Bauxite residue uses: successes, failures and ?

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August 2016
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• Background
• Scale of the problem and bauxite residue generation
• Overview of management methods
• Applications
• Successes, failures and ?
• Challenges to implementation
• Lowering the barriers
• New driving forces and the future
Red mud to Bauxite residue

- Red mud
- Bauxite residue
- Red oxide sand
- Red Sand™
- ReadyGrit™
- Alkaloam™
- Bauxaline®
- Feraloks
- Ferroalumina
- Cajunite™
- BPR – Bayer Process Residue
- Bauxite tailings

- ARR – Alumina Refinery Residue
- ART - Alumina Refinery Tailings
- DBR - Dried Bauxite Residue
- RMG
- Redmedite
- Bauxsol®
- ViroMine™
- ViroSewage™
- ViroSoils™
- Terra B™
Where does bauxite residue fit?

• Normally the last part of any meeting
• The last part of the Bayer process
• Historically the last thing on the alumina refinery manager’s mind
Until
Possible consequence if not properly stored
Ajka Alumina Plant – October 2010
Kolontár – October 2010
Kolontár – October 2010
Kolontár – October 2010
Wanji alumina plant – August 2016
Wanji alumina plant – August 2016
Wanji alumina plant – August 2016
Impact of Ajka incident

• Over 700,000 m³ of caustic bauxite residue slurry released as a result of a dam failure
• 10 people killed
• 150 people hospitalised
• Three local settlements overwhelmed - Devecser, Kolontár and Somlóvásárhely
• 300 houses destroyed or severely damaged
• 14 km² of agricultural land along Torna and Marcal waterways inundated with caustic liquor/ bauxite residue
• Extensive contamination of the River Danube
• Negative publicity – radioactivity, arsenic etc
Reactions following Ajka incident

- Heightened interest by authorities and activities
- IAI/EA Best practice document issued
- Concern of EU and national regulators - possible changes in waste directives and classification
- Increased attention to the important of making all sites as safe as possible
- More frequent and regular inspections
- Need to take into account natural disasters eg earthquakes, storms, in planning
- Increased motivation to find uses
- Meetings like this
  - would we be here if the incident hadn’t happened?
Scale of the problem

• Alumina production in 2015 was 115 million t/y - 95% via Bayer process
• Bauxite residue produced per tonne of alumina – range 0.5 to 4 t/t alumina
• Annual arising – over 155 million tonnes and growing
• Number of active alumina refineries – about 80
• Number of closed residue disposal sites – over 50
• All disposal in estuaries and the sea ceased at the end of 2015
• Amount stockpiled – 3,000 million tonnes an enormous deposit to mine as a future resource!
Growth in bauxite residue generation

- Aluminium demand to double between 2010 and 2050
- Allowing for recycling - estimates primary aluminium requirement 80 - 100 million t/y by 2050
- Equivalent to 160 - 200 million t/y of metallurgical alumina plus 8 million t/y chemical grade alumina
- Bauxite residue produced over 210 -250 million t/y

Where will this be:
- USA alumina production declining
- Europe static/decline
- China will grow
- Brazil will grow
- Middle East will grow
- Indonesia will grow
- Vietnam will grow
- Malaysia will grow
- Guinea should grow if political problems can be solved
Amount of bauxite residue generated

• Bauxites - alumina content ranges typically from just over 30% to 67%
• Amount of bauxite residue per tonne of alumina depends on bauxite and extraction conditions
• Very wide range - 0.5 to 4 t of bauxite residue/t of alumina
• World average (2010) - 1.35 t of bauxite residue/t of alumina
• European average (2013) - 0.67 t of bauxite residue/t of alumina
Bauxite: types and distribution

• Types of bauxite:
  – Lateritic – high in gibbsite – generally found in equatorial regions: Australia, Brazil, Ghana Guyana, etc
  – Karst – high in Boehmite – generally found in temperate zones: Australia, Guinea, Greece, Hungary etc

• Aluminous compounds present - Al₂O₃ content 30 to 67%
  – Gibbsite (Al(OH)₃)
  – Boehmite (AlOOH)
  – Diaspore (AlOOH)

• Main impurities
  – Oxides of iron, titania, calcia, silica (reactive(kaolin) and crystalline(quartz)), organics

