Insights Session

Cyanide Destruction & Recovery From Tailings
Including Possible Resin Technology

Presented by:
Peter Steckis,
Metallurgical Manager
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Midas Office Locations

Noosa-
Brisbane-
Newcastle-
Sydney-
Melbourne-
Perth-
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
Introduction

- More projects required by law to destroy cyanide in tailings
- Minimise exposure to wild life
- Cyanide forbidden in some states in the USA
- OH&S issues
- Environmental issues
- Cyanide DETOX
- Cyanide recovery
- Case studies
Introduction

• Remediation Methods
  — Destruction (oxidation)
  — Separation (physical, adsorption and complexation)
    > Non-destructive: use to concentrate and recover cyanide for recycling purpose
    > Toxicity of cyanide remained ➔ disposal problem
• Recovery Methods

<table>
<thead>
<tr>
<th>Complexation Method</th>
<th>Physical Methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acidification/volatilisation, metal addition, flotation</td>
<td>Dilution, membranes, electrowinning and hydrolysis/distillation</td>
</tr>
<tr>
<td>and solvent extraction</td>
<td></td>
</tr>
<tr>
<td><strong>Oxidation Methods</strong></td>
<td><strong>Adsorption Methods</strong></td>
</tr>
<tr>
<td>Biological, catalytic, electrolytic, chemical and</td>
<td>Minerals, activated carbons and resins adsorb cyanide from the</td>
</tr>
<tr>
<td>photolytic methods</td>
<td>solution. Various contact vessels can be used, ie: elutriation</td>
</tr>
<tr>
<td></td>
<td>columns, agitated cells, packed-bed, columns and loops, etc…</td>
</tr>
<tr>
<td></td>
<td>Afterwards it is screened by flotation or gravity separation</td>
</tr>
</tbody>
</table>
## Toxicity of Cyanide

### Table 1: The toxicity of poisons derived from plants and animals compared with sodium cyanide (adapted from Mann, 1992)

<table>
<thead>
<tr>
<th>Poison</th>
<th>Lethal dose (µg/kg bodyweight for the mouse)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Botulinus toxin</td>
<td>0.03</td>
</tr>
<tr>
<td>Tetanus</td>
<td>0.07</td>
</tr>
<tr>
<td>Cobra neurotoxin</td>
<td>0.30</td>
</tr>
<tr>
<td>Strychnine</td>
<td>500</td>
</tr>
<tr>
<td>Sodium cyanide</td>
<td>10 000</td>
</tr>
</tbody>
</table>

