Arsenic Fixation by the DMSP®
- DOWA Metals & Mining Scorodite Process -

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DOWA Metals & Mining Co., Ltd.

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DOWA Group Works

Nonferrous Metals
Gold, silver, copper, zinc, platinum, gallium, indium and other nonferrous metals

Electronic Materials
LEDs, silver powders, ferrite powders, metal powders and other materials

Metal Processing
Copper alloy strips, platings, metal ceramic substrates and other metal processing

Heat Treatment
Heat treatment of automotive parts, sales and maintenance of heat treatment furnaces

Sustainable Business on Circulating Resources

Managed landfill facility to minimize environmental risks

Waste treatment, soil remediation, metal recycling, consulting and other services

Recycling, resource utilization and detoxification

PCs, solar battery mobile phones, batteries, magnetic blank tape media, automobile parts, and other products

Provide high value-added materials

Integration into end products
1. Technical Outline of DMSP®

2. Operational results of DMSP® plant
   1. For Cu$_3$As & As$_2$S$_3$ compound ~ basic case

3. Test results of improved DMSP®
   1. Crystallization using iron oxide
   2. For smelting flue dust ~ high impurity case

4. Proposal for As removal and fixation
# Characteristics of Arsenic Compounds

<table>
<thead>
<tr>
<th>Substance Name</th>
<th>Chemical Formula</th>
<th>Evaluation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Amorphous Iron Arsenate</strong></td>
<td>FeAsO$_4$·XH$_2$O</td>
<td>○ 20mg/l (solubility experiment) Stable at high Fe/As ratio ○ × Much iron consumption</td>
</tr>
<tr>
<td><strong>Crystalline Iron Arsenate</strong></td>
<td>FeAsO$_4$·2H$_2$O</td>
<td>◎ 0.02mg/l (solubility experiment) The least soluble of all the arsenic compounds ○ ○</td>
</tr>
<tr>
<td><strong>Arsenic Sulfide</strong></td>
<td>As$_2$S$_3$</td>
<td>△ 0.8mg/l (document) Soluble in alkaline solution Changing into arsenic oxide in air ○ △</td>
</tr>
<tr>
<td><strong>Arsenicous Acid</strong></td>
<td>As$_2$O$_3$</td>
<td>× 20g/l at 25°C (aqueous solubility) × ○</td>
</tr>
<tr>
<td><strong>Calcium Arsenate</strong></td>
<td>Ca$_3$(AsO$_4$)$_2$</td>
<td>△ &gt;750mg/l at pH &gt;8 (document) Soluble in alkaline solution, substituted by dissolved CO$_2$ △ ○</td>
</tr>
<tr>
<td><strong>Copper Arsenide</strong></td>
<td>Cu$_3$As</td>
<td>× 1,500mg/l (solubility experiment) Readily soluble in acidic solution with sulfuric acid ○ ○</td>
</tr>
</tbody>
</table>

"Amount of Precipitation" is evaluated in consideration of arsenic concentration, moisture content, bulk density, and so on.

Crystalline iron arsenate (scorodite) is the best, especially in stability.
H$_3$AsO$_4$ + Fe$^{2+}$ + 1/4O$_2$ + 3/2H$_2$O = FeAsO$_4$·2H$_2$O + 2H$^+$ at Ambient Pressure, 95°C
Configuration of Scorodite by DMSP®

- Scorodite by DMSP®: Large particle size with smooth surface
- Scorodite by High TEMP AC process
- Amorphous Iron Arsenate

Improvement of stability
High sedimentation velocity
Excellent washing properties
Volume reduction

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As Solubility of Scorodite by DMSP®


Leaching test result by TCLP

<table>
<thead>
<tr>
<th>Criterion value</th>
<th>As (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test result</td>
<td>&lt;0.2</td>
</tr>
</tbody>
</table>

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Application to Copper Smelting

As Rich Concentrates

Cu Smelter

Anode

Cu Electrolysis

Cu Electrolyte

Electrolytic Cu

Cu Liberation

Slime

Liberation slime

Flue Dust

Acid-Plant Effluent

(As As Sulfide)