• Minor impurities
  – Magnesium, manganese, chromium, vanadium, zinc, zirconium, rare earths, thorium, uranium etc
Digestion processes

Varies by type of bauxite:

• Gibbsitic
  – 140 to 155°C, pressure 3 atmospheres, sodium hydroxide concentration 2.4 to 2.75 M

• Boehmitic
  – 240 to 250°C, pressure 6 atmospheres, sodium hydroxide concentration 3.5 to 3.75 M

• Diasporic
  – 250 to 280°C, pressure up to 80 atmospheres, concentrations of 230-350 g/L Na₂CO₃
Bauxite residue generation

• Balance between aluminous content of the bauxite, type of aluminium containing compound, local energy cost, transport cost, silica content (reactive more important than crystalline)

• When plants located very distant from the bauxite source, they tend to use high alumina bauxite and high temperature/aggressive extraction conditions
  – Common in parts of Europe, Canada

• Plants located close to the bauxite have a lower requirement to extract all the alumina and may use a poorer quality bauxite
  – Common in Western Australia
Alumina plant locations

• Main considerations
  – Energy source – coal including lignite, gas
  – Proximity to bauxite
  – Proximity to smelter which need cheap electricity

• Historically - close built to energy source and where the alumina was needed
  – France Gardanne 1893
  – UK Larne 1894
  – USA East St Louis 1902
  – Germany Martinswerk 1913
  – UK Burntisland 1917

• More recently – close to bauxite deposits
  – Western Australia
  – Queensland
  – Brazil
  – India
  – Ma’aden
  – Indonesia
  – China (though large quantities of bauxite still imported)
Historic management approaches

• Lagooning in ponds, impounded areas
• Disposal to quarries, depressions, dammed valleys, captured by sea walls
• River, estuarine, sea disposal (pipeline and ship)
• Mud farming
• Dry mud stacking
• Filtration – drum filters, plate and frame etc
• Seawater neutralisation/pH reduction
• Acid neutralisation
• Carbon dioxide neutralisation
• Sulfur dioxide neutralisation
• Use
Ajka pond on September 2010
Lagooning – early stages
Lagooning – later stages
Impounded storage area
Disposal in old quarries
Sea disposal
Sea/estuarine disposal - land reclamation
Mud farming
Mud farming
Dry mud stacking

DILUTE MUD/SAND SLURRY FROM PLANT → CYCLONES → MUD THICKENER

SAND SEPARATION PLANT

MUD THICKENER

DILUTE MUD SLURRY → CYCLONES → DILUTE MUD SLURRY

OVERFLOW RECYCLE → HIGH PRESSURE MUD PUMPING → UNDERFLOW HIGH DENSITY MUD

THICKENER

SAND TOWERS

DILUTE MUD SLURRY → CYCLONES → DILUTE MUD SLURRY

RECYCLE TO PROCESS

RUNOFF -> DECANT

DRY DISPOSAL AREA

SPRINKLERS → EVAPORATION

SUN

UNDER DRAINAGE

TO MUD DROPPERS VIA MUD LINE
Dry stacking
Filtration – plate and frame press
Filtration
Solids content after disposal

• Lagooning in ponds
  – Range 15–30% solids; generally 18-22%
  – Stays at that concentration
• Mud farming/Dry mud stacking
  – When discharged 45-50%
  – After mud farming >60%
  – After a prolonged period ~ 70%
• Filtration – drum filters, plate and frame etc
  – Press filter 62 – 70%
  – Hyperbaric filter 75%
Applications
Historic driving forces for dealing with bauxite residue

• Recovery of caustic soda for reuse in the process
• Lowest cost compatible with minimum effect on the environment
• A desire for use but needed to be a cost effective solution
• Occasional attempts to use – for example in times of war – used in iron and steel production
• Disposal cost
  – 5% of total cost alumina sometimes suggested
  – US$ 4 to 12/t more typical
• Closure costs often ignored – “not present local management’s problem”
### Chemical composition – range (wt%)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Range (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₂O₃</td>
<td>5 – 60</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>5 – 30</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.3 – 15</td>
</tr>
<tr>
<td>CaO</td>
<td>2 – 14</td>
</tr>
<tr>
<td>SiO₂</td>
<td>3 – 15</td>
</tr>
<tr>
<td>Na₂O</td>
<td>1 – 10</td>
</tr>
<tr>
<td>As, Ba, Be, C, Cd, Cr, Cu, Ga, Hg, K, P, Pb, Mg, Mn, Mo, Ni, S, Sc, Se, Th, U, V, Y, Zn, Zr + lanthanides</td>
<td></td>
</tr>
</tbody>
</table>