### Table 2: The toxicity of industrial poisonous gases compared with hydrogen cyanide (adapted from Richardson, 1992)

<table>
<thead>
<tr>
<th>Poisonous Gas</th>
<th>Threshold Limit Value (ppm)</th>
<th>Short-term Limit (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon monoxide</td>
<td>25</td>
<td>300</td>
</tr>
<tr>
<td>Chlorine</td>
<td>0.5</td>
<td>1</td>
</tr>
<tr>
<td>Hydrogen cyanide</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>Hydrogen sulphide</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Nitrogen dioxide</td>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td>Sulphur dioxide</td>
<td>2</td>
<td>5</td>
</tr>
<tr>
<td>Date</td>
<td>Location</td>
<td>Description</td>
</tr>
<tr>
<td>----------</td>
<td>----------</td>
<td>--------------------------------------------------</td>
</tr>
<tr>
<td>Aug 95</td>
<td>Guyana</td>
<td>3.2 billion litres of tailings into a river system</td>
</tr>
<tr>
<td>Dec 00</td>
<td>Guyana</td>
<td>Further spill into same river</td>
</tr>
<tr>
<td>Jan 00</td>
<td>Romania</td>
<td>130,000m³ of tailings into river systems</td>
</tr>
<tr>
<td>Jun 01</td>
<td>PNG</td>
<td>Cyanide spill into ocean</td>
</tr>
<tr>
<td>Oct 01</td>
<td>Ghana</td>
<td>2 spills, 1 mine wastewater, 1 cyanide</td>
</tr>
<tr>
<td>Nov 01</td>
<td>China</td>
<td>Liquid NaCN spill into a river</td>
</tr>
<tr>
<td>May/Jun 02</td>
<td>USA</td>
<td>24,000/40,000 gallon spills of cyanide solution</td>
</tr>
<tr>
<td>Jan 03</td>
<td>Western Honduras</td>
<td>Massive spill into river</td>
</tr>
<tr>
<td>Jan 03</td>
<td>Nicaragua</td>
<td>Cyanide solution spill into river</td>
</tr>
<tr>
<td>Mar 04</td>
<td>Romania</td>
<td>Contaminated water spill into river ~10 tonnes</td>
</tr>
<tr>
<td>Jun 04</td>
<td>China</td>
<td>7 lethal releases of chemicals</td>
</tr>
<tr>
<td>Oct 04</td>
<td>Australia</td>
<td>Report of mine tailings leaking into groundwater at Kalgoorlie</td>
</tr>
<tr>
<td>Jun 05</td>
<td>Laos</td>
<td>Cyanide spill into river</td>
</tr>
<tr>
<td>Oct 05</td>
<td>Philippines</td>
<td>2 spills of process treatment water</td>
</tr>
<tr>
<td>Jun 06</td>
<td>Ghana</td>
<td>Spill into river</td>
</tr>
<tr>
<td>Dec 06</td>
<td>Alaska</td>
<td>Cyanide found leaking into ground from tailings</td>
</tr>
</tbody>
</table>
Cyanide Form

- **Free cyanide**
  - Includes the cyanide ion and hydrogen cyanide
  - $\text{CN}^- + \text{HCN}$

- **Simple cyanide**
  - A salt which dissociated to form a cyanide ion
  - $\text{NaCN}$

- **Complex cyanide**
  - Dissociates to form another cyanide compound
  - $\text{Au(CN)}_2^-$

- **WAD cyanide**
  - **Weak acid dissociable**, cyanide that is readily released from cyanide containing compounds when the pH is lowered
  - $\text{Cd(CN)}_2$

- **SAD cyanide**
  - **Strong acid dissociable**, cyanide that is released from cyanide containing compounds under highly acidic conditions
  - $\text{Co(CN)}_6^{4-}$
Process Selection Criteria

• Recovery is favoured over destruction with high cyanide consuming ores

• Each project is unique with respect to species in the tailings

• Environmental regulations vary with respect to allowable concentration limits in the treated tailings

• There is a large choice of different cyanide destruction methods

• The cost and efficiency of each method varies

• Legislation varies from country to country
The cost of destroying cyanide can be a significant percentage of total operating costs, and unlike other costs it generates no income. It is therefore important, for both regulatory and economic reasons, to select the correct process.

- The cost for cyanide destruction, particularly for sodium metabisulfsulfite. E.g. in the INCO process, it can be a large cost, as high as $A0.50 to $2.00/tonne of tailings treated plus the new cyanide cost of approximately $1.50/tonne.

- On the other hand the cost of recovering cyanide can be as low as $0.50/tonne of tailings when copper credits are added back.

The CAPEX cost is a serious consideration when cyanide recovery is involved compared to cyanide destruction. The AVR or SART processes treat solution tailings rather than pulp and therefore the CAPEX cost of solid liquid separation has to be added.

Recycled cyanide is much cheaper than new cyanide and also has the advantage of less environmental risk. Less new cyanide is required so there are less transport, storage and handling issues.
DETOX Alternatives

- Natural attenuation/degredation
- Alkaline chlorination
- INCO/\(\text{SO}_2\) and air
- Hydrogen peroxide
- Ferrous sulphate
- Caros acid
- Ozonation
- Electrolytic oxidation
- Bio degradation
- Mainly related to the volatilisation of HCN from TSFs
- No reagents required, the final product is usually HCN

Table showing the efficiency of cyanide removal in tailing impoundments by natural degradation

