IMPURITY REMOVAL IN THE BAYER PROCESS

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Presented by: Steven Rosenberg
Presenter’s Bio

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• Present position: Director, Bauxite Residue R&D

• Work experience: Over 30 years in technical management and research roles in Bauxite/Alumina with companies such as Alcoa, Worsley Alumina and BHP.
Contents

• Introduction
• Bauxite and Other Impurity Sources
• How Impurities Affect Productivity
• Major Impurities and Removal Technologies
• Bauxite Residue Impacts
• Conclusions
Introduction

- Refineries are designed around the bauxite.
- Impurities can play a substantial role in design and operation.
- Most impurities are managed through ‘natural’ sinks.
- High relative inputs require dedicated removal processes.
- Impurities that mostly affect product quality are not covered in this talk.
- Thousands of impurity removal concepts, very few in commercial use.
### Some Typical Bauxite Ores

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<tr>
<th>Species</th>
<th>Guinea</th>
<th>Brazil</th>
<th>Weipa</th>
<th>WA (1)</th>
<th>WA (2)</th>
<th>India</th>
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<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.02</td>
<td>1.13</td>
</tr>
<tr>
<td>C inorganic</td>
<td>0.06</td>
<td>0.01</td>
<td>0.03</td>
<td>0.1</td>
<td></td>
<td></td>
<td>0.4</td>
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<tr>
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<td>0.11</td>
<td>0.03</td>
<td>0.23</td>
<td>0.2</td>
<td>0.2</td>
<td>0.11</td>
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<td>0.04</td>
<td>0.03</td>
<td>0.09</td>
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<td>0.02</td>
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Bauxite

- Wide range of impurities both inorganic and organic.
- Wide range of species extracted under Bayer conditions.
- Most impurities are controlled to ‘acceptable’ levels through DSP and soluble losses.
- Most refineries have effective control systems for carbonate and oxalate.
  - Not always efficient.
- Ideal solutions for TOC, sulphate and some other impurities yet to be found.
- Drive for Bauxite residue use puts pressure on purging for impurity control
How Impurities Affect Productivity

- Increase in ionic strength alters OH\(^-\) and Al(OH\(_4\))\(^-\) activities.
- Yield effects
- Product quality controls (e.g. oxalate).
- TS limits ‘C’.
- Surface chemistry effects (e.g. rate).
- Scale (availability and op factor).
Carbonate

- Relatively small inorganic input
- Most carbonate formed through base-catalysed cleavage of organics in digestion
- Some carbonate enters via lake water by CO$_2$ dissolution or photocatalytic breakdown of organics
- Removal via:
  - Intercalation in DSP
  - Causticisation
  - Salting-out
Carbonate Removal

- Lime / Caustic
- Bauxite Mills
- Desilication
- Digestion
- Clarification
- Precipitation
- Classification
- Calcination
- Gas / Coal
  - Steam / Utilities
  - Mud Washing / Filtration
  - Causticisation
  - Residue storage or use
- Salting Out
- Evaporation

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Causticisation

- **Causticisation reactions**
  - \[4\text{Ca}(	ext{OH})_2 + 2\text{Al(OH)}_4^- + \text{CO}_3^{2-} \rightarrow \text{Ca}_4[\text{Al(OH)}_6]_2 \cdot \text{CO}_3 + 4\text{OH}^-\]
    - (Hydrocalumite hemicarbonate or monocarbonate)
  - \[\text{Ca}_4[\text{Al(OH)}_6]_2 \cdot \text{CO}_3 + 3\text{CO}_3^{2-} \rightarrow 4\text{CaCO}_3 + 2\text{Al(OH)}_4^- + 4\text{OH}^-\]
    - Formation of calcium carbonate
  - \[3\text{Ca}_4[\text{Al(OH)}_6]_2 \cdot \text{CO}_3 + 2\text{Al(OH)}_4^- + 4\text{OH}^- \rightarrow 4\text{Ca}_3[\text{Al(OH)}_6]_2 + 3\text{CO}_3^{2-}\]
    - TCA formation

- **Overall Reactions**
  - \[\text{Ca(OH)}_2 + \text{CO}_3^{2-} \rightarrow \text{CaCO}_3 + 2\text{OH}^-\]
  - \[3\text{Ca(OH)}_2 + 2 \text{Al(OH)}_4^- \rightarrow \text{Ca}_3[\text{Al(OH)}_6]_2 + 2\text{OH}^-\]

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Causticisation

• **Causticisation**
  – Typical lime efficiency is about 50%
  – Can increase this to over 90% by limiting TCA formation
    • Worsley TCA inhibitor
    • Worsley and Alcoa – High Temperature Causticisation (HTC)

• **Salting Out**
  – Deep evaporation of spent liquor
  – Product often includes other species including sulfate and oxalate
  – HMW organics tend to produce a sticky cake that is difficult to handle
  – Disposal an issue
Effect of TCA Inhibitor

