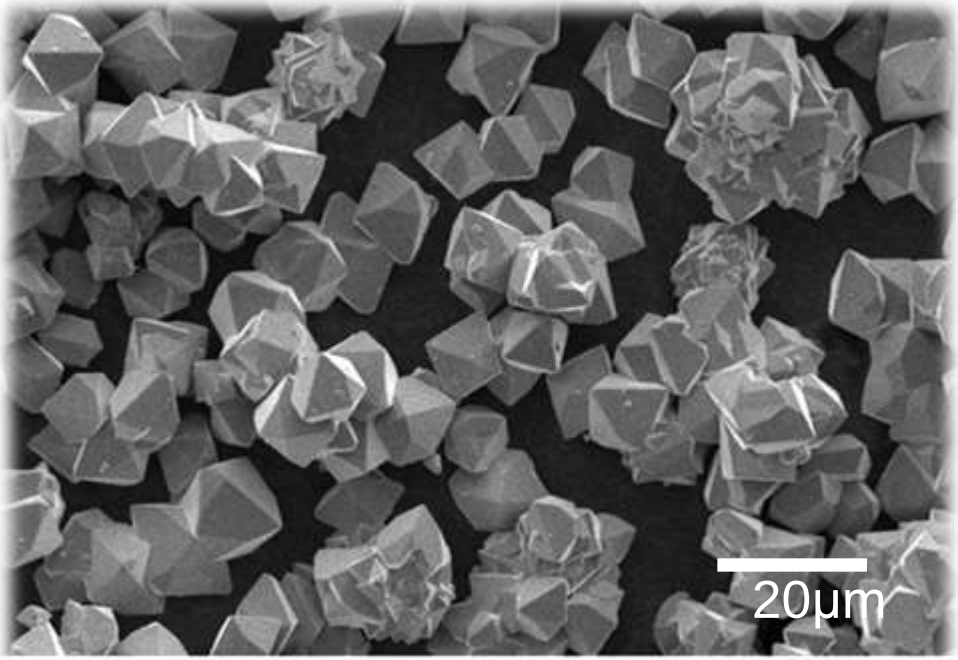
Arsenic Fixation by the DMSP®

- DOWA Metals & Mining Scorodite Process -



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DOWA Metals & Mining Co., Ltd.

Oct. 17, 2018 TOKYO

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

Environmental Management & Recycling

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

Managed landfill facility to minimize environmental risks

Integration into end products

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

CONTENT

Characteristics of Arsenic Compounds

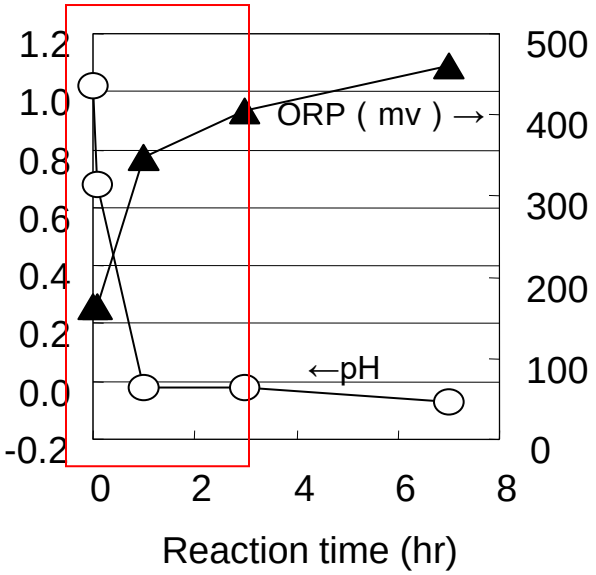
Arsenic Compound		Evaluation		
Substance Name	Chemical Formula	Solubility and Stability (Related with pH)	Removal Rate	Amount of Precipitation
Amorphous Iron Arsenate	$FeAsO_4 \cdot XH_2O$	○ 20mg/l (solubility experiment) Stable at high Fe/As ratio	○	× Much iron consumption
Crystalline Iron Arsenate (Scorodite)	$FeAsO_4 \cdot 2H_2O$	◎ 0.02mg/l (solubility experiment) The least soluble of all the arsenic compounds	○	○
Arsenic Sulfide	As_2S_3	△ 0.8mg/l (document) Soluble in alkaline solution 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) Soluble in alkaline solution, substituted by dissolved CO2	△	○
Copper Arsenide	Cu_3As	× 1,500mg/l (solubility experiment) 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.

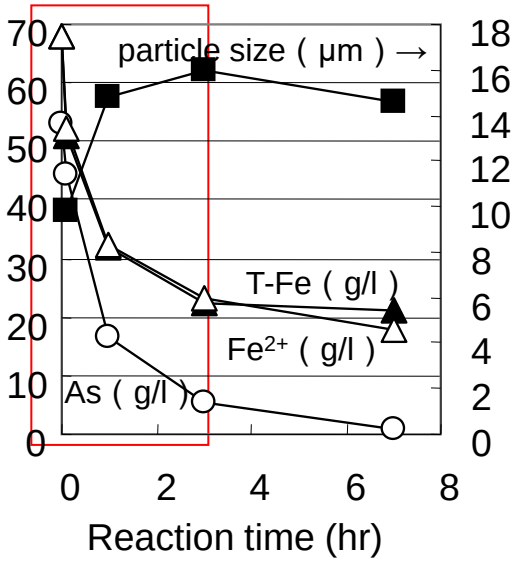
Crystalline iron arsenate (scorodite) is the best, especially in stability.

