EFFECT OF COOLING RATE ON PHASE AND MICROSTRUCTURE IN COPPER SLAG

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Outline

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- **Experimental**
  - Sample preparation
  - Evaluation
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  - Elution test results
- **Conclusion**
  - Key point and conclusion
  - Acknowledgments

Introduction

[Background]

Copper smelting ⇒ Oxidation reaction of copper ore with SiO_2 and O_2

- Copper-concentrated sulfide matte melt
- Impurities-concentrated **oxide slag melt**

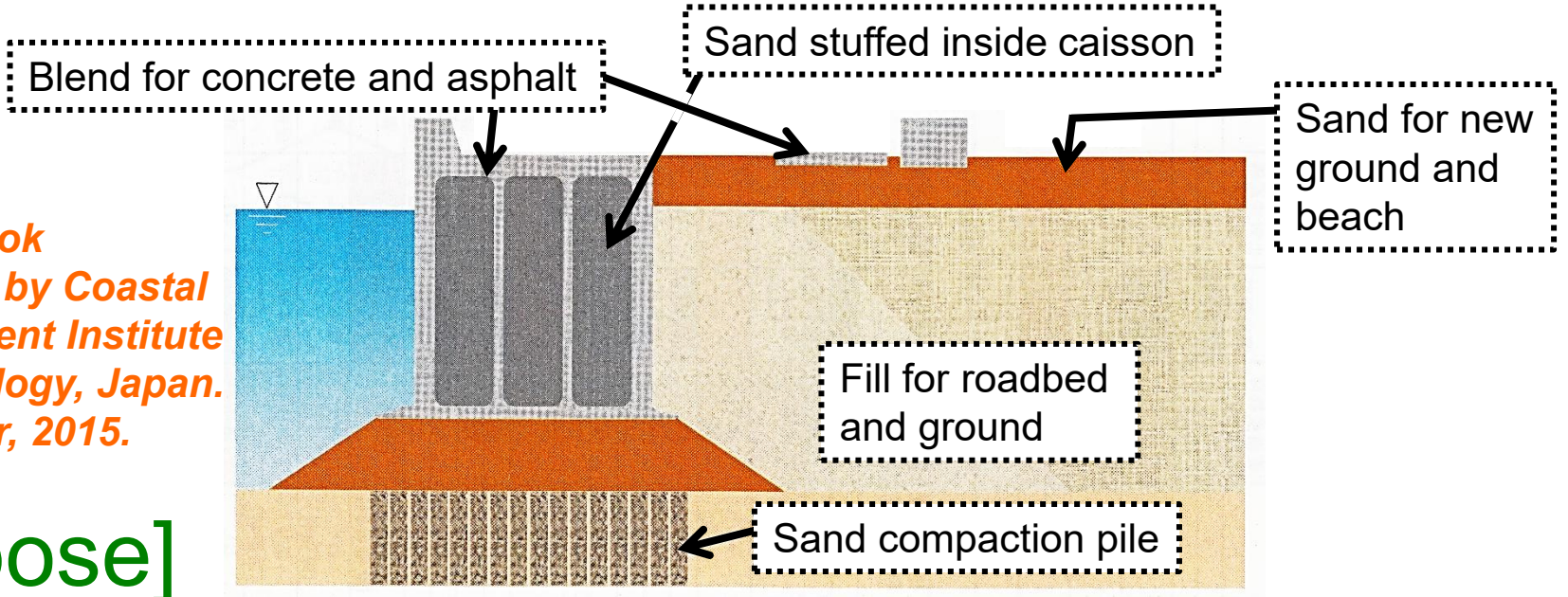
Lower concentration of Cu in copper ore
⇒ **Larger** amounts of copper slag

For sustainable copper process metallurgy,

Utilization of copper slag

Potential applications and purpose

Feature of copper slag: Stable & larger density



From a book published by Coastal Development Institute of Technology, Japan. September, 2015.

[Purpose]

To satisfy the guideline of **JIS K 0058-2** in **1mol/L HCl aqueous solution** immersion test under the notification of Ministry of the Environment of the Japanese Government.

Elution properties of heavy metals (Pb, As)
⇔Phase & microstructure in crystallized slag

Composition feature of copper slag

$2FeO \cdot SiO_2$ **Fe/SiO_2 =1.86 (mass%)**

Ideal for fayalite composition for the oxidation reaction of chalco-pyrite with SiO_2 and O_2

FeO_x (FeO-Fe_3O_4)–SiO_2–CaO, –Al_2O_3 etc.

Fe/SiO_2 =1.0~1.2 (An example of practical composition)

- SiO_2-rich composition, compared to fayalite
- Fe_3O_4 precipitation (FeO_x-rich)

→ **Microscopically heterogeneous**

☐ **Control of cooling rate → How do phase and the distribution of Pb and As change ?**

Experimental : Sample preparation

Sealing

Silica ampoule,
$\leq 5\times10^{-3}$ Pa

Melting

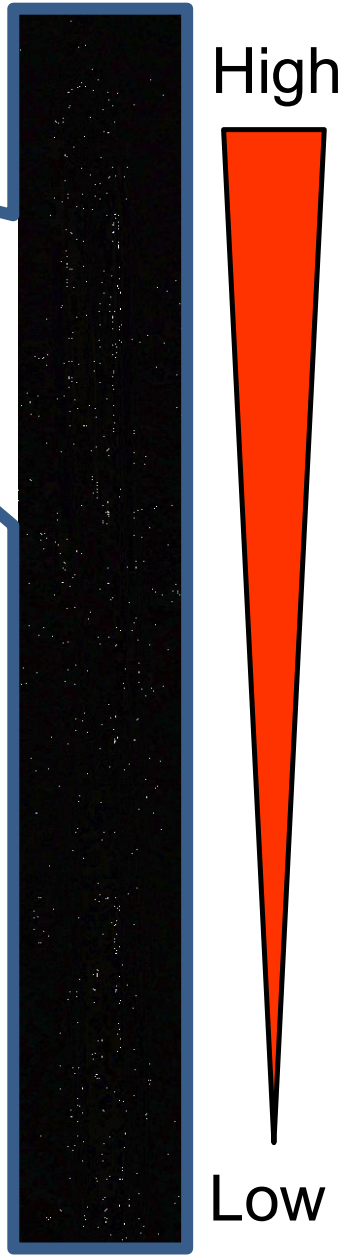
1250 ºC, 1h

Cooling

Method (Estimated cooling rate)
- Water-quenched (~ 3×10^{3})
- Cooled in air (~ 3×10^{2})
- Cooled in a furnace (~ 3) [ºC/min]

