ALTA 2014

Options For Removing Uranium & Thorium From Zircon Mineral Sands

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• ACKNOWLEDGEMENTS
This document is a dynamic record of the knowledge and experience of personnel at Mineral Engineering Technical Services Pty Ltd. As such it has been built upon over the years and is a collaborative effort by all those involved. We are thankful for the material supplied by and referenced from various equipment manufacturers, vendors, industry research and project partners.
Key Attributes

*Pragmatic, efficient, complete engineering through quality, personalised & exceptional service delivery*

- Working globally since 1988
- Dynamic and innovative niche consultancy
- Dedicated team providing customised service
- Specialist in Mineral Processing & Engineering Projects
- Unique solution finder
• Zircon is a valuable by-product from mineral sands operations

• The demand for zircon is growing as evidenced by increasing prices.

• Natural zircon contains uranium and thorium in varying quantities and from an environmental aspect this is problematic.

• The industry accepted standard is U+Th <500 ppm.

• High brightness is a marketing advantage.

• Removal of uranium and thorium achieves the production of a premium product.

• Sell a zircon sand to the ceramic market.
Mineral Sands-Zircon By-product

Wet Mineral Sands Concentrate

Electrostatic Separation

Non-Conductors (Monazite & Zircon)

Conductors (Rutile & Ilmenite)

Magnetic Separation

Product For Sale

Non-Mags

Mags

Non-Mags

Mags

Zircon

Monazite

Rutile

Ilmenite
Zircon Uses

- Pure ZrSiO$_4$
- Usually Zr,U,Th,TiO$_2$,SiO$_4$
- Very inert and refractory
- Opacifier in ceramics, zircon flour, zircon wash, fired in a kiln
- Kitchen crockery
- Floor tiles
- Minor zircon chemicals
- Minor zircon metal
• Recovered as a by-product from mineral sands

• Very high unit value $/t

• Very few producers- tight supply market

• Production, prices and demand have been rising

• Company’s like Iluka are brilliant at marketing and can affect market prices for zircon
Australian zircon sand export prices chart 2009-2013 Aug

Unit: USD/mt

Australia zircon sand 66% (CIF China)
Uranium & Thorium Radioactivity

• Contains from 10 ppm up to 1% uranium & thorium. Very variable depending on source of zircon-cation substitution at the time of formation in original host rock.

• Market requirements of <500 ppm total uranium & thorium.

• There are also transport limits of 50 Bq/gram and if exceeded radioactive stickers are required.

• The aim is to have the zircon classed as non radioactive to minimise all the issues that arrive from a radioactive classification.

• The uranium and thorium recovered can be precipitated and sold to a nuclear authority so there is no environmental issue with waste storage.
• Live in a no fault generation

• US FDA (Food & Drug Administration) test ceramics for leaching of metals

• Zircon flour or wash is the base of ceramic glazes

• Reducing radioactivity and impurities is market desirable - premium product

• If fired at the correct temperature the risks should be very low
Scanning Electron Microscopy

- An imaging technique using backscattered electrons to identify mineral phases in a ore / rock sample
  - Need to be coupled with energy dispersive spectrometry (EDS) for definitive identification
- Image contrast used to identify the ore minerals and their associations with other minerals
  - Higher the atomic number, the brighter the image

Back-scattered electron image (BS)

- Silver mineral acanthite $\text{Ag}_2\text{S}$ (bright)
- In a copper mineral malachite $\text{Cu}_2\text{CO}_3(\text{OH})_2$ (dark)
QEMSCAN – A Technology for Rapid Mineralogical Analysis

• Third generation of automated mineral analysis system that began with the QEM*SEM at CSIRO

• The system consists of:
  – A scanning electron microscope
  – Four X-ray detectors
  – A software package based on procedures developed by CSIRO

• Capable of identifying ore- and rock-forming minerals in milliseconds
  – A scanning electron microscope
  – Four X-ray detectors
  – A software package based on procedures developed by CSIRO
(Zr,Hf,U,Th,Y)SiO$_4$

The uranium and thorium based on SEM work is associated around the surface of the zircon grains or in micro cracks.

SEM is brilliant at detecting the radioactivity.

The zircon is inert but has some porosity.

Leaching removes the uranium and thorium to varying extents.
Historical Work

- Westralian Sands 1992
- Rio Tinto WIM project studies and testwork
- Hydrometallurgical studies by Hart, 1993; Hawkins & Aral 1995-CSIRO
- Patent search reveals numerous patents
- Hot acid leaching more effective than ambient leaching
- Zircon inert- small loss
- Mineralogical differences (porosity, impurities, age) result in different efficiencies
Process Review

• Various patented processes are referred to in the public domain
  
  – CSIRO pure zircon process
  
  – Pressure alkaline leaching
  
  – Acid leaching & hot acid leaching
  
  – PlaTCOM process
  
  – Alkane process-Dubbo Zirconia process
CSIRO Pure Process

- CSIRO has developed a process which reduces the radiation level of zircons by using a heat process followed by leaching to extract the radio nuclides.

- The stages involved in the Pure Zircon Process are:
  - grinding the sample to achieve a particle size of 15-20 μm
  - calcining the sample with a borate mineral at 1200°C for four hours
  - leaching the calcine with a dilute acid solution
  - economics not known - no commercial plants

The new process for treating zircon reduces radiation levels and removes impurities.
Pressure Alkaline leaching

• Pyrometallurgical methods include fusion with caustic soda and the formation of acid soluble zirconate

• This is followed by pressure leaching

• Time, temperature, grind size and caustic strength lead to the conclusion it was chemically controlled

• No plants, probably not commercial and product not suitable for ceramics industry
Acid & Hot Acid Leaching

- Lots of work done in this area
- Heat pre treatment
- Cold & hot Acid leaching
- Nitric, sulphuric and hydrochloric acid
- Variable efficiency and practicality
- Materials of construction
- Acid recovery?