Scorodite Formation by the Conventional DMSP®

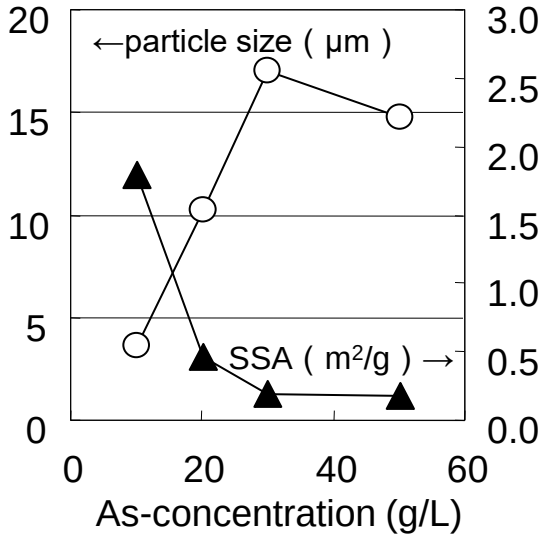
pH, ORP trend



Fe, As, particle size trend



Effect of initial As concentration

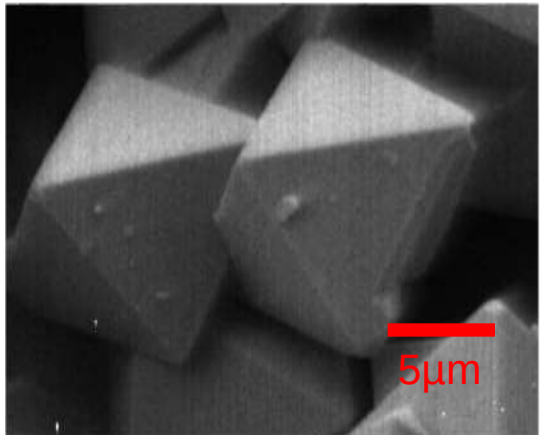


- $H_3AsO_4 + Fe^{2+} + 1/4O_2 + 3/2H_2O = FeAsO_4 \cdot 2H_2O + 2H^+$

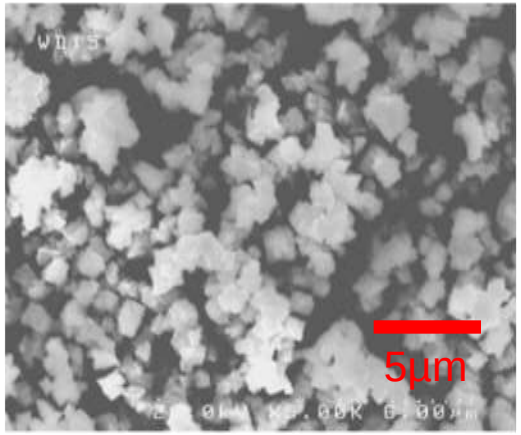
at Ambient Pressure , 95℃

Configuration of Scorodite by DMSP®

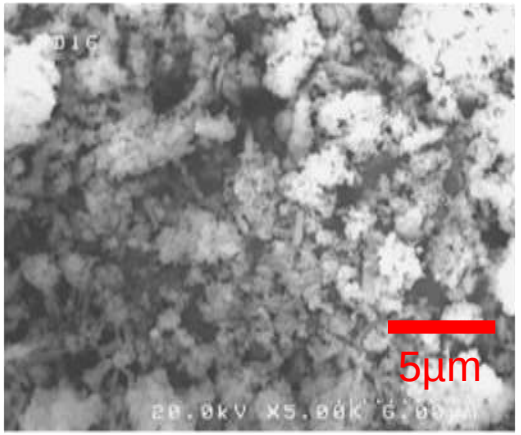
Scorodite by DMSP®