<table>
<thead>
<tr>
<th>Mine</th>
<th>CN entering the tailings system (mg.L⁻¹)</th>
<th>CN discharging from the tailings system (mg.L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lupin, NWT, Canada</td>
<td>184</td>
<td>0.17</td>
</tr>
<tr>
<td>Holt McDermott, Ontario, Canada</td>
<td>74.8</td>
<td>0.02</td>
</tr>
<tr>
<td>Cannon, Washington, USA</td>
<td>284</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>Ridgeway, South Carolina, USA</td>
<td>480</td>
<td>0.09</td>
</tr>
<tr>
<td>Golden Cross, New Zealand</td>
<td>6.8 (WAD CN)</td>
<td>0.33 (WAD CN)</td>
</tr>
<tr>
<td>Kurara</td>
<td>120</td>
<td>0.5</td>
</tr>
<tr>
<td>Gabanintha</td>
<td>250</td>
<td>120</td>
</tr>
</tbody>
</table>
Advantages and Disadvantages of Alkaline Chlorination

- **Advantages**
  - Well established process
  - Produce low residual effluent of free cyanide and WAD cyanide
  - Process can be adapted to continuous or batch operation
  - Process can be employed for treating pulp
  - Cyanate and ammonia can be removed through breakpoint chlorination

- **Disadvantages**
  - Not suitable for treating high levels of cyanide
    - Increase in reagent costs
  - Close control of pH to avoid release of cyanogen chloride gas (CNCl) (harmful if inhaled)
  - Inefficient for removal of iron complexed cyanides in particular under ambient conditions
  - Requires further treatment for removal of free chlorine and chloramines prior to discharge
  - May produce high concentration of cyanate that can potentially increase the ammonia concentration
Oxidation Method – INCO/\(\text{SO}_2\) Process

- Involves the mixing of sulphur dioxide and air with free cyanide, metal-complexed cyanide, thiocyanate to produce cyanate (can also use SMBS)
- Reaction can be catalysed with cupric or nickel cations (Copper Sulphate)
- Ineffective for reactive sulphide ores
- Can potentially lead to the production of by-products such as sludge and gypsum
- Been incorporated in mining operations in Canada and U.S. since 1983
Advantages and Disadvantages of INCO Process

• **Advantages**
  
  – Yields low effluent cyanide and metal concentration
  
  – Effective in treating slurries and solutions
  
  – Suitable for batch or continuous operations
  
  – Capital and operating costs are comparable to other chemical treatments

• **Disadvantages**
  
  – Not suitable for treating high levels of cyanide
    
    • increase in reagent costs and high power consumption due to air requirements
  
  – May generate high levels of sulfate in the treated solution
  
  – Additional treatment may be required to remove iron cyanide, thiocyanate, cyanate, ammonia, nitrate and/or metal before discharged to the environment
Detoxification of cyanide by hydrogen peroxide in gold mines

<table>
<thead>
<tr>
<th>Case study</th>
<th>Before treatment (mg/L)</th>
<th>After treatment (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total cyanide</td>
<td>WAD cyanide</td>
</tr>
<tr>
<td>Case study #1 Pond Overflow (1)</td>
<td>19</td>
<td>19</td>
</tr>
<tr>
<td>Case study #2 Barren Bleed (2)</td>
<td>1,350</td>
<td>850</td>
</tr>
<tr>
<td>Case study #3 Heap Leach Solution (3)</td>
<td>353</td>
<td>322</td>
</tr>
</tbody>
</table>

(Source: Griffiths, 1989)

Notes:
1) Preliminary plant results from pre-operational test runs
2) Typical results during first six months of operation
3) Average of 25 measurements made over ten days of plant operation
4) Value dropped from 1.0 to 0.4 over four days due to coagulation and settling
Advantages and Disadvantages of Hydrogen Peroxide Process

• Advantages
  — Process is simple in design and operation
  — By combining oxidation and precipitation, it is efficient for removal of all forms of cyanide
  — Adaptable to batch or continuous operations
  — Does not require close pH control
  — Produces low quantities of waste sludge
  — Effective during bench, pilot and full-scale operation