A rich source of elements but bauxite residues extremely variable in composition
Mineralogical components – range (wt%)

- Sodalite \(3\text{Na}_2\text{O.}\text{Al}_2\text{O}_3.2\text{SiO}_2.0-2\text{H}_{2}\text{O.}2\text{NaX}\) 4 – 40
  where X could be \(\text{CO}_3^{2-}, \text{Cl}^-, \text{OH}^-, \text{SO}_4^{2-}\) or \(\text{Al(OH)}_4^{-}\)
- Al - goethite \(((\text{Fe,Al})_2\text{O}_3.\text{nH}_{2}\text{O})\) 1 - 55
- Haematite \((\text{Fe}_2\text{O}_3)\) 10 – 30
- Magnetite \((\text{Fe}_3\text{O}_4)\) 0 - 8
- Silica \((\text{SiO}_2)\) crystalline and amorphous 3 - 20
- Calcium aluminate \((3\text{CaO.}\text{Al}_2\text{O}_3.6\text{H}_{2}\text{O})\) 2 - 20
- Boehmite \((\text{AlOOH})\) 0 - 20
- Titanium Dioxide \((\text{TiO}_2)\) anatase and rutile 2 - 15
- Muscovite \((\text{K}_2\text{O.}3\text{Al}_2\text{O}_3.6\text{SiO}_2.2\text{H}_{2}\text{O})\) 0 - 15
- Calcite \((\text{CaCO}_3)\) 2 - 20
- Kaolinite \((\text{Al}_2\text{O}_3.2\text{SiO}_2.2\text{H}_{2}\text{O})\) 0 - 5
- Gibbsite \((\text{Al(OH)}_3)\) 0 - 5
- Perovskite \((\text{CaTiO}_3)\) 0 -12
- Cancrinite \((\text{Na}_6[\text{Al}_6\text{Si}_6\text{O}_{24}]2\text{CaCO}_3)\) 0 - 5
- Diaspore \((\text{AlOOH})\) 0 - 5
Mineralogical components - minor

- Brookite (an orthorhombic variant of TiO$_2$)
- Ilmenite (FeTiO$_3$)
- Carnegieite (Si$_4$Al$_4$Na$_4$O$_{16}$)
- Dolomite (CaMg(CO$_3$)$_2$)
- Hydrogarnet (Ca$_3$Al$_2$(O$_4$H$_4$)$_3$)
- Hydroxycancrinite/Cancrinite (Na$_6$Ca$_2$(Al$_6$Si$_6$O$_{24}$)(CO$_3$)$_2$·2H$_2$O)(Na,Ca)$_8$(Al,Si)$_{12}$O$_{24}$(CO$_3$)·4H$_2$O)
- Cancrinite-NO$_3$ (Na$_{7.92}$Si$_6$Al$_6$O$_{31.56}$N$_{1.74}$)
- Cancrisilite-CO$_3$ (Na$_{7.86}$(AlSiO$_4$)$_6$(CO$_3$)(H$_2$O)$_{3.3}$)
- Katoite-Si (Ca$_3$Al$_2$(SiO$_4$)(OH)$_8$)
- Lawsonite (CaAl$_2$Si$_2$O$_7$(OH)$_2$·H$_2$O)
- Nepheline (Na$_2$KAl$_4$Si$_4$O$_{16}$)
- Nosean (Na$_8$Al$_6$Si$_6$O$_{24}$(SO$_4$))
- Portlandite (Ca(OH)$_2$)
- Schaeferite ($(\text{Na}_{0.7}\text{Ca}_{2.3})(\text{Mg}_{1.85}\text{Mn}_{0.15})(\text{VO}_4)_{2.88}(\text{PO}_4)_{0.12}$)
- Sodium titanate (Na$_2$TiO$_3$)
- Zircon (ZrSiO$_4$)
Elements may be present in different forms e.g. sodium

