総説

Review

Review of Iron Recovery and Cleaning of Copper Slag*

by Yong FAN^{1,3}, Etsuro SHIBATA^{2*},
Atsushi IIZUKA² and Takashi NAKAMURA²

Copper slag from copper matte smelting contains iron, which forms fayalite (Fe_2SiO_4) as the major constituent. Because of its favorable physico-mechanical properties, copper slag has uses such as concrete aggregates, ballast, and abrasives. However, the demand for copper slag for such applications is decreasing in advanced countries such as Japan. In recent years, the depletion of high-grade iron ores and increasing demands for iron resources have resulted in an interest in the development of methods for iron recovery from low-grade metallurgical wastes. This paper gives a review of various processes such as pyrometallurgy, hydrometallurgy, and beneficiation for iron recovery and slag cleaning. Authors also proposed a new process for iron recovery from copper slag, and related simple thermodynamic calculations are provided.

KEY WORDS : Copper Slag, Iron Recovery, Cleaning, Recycling

1. Introduction

1・1 General

In recent years, metal production has increased, and ore quality has been degraded. As a result, the amounts of wastes from such processes have increased. Huge quantities of slag, a solid waste product of pyrometallurgical operations in the metals industry, are dumped around the world; other cost-effective methods for using them are limited, and these slags pose a potential environmental threat from contained heavy metals. Copper slag, which is produced during the pyrometallurgical production of copper from copper concentrates, contains valuable metals such as copper, zinc, lead, cobalt, and nickel. For every tonne of metal produced, about 2.2–3 tonnes of slags, mainly copper smelter and converter slags, are generated. The conventional methods for treating slags are disposal in slag dumps or stockpiles. The increasing dumping of slags not only occupies large areas of land, but also wastes resources, and potentially has an impact on the environment as a result of water pollution. In addition, environmental regulations are becoming stricter. It is therefore desirable to use slags by the current options of recycling, metal recovery, and production of high-value-added materials.

The recovery of metals depends on the type of slag. Recycling copper converter slag back to the flash furnace has been practiced and leads to an increase in the matte grade. Because of the favorable physico-mechanical characteristics of

copper smelter slag, it can be used to make products such as cement, fillers, ballast, abrasives, aggregates, roofing granules, glass, and tiles. However, the demand for copper slag for these purposes is decreasing in advanced countries such as Japan. Various methods of recovering metals from copper smelter slag, particularly pyrometallurgical, hydrometallurgical, and mixed pyro/hydrometallurgical processes, have been extensively studied. At the end of the metal recovery process, iron, which is a major constituent of slag, usually remains as a residue (fayalite); this residue has little commercial value and requires disposal. Iron resources are now becoming scarce because of the very high demands in developing countries. The recovery of iron from such resources is once again being considered.

1・2 World copper production

In 2011, the global production of copper by smelting reached 15.8 million tonnes. The major copper-smelting countries, with quantities produced, are listed in Table 1¹⁾.

China, the world's major copper producer, generates annual copper slag emissions of more than 8 million tonnes. However, China's rate of copper slag use remains low, and most of the copper slag is dumped without being fully used; this causes serious environmental pollution and is a huge waste of resources.

The major slag-producing regions, with quantities produced, are shown in Fig. 1²⁾. Asia's share of world copper smelter output has increased from 27 % in 1990 to over 54 % in 2011, as smelter production in China has expanded rapidly with increasing demand. In the North and South America region, copper production by smelting has decreased to 3 million tonnes.

The bulk of the world's copper-smelting capacity is moving to Asia. Currently, 45% of global copper-smelting capacity, mostly from non-integrated smelters, is located in

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1. Graduate School of Environmental Studies, Tohoku University, 6-6-20, Aramaki, Aoba-ku, Sendai, 980-8579, Japan
2. Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University, 2-1-1 Katahira, Aobaku, Sendai 980-8577, Japan
3. School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, Beijing 100083, China
[For Correspondence] Email: etsuro@tagen.tohoku.ac.jp

Table 1 Copper smelter production in various countries ($\times 1000$ tonnes)¹⁾.

	2006	2007	2008	2009	2010
China	1917.5	2111.5	2453.4	2648.3	2772.2
Chile	1565.4	1514.3	1369.2	1522.3	1559.8
Japan	1361.8	1383.4	1335.8	1302.1	1356.3
India	609.6	699.9	651.0	705.1	653.9
USA	501.3	617.0	573.8	597.4	601.2
Russia	635.0	650.0	627.0	579.6	590.0

Note: This table shows primary metal in the form of blister and anode produced from concentrates, and may include copper produced from scrap.