Scorodite by High TEMP AC process



Amorphous Iron Arsenate

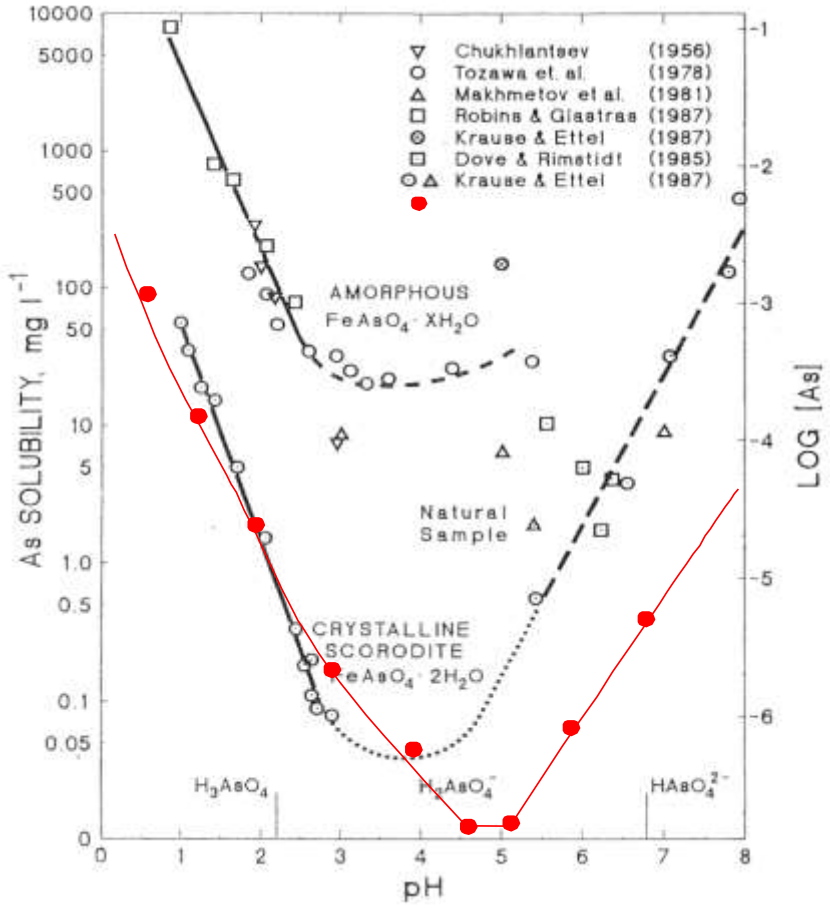


Large particle size with smooth surface

→

- **Improvement of stability**
- **High sedimentation velocity**
- **Excellent washing properties**
- **Volume reduction**

As Solubility of Scorodite by DMSP®

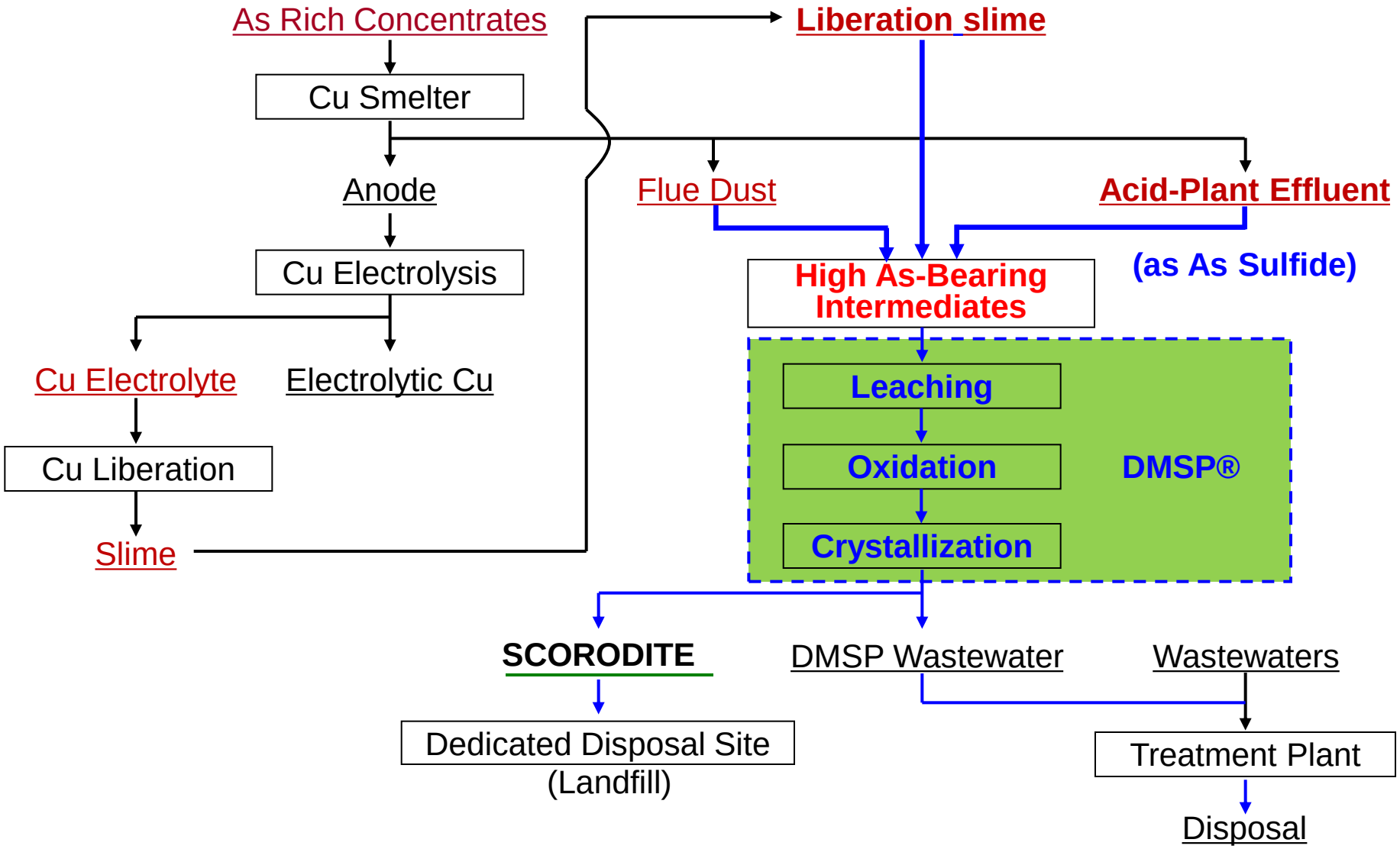


from Krause, E., Ettel, V.A., 1989. Solubilities and stabilities of ferric arsenate compounds. Hydrometallurgy, 22, 311-337