Sodium is one of few elements not widely present in the bauxite. May be present as:

- Soluble sodium compounds - residual sodium aluminate/sodium carbonate
- DSP Desilication product - $3\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 0\cdot2\text{H}_2\text{O} \cdot 2\text{NaX}$ where X could be $\text{CO}_3^{2-}$, $\text{Cl}^-$, $\text{OH}^-$, $\text{SO}_4^{2-}$, or $\text{Al(OH)}_4^-$ arising from the reaction between sodium aluminate and soluble sodium silicates
- Level typically 4 – 40%; up to 50% in Eurallumina
- Form of sodium will effect some applications
Bauxite residue possible applications

Hundreds of thousands of ideas, thousands of trials, hundreds of patents, a few tens of industrial applications

• Use as a bulk material (sometimes with fly ash, lime or cement)
  - Bricks, tiles, roads, dam/levee construction, landfill capping, soil amelioration, filling mine shafts

• Use for its chemical components
  - Cement, pigment, geopolymers, catalysts, refractories, phosphate removal, acid mine drainage treatment, heavy metal removal

• Extraction of chemical constituents
  - Iron, aluminium, titanium, gallium, rare-earths, scandium, yttrium
Some proposed applications

Bricks, tiles, roads, dam/levee construction, landfill capping, soil amelioration, wood substitution, mineral wool manufacture, plastic (PVC) filler, railway ballast, treatment of acid soil, drainage pipe filler, glass ceramics, light weight aggregates, foamed aggregates, filling former mine shafts, land reclamation

Cement (OPC clinker), Sulfo-aluminate cements, pozzolanic material for mortar, supplementary cementitious additives, concrete additive, paint pigment, pigment for plastics, dye, geopolymers, catalysts, refractory lining to replace ilmenite, refractory bricks, gravel

Phosphate removal, water treatment chemical, arsenic removal, fluoride removal, chromium and other heavy metal removal, acid mine drainage, sulfide oxidation, fertiliser, titanate-Mullite composites, plasma spray coatings

Extraction of iron, aluminium, titanium, gallium, scandium, vanadium, yttrium, lanthanides and other rare earths
Bauxite residue uses - history

- 1880s – iron recovery by Bayer
- 1910s – internal roads and dykes in refineries and residue disposal areas
- 1930s - cement
- 1940s – iron and steel production
- 1950s – pigments
- 1980s - bricks
- 1990s – cement, brick colouration, sulfo aluminate cements, capping, soil amelioration
- 2000s - acid mine drainage, phosphate removal
- 2010s – capping, metal recovery
Bayer patents 1888

Karl Joseph Bayer

- German patent 43,977
- US patent 382,505
- UK patent GB 10,093

“The red, iron containing residue after digestion settles well and, with sufficient practice, can be filtered and washed. Due to its high iron and aluminium oxide content, it can be, in an appropriate manner, treated or with other iron ores, be smelted to iron.”
Success
Dykes/levees

• Widespread used for many decades in dyke/levee construction

• When compacted good low permeability characteristics
  – $3 \times 10^{-5}$ cm/s to $4.6 \times 10^{-7}$ cm/s
  – $4.6 \times 10^{-7}$ cm/s at 24% moisture
  – $1.3 \times 10^{-7}$ cm/s achievable when compacted and under favourable conditions

• Use intermittent at any particular refinery.

• Sometimes mixed with fly ash
Levee construction
BR used in impoundment walls
Limited success
Use in bricks, tiles etc

• Successful trials and production over decades in Australia, China, Hungary, India, Jamaica, South Korea

However:
• Only moderate usage
• Routes
  – Sodium silicate
  – Firing
  – Addition of lime and cement
• China success insulation blocks/bricks: cement 15% + lime 12-15% + sand 33-35% + bauxite residue 35-40%
Building at JBI, unfired bricks
Building in Kingston
Radiological properties Jamaican buildings

• Pinnock UWI – 1991
• Gamma radiation measured by thermo-luminescence detector
• Radon using strips of CR 39 plastic to register tracks
• Building Research Institute 50% bauxite residue
Radiological properties Jamaican buildings

