Trends of Arsenic in Copper Raw Materials and its Technical Countermeasure in the Copper Industry

October 17, 2018

Metal Economics Research Institute, Japan
Nobuo YAMAZAKI
Contents

1. Trends and its Future Prospects of Arsenic Grade in Copper Concentrate
2. Current Status and Future of Impurity Regulation
3. Current Status and Issues of Arsenic Removal from Copper Raw Materials
4. Immobilization and Storage of Arsenic
5. What should we do?
Trend of As in main copper concentrate for Japanese Smelters

It used to be beautiful conc., but not now

**Escondida**

**Collahuasi**

**Los Pelambles**

**Northparks**

Source: MERIJ作成
As & Cu Trend of Imported Copper Concentrate for Japan

As & Cu Ratio: 2.8 !!

As: 0.04 ➔ 0.09%

Cu: 32 ➔ 26%

Source: MERIJ作成
How far will As grade of copper concentrate rise?

High As-Cu Mine Project (Planned for Development after 2021)

- 60kt-As increase ➔ 0.09% As UP ➔ 0.31% As in Conc

0.31%?

Tampakan, Marcapunta Oeste, El Galeno, La Granja, Pascua Lama, Wafi-Golpu, Canariaco Norte, Others

Chelopech, Chuquicamata, El Brocal, Toromocho, others

Source: Teck-Aurubis, CESLからMERI/J作成
Current Status and Future of As Regulation

① Regulation of impurity acceptance of concentrate ⇒ China
② Environmental regulation of air and water quality ⇒ Chile
③ Regulation of marine transportation of concentrate ⇒ IMO
④ Basel regulation of smelting byproduct ⇒ As, Pb grade in copper slag?

① Regulation of China’s imported concentrate acceptance (2006~ )

<table>
<thead>
<tr>
<th></th>
<th>As</th>
<th>Hg</th>
<th>Pb</th>
<th>Cd</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu Conc</td>
<td>0.5%</td>
<td>100ppm</td>
<td>6.0%</td>
<td>0.05%</td>
<td>0.10%</td>
</tr>
<tr>
<td>Pb Conc</td>
<td>0.7%</td>
<td>500ppm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn Conc</td>
<td>0.6%</td>
<td>600ppm</td>
<td></td>
<td>0.3%</td>
<td></td>
</tr>
<tr>
<td>Bulk Conc</td>
<td>0.45%</td>
<td>500ppm</td>
<td></td>
<td></td>
<td>0.4%</td>
</tr>
</tbody>
</table>

Source: GB20242-2006
Comparison of actual As emission of Chilean smelting (2014) and new regulation value (The Decree №28)

- **Chuquicamata**:
  - Emissions: 730 (T/Y)
  - Regulation Limit: 476 (T/Y)
  - Collection Efficiency: 90%
  - As Regulation Limit for CE: 99%

- **Paipote**:
  - Emissions: 35 (T/Y)
  - Regulation Limit: 17 (T/Y)
  - Collection Efficiency: 88%
  - As Regulation Limit for CE: 99%

- **Chagres**:
  - Emissions: 29.6 (T/Y)
  - Regulation Limit: 35 (T/Y)
  - Collection Efficiency: 90%
  - As Regulation Limit for CE: 99%

- **Altonorte**:
  - Emissions: 128 (T/Y)
  - Regulation Limit: 126 (T/Y)
  - Collection Efficiency: 90%
  - As Regulation Limit for CE: 99%

Possible for 35% reduction?
Possible for 9% improvement?

Source: Codelco Sustainability Report 2014

51% reduction
## Arsenic Balance of Copper Conc. in the World

<table>
<thead>
<tr>
<th>Source</th>
<th>As (t/y)</th>
<th>Ratio (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Whole World</td>
<td>150,000</td>
<td>100</td>
</tr>
<tr>
<td>Custom Smelter</td>
<td>50,000</td>
<td>33</td>
</tr>
<tr>
<td>Outside China</td>
<td>10,000</td>
<td>6</td>
</tr>
<tr>
<td>Self Treatment</td>
<td>100,000</td>
<td>67</td>
</tr>
<tr>
<td>De-As Roasting</td>
<td>24,000</td>
<td>16</td>
</tr>
<tr>
<td>Integrated Mine/Smelter</td>
<td>76,000</td>
<td>51</td>
</tr>
</tbody>
</table>

### Destination of Arsenic

- **Custom Smelter**: 33%
- **Integrated Mine & Smelter**: 51%
- **De-As Roasting**: 16%

### As for China:

\[
\text{Imported Conc} \times 17,333 \text{kdmt} \times 0.25\% = 43,000 \text{ t / y}
\]
Current Status and Issues of Arsenic Removal

Where should Arsenic be separated / removed?

Separation from Ore

Mining/Grinding/Flotation

Removal from Concentrates

Direct Leaching
De-As Roasting

Integrated Smelter

SX/EW

Flue Dust
Waste water from Acid Plant
Matte, Blister, Electorolyte, Slag

Removal from Intermediates

Fixation
Immobilization

E • Cu

Intermediates
Current Status and Issues of Arsenic Removal

Where should As be separated / removed? (Mine or Smelter?) depending upon Economic and Market Condition?