Leaching test result by TCLP

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

Application to Copper Smelting

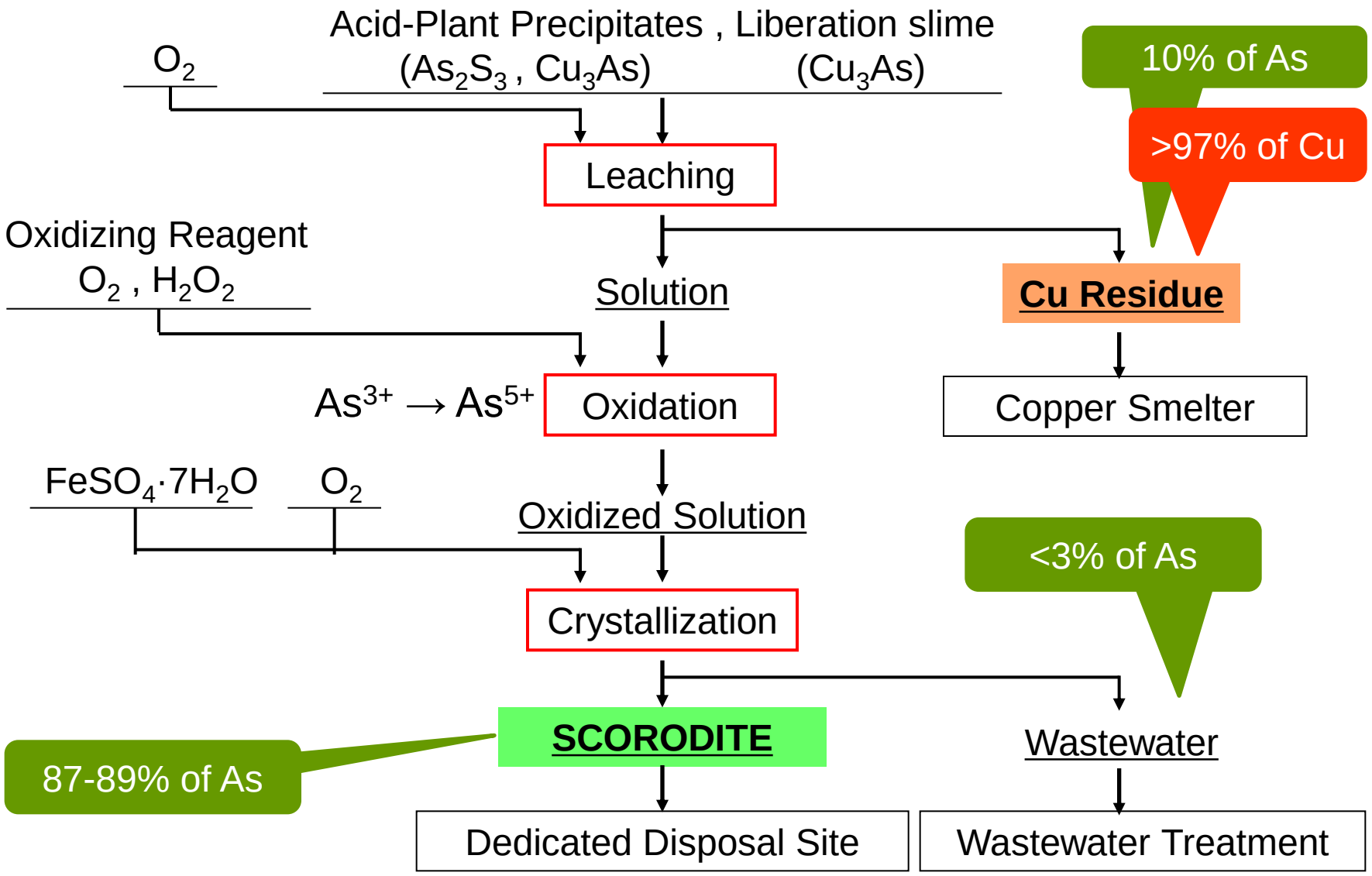


CONTENT

DMSP® Commercial Plant

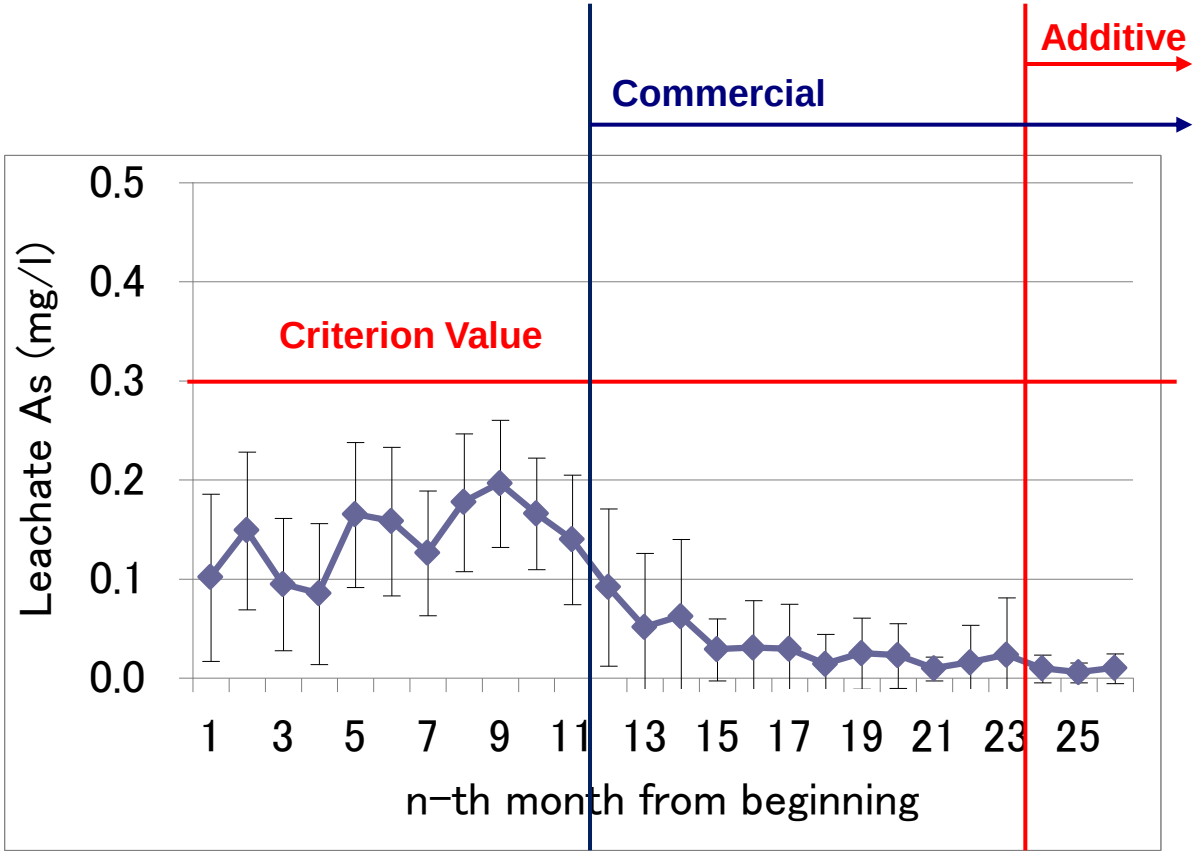
- Operation Term : 2008-2013
- Location : Kosaka Smelter
- Plant capability : 30 [t-As/M]
  150 [t-raw materials/M]
- Operator 5 [people/D]
- Shift 3 8-hr shifts