- Pinnock UWI – 1991
- Gamma radiation measured by thermo-luminescence detector

<table>
<thead>
<tr>
<th>Type of house</th>
<th>Gamma component (msv)</th>
<th>Radon component (msv/y)</th>
<th>Total (msv/y)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BRI 50% BR</td>
<td>0.80</td>
<td>0.66</td>
<td>1.44</td>
</tr>
<tr>
<td>100% Bauxite residue</td>
<td>1.25</td>
<td>0.82</td>
<td>2.07</td>
</tr>
<tr>
<td>Typical concrete</td>
<td>0.51</td>
<td>0.35</td>
<td>0.86</td>
</tr>
</tbody>
</table>
Success
Clinker production
Bauxite residue in clinker

• Ordinary Portland cement composition – 5% Al$_2$O$_3$, 3% Fe$_2$O$_3$, 21% SiO$_2$, 62% CaO
• Provides iron – driving force at some plants
• Provides alumina – driving force at some plants
• Silica and calcia useful although less critical
• Possible usage
  – Up to 5%
  – Global production of cement 4,600 million tonnes so large potential
Industrial uses in clinker

- Nikolayev alumina plant in the Ukraine
  - Up to 250,000 t/y in 10 cement plants in Ukraine, Russia, Georgia, Moldova and Belarus
    - Transported up to 1,200 km
    - Used predominantly for iron but also alumina value

- AoG, Distomon, Greece
  - 9,000 t/y cement plant in Greece
    - Driven by alumina value
    - Limits on soda and moisture
Success
Landfill capping Provence
Landfill capping Provence (methane collection)
Landfill capping Provence

Limits to municipal landfills

• Distance to landfill
• Capping of landfill is intermittent
• Moisture content of bauxite residue
Success
Roads

• Substantial use in internal roads in bauxite residue disposal areas at refineries
Road construction in Western Australia

(slide courtesy of Alcoa)
Road construction in Western Australia

- Substantial joint work between Curtin University and Alcoa Kwinana
  - Alcoa plants in Western Australia (Kwinana, Pinjarra, Wagerup) - 30,000 t/d of mud and 18,000 t/d of coarse sand residue
  - After carbonation marketed as Red Sand™ or ReadyGrit™

- Target to replace virgin sand and crushed limestone for sub-grade and top dressing
  - For each cubic metre of virgin sand replaced savings of 4.4 and 2.7 MJ respectively in energy conservation
  - Lower carbon footprint
  - Reduces loss of vegetation as avoids use of quarries
  - Cost savings
  - Less water used
  - Reduced eutrophication
Failure
Pigments for paint
Success
Iron and steel production

- Bauxite residue contains up to 60% iron oxides
- Used industrially during the second world war
- Considerable success in Russia and China
- Estimated over 1 million t/y used
- Some use of superconducting magnets as preliminary beneficiation stage
Iron and steel developments

- Recent research in Russia using low alkaline bauxite residue and bentonite has been very effective in raising the iron content, improving agglomeration quality and thereby give greater yields in the production of iron ore pellets.
- Moscow Institute of Steel and Alloys (MISiS) have developed a new generation furnace to process bauxite residue and produce pig iron and slag products - reduced energy consumption and improved metal quality.
- Several approaches using high temperature furnaces to recover iron and titanium leaving behind an inert material – Roszin, ENEXAL process (reductive smelting) AMRT/NTUA/AoG
ENEXAL process

• Extensive work by the National Technical University of Athens in conjunction with AoG
• Fine bauxite residue with 48% Fe$_2$O$_3$
• Mixed with coke fines and fluxes
• Feed to an electric arc furnace (melt surface 1,400 – 1,600°C) - 95% pig iron (97% recovery of iron) and slag produced
• Slag possible use is for mineral wool for insulation
The jury is still out
Bauxite residue as a supplementary cementitious material

- Considerable work in this area – Brazil, China, Greece, India, Portugal
- Effective as a pozzolanic material so can be incorporated into cement mixes (mortar and concrete)
- Can be used in cement blends and provide beneficial mechanical properties
- Levels up to 50% possible but lower levels at 5 to 10% more typical
- Downside:
  - Calcination is necessary in some circumstances, >800°C, some studies up to 1,300°C
  - Some studies have used neutralised bauxite residue
The jury is still out
Use in special cements