High As-Bearing Intermediates

Leaching

Oxidation

Crystallization

DMSP®

DMSP Wastewater

Wastewaters

SCORODITE

Dedicated Disposal Site (Landfill)

Treatment Plant

Disposal
1. Technical Outline of DMSP®

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DMSP® Commercial Plant

- Operation Term: 2008-2013
- Location: Kosaka Smelter
- Plant capability:
  - 30 [t-As/M]
  - 150 [t-raw materials/M]
- Operator: 5 [people/D]
- Shift: 3 8-hr shifts
Commercial DMSP® Process Flow

Acid-Plant Precipitates, Liberation slime (As$_2$S$_3$, Cu$_3$As) (Cu$_3$As)

O_{2} \quad \text{Leaching}

Oxidizing Reagent $O_{2}$, $H_2O_2$

As$^{3+}$ → As$^{5+}$

FeSO$_4$·7H$_2$O $O_{2}$ \quad \text{Oxidized Solution}

Oxidized Solution

Crystallization

SCORODITE

Dedicated Disposal Site

Wastewater

10% of As

>97% of Cu

Copper Smelter

<3% of As

Wastewater Treatment

87-89% of As

10% of As

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Stability of Scorodite in Operation

As Solubility ~ Japanese Standard

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Stability of Scorodite in Operation

As Solubility ~ Japanese Standard

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Stability of Scorodite in Operation

As Solubility ~ After Long Storage

 Criterion Value
Stability of Scorodite in Operation

As Solubility ~ Various Methods

<table>
<thead>
<tr>
<th>Method</th>
<th>Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>Notification No. 13 (Japan)</td>
<td>a 0.06 b 0.07 c 0.03</td>
</tr>
<tr>
<td>TCLP (U.S. EPA Method 1311)</td>
<td>a 0.053 b 0.038 c 0.034</td>
</tr>
<tr>
<td>Availability Test (NEN 7341)</td>
<td>a 0.070 b 0.088 c 0.031</td>
</tr>
<tr>
<td>EP (U.S. EPA Method 1310B)</td>
<td>a 0.045 b 0.040 c 0.028</td>
</tr>
<tr>
<td>MEP (1) (U.S. EPA Method 1320)</td>
<td>a 0.31 b 0.24 c 0.24</td>
</tr>
<tr>
<td>MEP (2)</td>
<td>a 0.26 b 0.32 c 0.37</td>
</tr>
<tr>
<td>MEP (3)</td>
<td>a 0.46 b 0.48 c 0.54</td>
</tr>
<tr>
<td>MEP (4)</td>
<td>a 0.31 b 0.31 c 0.36</td>
</tr>
<tr>
<td>MEP (5)</td>
<td>a 0.37 b 0.33 c 0.37</td>
</tr>
<tr>
<td>MEP (6)</td>
<td>a 0.23 b 0.29 c 0.32</td>
</tr>
<tr>
<td>MEP (7)</td>
<td>a 0.23 b 0.29 c 0.31</td>
</tr>
<tr>
<td>MEP (8)</td>
<td>a 0.25 b 0.26 c 0.32</td>
</tr>
<tr>
<td>MEP (9)</td>
<td>a 0.28 b 0.51 c 0.33</td>
</tr>
</tbody>
</table>
Dedicated Disposal Site

Scorodite Landfill  2,300t

Effluent Monitor  OK!
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Pilot Plant for Flue Dust

- Contract Research from JOGMEC
- Operation Term: 2011-2012
- Location: Kosaka Smelter
- Batch operation
  - 140kg-dust/B
  - 34kg-scorodite/B
DMSP® Flow for Flue Dust

1. **First Leaching**
   - pH 2-3, 30°C
   - Sulfuric acid
   - Ca(OH)₂
   - Flue dust
   - Oxygen
   - Cu solution
   - Cu recovery

2. **Second Leaching**
   - pH 0.2, 70°C
   - Residue
   - Oxygen
   - Cu solution
   - Cu recovery

3. **Purification**
   - pH 1, 40°C
   - As solution
   - Oxygen
   - Second Residue
   - Smelting
   - 30-40% of As
   - <3% of As