Asia, compared with only 2% in the period from the 1970s to the 1990s. Copper smelters throughout the world currently operate using a mixture of technologies, including the recent Isasmelt and the older flash and reverberatory furnaces. Environmental and other requirements will probably drive the industry to incorporate different technologies. Pyrometallurgy is the process most used in treating copper concentrates. In this type of technology, which is used in many countries, flash furnaces are installed to facilitate recovery of valuable elements from copper concentrates.

1 · 3 Formation of copper slag

The primary supply of raw materials in copper metallurgy involves mining copper ores, which generally come in two forms: copper sulfides or copper oxides. Ores are processed by one of two methods, depending on the type of ore. Copper sulfide ores are first concentrated, and then smelted and refined; each of these stages is a separate process and can be carried out at a different location. Copper oxide ores are crushed and the copper is then extracted from the crushed ore by dissolving the copper in acid and then recovering the copper from the acid via electrolysis. This process is called solvent-extraction–electrowinning (SX-EW), and accounts for some 15 % of primary copper production.

After the ore has been mined, it is crushed and ground, followed by concentration by flotation. Pyrometallurgy and hydrometallurgy are the methods used in treating copper concentrates. The latter is a new technology and is not widely used in ore treatment. The obtained copper concentrates typically contain around 30 mass% of copper, but grades range from 20 to 40 mass%. In the subsequent smelting process, the copper is transformed into a “matte” containing 50–70 mass% copper. The molten matte is processed in a converter, resulting in so-called blister copper with a copper content of 98.5–99.5 mass%. In the next step, the blister copper is fire-refined in the traditional process, or, increasingly, remelted and cast into anodes for electro-refining.

In the ores, the oxides and sulfides combine covalently to form a Cu–Fe–O–S phase in the absence of silica (SiO₂). During smelting, when SiO₂ is added, it combines with the oxides to form strongly bonded silicate anions, which group together to form the slag phase:

Sulfides show no tendency to form anionic complexes

Fig.1 Copper smelter production by region, 2007–2011²⁾.

and hence they remain as a distinct covalent matte phase, quite different from the silicate slag. SiO₂ is added directly for the most complete isolation of copper in the matte, which occurs at near saturation concentration of SiO₂. Certain amounts of lime and alumina (Al₂O₃) are added to stabilize the slag structure. The molten slag is discharged from the furnace at 1000–1300°C. Slag is a solution of molten oxides. These oxides include ferrous oxide (FeO) and ferric oxide (Fe₂O₃) from iron oxidation, SiO₂ from the flux, Al₂O₃, lime (CaO), magnesia (MgO), and oxide impurities from the concentrate. Small amounts of sulfides can also be dissolved in FeO–SiO₂ slags, but lime and Al₂O₃ in slags decrease the sulfide solubility.

1 · 4 Properties of copper smelter slag

When a liquid slag is cooled slowly, it forms a dense, hard, crystalline product, whereas quick solidification, by pouring the molten slag into water, gives an amorphous granulated slag. The commonest copper slag is an impure iron silicate glass with small inclusions of copper and copper matte. The chemical composition of the slag varies with the type of furnace or treatment process. A typical copper slag composition from flash smelter is as follows: Fe = 30–40 mass%, SiO₂ = 35–40 mass%, Al₂O₃ ≤ 5 mass%, CaO ≤ 5 mass%, Cu = 0.5–1 mass%, Pb ≤ 1 mass%, Zn ≤ 2 mass%, and As ≤ 0.1 mass%.

The chemical compositions of copper slags from different origins are shown in Table 2. Most of components in slag are oxides, however it contains a small amount of sulfides. The total sulfur contents in each slag are from 0.11 to 3.57 mass% as shown in Table 2. Generally, the main components in copper slags are iron oxides and SiO₂, in amounts of 25–50 mass% each. Almost all copper slags contain considerable amounts of copper (0.5–3.7%) close to, or even higher, than those in copper ores. Depending on the origin, some slags contain cobalt and/or nickel at levels worth recovering and using. Toxic elements (arsenic) and heavy metals (lead) are present in some copper slags.