Evaluation

- XRD
- SEM-EDS
- ICP-MS



High

Low

Water-quenched



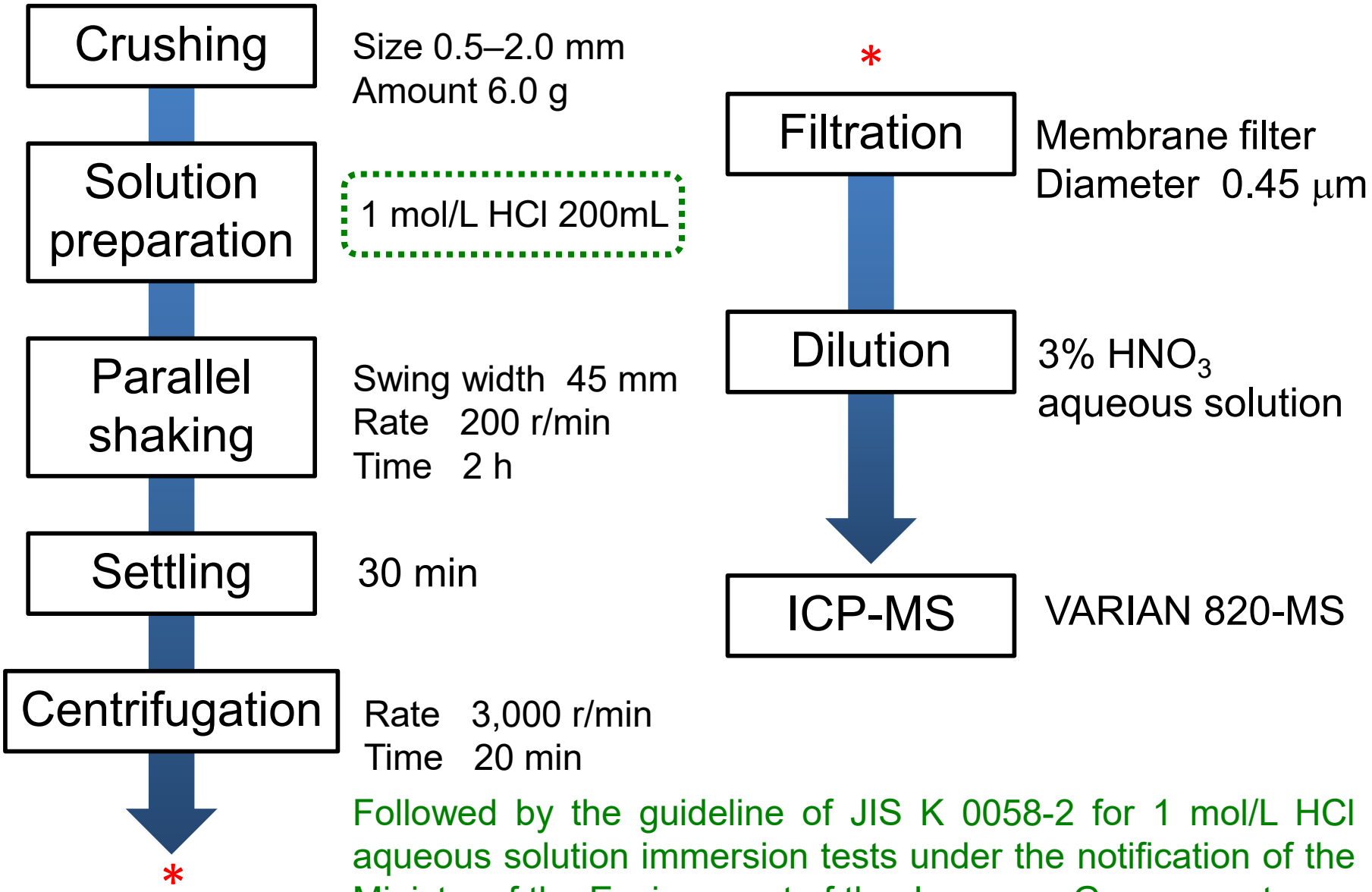
Cooled in air



Cooled in a furnace

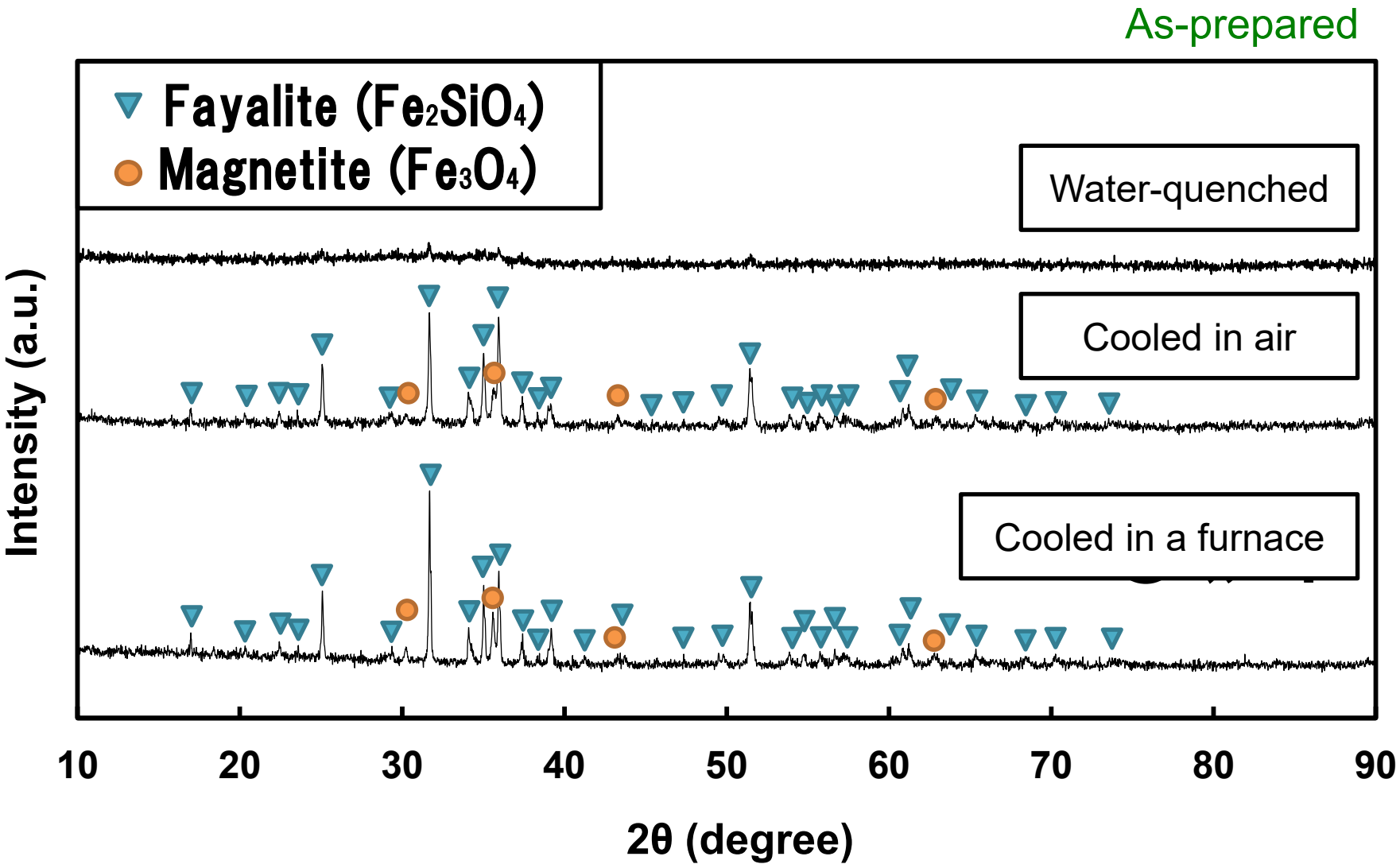


Experimental : Elution properties

