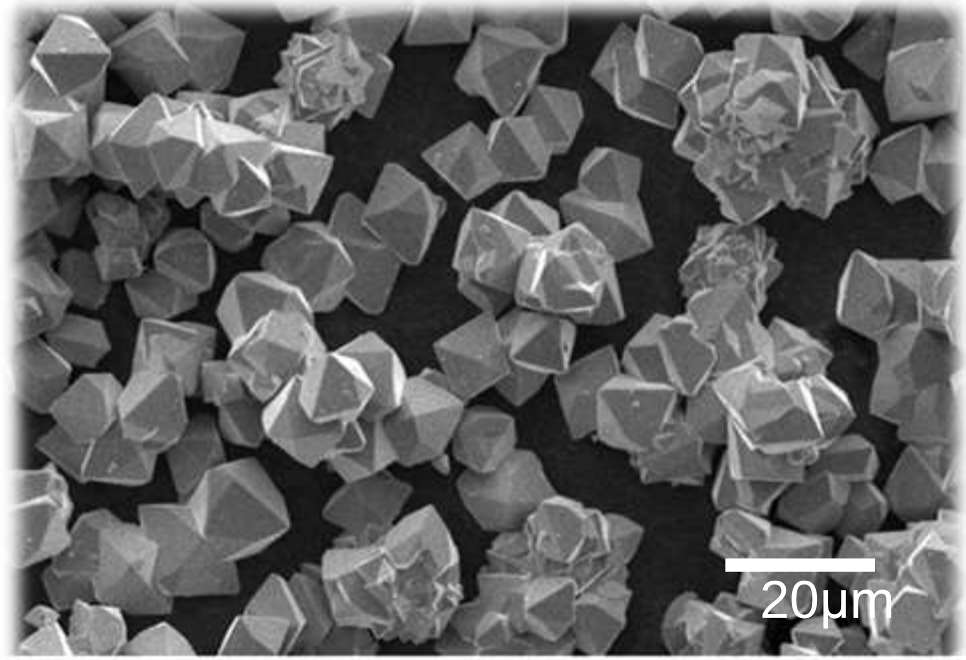
# Arsenic Fixation by the DMSP®

## - DOWA Metals & Mining Scorodite Process -

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# DOWA Group Works

## Nonferrous Metals

**Production of materials**

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

**Provide high value-added materials**

***Sustainable Business on Circulating Resources***

**Recycling, resource utilization and detoxification**

***Integration into end products***

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

## Environmental Management & Recycling

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

Managed landfill facility to minimize environmental risks

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1. Technical Outline of DMSP®
2. Operational results of DMSP® plant
    1. For $Cu_3As$ & $As_2S_3$ 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

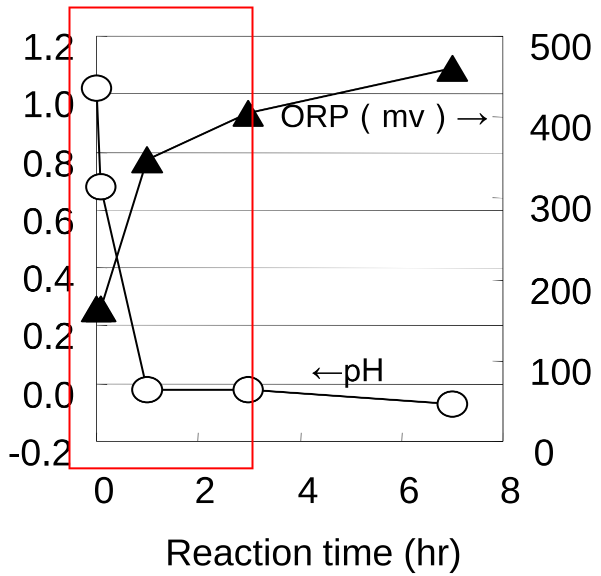
| Arsenic Compound | | Evaluation | | | | |
|---|---|---|---|---|---|---|
| Substance Name | Chemical Formula | Solubility and Stability (Related with pH) | | Removal Rate | Amount of Precipitation | |
| Amorphous Iron Arsenate | $FeAsO_4 \cdot XH_2O$ | ○ | 20mg/l (solubility experiment)<br>Stable at high Fe/As ratio | ○ | × | Much iron consumption |
| Crystalline Iron Arsenate (Scorodite) | $FeAsO_4 \cdot 2H_2O$ | ◎ | 0.02mg/l (solubility experiment)<br>The least soluble of all the arsenic compounds | ○ | ○ | |
| Arsenic Sulfide | $As_2S_3$ | △ | 0.8mg/l (document)<br>Soluble in alkaline solution<br>Changing into arsenic oxide in air | ○ | △ | |
| Arsenious Acid | $As_2O_3$ | × | 20g/l at 25℃ (aqueous solubility) | × | ○ | |
| Calcium Arsenate | $Ca_3(AsO_4)_2$ | △ | >750mg/l at pH >8 (document)<br>Soluble in alkaline solution, substituted by dissolved CO2 | △ | ○ | |
| Copper Arsenide | $Cu_3As$ | × | 1,500mg/l (solubility experiment)<br>Readily soluble in acidic solution with sulfuric acid | ○ | ○ | |

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

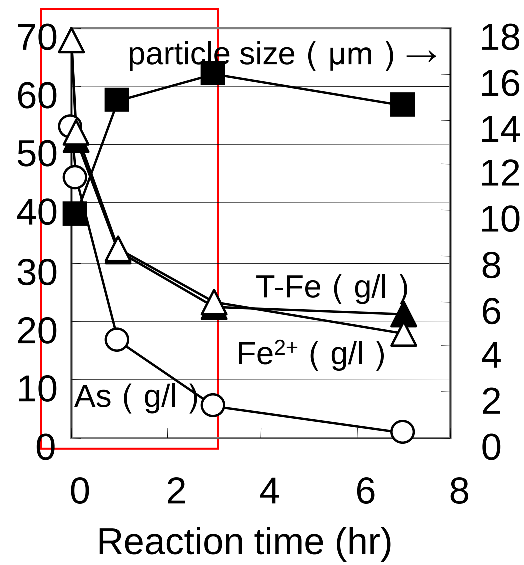
**Crystalline iron arsenate (scorodite) is the best, especially in stability.**