4. **Crystallization**
   - 60-70% of As
   - SCORODITE

**Waste water**
# Configuration of Scorodite from Flue Dust

<table>
<thead>
<tr>
<th>No.</th>
<th>Moisture (%)</th>
<th>Median (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial</td>
<td>11</td>
<td>22.5</td>
</tr>
<tr>
<td>F1</td>
<td>20.5</td>
<td>3.7</td>
</tr>
<tr>
<td>F2</td>
<td>12.2</td>
<td>8.8</td>
</tr>
</tbody>
</table>

Commercial Sample  
Pilot No.F1 from dust  
Pilot No.F2 from dust
### Solubility of Scorodite from Flue Dust

<table>
<thead>
<tr>
<th>Japanese Regulation</th>
<th>Pour size (µm)</th>
<th>As (mg/L)</th>
<th>Pb (mg/L)</th>
<th>Cd (mg/L)</th>
<th>Se (mg/L)</th>
<th>Cr (mg/L)</th>
<th>Hg (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Criterion Value</td>
<td>1.0</td>
<td>&lt;0.3</td>
<td>&lt;0.3</td>
<td>&lt;0.3</td>
<td>&lt;0.3</td>
<td>&lt;1.5</td>
<td>&lt;5</td>
</tr>
<tr>
<td>F1</td>
<td>1.0</td>
<td>63</td>
<td>0.09</td>
<td>0.10</td>
<td>&lt;0.02</td>
<td>&lt;0.01</td>
<td>&lt;0.05</td>
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<tr>
<td>F2</td>
<td>1.0</td>
<td>0.29</td>
<td>&lt;0.01</td>
<td>0.01</td>
<td>&lt;0.02</td>
<td>&lt;0.01</td>
<td>&lt;0.05</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>TCLP</th>
<th>Pour size (µm)</th>
<th>As (mg/L)</th>
<th>Pb (mg/L)</th>
<th>Cd (mg/L)</th>
<th>Se (mg/L)</th>
<th>Cr (mg/L)</th>
<th>Hg (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Criterion Value</td>
<td>0.6-0.8</td>
<td>&lt;5.0</td>
<td>&lt;5.0</td>
<td>&lt;1.0</td>
<td>&lt;1.0</td>
<td>&lt;5.0</td>
<td>&lt;200</td>
</tr>
<tr>
<td>F1</td>
<td>0.7</td>
<td>&lt;0.2</td>
<td>&lt;0.1</td>
<td>&lt;0.05</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;10</td>
</tr>
<tr>
<td>F2</td>
<td>0.7</td>
<td>0.3</td>
<td>&lt;0.1</td>
<td>&lt;0.05</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;10</td>
</tr>
</tbody>
</table>
CONTENT

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Essential Reaction Equation of Scorodite Formation Caused By Fe-Form

The Conventional DMSP® Method

- $\text{H}_3\text{AsO}_4 + \text{Fe}^{2+} + \dfrac{1}{4}\text{O}_2 + \dfrac{3}{2}\text{H}_2\text{O} = \text{FeAsO}_4 \cdot 2\text{H}_2\text{O} + 2\text{H}^+$

The Hematite Addition Method (the HA method)

- $\text{H}_3\text{AsO}_4 + \dfrac{1}{2}\text{Fe}_2\text{O}_3 + \dfrac{1}{2}\text{H}_2\text{O} = \text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$

The Magnetite Addition Method (the MA method)

- $\text{H}_3\text{AsO}_4 + \dfrac{1}{2}\text{Fe}_3\text{O}_4 + \text{H}_2\text{O} = \text{FeAsO}_4 \cdot 2\text{H}_2\text{O} + \dfrac{1}{2}\text{Fe}^{2+} + \text{OH}^-$
- $\text{H}_2\text{AsO}_4^- + \dfrac{1}{2}\text{Fe}_3\text{O}_4 + 2\text{H}_2\text{O} = \text{FeAsO}_4 \cdot 2\text{H}_2\text{O} + \dfrac{1}{2}\text{Fe}^{2+} + 2\text{OH}^-$
## Effect of Iron Source on Crystallization