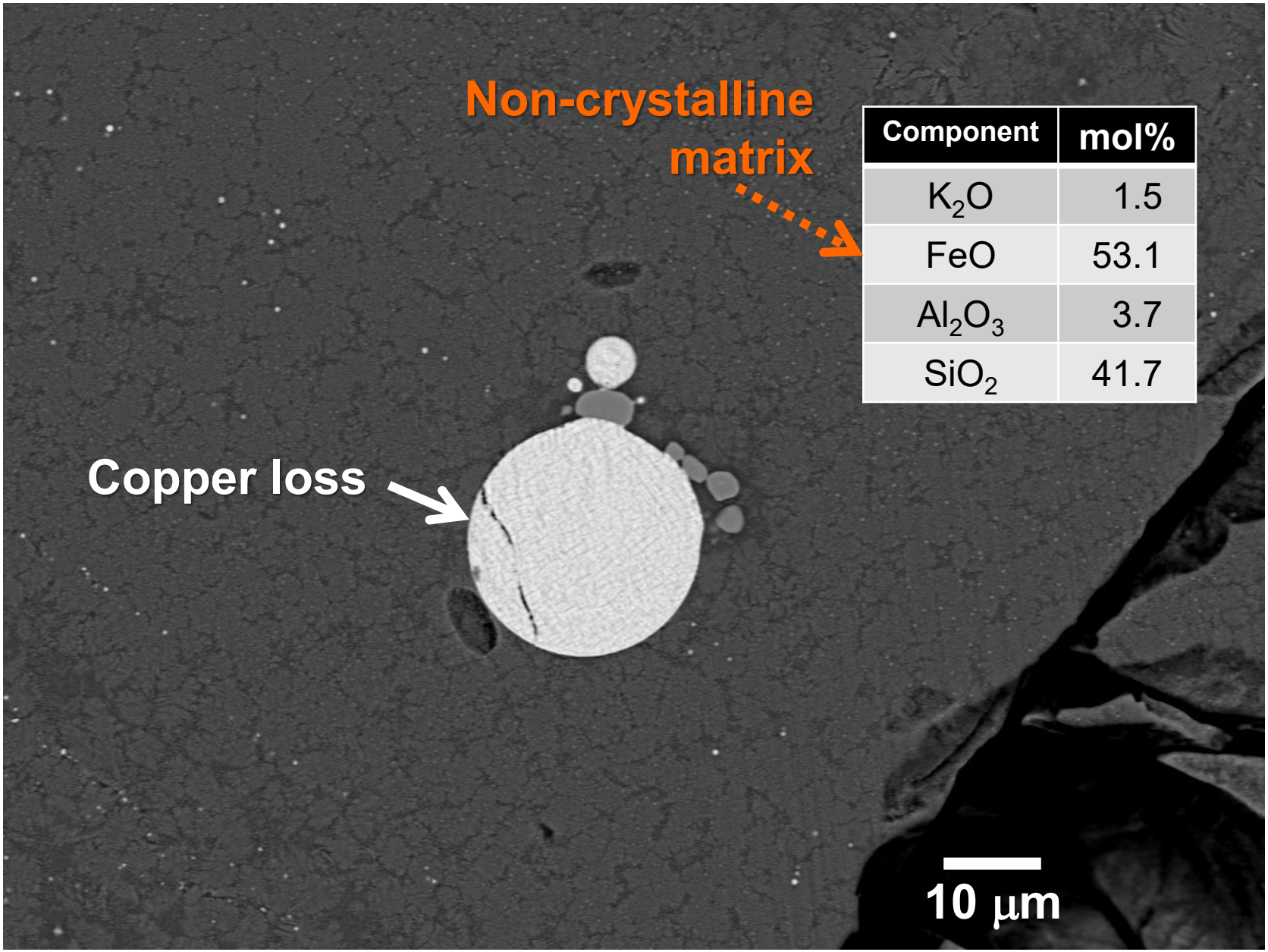


Followed by the guideline of JIS K 0058-2 for 1 mol/L HCl aqueous solution immersion tests under the notification of the Ministry of the Environment of the Japanese Government.