Equilibrium C/S showing the effect of a TCA inhibitor

- without TCA inhibitor
- with TCA inhibitor

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Sulfate - Inputs

• Mostly enters via sulfate/sulfide minerals
  – Kaolin, jarosite, oxidation of pyrite or marcasite

• Other sources:
  – Gypsum
  – Sulfides added for Zinc control
  – Degradation of sulfur-containing organics
  – Cleaning acid
Sulfate – outputs

• Major sinks are DSP and soluble losses
  – Most sulfate removed via intercalation in sodalite (templates around sulfate anion)
  – Less so with cancrinite
  – Entrained liquor in residue
Sulfate – outputs

• **Other Removal Strategies:**
  – **Salting out** \((\text{Na}_2\text{CO}_3.2\text{Na}_2\text{SO}_4, \text{Na}_2\text{SO}_4.\text{NaF})\)
    • Cake performance due to organics, disposal
  – **Salting out / liquor burning**
    • Filtration issues
  – **Cooling** \((\text{Na}_2\text{SO}_4.10\text{H}_2\text{O})\)
    • Energy, scale formation
  – **Layered double hydroxides** (hydrocalumite, Lithium LDH)
    • Cost, alumina loss
Organics - inputs

• Vast range of organic species in bauxite
  – Intact materials (plant and animal matter)
  – Cellulose, lignin, humic and fulvic acids (HMW)
  – Degraded matter (simpler organics)

• HMW organics cause the most problems due to tendency to absorb on surfaces
  – Surface chemistry impacts such as impurity incorporation, yield effects, morphology changes, and filtration problems

• Base-catalysed hydrolysis results in simpler organics and ultimately carbonate, oxalate and other carboxylates

• Can contribute substantially to ionic strength
Organics Removal

Lime / Caustic

Bauxite

Mills

Desilication

Digestion

Wet Oxidation

Clarification

Precipitation

Adsorbants P-DADMAC

Calcination

Mud Washing / Filtration

Gas / Coal

Steam / Utilities

Residue storage or use

Liquor Burning Salting out

Evaporation

ICSOTA

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Organics – HMW Removal

• **Adsorption**
  – Inert, high surface area materials
    • Activated charcoal, magnesia, dolomite, hydrotalcite, TCA, alumina
  – Problems: Separation, poor performance/cost, efficacy

• **Membranes**
  – Polysulfone based ultra- and nano-filtration, cross flow systems
  – Problems: poor permeate flux rates, fouling (including suspended solids), doesn’t really *remove* organics, costly.

• **Anion Exchange (polyDADMAC)**
  – Effective for some HMW organics, in relatively common use.
  – Problems: Expensive, exchanges organics for chloride
Organics – Broad-range Removal

• Wet Oxidation
  – Effective for many organics (esp HMW), relatively economical to install/run.
  – Problems: Hydrogen explosion risk, extreme conditions required for refractory organics, Separation, poor performance/cost, efficacy

• Liquor Burning
  – Highly effective – removes all organics in treatment stream
  – SLC a viable option, with few reported incidents.
Organics – Other Removal Options

• Bauxite Roasting
  – Calcination of bauxite prior to digestion, producing transition aluminas and goethite-haematite conversion
  – Problems – demonstrated at pilot scale, but never applied. Likely very high Capex/Opex, energy/GHG, odour and dust control issues.

• Other techniques
  – Oxidative: MnO$_2$, plasma torch
  – Biological – Demonstrated for oxalate, could be extended to other carboxylates.
  – Geopolymer – reaction of a side-stream of liquor with active silica to produce a geopolymer solid that supposedly entombs all impurities.
Oxalate - Inputs

- Most oxalate produced through base-catalysed cleavage of more complex organics
- Small amount adsorbed on mineral surfaces
- Some oxalate present as oxalic acid (mainly in bauxite overburden)
Side-stream Oxalate Removal

- Lime / Caustic
- Bauxite Mills
- Desilication
- Digestion
- Clarification
- Precipitation
- Classification
- Calcination
- Oxalate Removal
- Evaporation
- Oxalate Destruction

- Gas / Coal
  - Steam / Utilities
  - Mud Washing / Filtration
  - Residue storage or use

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Evaporation/crystallisation

- Very common, reliable removal method. Moderate evaporation, with recycled oxalate seed. Crystals separated by filtration and discarded or destroyed,
- Problems: Oxalate morphology (filtration), yield can be poor, strongly affected by HMW organics and other surfactants. P-DADMAC can help.
Oxalate – Side stream removal

• **Salting Out (deep evaporation)**
  – Commonly used, removes multiple impurities
  – Problems: poor oxalate morphology, often heavily contaminated with HMW organics. Very difficult to filter or settle.

• **“Drowning” out**
  – Alternative to Salting Out, decreases water activity by addition of partially miscible alcohols to supersaturate oxalate
  – Problems: Cost (solvent recovery), flammability, odours.