# Scorodite Formation by the Conventional DMSP®

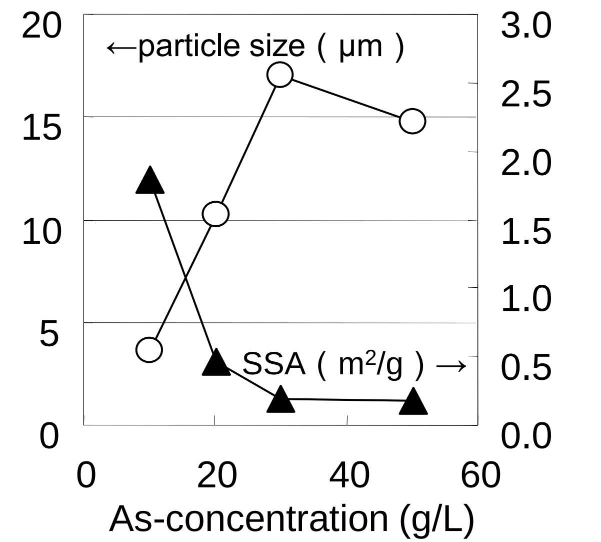
pH, ORP trend




Fe, As, particle size trend




Effect of initial As concentration

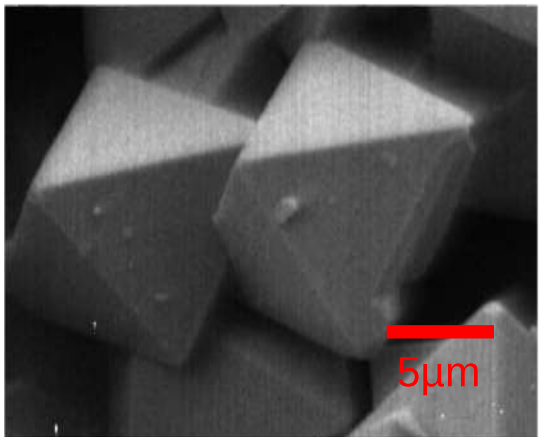



- $H_3AsO_4 + Fe^{2+} + 1/4O_2 + 3/2H_2O = FeAsO_4 \cdot 2H_2O + 2H^+$

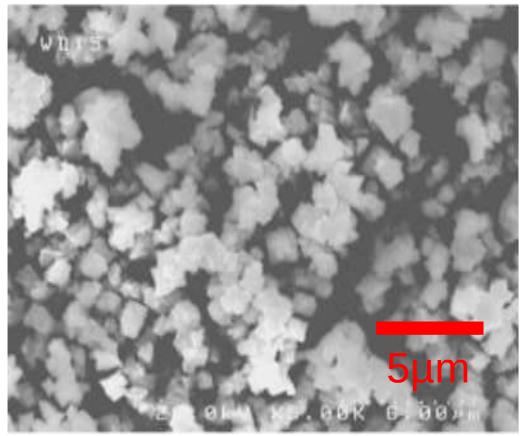
**at Ambient Pressure , 95℃**

# Configuration of Scorodite by DMSP®

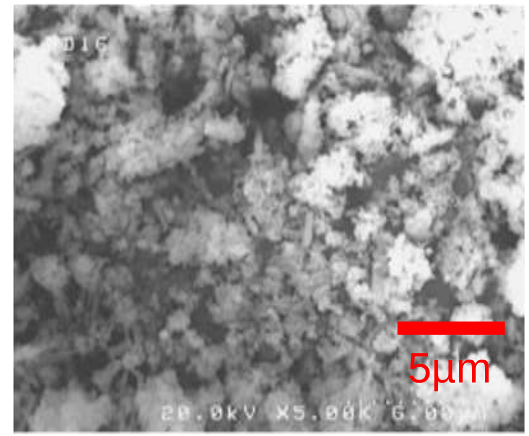
Scorodite by DMSP®