Some physical and mechanical properties of copper slag are given in Table 3¹⁾. Air-cooled copper slag is black and has a glassy appearance. The densities of copper slags vary from 3.16 to as high as 3.87 g/cm³, depending on the iron content. In general, water absorption by copper slags is very low. Granulated copper slags are more porous and therefore have lower specific gravities and higher absorption capacities than air-cooled copper slags. When a liquid slag is cooled slowly, it forms a dense, hard, crystalline product, whereas quick

Table 2 Typical chemical compositions of copper slags.

Elements (mass%)	Cu	Fe	S	Si	Ca	Al	Mg	Others
Slag 1	1.0	63.9	0.5	27.8	1.2	2.9	1.1	NR
Slag 2	0.58	38.6	0.93	17.40	1.11	2.51	1.65	Ni: 0.57 Co: 0.21
Slag 3	3.23	Fe ₃ O ₄ : 11.8	3.57	SiO ₂ : 27.7	NR	NR	NR	NR
Slag 4	1.25	43.75	NR	SiO ₂ : 32.18	CaO: 12.31	Al ₂ O ₃ : 6.54	MgO: 3.23	Ni: 0.20 Pb: 0.32 Zn: 1.45
Slag 5	1.06	38.55	0.52	SiO ₂ : 34.08	CaO: 2.77	Al ₂ O ₃ : 3.90	MgO: 1.14	17.98
Slag 6	1.45	39.96	0.72	SiO ₂ : 20.16	CaO: 2.0	Al ₂ O ₃ : 2.99	MgO: 0.76	P: 0.30 Zn: 0.85 Pb: 0.77 Co: 2
Slag 7	1.4	FeO: 29	0.6	SiO ₂ : 31	CaO: 10	Al ₂ O ₃ : 7	MgO: 5	ZnO: 10 PbO: 0.5 Zn: 1.70 Co: 4.09 Pb: 1.16
Slag 8	1.35	28.43	0.11	15.38	5.13	3.22	2.15	

Slag 1: Fayalite from EL Teniente of Sterlite Industries India Limited³; Slag 2: Slow-cooled slag from INCO's flash smelting furnace in Sudbury, Ontario, Canada⁴; Slag 3: Flash smelting furnace slag from Chilean Smelter Industry⁵; Slag 4: Quenched smelter slag from YunNan Copper Smelter Industry, China⁶; Slag 5: Quenched smelter slag from YunNan Copper Smelter Industry, China⁷; Slag 6: Quenched smelter slag from JiangXi Copper Smelter Industry, China⁸; Slag 7: Slag from ex-water-jacket furnace in the Lubumbashi plant in the Democratic Republic of the Congo⁹; Slag 8: Slag from a copper smelter in Guangdong Province of China¹⁰; NR: No Report.

solidification, by pouring the molten slag into water, gives a granulated amorphous slag.

2. Iron Recovery and Beneficiation Technologies

Researches related with copper slag have been extensively conducted for long time¹². There are reports on the recoveries of copper, nickel, and cobalt from copper slags¹³⁻¹⁶. However, these processes leave behind substantial amounts of materials to be disposed of or otherwise used. Over the years, several uses for smelting slags have been found, including cement and concrete, abrasive grit, land reclamation, and ceramic tiles. Other potential uses of copper slags include roofing granules, hot-mixed asphalt, and cutting tools. However, all of these applications are cost-sensitive, and the cost of transporting the slag from a remote location to a manufacturing facility often makes its use uncompetitive. As a result, most slag is still landfilled after processing.

Although the iron content in copper slags is high, iron recovery has rarely been reported. The main reason is that the iron is present as fayalite, not as Fe₃O₄ or Fe₂O₃. The traditional methods for iron recovery from minerals are therefore not effective. In order to recover iron efficiently, it would be better to convert the fayalite into other iron phases such as metallic iron and magnetite. Recently, a number of methods for iron concentration and recovery from copper slags have been reported, and these are reviewed below.

2.1 Metal extraction for iron concentration

2.1.1 Reduction methods During pyrometallurgical processing of non-ferrous metals, smelting residues such as smelter slags and flue gas dusts containing valuable metals and harmful substances are inevitably generated as secondary

Table 3 Physical properties of copper slags¹¹.

Appearance	Black, glassy, more vesicular when granulate
Density, g/cm ³	3.16-3.87
Absorption, %	0.15-0.55
Soundness, %	0.8-0.9
Conductivity, μ S/cm	500
Specific gravity	2.8-3.8
Hardness, mohs	6-7
Moisture, %	< 5
Water soluble chloride, ppm	< 50
Abrasion loss, %	24.1
Sodium sulphate soundness loss, %	0.9

products. To reduce environmental loading and to recover valuable metals, such materials require appropriate treatment, with the aim of maximizing metal recovery and iron concentration.

