> precipitates as a double salt. Even higher TC (>400 g/L) concentrations lead to Oxalate precipitation and explains why prior oxalate removal is preferable as a first step. On treating the Oxalate Building liquor discharge a 2-stage removal process could be considered with a progressive increase in TC in the evaporated liquor.

Stage 1 – Fluoro/sulphate removal

Stage 2 – Na<sub>2</sub>CO<sub>3</sub> removal

The final mud waste stream and associated liquor loss represents an important impurity exit stream. This stream can be controlled to increase the liquor exit when liquor volumes, enriched in

impurities, need to be urgently discharged from the refinery. However, during refinery operations attempts are often made to reduce soluble soda losses and meet financial and environmental targets. While significant savings in caustic usage may be possible, this will cause an increase in Na<sub>2</sub>SO<sub>4</sub>, NaF and NaCl concentrations in the liquor through an increased recirculation of impurities.

Numerous processes have been suggested for the removal of Ga from liquors, these include using carbonation or mercury amalgam [8, 9]. However, these steps are often targeting the production and sale of small quantities of Ga, rather than attempting to dramatically lower liquor concentrations to impact on product quality. Large scale processing would require an SX (solvent extraction) or IX (Ion Exchange) process plant which could realistically lower Ga in the Bayer liquor. Literature suggests SX is capable of stripping 60 to 70 % of Ga from a spent liquor stream. Daily Processing and removal of a significant amount of the Daily Input of Ga would be required (e.g. Bauxite Tonnage used x Ga content).

**Table 8. Currently available impurity removal technologies.**

<b>Technology*</b>	<b>Precipitation Process</b>
Salting Out Evaporation (SOE) (<100 °C)	Na <sub>2</sub> CO <sub>3</sub> .2Na <sub>2</sub> SO <sub>4</sub> , Na <sub>2</sub> SO <sub>4</sub> .NaF. nNa <sub>2</sub> SO <sub>4</sub> and Na <sub>2</sub> CO <sub>3</sub> . Na <sub>2</sub> CO <sub>3</sub> .2Na <sub>2</sub> SO <sub>4</sub> (range of double salts - NaF.2Na <sub>3</sub> XO <sub>4</sub> .19H <sub>2</sub> O where X = V, P, As) NaCl not removed – as it is highly soluble Product filtration may be an issue when liquor is viscous Unseeded evaporative crystallization
Salting Out Evaporation (SOE) (deep evaporation)	Commonly used, removes multiple impurities, including oxalate also removed. Products may be very difficult to filter or settle. Salt cake processing required
Liquor Burning	Treats oxalate residues and removes organics from the liquor Liquor Burning – Highly effective and removes all organics in treatment stream Problems: high capex/opex. Can be unreliable. Odors, halide emissions and caustic dust. Highly energy inefficient. Workforce/community issues.
Liquor Cooling	Na <sub>2</sub> SO <sub>4</sub> .10H <sub>2</sub> O removed when liquor taken to low temperatures (minus 20 °C).
Solid Liquid Calcination (SLC)	Used with high organic bauxites which generate a high content of Na <sub>2</sub> CO <sub>3</sub> . E.g. San Ciprian [6]. SLC a viable option, with few reported incidents
Geopolymer encapsulation	Discharge volumes of hot SL combined with BFS or metakaolin to form a useable concrete-type final product.

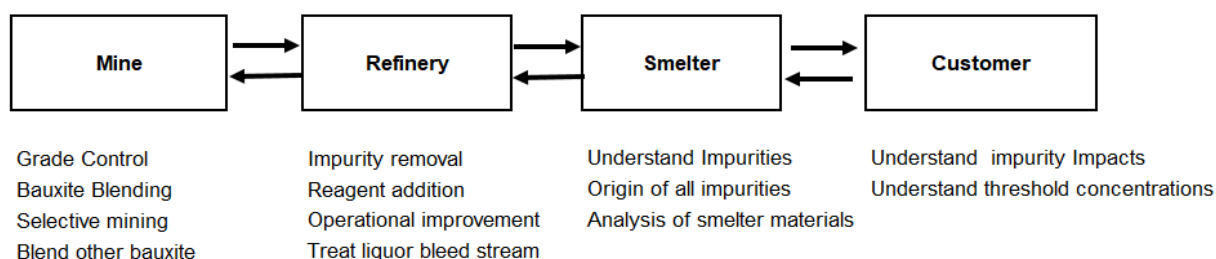
\*Table adapted from [7]

## 8. Conclusion

Experience has taught the alumina industry to never underestimate the possibility of unplanned impurity related problems occurring. Process technologies are available to lower the liquor impurity loads but these come at a high price. Prior to any expenditure it is recommended to investigate low cost options for incremental impurity removal and control. Continuous monitoring of impurity loads and bauxite chemistry can give a good indicator of future F problems (related to CaO usage) or SO<sub>4</sub> problems (related to reduced RSiO<sub>2</sub> concentrations = DSP).

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.**

## 9. References

1. P. Smith, Reactions of lime under high temperature Bayer digestion conditions. *Hydrometallurgy*. V170, P16-23, 2017.
2. D. Wilson, et al, Fluoride chemistry in the Bayer Process. *Proceedings of the 6th International Alumina Quality Workshop 2002*. P281 to 287.
3. G.W. Riley et al. A generic system of plant impurity balance models. *Proceedings of the 6th International Alumina Quality Workshop 2002*.
4. G.W. Riley et al. Plant impurity balances and impurity inclusion in DSP. *Proceedings of the 5th International Alumina Quality Workshop 1999*.
5. J. Vind, et al. Distribution of Selected Trace Elements in the Bayer Process. *Metals - Open Access Metallurgy Journal*. 8 (5), 327 May 2018
6. J. Pulpeiro, and M. Gayol, A year of operation of the solid-liquid Calcination (SLC) Process. *Light Metals 2000*, Ray D. Peterson, Editor.
7. S. Rosenburg, Impurity removal in the Bayer Process. *ICSOBA 2017*, Hamburg, 2 – 5 October, 2017.
8. Z. Zhao, Y. Xiao, Y. Fan, Recovery of gallium from Bayer liquor: A review. *Hydrometallurgy* V125–126. P115–124, 2012.
9. S. Lahirir, R. Meyappan, A. Varadharaj. Gallium Recovery – Technological Alternatives. *Bull. Electrochemistry* 12(5-6) P342-345, 1966.