Scorodite by High TEMP AC process




Amorphous Iron Arsenate




**Large particle size with smooth surface**

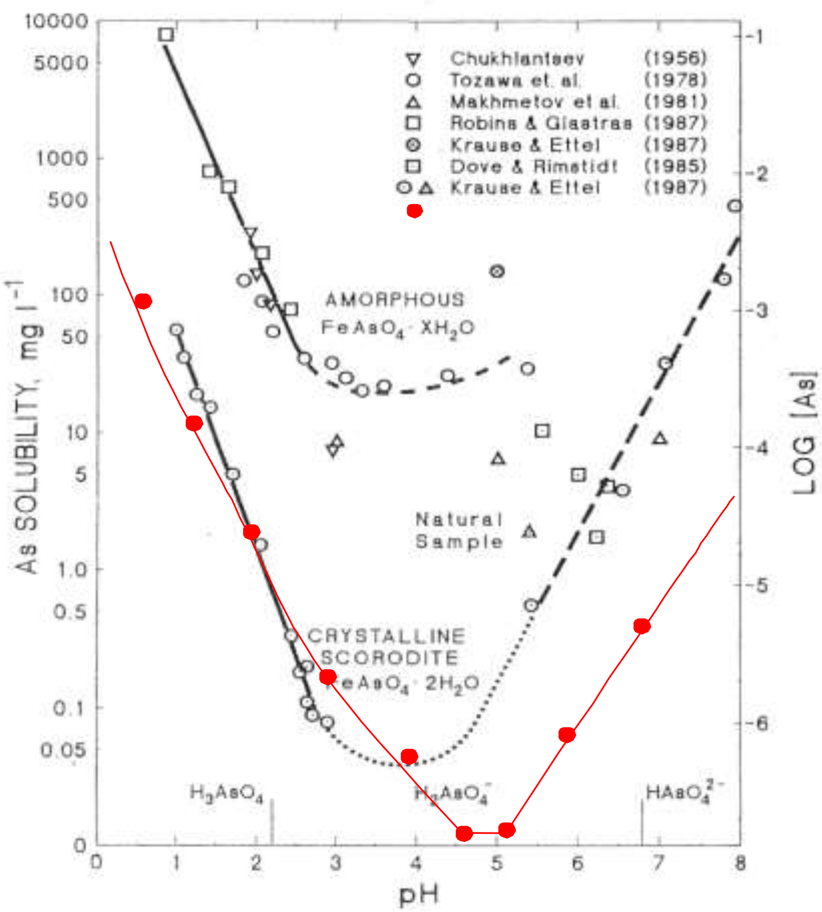
**Improvement of stability**

**High sedimentation velocity**

**Excellent washing properties**

**Volume reduction**

# As Solubility of Scorodite by DMSP®

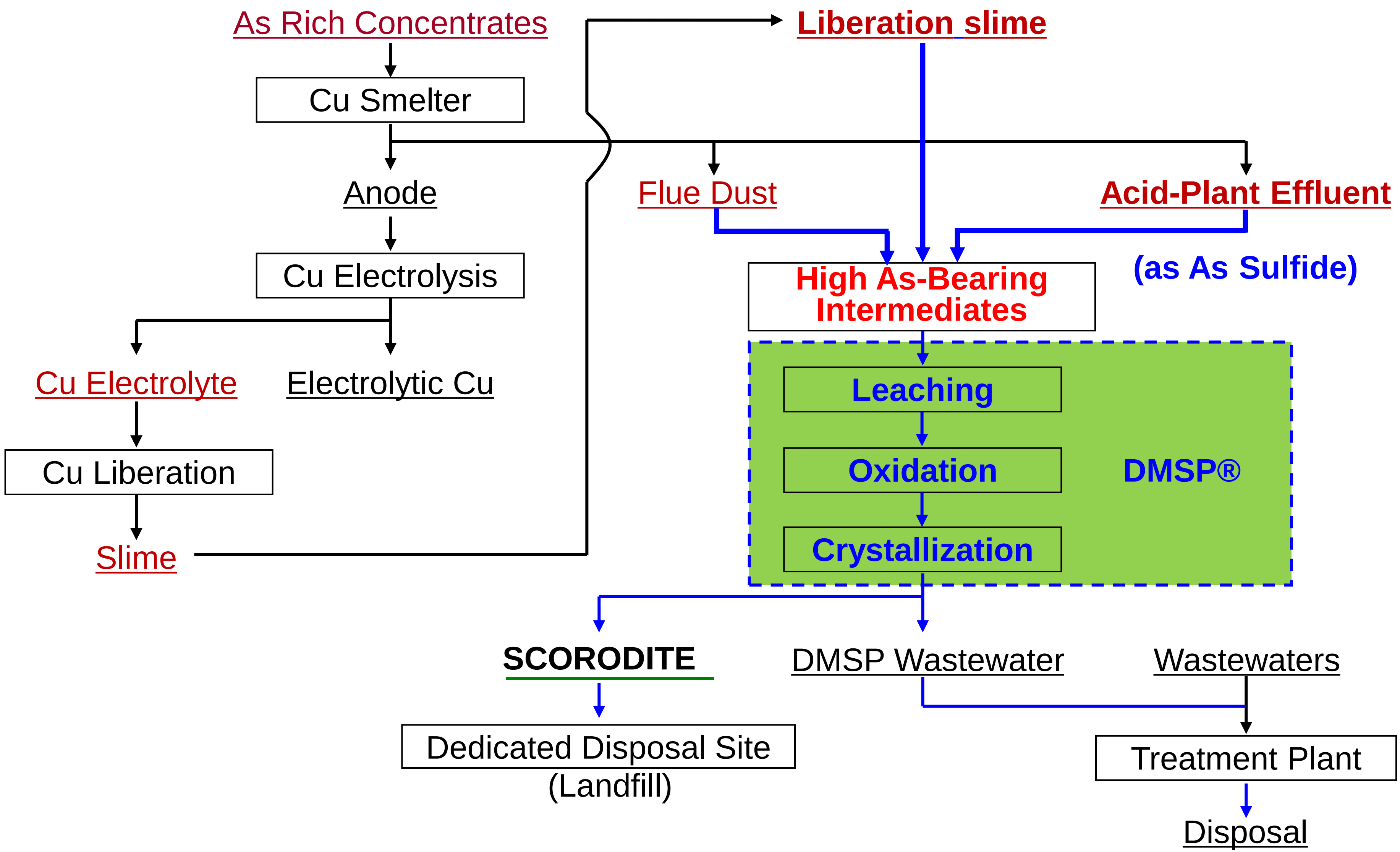



from Krause, E., Ettel, V.A., 1989.
Solubilities and stabilities of ferric arsenate compounds. Hydrometallurgy, 22, 311-337