<table>
<thead>
<tr>
<th>Trigger</th>
<th>Penalty (US$/dmt)</th>
<th>US$/t-As</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1% &lt; As &lt; 0.5%</td>
<td>3-4 $/0.1%</td>
<td>US$3-4K</td>
</tr>
<tr>
<td>0.5% &lt; As &lt; 1.0%</td>
<td>4-6 $/0.1%</td>
<td>US$4-6K</td>
</tr>
<tr>
<td>1.0% &lt; As &lt; 5.0%</td>
<td>5-8 $/0.1%</td>
<td>US$5-8K</td>
</tr>
<tr>
<td>5.0% &lt; As &lt; 10.0%</td>
<td>8-10 $/0.1%</td>
<td>US$8-10K</td>
</tr>
<tr>
<td>10.0% &lt;</td>
<td>10-15 $/0.1%</td>
<td>US$10-15K</td>
</tr>
</tbody>
</table>

Converted Value to 1ton of As

Source: Codelco 2015

Source: 聴取によりMERIJ作成

Costo Tratamiento del Arsenico (US$/tms)
Current status and issues of As removal from Cu Conc.

Cu Conc. (16)

Hydrometallurgy (15)
- POX
- CESL
- FLSmidth
- Ferric Leaching
- Galvanox
- PLATSOL
- BioCop
- Albion
- Hydro Copper
- INTEC
- Nikko Chlorination
- Sumitomo Chlorine
- Toowong
- Equity Silver
- Poly Sulfide

Pyrometallurgy (1)

Atomosphere (12)
- FLSmidth
- Ferric Leaching
- Galvanox
- BioCop
- Albion
- Hydro Copper
- INTEC
- Nikko Chlorin.
- Sumitomo Chlori.
- Toowong
- Equity Silver
- Poly Sulfide

Sulfuric (5)
- FLSmidth
- Ferric Leaching
- Galvanox
- BioCop
- Albion

Chloride (4)
- Hydro Copper
- INTEC
- Nikko Chlorin.
- Sumitomo Chlorn.

Alkali (3)
- Toowong
- Equity Silver
- Poly Sulfide

Partial Roasting
- Ministero Hales

Pressurization (3)
- POX
- CESL
- PLATSOL

Roasting
**CESL Cu-As Process (Visit on Sept. 2017)**

4Cu₃AsS₄(s) + 31O₂(g) + 2Fe₂(SO₄)₃(aq) + 2H₂O → 12CuSO₄(aq) + 4FeAsO₄・2H₂O(s) + 8S⁰(s) + 2H₂SO₄(aq)

**Condition**
- Temp.: 150℃
- Total P.: 13.6 atm
- O₂ P.: 9.5 atm R.T.
- 60~90 min.
- Re-ground to 10 μm

**Leaching Catalyst:** Chloride 12g/l

Source: CESL
Scorodite from CESL Process

Scorodite + BFAS

- As Residue
- Silica
- Scorodite Phase

Scorodite + BFAS

Clay 4%
Silicates 6%

Long Stability Test (TCLP)

As Limit: 5ppm
As in leachate
800 days

Source: CESL

Source: CESL
Partial Roasting at Ministro Hales (Visit on Oct.2017)  

<table>
<thead>
<tr>
<th>Conc.</th>
<th>Calcine</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>5%</td>
</tr>
</tbody>
</table>

2Cu₃AsS₄(s) → 3Cu₂S(s) + As₂S₃(g) + S₂(g)

680°C

Top of Roaster

Conc. to Roaster

Calcine Hopper

Roaster&Cyclone

ESP

Work Equipment

2As₂S₃(g) + 9O₂(q) → 2As₂O₃(q) + 6SO₂(q)

As₂O₃ + H₂O → 2HAsO₂

2HAsO₂ + 3Ca(OH)₂ → Ca₃(AsO₃)₂ + H₂O

Ca/As Filtration by LAROX

To Chuquicamata

Disposal to Monte Cristo
A part of Arsenic Removal from Circuit as:

- $\text{Ca}_3(\text{AsO}_4)_2$
- $\text{As}_2\text{S}_3$
- $\text{FeAsO}_4$
- $\text{Cu}_3\text{As}$
- $\text{FeOOH} \cdot \text{AsO}_4$

**Flowchart: Arsenic Removal at Copper Smelter**

1. **Blended Cu Conc.** → **FSF** → **Gas** → **Boiler** → **EP** → **Gas Cooler** → **Acid Plant**
2. **Slag** → **Anode Furnace** → **Gas** → **Boiler** → **EP**
3. **PSC** → **Gas** → **Boiler** → **EP**
4. **Anode** → **Leaching** → **Flue Dust**
5. **PSC** → **Floatation** → **Slag Conc.** → **Iron Conc.**
6. **Tank House** → **Slime** → **E Cu** → **Electrolyte** → **Decopperizing Tank** → **Ion Exchange Tower** → **Sb, Bi Residue**
7. **Liberated E Cu** → **Ni Sulfate** → **Evaporation**
Concept of Basel regulated objects
Those containing As, Cd and Pb at 0.1 wt% or more are applicable (Appended Table 3)