XRD patterns of slag samples

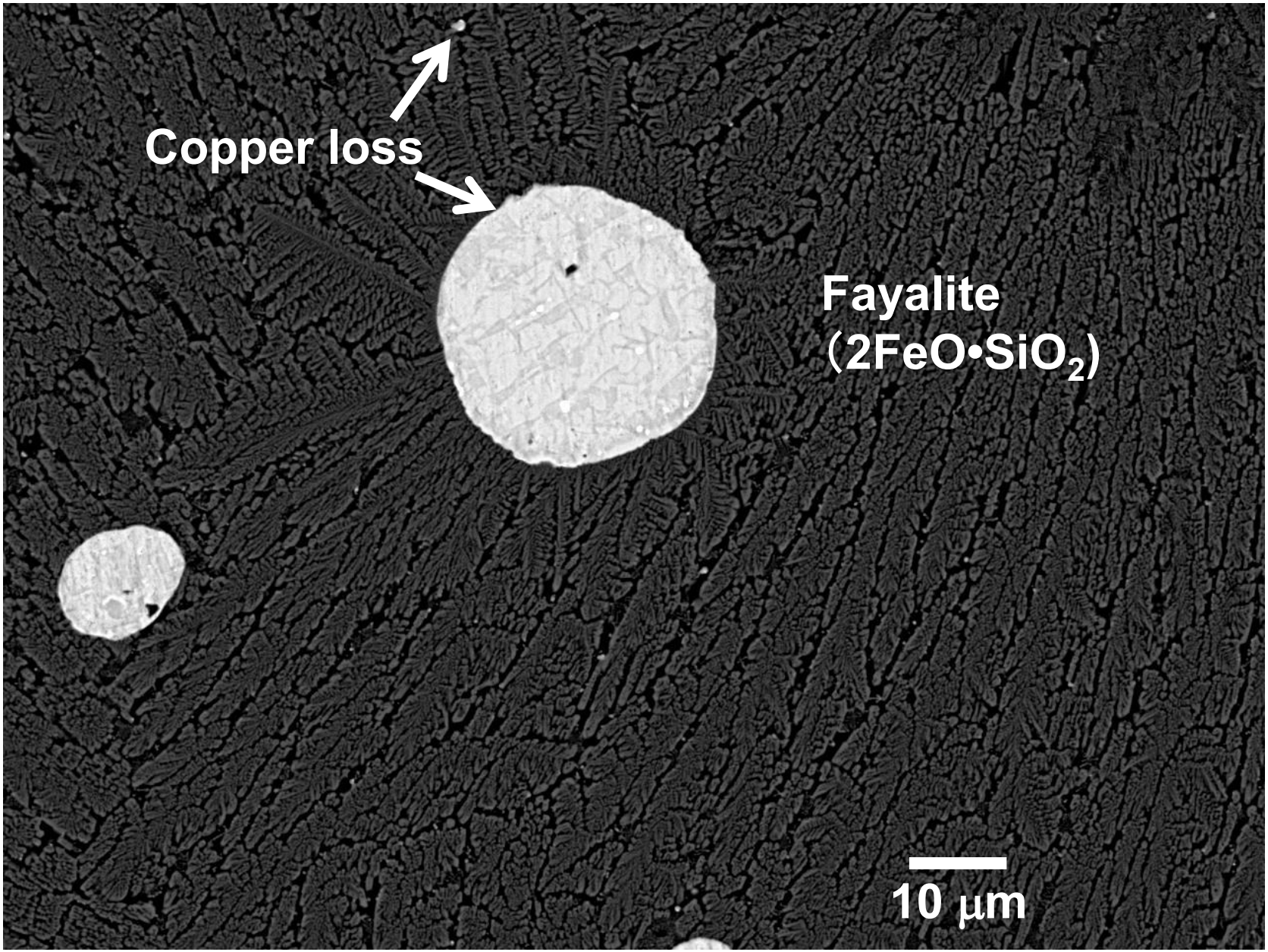


SEM image of water-quenched slag

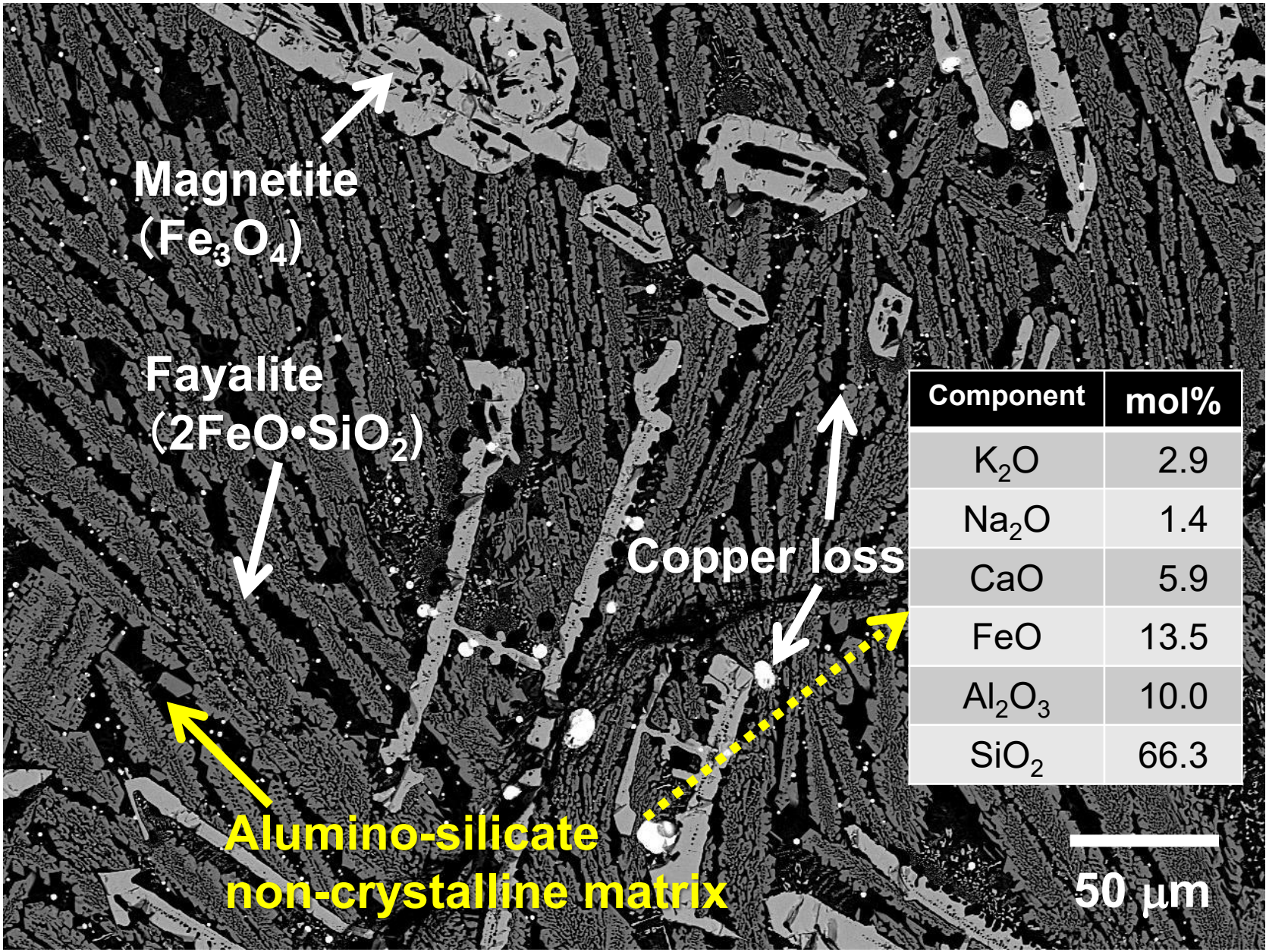


Component	mol%
K_2O	1.5
FeO	53.1
Al_2O_3	3.7
SiO_2	41.7

SEM image of slag cooled in air