Leaching test result by TCLP

| | As (mg/L) |
|---|---|
| Criterion value | <5.0 |
| Test result | <0.2 |

# Application to Copper Smelting



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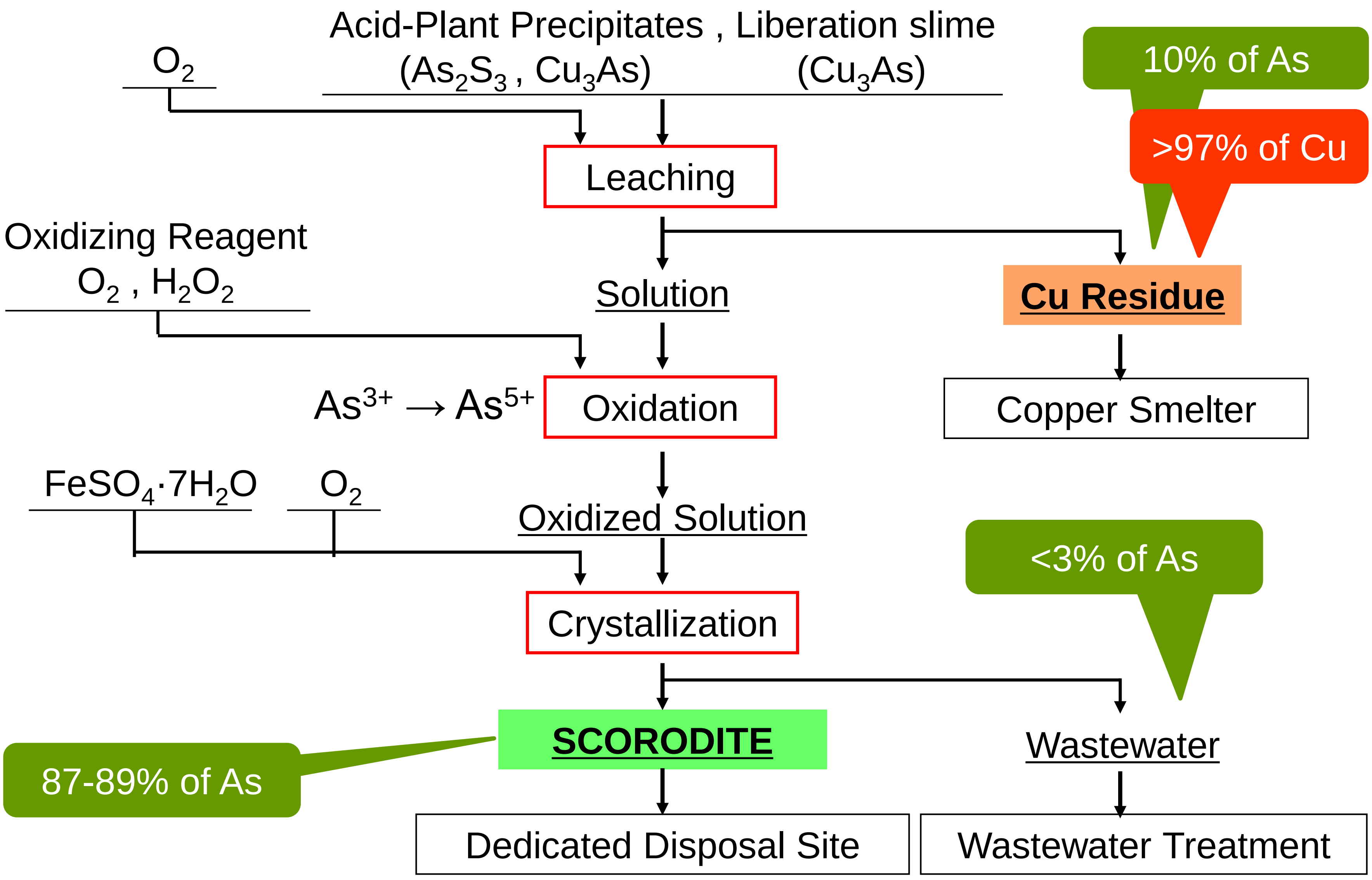
# DMSP® Commercial Plant

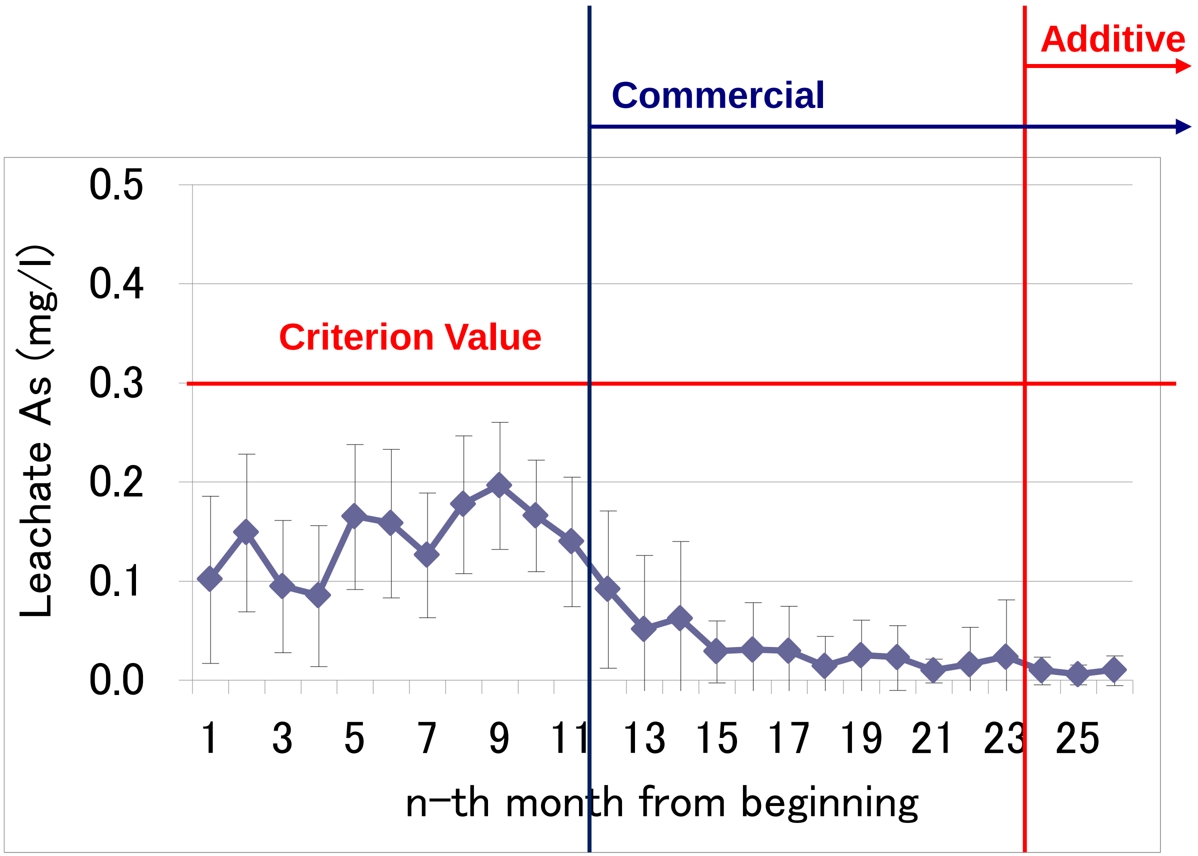
- Operation Term : 2008-2013
- Location : Kosaka Smelter
- Plant capability : 30 [t-As/M]
  150 [t-raw materials/M]
- Operator 5 [people/D]
- Shift 3 8-hr shifts