Calcium sulfo-aluminate/belite based
\[ Ca_4(AlO_2)_6SO_4 \]

- **Benefits**
  - Reduced carbon dioxide emissions
    - Less carbonate
    - Lower firing temperature
  - Rapid setting
  - High strength, particularly early strength
  - Can use waste from flue gas scrubbing

- **Problems**
  - Poor workability
  - Large capital investment for new plant

- Considerable usage of calcium sulfo-aluminate cements in China
The jury is still out
Acid mine drainage

• Treatment of contaminated water from old mine sites – removal of As, Ca, Cr, Cu, Ni, Pb, Zn etc.
• Southern Cross and Virotec patents 2002
• Basecon process - Bauxsol®
• Bauxite residue mixed with brines: Mg to Ca ratio critical to effectiveness
• Very promising results in some quite large trials never fully successful on a significant scale
Water treatment

• Many patents and approaches, processes based on:
  – Brine treatment
  – Acid neutralisation
  – Heat activation
• Products
  – Ferrifloc 1980s
  – Bauxsol®
  – Redmedite
• Pellets used in phosphate removal
• Several successful quite large scale trials
Acid mine drainage – Virotec/Redmedite

- Products made from brine treatment of bauxite residue – Bauxsol® and Redmedite
- Historically a considerable amount of work at Southern Cross University
- Current trials at Wheal Augusta, former barytes mine in UK with Plymouth University on contaminant removal from leachate and remediation of contaminated soil

**Removal of contaminants**
- Al – 91%
- As – 65%
- Cd – 73%
- Co – 81%
- Cr – 95%
- Cu – 99%
- Fe – 98%
- Mn - 26%
- Ni - 28%
- Pb – 99%
- Zn – 74%
Acid mine drainage - Redmedite
Failure
Not technical but PR
Soil amelioration

• In 1996 a large trial using partially neutralised bauxite residue (Alkaloam®) was undertaken on a 4,360 ha area on an estuarine area in Western Australia with acidic sandy soils which suffered from eutrophication, excessive algae growth and fish deaths

• Bauxite residue added at about 250 tonne/ha to sandy soil together with 5% gypsum

• The resulting soil had:
  – Higher water retention
  – Higher nutrient utilisation ability
  – Better phosphorus availability
  – Reduced leachability of phosphorus and thereby the amount of phosphorous escaping into the estuary and hence the occurrence of algal blooms and fish deaths
Soil amelioration

No issues were found with metal contamination or radioactivity levels

BUT
“The great red mud experiment that went radioactive”

May 2002
Quentin Treasure was a member of a local land-care group when he was approached to take part in an unusual experiment by the West Australian Agricultural Department.
The department wanted to spread a reddish substance over his farmland to see if it would stop unwanted phosphorus from entering waterways.
The bonus, Mr Treasure was assured, was not just environmental. He could look forward to vastly increased crop yields using a soil-improving agent that would cost him just 50 c a tonne.
But this was no ordinary product. It was industrial waste.
The trucks dumping tonne after tonne of the ochre-like material were coming straight from settling ponds at the nearby Alcoa aluminium refinery, which was co-funding the project.

"We never talked a lot about whether it was safe or not," Mr Treasure said. "We were just told it was dirt from the hills that came from Alcoa. And being a little bit naive at the time, that is all we assumed it was."
The experiment, now being used to justify an extraordinary proposal for large-scale use of industrial waste on West Australian farms, remains a bitter memory for a small group of farmers that originally took part.
What Mr Treasure did not fully understand when he agreed to the proposal was that, apart from having fertilising potential, the red mud was also laced with dangerous materials.
Sprinkled over each hectare were up to 30 kilograms of radioactive thorium, six kilograms of chromium, more than two kilograms of barium and up to one kilogram of uranium.
On top of that there were 24 kilograms of fluoride, more than half a kilogram each of the toxic heavy metals arsenic, copper, zinc, and cobalt, as well as smaller amounts of lead, cadmium and beryllium.
Ephemeral successes

• 1960s - Pigment production in Northern Ireland

• Late 1990s – Clinker in India – 2.5 million tonnes

• 1980s and 1990s – Colourant for bricks UK ~5% addition

• Use in OPC clinker in China – change in standards

• Use in refractories in Romania 50,000 – 60,000 t/y
Some future potential success stories?
EU MSCA-ETN RED MUD project