SEM image of slag cooled in a furnace



Component	mol%
K_2O	2.9
Na_2O	1.4
CaO	5.9
FeO	13.5
Al_2O_3	10.0
SiO_2	66.3

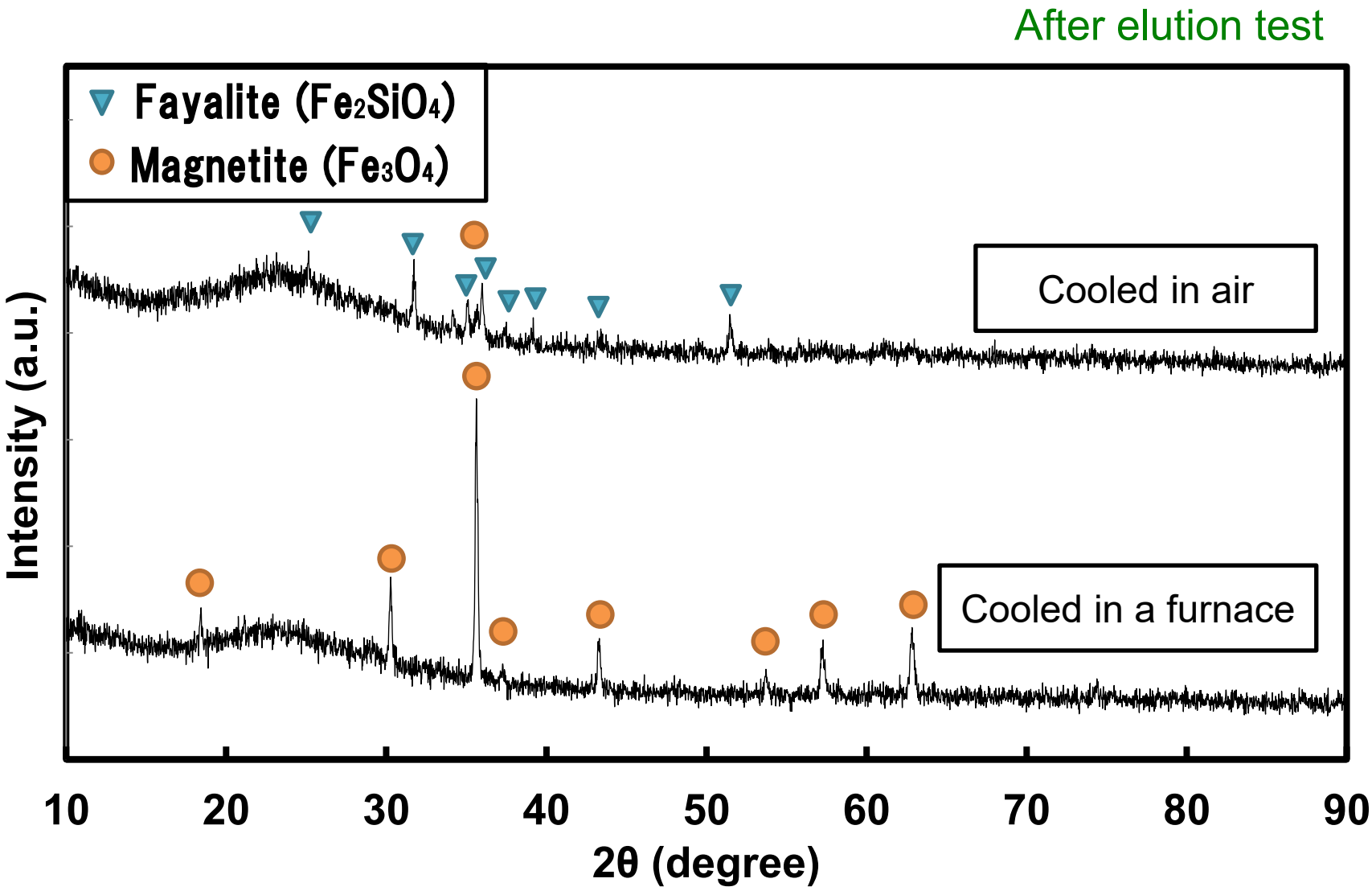
Elution test results in 1 mol/L HCl aqueous solution