Commercial DMSP® Process Flow



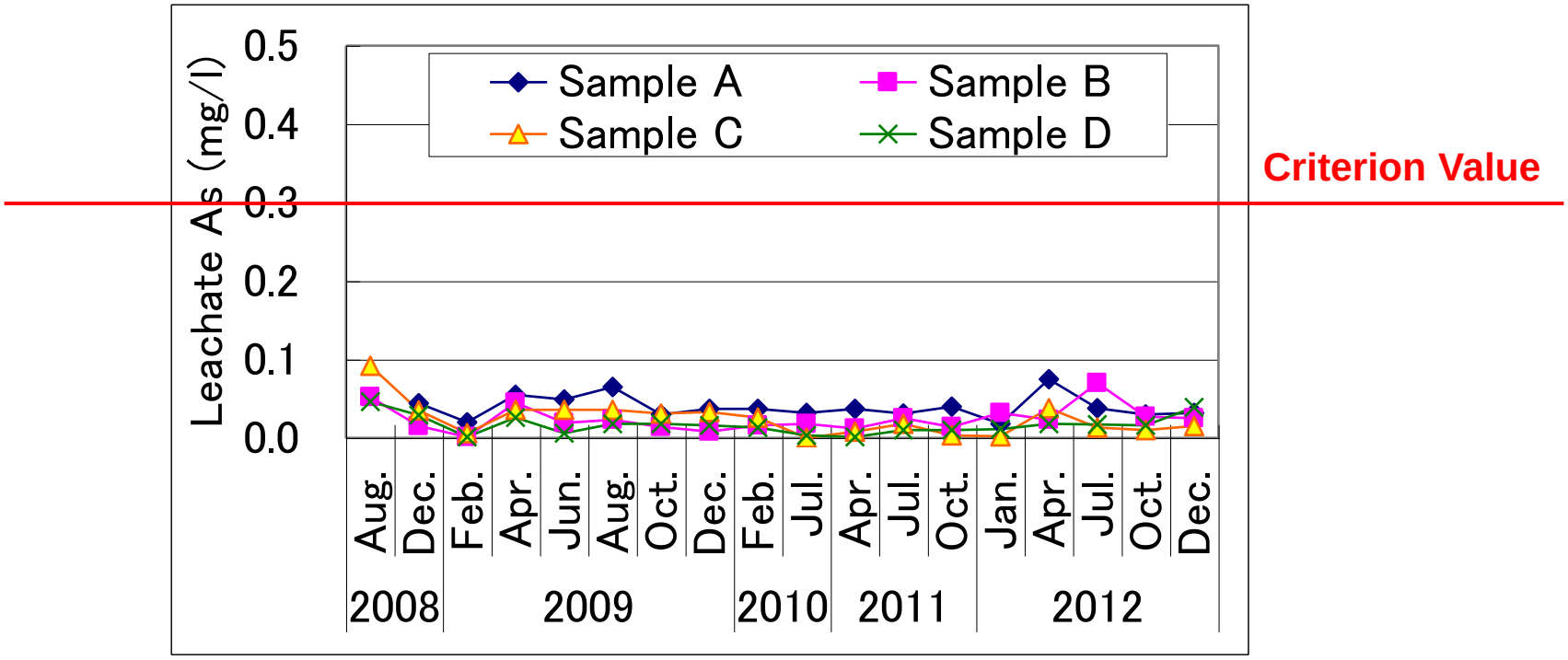
Stability of Scorodite in Operation

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

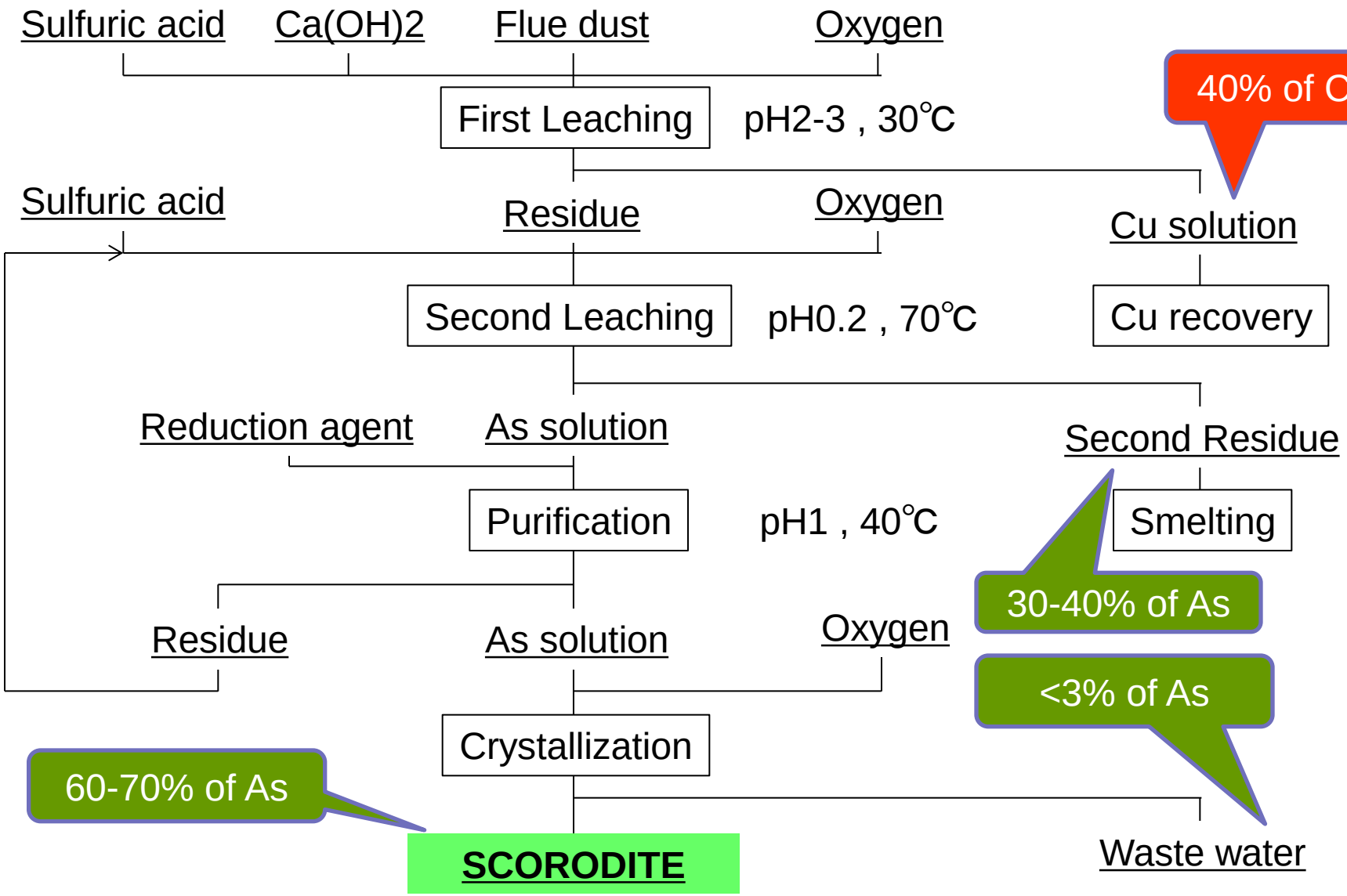
Effluent Monitor **OK!**

CONTENT

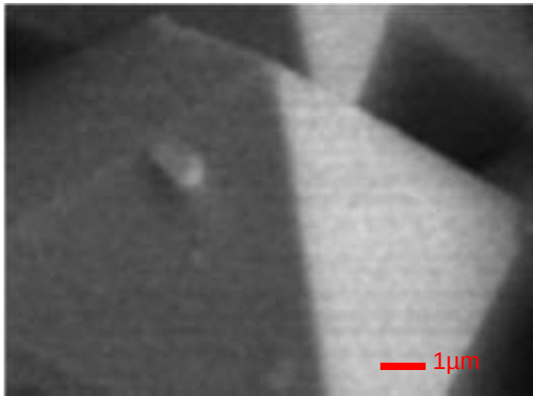
Pilot Plant for Flue Dust

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