# Commercial DMSP® Process Flow



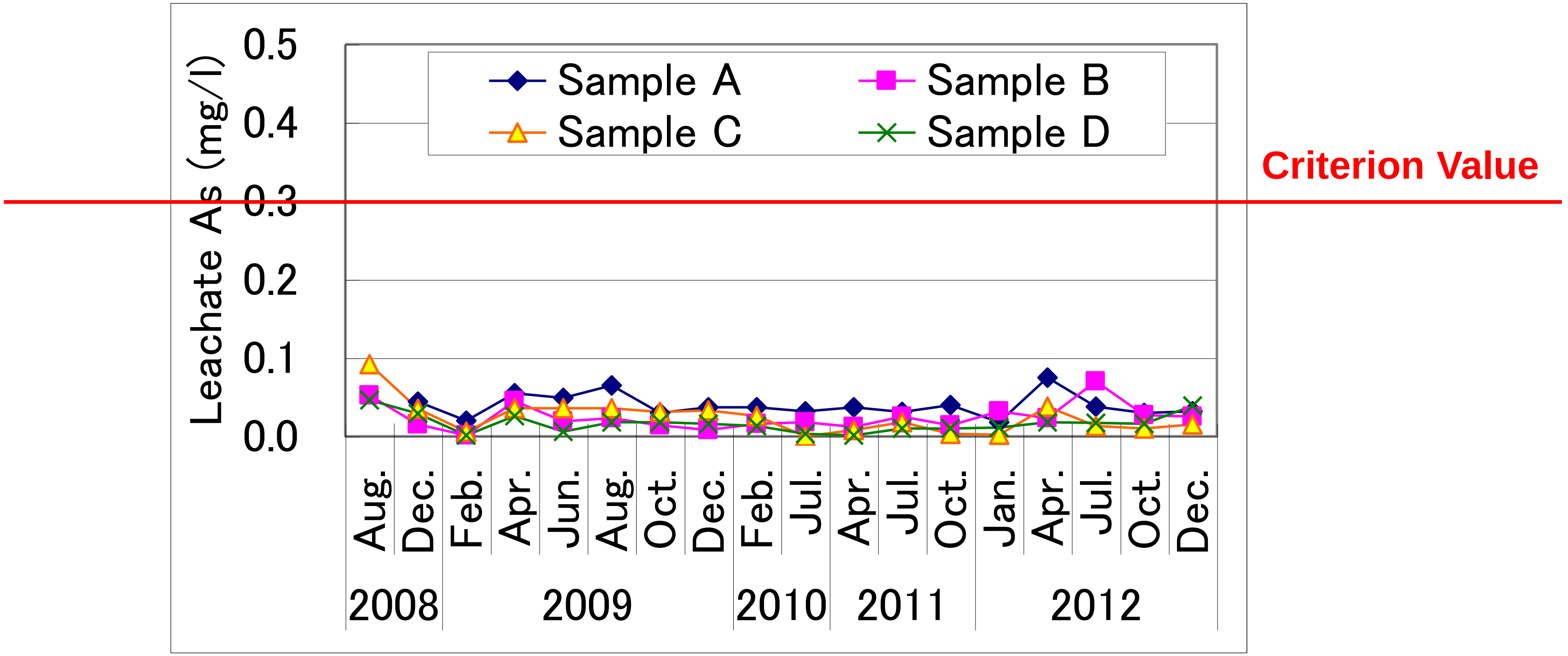
# Stability of Scorodite in Operation

## As Solubility ~ Japanese Standard



# Stability of Scorodite in Operation

## As Solubility ~ After Long Storage



# Stability of Scorodite in Operation

## As Solubility ~ Various Methods

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

# Dedicated Disposal Site

**Scorodite Landfill 2,300t**

**Effluent Monitor** **OK!**

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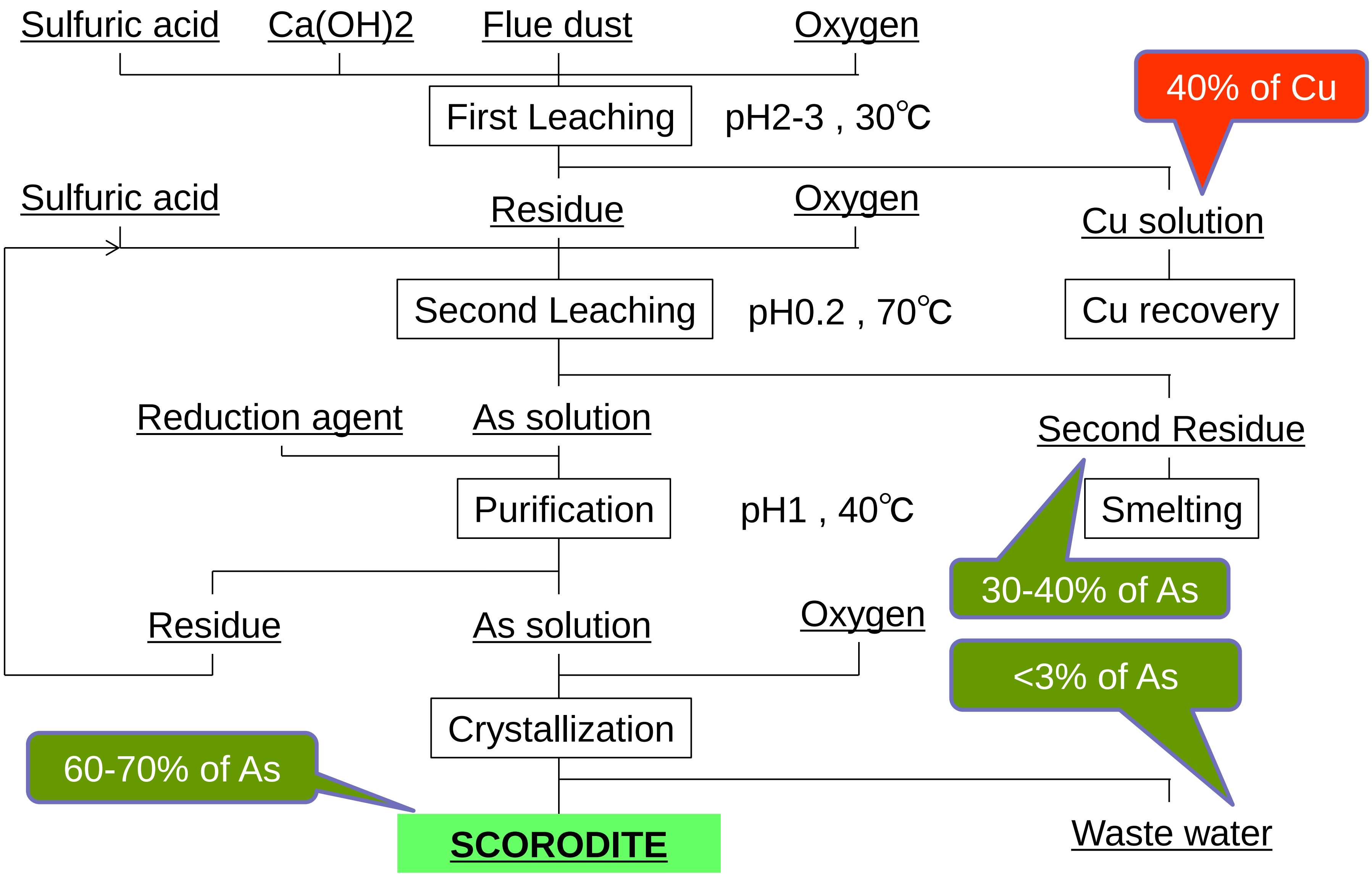
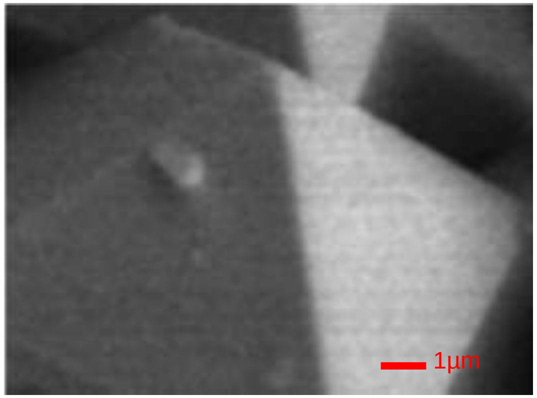
# Pilot Plant for Flue Dust

- Contract Research from JOGMEC
- Operation Term : 2011-2012
- Location ： Kosaka Smelter
- Batch operation
  - 140kg-dust/B
  - 34kg-scorodite/B

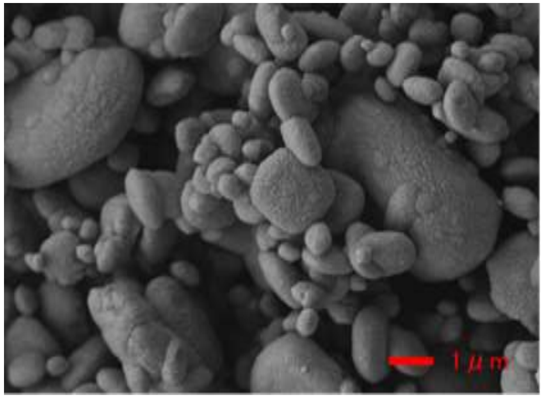
# DMSP® Flow for Flue Dust



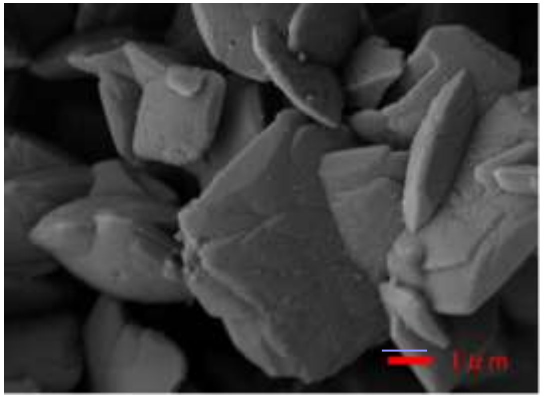