<table>
<thead>
<tr>
<th>Time</th>
<th>Hematite</th>
<th>Hematite + Fe(Ⅱ)</th>
<th>Magnetite</th>
<th>Magnetite + Fe(Ⅱ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5hr</td>
<td>![Image]</td>
<td>![Image]</td>
<td>![Image]</td>
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</tr>
<tr>
<td>1.5hr</td>
<td>![Image]</td>
<td>![Image]</td>
<td>![Image]</td>
<td>![Image]</td>
</tr>
<tr>
<td>3.0hr</td>
<td>![Image]</td>
<td>![Image]</td>
<td>![Image]</td>
<td>![Image]</td>
</tr>
<tr>
<td>6.0hr</td>
<td>![Image]</td>
<td>![Image]</td>
<td>![Image]</td>
<td>![Image]</td>
</tr>
<tr>
<td>Condition</td>
<td>Fe/As of Source (mol/mol)</td>
<td>Initial Solution (g/L)</td>
<td>Reaction Time (hr)</td>
<td>Temp. (℃)</td>
</tr>
<tr>
<td>--------------</td>
<td>---------------------------</td>
<td>------------------------</td>
<td>--------------------</td>
<td>-----------</td>
</tr>
<tr>
<td></td>
<td>Fe(II)</td>
<td>Oxide</td>
<td>As (V)</td>
<td>Fe(II)</td>
</tr>
<tr>
<td>Conventional</td>
<td>1.5</td>
<td>0</td>
<td>45</td>
<td>50</td>
</tr>
<tr>
<td>Hematite</td>
<td>0.3</td>
<td>1.1</td>
<td>45</td>
<td>10</td>
</tr>
<tr>
<td>Magnetite</td>
<td>0.1</td>
<td>1.5 (1.05)</td>
<td>45</td>
<td>3.3</td>
</tr>
</tbody>
</table>
Effect on Crystallization by various Iron sources

◇ Conventional DMSP® Method
- Post reaction solution
  - As = 2 g/L
- Reaction time
  - $\geq 6$ hr

△ Hematite Addition Method

□ Magnetite Addition Method
- Post reaction solution
  - As < 0.1 g/L
- Reaction time
  - $\leq 2$ hr

Fig. As concentration in reaction solution of conventional DMSP & magnetite addition method
Characteristics of Scorodite by various Iron sources

<table>
<thead>
<tr>
<th>Test Scorodite Characteristics</th>
<th>Content (%)</th>
<th>Moisture (%)</th>
<th>D50 (µm)</th>
<th>Post Solution (g/L) As</th>
<th>Leachate As (mg/L) Japan</th>
<th>Leachate As (mg/L) TCLP</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe</td>
<td>As</td>
<td>D50</td>
<td>As</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Criterion Value</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Conventional</td>
<td>31</td>
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<td>22</td>
<td>1.92</td>
<td>23</td>
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<tr>
<td></td>
<td>0.3</td>
<td>5.0</td>
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<tr>
<td>Hematite</td>
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<tr>
<td></td>
<td>0.09</td>
<td>0.3</td>
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</tr>
<tr>
<td>Magnetite</td>
<td>31</td>
<td>24</td>
<td>16</td>
<td>3.9</td>
<td>0.018</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>0.07</td>
<td>&lt;0.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
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Proposal of As fixation

- Low As concentrated wastewater
- High As concentrated wastewater
- (Mixed) Solid compound:
  - Amorphous Iron Arsenate
  - Arsenic Sulfide
  - Arsenic Oxide
  - Calcium Arsenate
  - Copper Arsenide
  - Smelting Intermediates
  - Liberation Slime
  - Purification sludge

Neutralization with Fe$^{3+}$
  - Low cost

Amorphous Scordite
  - Fe(OH)$_3$ Precipitates
  - Co-precipitated As
  - Adsorbed As

DMSP®
  - Fast !

Crystalline Scordite
  - High concentrated As
  - Huge size
  - Smart surface
  - Low lattice defect

  - Low solubility
  - High stability
  - Low moisture
  - High packing density
Thank you very much for your kind attention.

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