The copper slag generated at Kure in Turkey has been investigated by Acma et al.¹⁷ for the recovery of copper and cobalt, and the production of magnet-grade iron oxides such as γ -Fe₂O₃, by a pyro/hydrometallurgical route. A flow diagram of the process is shown in Fig. 2. The fayalite slag, containing about 0.8 mass% copper and 0.4 mass% cobalt, is reduced with coke/graphite in a DC arc furnace to yield a liquid alloy rich in iron and containing about 3.8 mass% copper, 3.3 mass% cobalt, and 2.1 mass% sulfur. The alloy is leached with hot sulfuric acid so that the cobalt and iron are solubilized, leaving copper and other impurities in the residue. The leaching liquor is treated with H₂S to precipitate cobalt as a sulfide. The remaining liquor, containing mainly FeSO₄, is taken through a processing sequence consisting of goethite precipitation, dehydration, controlled reduction, and finally reoxidation, to obtain γ -Fe₂O₃ for magnetic applications¹⁷.

Rudnik et al.¹⁸ used a simple hydrometallurgical method for selective recovery of copper and cobalt from industrial copper converter slags. After roasting the slag under reducing conditions to produce a Cu-Co-Fe-Pb alloy, the alloy was electrochemically dissolved in an ammonia-ammonium chloride solution. The slime was then leached in an ammonia solution, and selective electro-winning of copper and cobalt was carried out as shown in Fig. 3. The copper deposit was of high purity (99.9 mass%), and the purity of the cobalt deposit was 92 mass%. A 27 mass% Cu-6 mass% Co-64 mass% Fe-1.5 mass% Pb alloy was formed after roasting, and did not dissolve uniformly during electrolysis. This resulted in separation of the metals; iron remained in the slime, whereas copper and cobalt were present in the slime, electrolyte, and cathodic deposit. A series of secondary processes also took place: precipitation of iron compounds, copper cementation with cobalt and iron, and adsorption of copper and cobalt ions on the iron precipitates.¹⁸

Mawejaa et al.⁹ found that a w value (coal-to-slag ratio) of 5 % enabled the simultaneous recovery of 70-90 % of copper, cobalt, and zinc after reduction of the molten slag for 30-60 min. After reduction, the cleaned slag contained only small

Fig.2 Flow diagram of Kure method¹⁷⁾. Fig.3 Flow diagram of selective copper and cobalt recoveries from copper converter slag¹⁸⁾. Fig.4 Flow diagram of arsenic removal from smelting residue and recovery of high-purity copper²⁶⁾.

amounts of copper and cobalt (<0.4 mass%). Fuming of lead and zinc was efficient as the lead content in the residual slag dropped to levels lower than 0.04 mass%. When coal is added to the molten slag, the optimum condition for direct reduction of the slag using a metallurgical coal, especially with the aim of maximizing metal recovery and reducing iron contamination, is to use a low w . For a reduction time of about 60 min, w values between 3.5% and 4% should be considered. Recoveries of higher than 70% for zinc and 80% for copper and cobalt from the slags can be achieved under these conditions⁹⁾.

2 · 1 · 2 Hydrometallurgical methods There are various hydrometallurgical methods for the direct treatment of slags, including leaching in sulfuric acid¹⁹⁾ or ferric chloride²⁰⁾, hydrochloric acid, ammonia, and cyanide, to selectively extract metals such as cobalt, copper, and zinc from copper smelter slags, with the aim of maximizing metal recovery and iron concentration. Cyanide was originally used, but was replaced by other leachants because of environmental problems. To increase the leaching efficiency, measures such as addition of H_2O_2 ²¹⁾, pressure leaching¹⁹⁾, or leaching in a Cl_2/Cl^- system¹⁵⁾ have been taken. A simpler and more effective method involving roasting the slag with sulfuric acid^{22, 23)}, ammonium sulfate²³⁾, ferric sulfate²⁴⁾, or under reducing conditions²⁰⁾, followed by acid leaching, has also been proposed.