# Configuration of Scorodite from Flue Dust




Commercial Sample



Pilot No.F1 from dust



Pilot No.F2 from dust

| No. | Moisture (%) | Median (μm) |
|---|---|---|
| Commercial | 11 | 22.5 |
| F1 | 20.5 | 3.7 |
| F2 | 12.2 | 8.8 |

# Solubility of Scorodite from Flue Dust

| Japanese Regulation | Pour size (μm) | As (mg/L) | Pb (mg/L) | Cd (mg/L) | Se (mg/L) | Cr (mg/L) | Hg (μg/L) |
|---|---|---|---|---|---|---|---|
| Criterion Value | 1.0 | <0.3 | <0.3 | <0.3 | <0.3 | <1.5 | <5 |
| F1 | 1.0 | 63 | 0.09 | 0.10 | <0.02 | <0.01 | <0.05 |
| F2 | 1.0 | 0.29 | <0.01 | 0.01 | <0.02 | <0.01 | <0.05 |

| TCLP | Pour size (μm) | As (mg/L) | Pb (mg/L) | Cd (mg/L) | Se (mg/L) | Cr (mg/L) | Hg (μg/L) |
|---|---|---|---|---|---|---|---|
| Criterion Value | 0.6-0.8 | <5.0 | <5.0 | <1.0 | <1.0 | <5.0 | <200 |
| F1 | 0.7 | <0.2 | <0.1 | <0.05 | <0.1 | <0.1 | <10 |
| F2 | 0.7 | 0.3 | <0.1 | <0.05 | <0.1 | <0.1 | <10 |