• Disadvantages
  — High reagents costs
  — May produce high concentration of cyanate that can potentially increase the ammonia concentration
  — Does not remove ammonia or thiocyanate
  — Not suitable for treating tailings slurries
  — May require addition treatment processes
Metal Sulphates

- Common metals used ➔ iron, zinc, aluminium, copper
- Commercial application ➔ Prussian blue precipitation (precipitation of $\text{Fe}_4[\text{Fe(CN)}_6]_3$ on the addition of $\text{FeSO}_4$) – unstable in alkaline solutions
- Applicable to SAD cyanide complexes, thiocyanate has a limited response
- Not a stand-alone process

(Source: Technische Universitat Kaiserslautern website, 2013)
Caro’s Acid

- Peroxymonosulfuric acid (H$_2$SO$_5$), also known as Caro’s acid, is a reagent used in a recently developed cyanide treatment process that has found application at some sites.

\[
\text{H}_2\text{SO}_5 + \text{CN}^- \rightarrow \text{OCN}^- + \text{SO}_4^{2-} + 2\text{H}^+
\]

- **Caro’s acid used in the process must be produced on-site** using sulfuric acid and hydrogen peroxide - Caro’s acid decomposes very quickly.

- **Caro’s acid is used in slurry treatment applications** -
  - The addition of a copper catalyst is not required.
  - Typically used in situations where the sulfur dioxide and air process is not suited.
    - The retro fitting of cyanide destruction into older operations where tankage is not in place.
  - In solution applications, other destruction processes, such as the hydrogen peroxide process are preferred.
Ozonation

- Treatment of cyanide bearing wastewater has been carried out using ozone

- Advantages of ozone oxidation include:
  - Extremely effective against all free and complexed cyanides
    - Used alone or in combination with UV light
  - Does not form any undesirable by-products such as chlorinated organics or ammonia
  - Does not require the purchase, storage or handling of dangerous chemicals on site
  - Ozone is produced on site from air using an ozone generator

The reaction with ozone does not require high temperatures or pressures
Electrowinning

- Applicable to SAD and WAD cyanides but not thiocyanate
- Low efficiency, however progress is continuing to make it economically viable
- Has been applied at CELEC regeneration system or high surface area (HAS) reactor

(Source: Precious Metals Processing Consultants website, 2013)
(Source: Allied Plating Supplies website, 2013)
Oxidation Method – Bio-Oxidation

- Converting cyanide into cyanate (a less toxic species) by means of bacteria, fungi, algae, yeasts and plants, enzymes and amino acid followed by hydrolysis to ammonium and bicarbonate ion.
- Final products depend on biomass used, cyanide species, initial cyanide concentration, pH and temperature.

Rotating biological contactor plant for the removal of cyanide and thiocyanate at the Homestake Mine.
Cyanide Recovery Alternatives

- Water recovery
- AVR
- SART
- Resin technology
- Cyanide can effectively be recovered and re-used by recycling cyanide-containing solutions within a metallurgical circuit

- This is commonly conducted using tailings thickeners or tailings filters to separate solution from tailings solids, with the solution being recycled in the grinding and leaching circuits

- Can be determined by a simple mass balance calculation including the improved economics.
- In the dry Australian climate water recovery is favoured because water is often scarce
• Reaction is favoured at low pH, typically the process is operated at pH between 1.5 and 2
• Also known as Mills-Crowe process
• New development ➔ Cyanisorb™ process
• Disadvantage ➔ consumes high amounts of acid and alkaline
• Advantage ➔ low energy consumption and increased volatilisation rate compared to hydrolysis/distillation process
• Effective for WADs and to a lesser extent for thiocyanate and SADs

(Source: Around of Mining and Metallurgy Blog, 2008)
The CYANISORB® process consists of four operations:

- Converting cyanide and metal-cyanide complexes to HCN
- Stripping HCN from tailings in a packed tower
- Recovering HCN gas into an alkaline solution
- Adjusting the pH of the detoxified tailings
The Golden Cross plant is currently operating with an average recovery of tailings WAD cyanide of 80–90%
Benefits

• Metallurgical Benefits
  – Reduced sodium cyanide costs
    – Less cyanide purchases required and lower transport and handling costs
    – Possibility of higher NaCN addition rates when required without NaCN loss with the tailings

• Tailings Treatment - Economic Benefits
  – Reduced exposure to NaCN price increases
  – Tailings detoxification costs are reduced
  – Cyanide recycling provides an approximately zero nett tailings detoxification cost
SART (Sulfidisation, Acidification, Recycle and Thickening) Process

• Alternative recovery route for high grade cyanide soluble copper slurries
  — Cu and CN are recoverable
  — Comparatively low OPEX and CAPEX costs
  — Bench scale testwork, pilot plant trials and feasibility study for the Telfer Gold Mine (WA, Australia)
  — Site personnel verify the route is effective and economical

• Sulfidisation, Acidification
  \[2\text{Na}_3\text{Cu(CN)}_4 + 3.5\text{H}_2\text{SO}_4 + \text{NaHS} \rightarrow \text{Cu}_2\text{S} + 3.5\text{Na}_2\text{SO}_4 + 8\text{HCN}\]

• Recycle - Fine Cu$_2$S is recycled as seed to previous step

• Thickening
  \[2\text{HCN} + \text{Ca(OH)}_2 \rightarrow \text{Ca(CN)}_2 + 2\text{H}_2\text{O}\]
Adsorption Method

- **Common adsorbents:**
  - **Mineral:**
    > Cyanide is adsorbed via ion exchange or precipitation
  - **Activated carbon:**
    > Packed bed system
    > Effective for dilute cyanide - in particular for WADs and SADs
    > Non-selective

- Needs to be coupled with screening, gravity separation or flotation
- Cyanide is desorbed into a low volume solution
Adsorption Method

- Common adsorbents:
  - Resins:
    > Can be selective and capacity depends on the chelating or ion-exchange properties
    > Predominantly used in packed bed system
    > More cost effective compared to activated carbon due to high resistant to fouling and fast desorption kinetics
    > Not effective for thiocyanate
Advantages and Disadvantages of Resins

**Advantages**
- Not poisoned by organics – no thermal regeneration
- Unaffected by clay ores
- Do not absorb calcium – reduced acid washing requirements
- Improve recovery in the presence of preg-robbing ores
- High selectivity resins offer advantages with Cu/Au ores
- High loading capacity (100,000 g/t) and faster loading kinetics
- Enhanced abrasion resistance over activated carbon
- Reduced capital costs for small to medium operations

**Disadvantages**
- Resin particle size – 0.8-1.2 mm – screening more difficult
- Strong base resins less selective for gold over base metals compared to activated carbon
- Resin is approximately ten times more expensive than carbon ($30,000/t)
- Database of experience is limited
Resins – Case Study

- **Operations in Environmentally sensitive area**
  - Tailings final product from CCD thickeners
  - Filtration of tailings using belt filters
  - Inefficient operation of belt filters when clay levels high

- **Cyanide increasing as well as some metal losses**
  - Investigated use of Resin in Pulp for metal scavenging and cyanide reduction
  - Testwork carried out in laboratory in Perth

![Graph showing cyanide concentration over time](image)
Resins – Case Study

- **Testwork (IXR)**
  - Tailings final product from recovery testwork
  - Testwork procedure was developed – Multi contact
  - Resin in Pulp scenario
  - A100/2412 (Metals) and A500/2788 (Gold silver and cyanide) resins tested
  - Bottle roll tests - sequential contact with resin
  - 12.5 g/L target concentration of resin – Slightly higher for A500/2788
  - Cyanide levels in pulp monitored
  - Assumes that cyanide is loaded onto the resin

- **Resin stripping**
  - Acidic conditions and HCN generated
  - Requirement to recover HCN gas in caustic solution

