Recycling of waste from the primary aluminium industry

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Reykjavik University
Seminar on aluminium, energy and environment
## Hazardous waste from Al industry in Iceland

<table>
<thead>
<tr>
<th></th>
<th>Alcoa</th>
<th>Norðurál</th>
<th>Rio Tinto Alcan</th>
<th>Sum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spent potlinings, SPL (t)</td>
<td>9.475</td>
<td>4.906</td>
<td>3.891</td>
<td>18.272</td>
</tr>
<tr>
<td>Dross (t)</td>
<td>2.106</td>
<td>2.238</td>
<td>2.368</td>
<td>6.712</td>
</tr>
<tr>
<td>Aluminium production(t)</td>
<td>335.560</td>
<td>298.388</td>
<td>205.051</td>
<td>838.999</td>
</tr>
</tbody>
</table>

- **SPL** – Average Iceland 22 kg/tonne aluminium
  - 20 – 30 kg/tonne worldwide

- **Dross** - Average Iceland 8 kg/tonne aluminium
  - Typically 15 – 30 kg/tonne aluminium (primary production)
  - Up 80 kg/tonne aluminium in secondary production

Data from company reports for 2104
Origin of spent pot linings (SPL)

Aluminium electrolysis cells renewed every 5 – 7 years

- Off-gas duct
- Alumina
- Anode rod
- Carbon anode
- Alumina
- Electrolyte
- Molten aluminium
- Cathode
- Current conductor
- Insulation
- Steel shell

SPL

1\textsuperscript{st} cut

2\textsuperscript{nd} cut
Composition of SPL

<table>
<thead>
<tr>
<th>Compound</th>
<th>1st cut wt%</th>
<th>2nd cut wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>0-10</td>
<td>10-50</td>
</tr>
<tr>
<td>C</td>
<td>40-75</td>
<td>0-20</td>
</tr>
<tr>
<td>Na</td>
<td>8-17</td>
<td>6-14</td>
</tr>
<tr>
<td>F</td>
<td>10-20</td>
<td>4-10</td>
</tr>
<tr>
<td>CaO</td>
<td>1-6</td>
<td>1-8</td>
</tr>
<tr>
<td>SiO₂</td>
<td>0-6</td>
<td>10-50</td>
</tr>
<tr>
<td>Metallic Al</td>
<td>0-5</td>
<td>0</td>
</tr>
<tr>
<td>CN total</td>
<td>0.01-0.5</td>
<td>0-0.1</td>
</tr>
<tr>
<td>CN free</td>
<td>0-0.2</td>
<td>0-0.05</td>
</tr>
</tbody>
</table>

- Aluminium penetrates into cracks formed in cathode and insulation
- Bath components (cryolite etc) can diffuse into cathode and insulation
- Composition of cut 2 is very variable because of different materials used by different aluminium producers
- Sodium diffuses into cathodes
  - \(2Na + 2C + N_2 = 2NaCN\)
- Aluminium nitride can form
  - \(2Al + N_2 = 2AlN\)
  - Can result in ammonia formation when treating SPL
    - \(AlN +3H_2O = Al(OH)_3 + NH_3\)
SPL, cut 1 and 2 is hazardous

• "Contact with water can generate flammable and toxic gases (ammonia, phosphine, hydrogen and methane). Phosphine gas can autoignite. Elevated temperature processing can generate hydrogen fluoride, hydrogen cyanide and sulfur oxides (SOx). Contact with acids can result in the formation and release of appreciable and potentially toxic amounts of hydrogen cyanide (HCN) and hydrogen sulfide (H2S) gases."

• Landfilling of SPL is banned in N-America
  • Because of leakage of cyanides, fluoride, ammonia, etc. into ground water
  • Remediation of some closed landfills is required

MSDS from Alcoa for cut 1 and cut 2
Best available techniques (BAT) for SPL treatment

• “In order to reduce the disposal of spent pot lining, BAT is to organise operations on the site so as to facilitate its external recycling. Including using one or a combination of the techniques shown below”
  • Use in cement manufacture
  • Use as a carburiser in the steel and ferro-alloy industry
  • Use as a secondary raw material (rock wool, salt slag recovery, etc.)

• Because of stricter environmental and safety regulations it has become more difficult for the above industries to accept untreated SPL
Treatment of SPL - examples

• Rito Tinto Alcan – Saguenay, Quebec, Canada
  • Capacity 80,000 tonnes/year of SPL
  • Process based on treatment of SPL with water and acidic and basic solutions
  • Products: Carbon, CaF$_2$ .......

• Alcoa – Gum Springs, Arizona, USA
  • SPL mixed with lime and calcium silicate and treated in a furnace at >700°C
  • Cyanides are destroyed, and fluorides bound in CaF$_2$
  • Product can be landfilled at a hazardous waste site

• BEFESA – UK
  • Co-processing of SPL and salt cake from recovery aluminium from dross
Treatment of SPL from Icelandic Al industry

- **Alcoa**
  - Sent to the UK for treatment

- **Rito Tinto Alcan**
  - Seashore deposits
    - No harmfull effects have been observed

- **Norðurál**
  - Landfill affected by the tide

**Alcoa policy:** Nothing to landfill

**Fluoride ions washed to sea**
Precipitation of CaF$_2$
Ammonia washed to sea
Cyanide?

[Diagram showing seawater levels and SPL during high and low tide]
What is dross?