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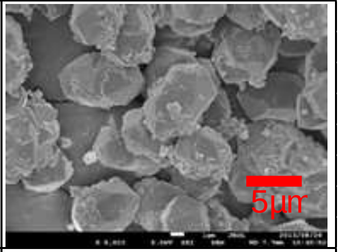
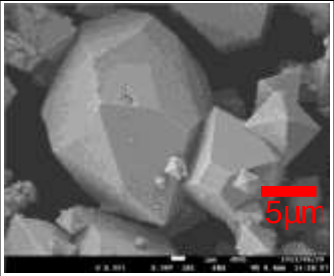
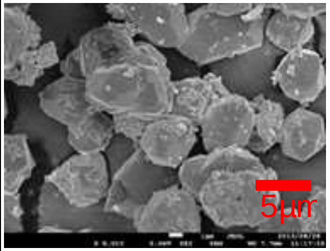
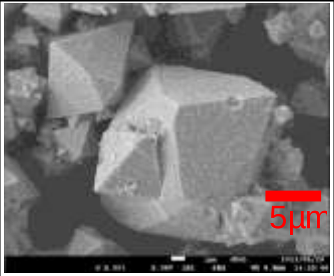
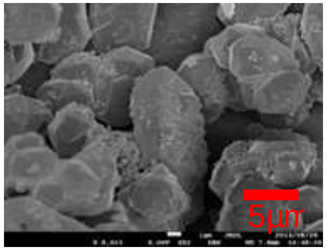
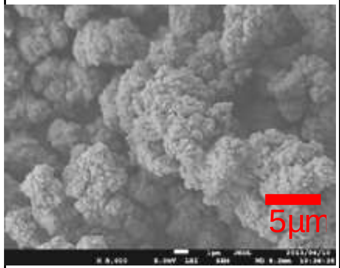
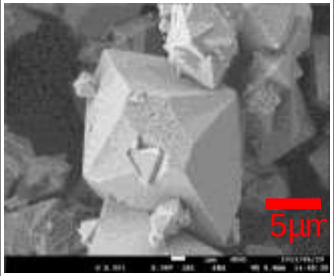
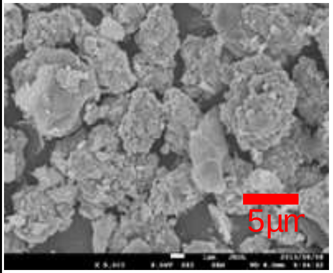
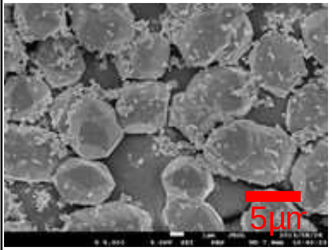
# Essential Reaction Equation of Scorodite Formation Caused By Fe-Form

- The Conventional DMSP® Method
  - $H_3AsO_4 + \mathbf{Fe^{2+}} + 1/4O_2 + 3/2H_2O = FeAsO_4 \cdot 2H_2O + 2H^+$
- The Hematite Addition Method (the HA method)
  - $H_3AsO_4 + 1/2\mathbf{Fe_2O_3} + 1/2H_2O = FeAsO_4 \cdot 2H_2O$
- The Magnetite Addition Method (the MA method)
  - $H_3AsO_4 + 1/2\mathbf{Fe_3O_4} + H_2O = FeAsO_4 \cdot 2H_2O + 1/2Fe^{2+} + OH^-$
  - $H_2AsO_4^- + 1/2\mathbf{Fe_3O_4} + 2H_2O = FeAsO_4 \cdot 2H_2O + 1/2Fe^{2+} + 2OH^-$

# Effect of Iron Source on Crystallization

| | Hematite | Hematite + Fe(Ⅱ) | Magnetite | Magnetite + Fe(Ⅱ) |
|---|---|---|---|---|
| 0.5hr | | | |  |
| 1.5hr | |  | |  |
| 3.0hr | |  | |  |
| 6.0hr |  |  |  |  |

# Lab-Test Condition

| Condition | Fe/As of Source (mol/mol) | | Initial Solution (g/L) | | Reaction Time (hr) | Temp. (℃) |
|---|---|---|---|---|---|---|
| | Fe(II) | Oxide | As (V) | Fe(II) | | |
| Conventional | 1.5 | 0 | 45 | 50 | 6.0 | 95 |
| Hematite | 0.3 | 1.1 | 45 | 10 | 6.0 | 95 |
| Magnetite (Hybrid) | 0.1 | 1.5 (1.05) | 45 | 3.3 | 6.0 | 95 |