The standard value: 150 mg/kg

Dissolved entirely		mg/kg
Pb	Water-quenched	739
	Cooled in air	833
	Cooled in a furnace	861
As	Water-quenched	345
	Cooled in air	559
	Cooled in a furnace	495

1 mol/L HCl		mg/kg
Pb	Water-quenched	368
	Cooled in air	21
	Cooled in a furnace	28
As	Water-quenched	179
	Cooled in air	4
	Cooled in a furnace	2

XRD patterns after elution test



Macroscopic appearance after elution test

[Water-quenched]





3 months later



[Cooled in a furnace]



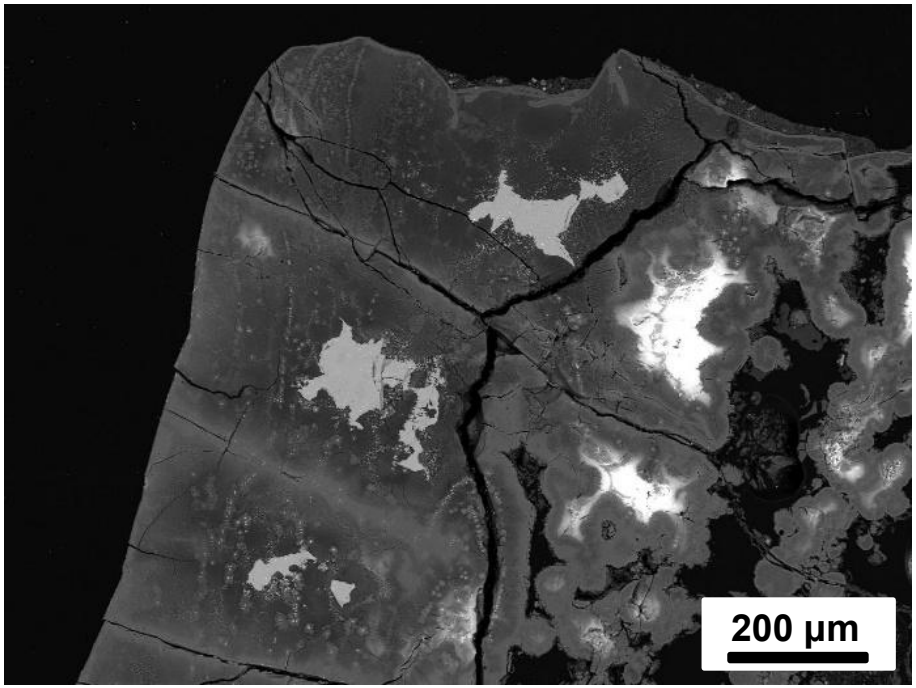


3 months later

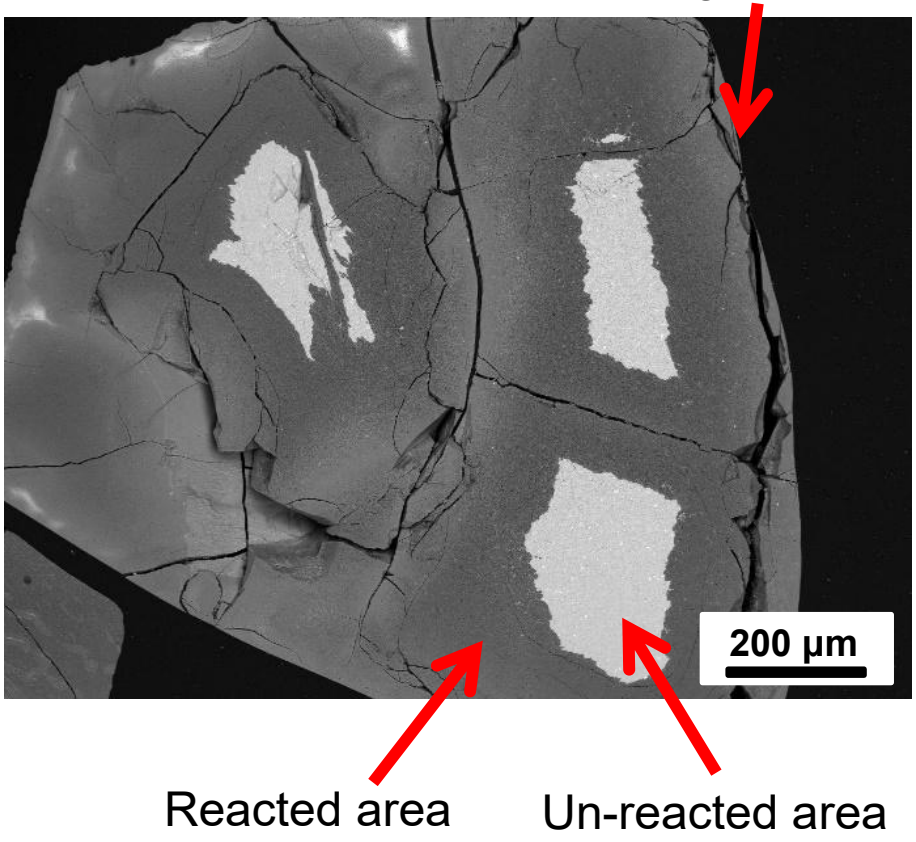


Microstructures after elution test

[Water-quenched]