Being Confidential to ETCL
Rare earth elements

• Extremely strong demand for rare earth elements (REEs), normally taken to mean the lanthanides plus scandium and yttrium
  – Light rare earth elements (LREE) - from lanthanum to samarium
  – Heavy rare earth elements (HREE) covering europium to lutetium
• Essential constituents of permanent magnets, nickel metal hydride batteries and lamp phosphors – demand driven by growth in electric and hybrid cars, wind turbines and compact fluorescent lights
• Very strong demand for scandium for use as a grain growth control agent in high strength aluminium alloys.
• REEs in bauxites from Olmedo in Sardinia, Vlasenica in Bosnia Herzegovina, Grebnik in Kosovo and Panassos-Ghiona, Marmara, Evia Island in Greece.
Rare earths elements

- REEs remain undissolved during the Bayer process – concentrate in the bauxite residue
- 1980s on Jamaican bauxite residues using dilute acid as the first stage leaving behind the iron and titanium oxides, the REEs were then recovered by selective precipitation
- Joint venture between the Jamaican Bauxite Institute and Nippon Light Metals to construct a pilot plant for extraction from locally arising bauxite residues
- Orbite -recovery of alumina, titania, iron oxide, magnesia and rare earth elements - 6 M hydrochloric acid at temperatures between 140 to 165°C and a pressure of 60 to 90 psi
- Significant theme of the EU MSCA-ETN REDMUD programme:
  - Selective leaching after sulfation roasting at KU Leuven
  - Cation exchange chromatographic techniques at the National Technical University of Athens
- British Geological Study and Camborne School of Mines assessment of the potential for REEs in bauxite residues (assuming a total REE content of 1,000 mg/kg and an extraction efficiency of 50%):
  - Over 200,000 t of REEs could be available from bauxite residue produced in Europe since 1972
  - Globally every year over 172,000 t of REEs ‘wasted’ in bauxite residue compares to 100,000 t of REEs produced
Construction products

- Purgo – trials combining different waste materials with bauxite residue to manufacture construction materials such as building panels, aggregates etc.
- Treatment process minimises the leaching of the heavy metal contaminants e.g. As, Cd, Cr, Hg, Mo, Pb, Se
- Treated material meet the ‘inert’ classification in the Waste Acceptance Criteria Testing standard BS EN 12457
- Moderate scale tonnage trials
Situation in China

- Alumina production in China in 2015 almost 60 million tonnes
- Expected to be the area of largest growth over the coming decades
- Bauxites used very wide range of compositions
- Historically a significant percentage of alumina is made using a sinter route or combined Bayer-sinter route
  - Indigenous bauxites relatively low grade, some high in silica
  - Calcined at ~1,000°C with limestone and sometimes soda
  - Results in much higher calcia and silica levels than standard Bayer process and high gibbsitic bauxite
  - High in $\beta$-2CaO·SiO$_2$
  - Low in iron
- 1965 cement plant built to consume residue from Shandong Alumina
  - By late 1990s over 6 million tonnes of residue used to make OPC and oil well cements
- However, standards for cement restricted sodium level content and progressive move to imported bauxites so decline in sinter processing except for chemical grade alumina
- Since 2005 very large scale effort to utilise more bauxite residue in many areas
  - High intensity magnetic separation to concentrate iron
  - Glass ceramics CaO - SiO$_2$ - Al$_2$O$_3$
  - Bricks (with lime fly ash)
  - Polymer filler
- Very demanding Government targets but current use estimate is < 10%
Bauxite residue use targets/goals

• Chinese Government target of 25% use by 2015
• Shandong Province target of 40% use by 2015
• Note, however, > 10% use achieved in China
• IAI Alumina Technology Roadmap strategic goal of 20% by 2025
Bauxite residue uses estimates