Table 1: 別表第一（対象外リスト） 長くず、細線くず等 53種類

Table 2: 別表第二（対象リスト） やつれ汚泥、煉焦塩泥、PCB等 59種類

Table 3: 別表第三

Source: 環境省

Current Status and Issues on Copper Slag

Transition of Export of Copper Slag from Japanese Copper Smelter

As Distribution
- Storage, others: 1,280 t/y (30%)
- Cu Slag: 3,500 t/y (70%)

Uses of Copper Slag
- Construction Works Material: 13%
- Sandblasting Material: 24%
- Aggregate for Concrete: 7%
- Cement material: 56%

Source: MERI作成

Uses of Copper Slag

Source: MERI/J

Copper Slag

Source: MERI/J
Arsenic Fixation from Flue Dust at Ecometales

Leaching of Flue Dust and Arsenic Fixation as Scorodite (Visit on October 2017)

**Flue Dust Leaching Step**
- Capacity
  - 5,000t-As/y
  - 50,000t-Flue Dust/y
  - 70,000m³-Waste
- Water/y

**Scorodite Formation Step**
- Conditions
  - Fe/As=1.2
  - 80℃ RT 24hr
  - pH
    - 0.7-1.1 at 1st
    - 1.3-1.5 at 2nd
- Scorodite 12%As, 10%Fe

Source: Ecometales Homepage
Immobilization & Storage of Arsenic

Fixation
Immobilization

Pyro

As$_2$O$_3$

High Purity Metal

Ca$_3$(AsO$_3$)$_2$

Encapsulation

Vitrification

Yukonite
(Scoro+Ca)

Scoro+HAP

HAP: Hydrated Aluminum Phosphate
(AlPO$_4$·1.5H$_2$O)

Hydro

Crystalline Scorodite

Amorphous Scorodite

Crystalline Ca$_3$(AsO$_4$)$_2$

Copper Arsenate

MERI/J
**Immobilization & Storage of Arsenic**

### Long Term Stability of Crystalline Scorodite (DOWA Process)

#### Solubility of Scorodite

<table>
<thead>
<tr>
<th>pH</th>
<th>As Solubility (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.05</td>
</tr>
<tr>
<td>6</td>
<td>0.1</td>
</tr>
<tr>
<td>7</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Source: Hydrometallurgy 1989, Ettel

#### Difference of Crystal Size

- **Amorphous Scorodite**
- **Crystalline Scorodite by DOWA**

Source: Copper 2016, Fujita

#### Quality of Scorodite

<table>
<thead>
<tr>
<th></th>
<th>As</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scorodite Theoretical Grade</td>
<td>32.4%</td>
<td>24.2%</td>
</tr>
<tr>
<td>DOWA</td>
<td>30.9%</td>
<td>24.1%</td>
</tr>
<tr>
<td>Ecometales</td>
<td>12%</td>
<td>10%</td>
</tr>
<tr>
<td>CESL</td>
<td>8%</td>
<td></td>
</tr>
</tbody>
</table>

Source: DOWA Cobre 2013, Copper 2016

#### NO.13 Leaching Test Result of MOE

<table>
<thead>
<tr>
<th>Month</th>
<th>As Leachate (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.3</td>
</tr>
<tr>
<td>2</td>
<td>0.25</td>
</tr>
<tr>
<td>3</td>
<td>0.2</td>
</tr>
<tr>
<td>4</td>
<td>0.15</td>
</tr>
<tr>
<td>5</td>
<td>0.1</td>
</tr>
<tr>
<td>6</td>
<td>0.05</td>
</tr>
<tr>
<td>7</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Source: MMJ March 2012, Mitsune

### Structure plan for Storage

- Filter Layer (Crushed Stone)
- Concrete Protective Layer
  - (Viscous Soil + Bentonite)
- External Liner Sheet
  - Reinforced Concrete Structure
  - Internal Concrete
- Backfill Stratum
  - Seepage Control Sheet
    - Concrete Floor
    - Crushed Stone for

Source: Fujita, TMS 2012
Examples of Current Status and Issues for Arsenic Storage

Tsumeb Smelter in Namibia & Ecometales in Chile

- **Tsumeb Smelter**
- **As Residue**
- **Landfill Area**
- **Ecometales**

Sources:
- Google Earth
- CEE bank watch Network
- Ecometales Homepage
What Should We Do?

1. Secure international competitiveness
2. Improvement of raw materials treatment capability
3. Improvement of environmental conservation

① Unified Management at Joint Arsenic Treatment Company in Japan
What Should We Do?

② International Approach to Preventing Arsenic Diffusion

International Inspection System for Arsenic

Europe
China
Japan
Chile/Peru

Crystalline Scorodite Production Plant

Toward Unified Management For Arsenic
Thank You for Your Attention

E-mail: yamazaki@merij.or.jp