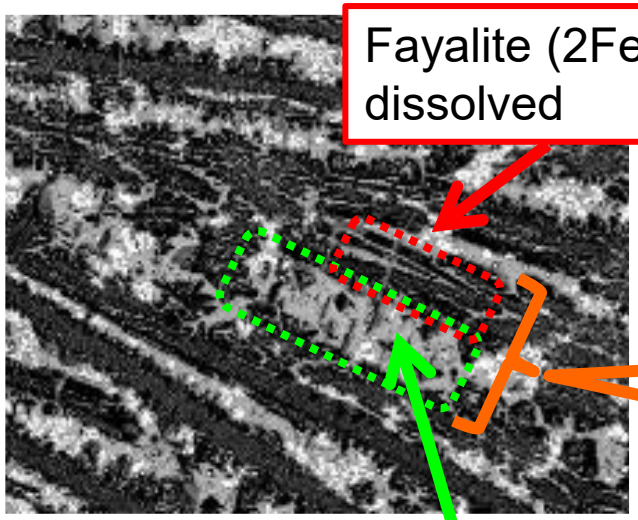


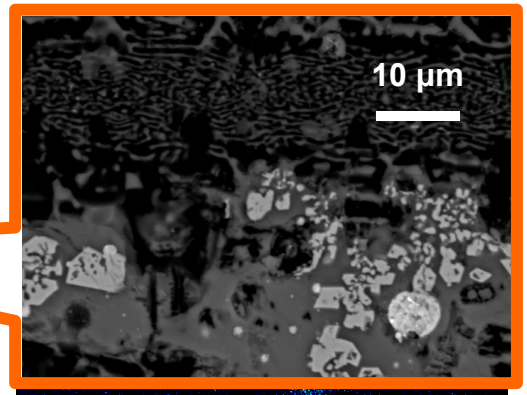
[Cooled in air]

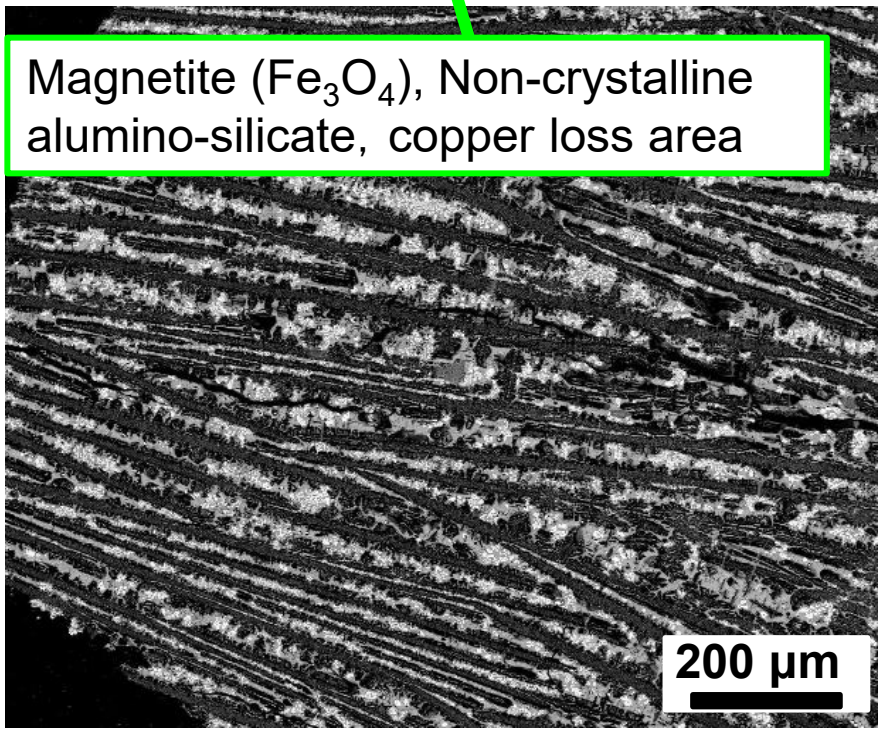


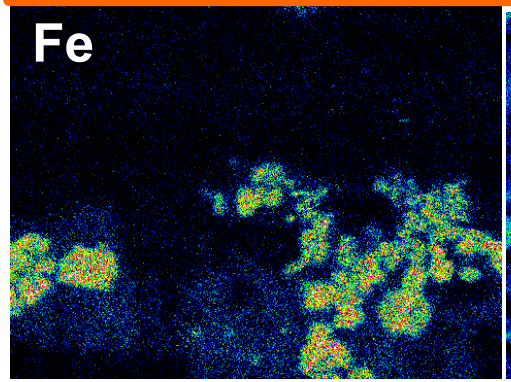
Microstructures after elution test

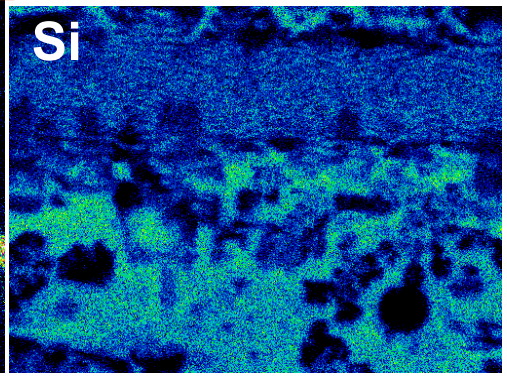
[Cooled in a furnace]