- Clinker – Ukraine, Greece, Russia, Georgia, Moldova, Belorussia, Romania, ~250,000 t/y + China
- Global estimate for clinker/cement additive 1 to 1.5 million t/y
- Use in iron and steel production 0.2 to 1.2 million t/y especially China
- Road construction, sometimes in conjunction with fly ash – Australia, France ~ 50,000 tonnes/y external
- Large but intermittent use internally in refineries for levees, dykes and roads – low millions of tonnes
- Capping landfill sites – France 70,000 to 100,000 t/y
- Building materials 0.5 to 1 million t/y
- Miscellaneous 300,000 t/y
- **TOTAL 2.4 to 7 million t/y**
Challenges to use

• Moisture level
• Sodium content and types of compound
• pH
• Hazardous categorisation
• Heavy metal content – especially chromium
• Radioactivity
• Location
• Liability concerns
• Cost
Amount of bauxite residue generated by region (million tonne/y)

- China 80 (growing)
- Australia 30
- South America 18
- North America 9 (declining sharply)
- Asia and Africa (excluding China) 8.5
- Eastern Europe 5.5
- Western Europe 4
- Middle East currently small but will grow substantially
More recent driving forces for dealing with bauxite residue

- Growing desire within the industry to present a favourable public image – referenced in annual environmental reports of all major companies
- Very strong concerns about storage following Ajka increased by Wanji
- Strong drive to recover caustic soda
- Government pressure in China to find uses
- Concerns about closure costs – in the early days, no plant was built with the expectation that one day it would close
Lowering the barriers to use
Lowering the barriers

- Lower moisture contents – easier handling, lower transport cost, reduced energy use in some applications
  - Use of plate and frame filter presses
  - Obtain by air drying if climate appropriate
  - <28% moisture content achievable; in the future even lower
- Sodium – reduced contamination or interference in some applications
  - Improved recovery systems within refinery operation
  - Improved filtration so more sodium extracted from residue
  - Improved washing
- Lower pH
  - Neutralisation – acid, sea water or brine
  - Better filtration
  - Accelerated carbonation
  - Alcoa Kwinana carbon dioxide capture
- Radioactivity - more a perception issue that a real issue but can be a problem with some bauxite residue and some bauxite sources
  - Dissemination of the appropriate information
  - Bauxite residue selection
- Hazardous categorisation
  - Testing – eye, skin, transport
  - REACH
- Co-operation – producers, users, universities, networking
- Innovation – new solutions to old problems
Bauxite residue – some further challenges

• Very many ideas have been considered and tried but the results have never been published
  – Confidentiality in some instances
  – Failure in others
  – Partial success but no desire to publish

• Competition
  – In spite of a more open attitude, there is still a reluctance to give away years of hard won information
  – Some industries operate on very narrow financial margins – e.g. cement
  – Some companies have invested substantial sums in R&D and want to see a financial payback

• Focus of large scale producers is on projects that will use large volumes

• Beware of solutions that only utilise part of the residue and leave a less desirable residue
  – Acid or solvent extraction process for REE

• Need holistic solutions that use all the material
Future driving forces for affecting bauxite residue use

- Disposal to the sea has now ceased so new challenges for some refineries, several have closed as a result
- Public attitude to green solutions becoming stronger
- Shareholder pressure on multi-nationals stronger
- Desire to reduce area of land rendered unusable for future use – LCI/LCA driven
- More open attitude to co-operation by producers
- Desire by the major producers to minimise the environmental impacts of generation and substantially increased R&D effort e.g. Rusal - recycling centre in Urals, Alcoa – carbon capture and university support
- Increased use of filtration so lower moisture and soda levels
- External funding for research available e.g. EU MSCA-ETN REDMUD, BRAVO
- Role of entrepreneurs
- The “brain power” / intellectual effort now being expended
In summary

- Despite the enormous amount of work current usage at 2 – 5% is disappointing

- However, conditions never better as increased desire to succeed, bauxite residues with lower moisture and soda levels becoming increasingly available, more funding and intellectual effort

- Short term opportunities
  - Cement/clinker
  - Building construction materials
  - Iron recovery
  - Soil amelioration
  - Capping
  - Road construction
  - Levees/dams

- Medium term opportunities
  - Heavy metal removal, phosphate removal, acid mine drainage
  - Supplementary cementious materials

- Longer term opportunities
  - Scandium and REEs
  - Geo-polymers – with silica
A final thought

Since I started talking this afternoon, the industry has produced .....
Over 1,500 of these filled with bauxite residue
Thank you for your kind attention