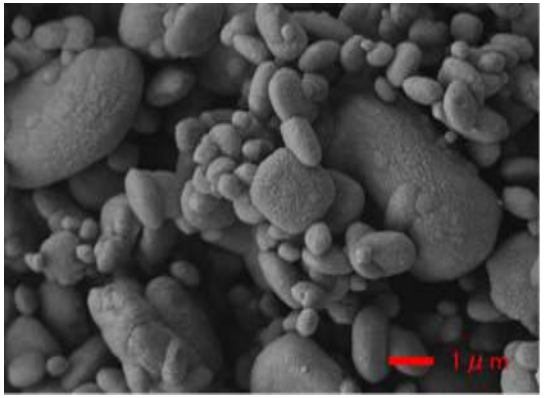
DMSP® Flow for Flue Dust



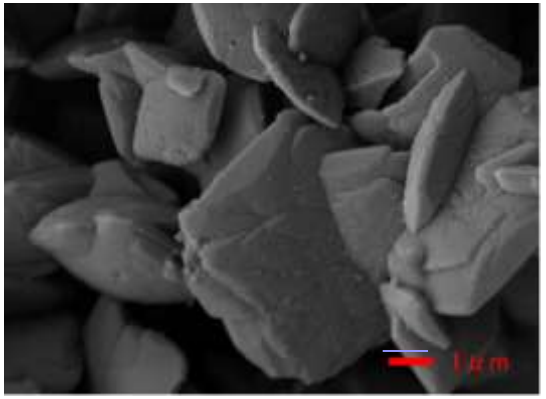
Configuration of Scorodite from Flue Dust



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

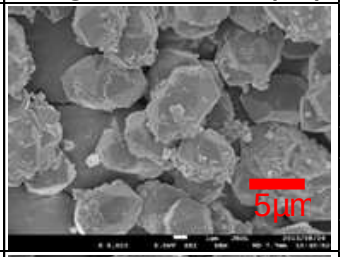
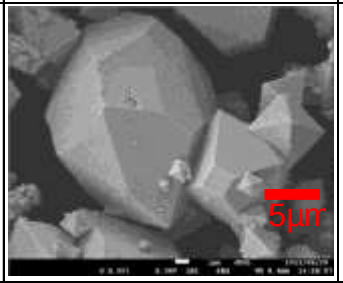
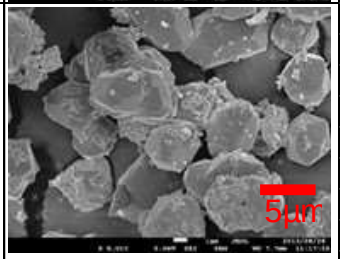
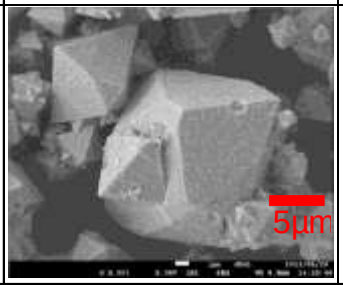
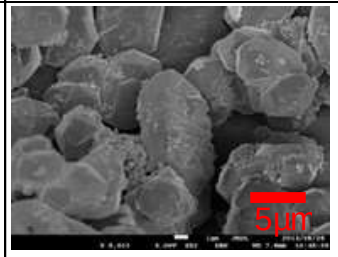