# Effect on Crystallization by various Iron sources

## ◇ Conventional DMSP® Method

- Post reaction solution
  - As = 2 g/L
- Reaction time
  - ≧ 6 hr

## △ Hematite Addition Method

## □ Magnetite Addition Method

- Post reaction solution
  - As < 0.1 g/L
- Reaction time
  - ≦ 2 hr

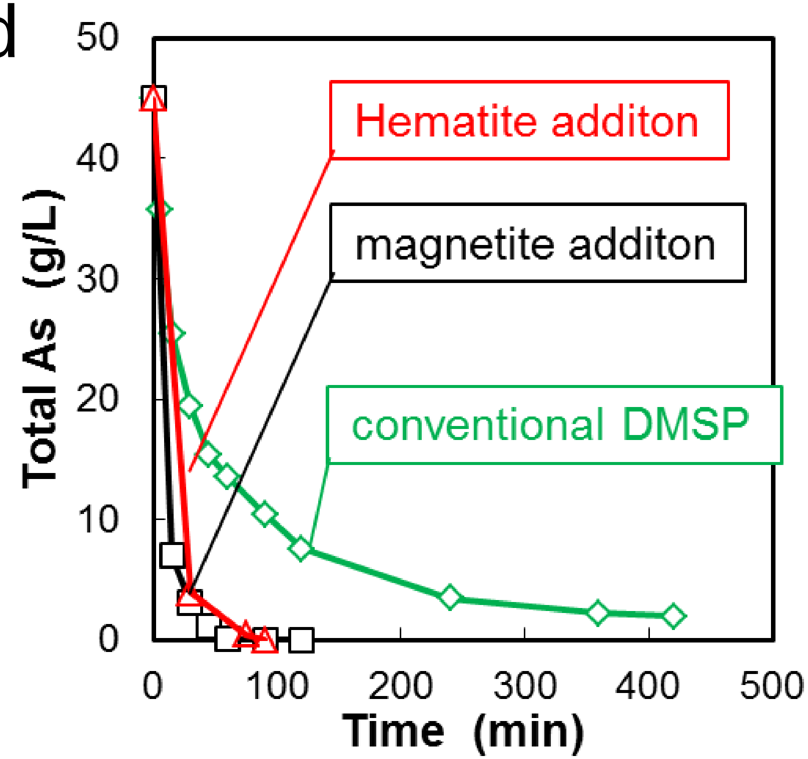
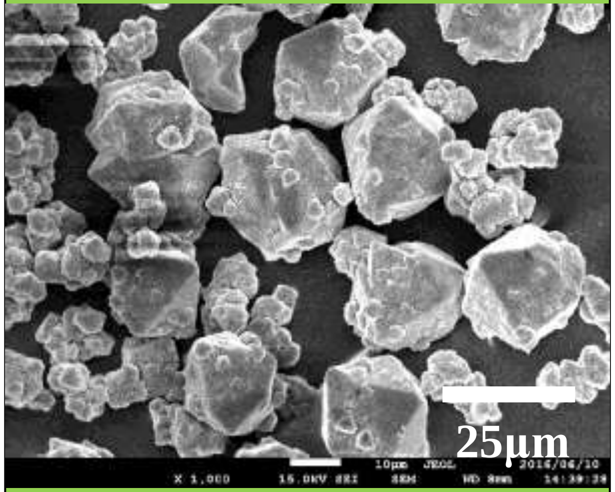
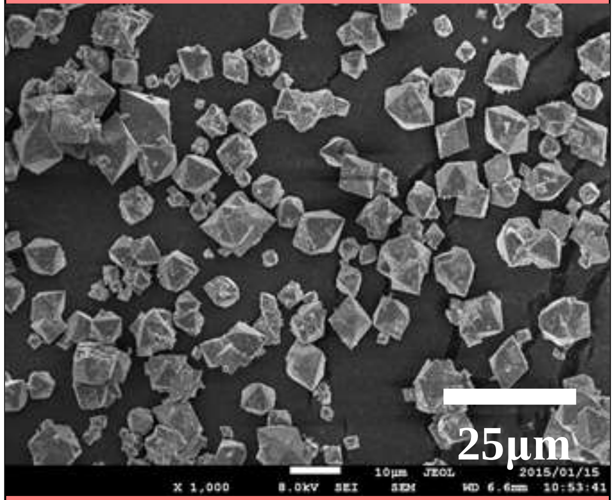



Fig. As concentration in reaction solution of conventional DMSP & magnetite addition method

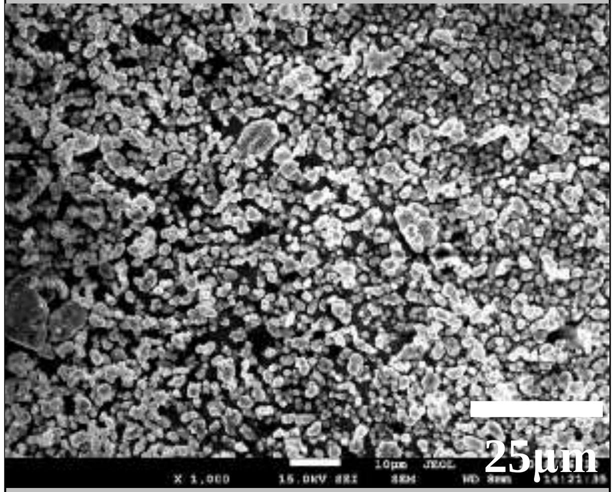
# Characteristics of Scorodite by various Iron sources




Conventional DMSP®(G-1)
D(50)=21.4µm




HA method under air (BD)
D(50)=9.2µm




MA method under air (M-5)
D(50)=3.9µm

| Test Scorodite Characteristics | Content (%) Fe | Content (%) As | Moisture (%) | D50 (µm) | Post Solution (g/L) As | Post Solution (g/L) Fe | Leachate As (mg/L) Japan | Leachate As (mg/L) TCLP |
|---|---|---|---|---|---|---|---|---|
| Criterion Value | | | | | | | 0.3 | 5.0 |
| Conventional | 31 | 24 | 11 | 22 | 1.92 | 23 | 0.03 | <0.2 |
| Hematite | 31 | 24 | 13 | 9.2 | 0.003 | 6.5 | 0.09 | 0.3 |
| Magnetite | 31 | 24 | 16 | 3.9 | 0.018 | 16 | 0.07 | <0.2 |

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# Proposal of As fixation

Low As concentrated wastewater

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

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

High As concentrated wastewater

(Mixed) Solid compound
- Amorphous Iron Arsenate
- Arsenic Sulfide
- Arsenic Oxide
- Calcium Arsenate
- Copper Arsenide

Smelting Intermediates
- Liberation Slime
- Purification sludge

**DMSP®**

Fast !

Crystalline Scorodite

- 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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