• **Sonocrystalisation**
  – Induces oxalate crystallisation by cavitation. Improved oxalate yield in pilot trials
  – Problems: Oxalate morphology, cake separation
Oxalate Co-precipitation

1. Lime / Caustic
2. Bauxite
   - Mills
   - Desilication
   - Digestion
   - Clarification
   - Precipitation
   - Classification
   - Calcination
3. Gas / Coal
   - Steam / Utilities
   - Mud Washing / Filtration
   - Oxalate Removal
   - Oxalate Destruction
   - Residue storage or use

Events:
- Evaporation

Source: ICSOBA

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Oxalate Removal - Coprecipitation

- Oxalate permitted to precipitate with gibbsite in precipitators
- Oxalate reports to fine seed and is washed out in counter-current washing tanks and filters.
- Fine seed must be (almost) oxalate-free to avoid severe product quality issues.
- Oxalate-rich washings must be treated to remove oxalate.
Oxalate Disposal and Destruction

- Sodium oxalate is toxic and soluble.
- Roasting/calcination
  - \( \text{Na}_2\text{C}_2\text{O}_4 + \frac{1}{2}\text{O}_2 \rightarrow \text{Na}_2\text{CO}_3 + \text{CO}_2 \)
  - Carbonate can be returned to process and causticised
  - Problems: Odour, dust emissions
- Causticisation
  - Very common means of destruction. Oxalate from seed-washing or cake redissolved in water is treated with slaked lime.
  - \( \text{Na}_2\text{C}_2\text{O}_4 + \text{Ca(OH)}_2 + \text{H}_2\text{O} \rightarrow \text{CaC}_2\text{O}_4\cdot\text{H}_2\text{O} + 2\text{NaOH} \)
  - Problems: Very lime inefficient (2-10%), alumina loss
- Two Stage Causticisation
  - Improved lime efficiency (hydrocalumite used for carbonate csn)
  - Problems: High Capex/Opex
Oxalate Disposal and Destruction

• **Photocatalytic Oxidation**
  - Seedwashing filtrate or cake dissolved in water.
  - Problems: Catalyst required for acceptable rates, slow or ineffective in alkali (oxidation potential).

• **Biological destruction**
  - Seedwashing filtrate or cake dissolved in water
  - Extremophile oxalate consuming bacteria up to pH 11 in moving bed bioreactor.
  - Very effective and simple to operate, produces sodium bicarbonate and sodium carbonate.
Fluoride

- Fluoride enters via clay, fluorspar etc.
- Typically removed with TCA
- Main issue is formation of sparingly soluble double salts that scale evaporators
  - \( \text{Na}_2\text{SO}_4\cdot\text{NaF} \) (kogarkoite), \( \text{NaF}\cdot\text{Na}_2\text{V}_2\text{O}_5 \) etc.
- With high sulfate, can also co-precipitate with gibbsite.
- At high concentrations, can remove by crystallising NaF.
Silicates

• Very well known impurity – love/hate relationship!
• Pre-Desilication required for removal, with significant caustic loss
• Also main impurity removal process for many refineries (intercalation).

• \[3\text{Al}_2\text{Si}_2\text{O}_6(\text{OH})_4 + 18\text{NaOH} \rightarrow 6\text{Na}_2\text{SiO}_3 + 6\text{NaAl(OH)}_4 + 3\text{H}_2\text{O}\]
  – No net alumina loss unless quartz is attacked

• \[6\text{Na}_2\text{SiO}_3 + 6\text{NaAl(OH)}_4 + \text{Na}_2\text{X} \rightarrow \text{Na}_6[\text{Al}_6\text{Si}_6\text{O}_{24}].\text{Na}_2\text{X} + 12\text{NaOH} + 6\text{H}_2\text{O}\]
Silicates

- **Sumitomo process**
  - Relies on relative dissolution rates of gibbsite vs kaolin
  - Short digestion times, followed by rapid solid/liquid separation under pressure
  - Liquor stream is separately desilicated, cooled and DSP filtered out. Possible soda and alumina recovery
  - Problems: Loss of extraction efficiency, complexity, not suitable for boehmitic bauxites.
Bauxite Residue Impacts

- Bauxite Residue (BxR) often considered the ‘sewer’ for the refinery
- For most BxR utilisation schemes, sodium is the main barrier
- High soluble losses or purging are incompatible with BxR use.
- Solid alkalinity (DSP, TCA, partially reacted lime solids) buffers pH and releases sodium
- Oxalate, sulphate and other impurities are also a problem.
Conclusions

- Thousands of impurity removal ideas have been proposed and tested, but relatively few have found commercial success.
- The reasons are mostly obvious: cost, operability and practicality.
- Impurity removal is an important part of refinery design
- Increasing pressure to make use of Bauxite residue demands that new ways to control impurities be found