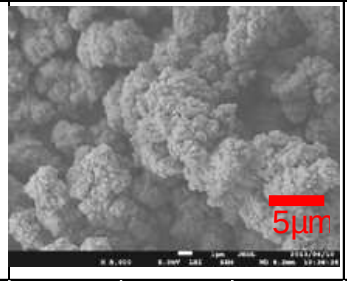
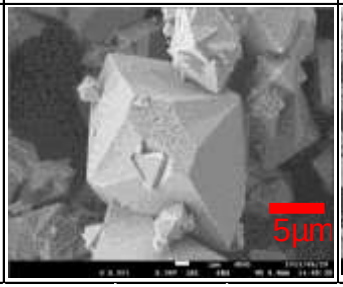
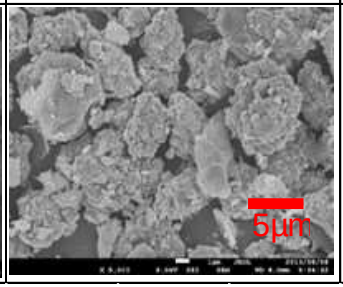
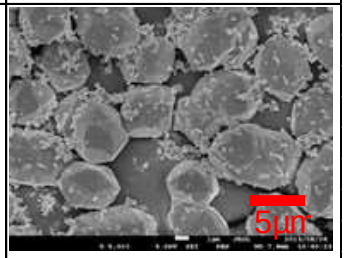
TCLP	Pour size (μm)	As (mg/L)	Pb (mg/L)	Cd (mg/L)	Se (mg/L)	Cr (mg/L)	Hg (μg/L)
Criterion Value	0.6-0.8	<5.0	<5.0	<1.0	<1.0	<5.0	<200
F1	0.7	<0.2	<0.1	<0.05	<0.1	<0.1	<10
F2	0.7	0.3	<0.1	<0.05	<0.1	<0.1	<10