- **Significant development required**
  - Resin type and selectivity
  - Stripping of the resin
  - Recovery of cyanide
Environmental Issues - Birds & Wildlife

- Contaminated ducks
- Bird fatalities
- Species in danger
Attempts at Minimizing Bird Fatalities due to Cyanide in Tailings

**Hazing techniques:**
- Propane gas gun
- Bird whalers
- Streamers
- Loud music
- Netting
- Flying kites
- Flagging tape
- Wine casks
- Fishing lines

(Source: Magnum Photos website, 2005)
Minimizing Bird Fatalities Due To Cyanide In Tailings

(Source: Bird B Gone Blog, 2012)

(Source: Zon Scare Cannons website, 2013)
The Motivation?

- No set regulation for management of cyanide
- Numerous spills and other incident involving cyanide solutions

Aug 1995: Omai, Guyana - dam failure
May 1998: Kyrgyz Republic – truck
Jan 2000: Baia Mare, Romania
Mar 2000: Papua New Guinea – helicopter
2002: Nevada, USA - pipe failures

(Source: International Cyanide Management Code website, 2013)
Established based on the collective efforts from 40 participants:

- Global mining industry
- Cyanide producers
- Non-Governmental Organisations
- Governments
- United Nations Environmental Programme (UNEP)
- International Council on Mining and Metals (ICMM)
- Gold Institute
- World Wildlife Fund for Nature (WWF)
- International Finance Corporation (IFC)
- European Commission
Case Studies

- Mt Muro
- Rapu Rapu
- Mina Sertao
- Andorinhas
Mt Muro INCO Process

POND SOLUTION STREAM

RAW WATER

HOIST

SPLITTER

MIX TANK

SODIUM METABISULPHITE STORAGE TANK

METERING PUMPS

CYANIDE DESTRUCTION REACTOR TANK 1

1600 Nm³/h (1000 scfm)

CYANIDE DESTRUCTION REACTOR TANK 2

1600 Nm³/h (1000 scfm)

LIME FEED

LIME STORAGE TANK

LIME FILTER

SILENCE

AIR BLOWER

AIR FILTER

AIR

AIR

3200 Nm³/h (2000 scfm)

DESIGN OPERATING CONDITIONS

Mt Muro INCO Process

(Source: METS Image Library 2014)
• Strong anti mining sentiment in the Philippines. NGO’s and church vocal

• Super typhoon (one in hundred year event) resulted in tailings dam overflow

• Overflow direct to ocean

• Fish kill immediate and obvious to local fishermen

• Company reacts. Government shuts facility

• Project re opened after mitigation steps put in place to ensure cannot happen again

Mitigation Steps:
• Overflow from tailings dam to ponds
• Ponds have cyanide destruction facilities
• Reed beds after ponds
• Cannot flow direct to ocean
Mina Sertao & Andorhinas (BRAZIL)

(Source: METS Image Library 2014)
Conclusions

• The historical spill incidents such as Baia Mare and Guyana have created an environment where regulators are wary of gold cyanide projects

• Either DETOX or cyanide recovery is seen as being responsible and minimising the potential environmental risk

• As indicated in the previous discussion, there are over nine cyanide treatment processes that have been successfully used worldwide for cyanide removal at mining operations

• The key to successful implementation of these processes is by considering site water and cyanide balances under both average and extreme climatic conditions and the range of cyanide treatment processes available and their ability to be used individually or in combination to achieve treatment objectives

• Proper testing, design, construction, maintenance and monitoring of both water management and cyanide management facilities are required

• Process selection is not straight forward and each project is unique in finding the best solution. With regards to cost effectiveness the economics have moved to cyanide recovery in preference to destruction

• Assessing the hazards of using cyanide should be based on the Australian Risk Assessment Standard. It is in the interests of all gold mining companies adopting the International Cyanide Management Code
What did you get out of this presentation?
Please share your thoughts in an informal discussion

Questions?
• METS Image Library 2014


THANK YOU

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