• Aluminum on the surface of molten aluminium is oxidised by oxygen in air
  • $2\text{Al} + 1,5\text{O}_2 = \text{Al}_2\text{O}_3$
• Aluminum can also react with $\text{N}_2$ from air to for aluminium nitride
  • $2\text{Al} + \text{N}_2 = 2\text{AlN}$
• Other alloying elements also oxidised on the surface of molten aluminum
  • Mg, Zn, Si......
• Oxides and nitrides are removed from the surface of the molten aluminium by skimming
  • Automatic
  • Manual
• The material removed is dross
  • Contains about 50% metallic aluminium
Dross is hazardous

- Contact with water can generate flammable and toxic gases
  - Ammonia: \[ \text{AlN} + 3\text{H}_2\text{O} = \text{Al(OH)}_3 + \text{NH}_3 \]
  - Hydrogen: \[ 2\text{Al} + 3\text{H}_2\text{O} = \text{Al}_2\text{O}_3 + 3\text{H}_2 \]
  - Phosphine: \[ \text{PH}_3 \]
  - Methane: \[ \text{CH}_4 \]

- Dross may not be kept outdoors
  - Outdoor heaps have resulted in ammonia “clouds“

- Transport is expensive

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<table>
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<tbody>
<tr>
<td>Al</td>
<td>40 – 60%</td>
</tr>
<tr>
<td>AlN</td>
<td>5 – 10 %</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>30 – 40%</td>
</tr>
<tr>
<td>Cryolite</td>
<td>1 – 10%</td>
</tr>
<tr>
<td>Other</td>
<td>1 – 10%</td>
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</table>
Aluminium recovery from dross

• Recovery with salt
  • Used by Alur/Kratus treat from dross from Rio Tinto Alcan
  • Dross is melted with salt in a rotary furnace
  • Salt protects metal from oxidation and facilitates removal of impurities
  • Molten aluminum is separated from molten salt and solids
    • Aluminium ingots are cast
    • Salt with solids solidified, resulting in salt cake
  • Salt cake is sent to the UK for recycling
    • Salt for reuse in process
    • Aluminium 5 – 10%
    • Al oxide and other oxides to cement
    • Ammonium sulfate
  • Alur/Kratus is planning to start recycling of salt cake

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<td>NaCl</td>
<td>60 – 70%</td>
</tr>
<tr>
<td>KCl</td>
<td>35 – 25%</td>
</tr>
<tr>
<td>CaF₂</td>
<td>5%</td>
</tr>
<tr>
<td>Al metal</td>
<td>2 – 8%</td>
</tr>
<tr>
<td>Salt</td>
<td>20 – 40%</td>
</tr>
<tr>
<td>AlN</td>
<td>5 – 15%</td>
</tr>
<tr>
<td>Other (Oxides, fluorides, ...)</td>
<td>40 – 70%</td>
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Aluminium recovery from dross

- Salt free processes
  - Dross is treated in a rotary furnace in reducing atmosphere to melt aluminum
  - Molten aluminum is separated from solids, non-metallic product (NMP)
    - Ingots of aluminium cast
  - Used by Alur/Kratus to treat dross from Norðurál
  - NMP remaining after aluminium recovery is hazardous
    - Same hazards as with dross
    - NMP from Alur has been treated in seashore flushing pits before landfilling
      - Ammonia formed is washed to sea (AlN +3H₂O = Al(OH)₃ + NH₃)
      - Fluoride ions partially washed out (CaF₂ precipitates in seawater)

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Water treatment of NMP

• Reaction of water and AlN in NMP is an exothermic reaction
  • $\text{AlN} + 3\text{H}_2\text{O} = \text{Al(OH)}_3 + \text{NH}_3$

1450 g NMP, 1450 g water
Process suggested for treatment of NMP

Water

NMP

> 0,5 mm

< 0,5 mm

> 2 mm (Al)

> 2 mm (Al)

Al to recycling

Off gas (NH₃, H₂,..)

Off gas

Wash water

Solution to waste treatment

Ammonia (28 - 30%)

Product
Recycling of SPL and dross in Iceland

• Quantity limited
  • SPL 18 000 tonnes/year
  • Dross 7 000 tonnes/year

• Can SPL, NMP and salt cake be treated with the same equipment?
  • On smaller scale than elsewhere?
  • Project with Alur/Kratus to develop such a process

• Utltimate goal: develop a process that can be set up close to aluminium smelters
  • No transport of hazardous materials
Small scale processing of waste

- Milling
- Sieving
- Water washing
  - 100 °C
  - NaOH, CaO
  - NaOCl
- Filtration

- Ammonia (25%), fertilser
- Al (1 – 10 mm)
- Crystallisation
- Washed NMP
- Washed SPL
- Salt
- Salt cake
- Wash solution
  CaF₂, AlF₃, ...
- NMP
- SPL
- Al metal
- Aluminium recovery
- Dross (50% Al)
- Brine
- Cement, rockwool, etc.
- Carbon as fuel (from cut 1)
- Cement (from cut 1 and cut 2)
Thank you

Innovation Center
Iceland