CONTENT

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

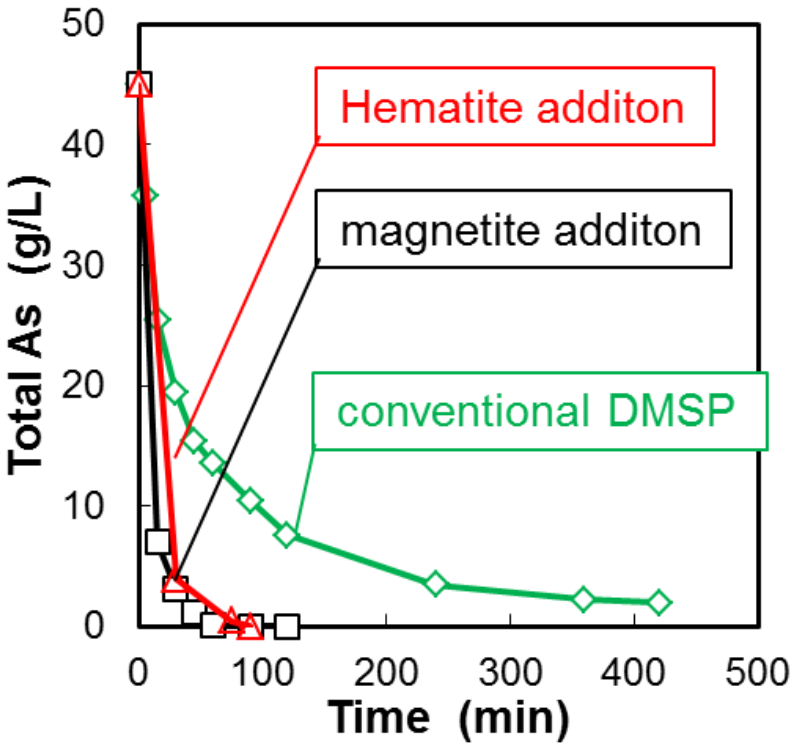
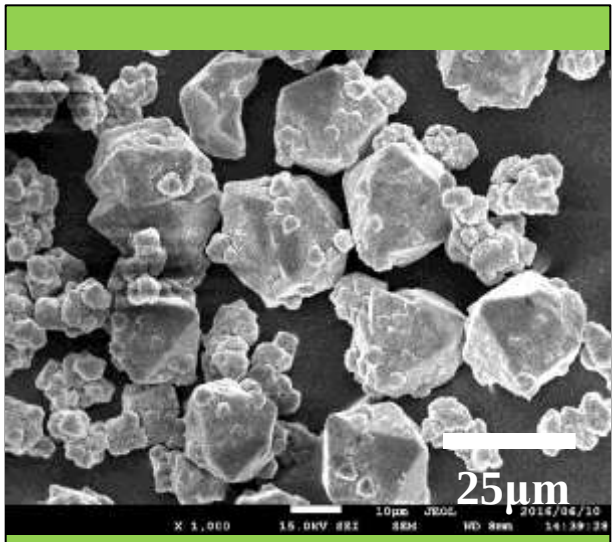
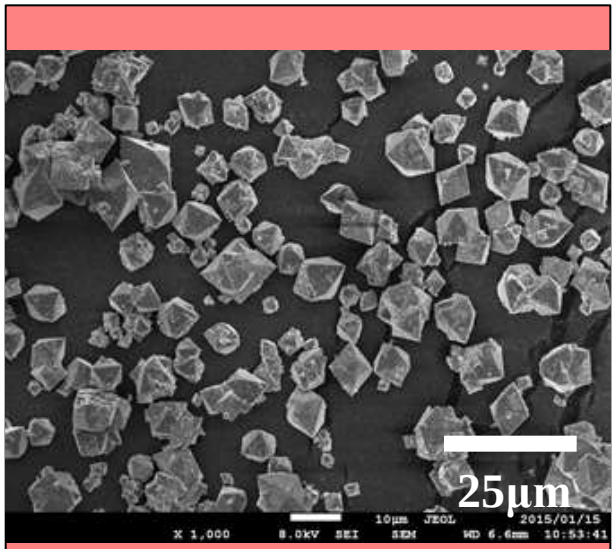


Fig. As concentration in reaction solution of conventional DMSP & magnetite addition method

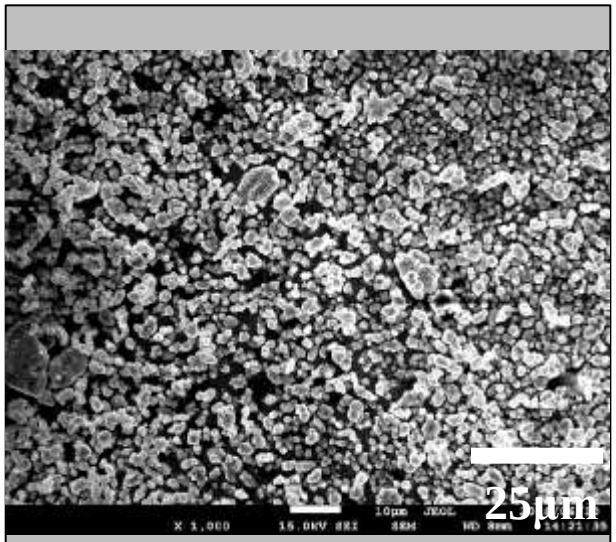
Characteristics of Scorodite by various Iron sources



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	As	Moisture (%)	D50 (μm)	Post Solution (g/L) As	Fe	Leachate As (mg/L) Japan	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

CONTENT

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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