Figure 1: The effect of heat treatment on uranium leaching of zircon Dengkil sand
Issues With Acid Leaching

- Acid cost and acid recovery
- Temperature limitations each acid
- Bonded silicon carbide vessels for leaching - highly corrosive
- w/w % solids/acid limitations
- Bench scale ok but continuous piloting required
## Typical Feed & Leached Product Results

<table>
<thead>
<tr>
<th></th>
<th>% ZrO₂</th>
<th>% Fe₂O₃</th>
<th>% TiO₂</th>
<th>% Al₂O₃</th>
<th>% SiO₂</th>
<th>ppm U</th>
<th>ppm Th</th>
<th>ppm U+Th</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Feed</strong></td>
<td>64.7</td>
<td>0.23</td>
<td>3.91</td>
<td>0.95</td>
<td>29.2</td>
<td>990</td>
<td>650</td>
<td>1640</td>
</tr>
<tr>
<td><strong>Product</strong></td>
<td>64.0</td>
<td>0.02</td>
<td>0.48</td>
<td>0.21</td>
<td>34.2</td>
<td>341</td>
<td>110</td>
<td>451</td>
</tr>
</tbody>
</table>

- U+Th below 500 ppm
- High recovery of zircon
- Grinding not required
- Premium brightness- removal of iron, alumina, titania
- Acid and conditions not quoted for confidentiality
PlaTCOM Process

- A patented Malaysian process for removing radioactive elements from zircon
- It reports minimal cost in removing radioactivity
- Does not involve grinding
- It suggests acid leaching is not cost effective
- Do not disclose how they process the zircon
Alkane-Dubbo Zirconia Process

Process Flow Sheet

- Simple open cut mining operation
- Crushing and grinding
- Sulphuric acid, roast, leach whole of ore
- Solvent extraction, separation & refining

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Product Value Enhancements

• Continuing Product Development for Increased Return
  • **Rare Earths:**
    - MOU with Shin-Etsu Chemical to produce suite of separated rare earth oxides
  
  • Sale of products to others excess to Shin-Etsu’s requirements
  • Further work to improve recoveries proceeding at ANSTO
  • **Niobium:**
    - Treibacher JV to produce FeNb product for direct sale to end users
  
  • **Zirconium:**
    - Zr development to produce value added zirconium products of variable particle size and quality for different applications: Production of yttria - stabilised zirconia microsphere grinding media
  
  • Production of PZT –piezoelectric lead zirconate titanate
  • Ceramic colours, eg. yellow using praseodymium
  • Glass and steel making refractories
Zircon Leaching Batch Tests

• Batch tests are very good at achieving preliminary tests

• Optimisation of reagents and temperature is more time consuming

• Test parameters:
  - Acid type
  - Concentration
  - Temperature
  - Residence Time
  - Leach density
  - Effect grind size
  - Product quality (brightness, U+Th)
Zircon Leach Pilot Plant

• Scale up is an issue – what’s acceptable?

• Re cycle streams

• How long to run

• Engineering and sampling data generation

• Significant cost but provides confidence in the process
CAPEX & OPEX Zircon Leach Plants

• CAPEX
  – Tonnages are small
  – Complexity can increase this significantly
  – CAPEX similar to a small gold plant
  – Country location can change this significantly (Malaysia vs Australia)
  – Materials of construction- bonded silicon carbide expensive
  – Environmental regulations
  – OH&S impacts

• OPEX
  – OPEX $/t high due to low throughput
  – Assigned value for uranium?
  – Will the market pay for the premium?
  – Possibly OK during high zircon prices
Zircon Leach Full Scale Plant

- Permitting & licence
- Process Flowsheet
- Plant layout
- Process design
- P&ID’s
- Equipment list
- Mass balance
- Water balance
- Process control
- OH&S
- Safety
- Environmental
- Project implementation
Zircon Leach Process Risks

- Never been done before at commercial scale
- Product acceptance
- Long term zircon price
- Variable geometallurgy
- Engineering & Scale up from bench scale
- Corrosion & materials of construction
- OH&S issues with radioactivity
- Social compliance and acceptance
- Premium product - excellent market acceptance
- High brightness
- Uranium & thorium, <500 ppm
- Other contaminants - TiO₂ low

Zircon Leach Final Product Brightness

Leached (1) RMB Tiwest Iluka
Leached (2) DMS Mozambique Sierra Leone
Conclusions

- Specific proprietary technical information has been intentionally withheld because of confidentiality.

- A number of process routes are available as listed in the public domain literature.

- Mineralogical differences result in different efficiencies of removal of U+Th.

- Project development will take several years from benchscale to production plant.

- No commercial plants have been built at this point in time - this could change in the next couple of years.

- Lack of transparency between producers because of competitive market is an issue in terms of who is doing what - very secretive industry, industrial minerals, marketing is the key.
Conclusions

• Growing market in China for ceramics - urbanisation and higher standard of living

• Premium products are more desirable
  – Ceramic glazes brightness is highly desirable
  – Competitive marketing
Acknowledgement

• Thanks to companies for permission to publish

• Thanks also to all colleagues, laboratory staff and other consultants for their help and contribution.

• Thanks to vendors for the photos
REFERENCES


• Ashraf M. Kinetics of Alkaline Pressure Leaching of Mechanically Modified zircon Concentrate. 2006.