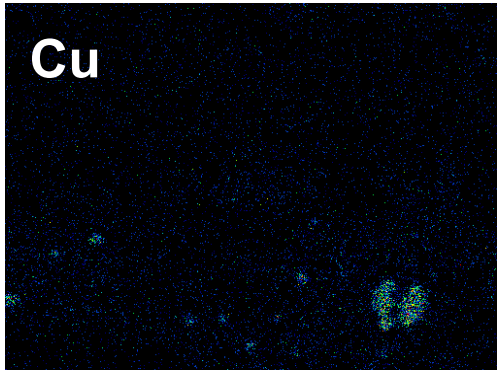


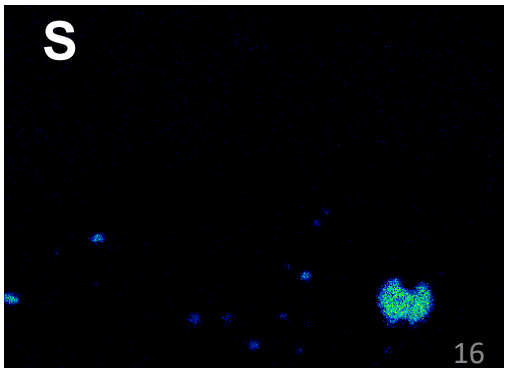




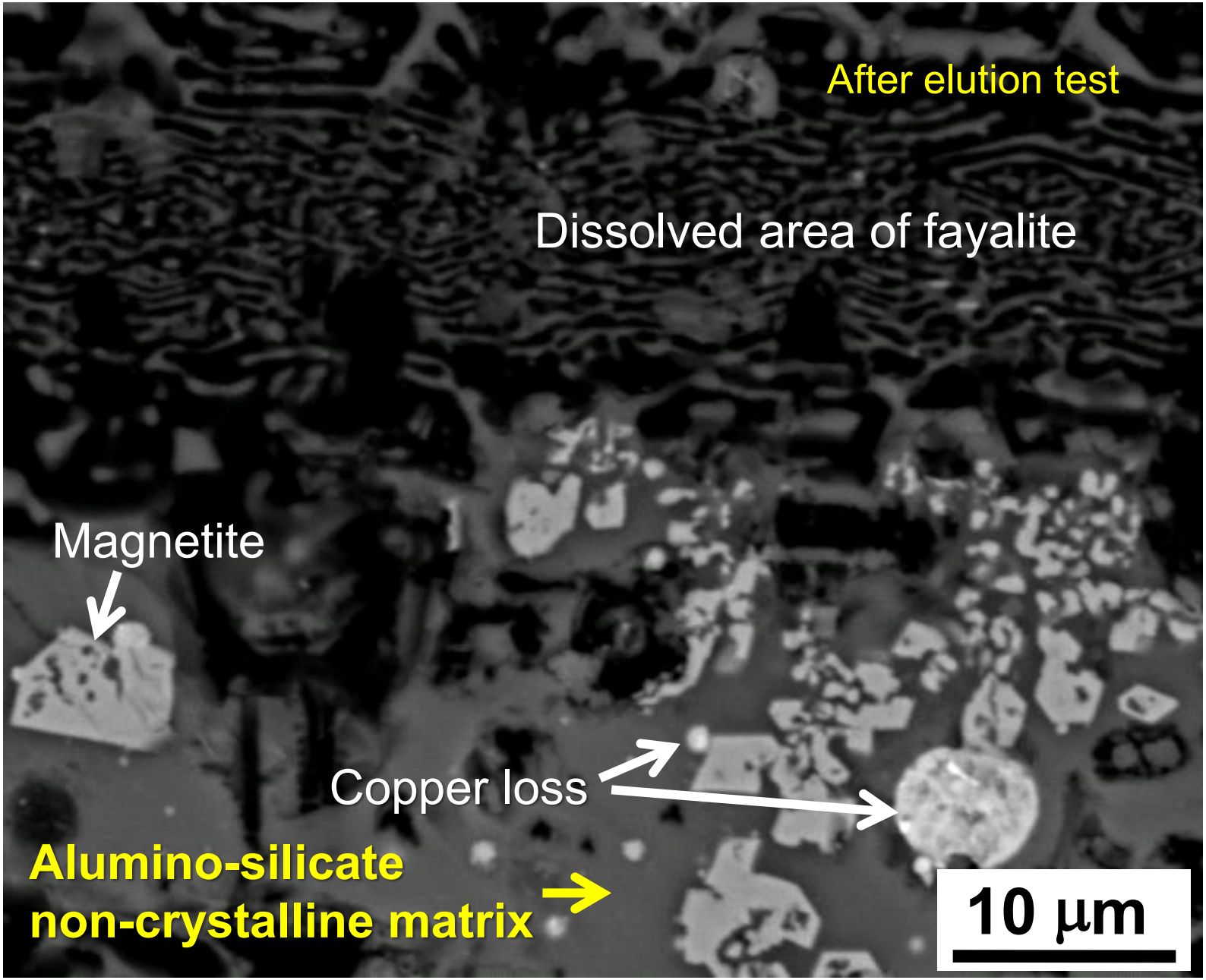








SEM image of slag cooled in a furnace



Change of composition distribution

[Water-quenched]

- **Non-crystalline matrix**

Component	mol%
K_2O	1.5
FeO	53.1
Al_2O_3	3.7
SiO_2	41.7

With Pb and As

[Cooled in a furnace]
(Slowest cooling rate)

- **Fayalite ($2FeO \cdot SiO_2$)**
- **Magnetite (Fe_3O_4)**
- **Non-crystalline matrix**

Component	mol%
K_2O	2.9
Na_2O	1.4
CaO	5.9
FeO	13.5
Al_2O_3	10.0
SiO_2	66.3

With Pb and As

Conclusion

Copper slag in smelting process was re-melted in vacuum-sealed ampoule and cooled with different rates for crystallization. Slower cooling to form the fayalite and magnetite phases results in the formation of SiO_2-rich alumino-silicate non-crystalline area.

The crystallized-copper slag with the SiO_2-rich (< 60 mol%) non-crystalline matrix containing Pb and As elements has a satisfaction to the standard of JIS K 0058-2 for 1 mol/L HCl aqueous solution immersion tests under the notification of the Ministry of the Environment of the Japanese Government.

Acknowledgments

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Thank you 

H. Takebe,S. Tomita, A. Saitoh, M. Kawahara, Y. Sueoka, M. Sakakibara, “Effect of Crystallization on Microstructure and Elution Proerties in Copper Slag”, *Journal of Sustainable Metallurgy*, **3**, (2017), 543-550.