Acid roasting of slags followed by hot-water leaching was carried out by Arslan et al.²²⁾ to dissolve valuable metals. Iron dissolution decreased to almost zero after 2 h of thermal treatment at 650°C. After filtration, copper and zinc in the

solution were recovered by H_2S precipitation and cobalt was precipitated by reduction with H_2 gas in an autoclave.²²⁾

Leaching tests of base metals contained in two smelter slags were undertaken in ammonia and nitric acid solutions by Mawejaa et al.⁹⁾, with the aim of recovering cobalt, copper, and zinc. Annealing these slags at 1180°C produced crystalline phases comprising diopside, magnetite, and fayalite. Copper and zinc were leached from the amorphous slag in ammonia at 25°C for 2 h. Another route involves leaching of cobalt, copper, and zinc from the crystallized slag at pH = 0 at 60°C. This route is a compromise between good recovery rates of the three metals and pollution of the pregnant leaching solutions by iron and lead. The leaching residues can be chemically stabilized by annealing, and used as landfills.⁹⁾

Tests using atmospheric sulfuric acid leaching for copper and zinc were carried out by Linblad et al.²⁵⁾ from an aged reverberatory dump slag. Recoveries of 85 % for copper and 93 % for zinc were obtained after an extensive aging period. However, a substantial amount of iron was leached along with the copper and zinc.²⁵⁾

An experimental procedure involving both pyrometallurgical and hydrometallurgical operations was used by Shibayama et al.²⁶⁾ to remove high levels of arsenic (≈ 20 mass%) and for high recovery of copper (>3.0 mass%) contained in a copper-smelting residue sample, as shown in Fig. 4. In the first stage, the original smelting residue was heated at temperatures from 700 to 800°C in a N_2 gas atmosphere to remove volatiles, targeting mainly reduction of the amount of arsenic and the overall weight of

Fig.5 Flow diagram of high-temperature pressure-oxidative acid leaching of slag⁷⁾.

the smelting residue to be treated in the leaching stage. After volatilization treatment, the heated residue was treated using a hydrometallurgical multistage process involving two-step leaching, the first to selectively dissolve arsenic and the second to dissolve copper and other metals, in sulfuric acid under various concentration conditions, followed by solvent extraction using LIX-84I to recover the copper. The results showed that over 90 % of arsenic and copper in the smelting residue was removed in the two stages.²⁶⁾

High-temperature pressure-oxidative acid leaching of copper smelter slags was investigated as a process to facilitate slag cleaning and for selective dissolution of base metals for economic recovery. A flow diagram is shown in Fig. 5. Extractions of >99 % for nickel and cobalt, >97 % for copper, >91 % for zinc, and <2.2 % for iron were achieved by Li et al.⁷⁾ for 20 mass% acid addition and 25% solids loading at a 200–300 kPa O₂ overpressure at 250°C in 2 h. The as-produced residue, containing less than 0.01 mass% of base metals and hematite, and virtually zero sulfidic sulfur, seems to be suitable for safe disposal. The process enables economic recovery of base metals from slags and is reliable and feasible.⁷⁾

Leaching of converter slag flotation tailings from the Svyatogor copper smelter (Sverdlovsk region, Russia) using sulfuric acid solutions containing ferric ions was investigated by Muravyov et al.²⁸⁾ The solutions were obtained by oxidation of ferrous sulfate using a consortium of moderately thermophilic, acidophilic, and chemolithotrophic microorganisms, including *Sulfobacillus* species. The flotation tailings contained 0.56 mass% copper and 4.74 mass% zinc. Copper was present mostly as digenite, bornite, and free metal. Zinc was present as a ferrite (franklinite; ZnFe₂O₄) and, to a lesser degree, as a silicate. Increasing the Fe³⁺ concentration was found to have an inhibitory effect on zinc and iron leaching, but not on copper leaching. The temperature had the most pronounced effect on the kinetics of copper and zinc leaching. A kinetic analysis was carried out, and the calculated activation energies for copper and zinc leaching were 51.3 and 53.8 kJ/mol, indicating that the process is controlled by a chemical reaction on particle surfaces.²⁸⁾

A novel hydrometallurgical method was developed by Yang et al.¹⁰⁾ for selectively extracting valuable base metal such as cobalt, zinc, and copper from copper smelter slags at atmospheric pressure. A flow diagram is shown in Fig. 6. The method involves leaching with sulfuric acid and sodium chlorate

Fig.6 Flow diagram of selective leaching of valuable metals¹⁰⁾.

oxidant, and neutralizing with calcium hydroxide, for better and faster filtration of the precipitate. The method significantly decreases or avoids the adverse effects of SiO₂ and ferric oxides on recycling or extracting target valuable metals. This leaching and selective precipitation process recovers about 98 % cobalt, 97 % zinc, and 89 % copper from the slag, and only 3.2 % silicon and 0.02 % iron are dissolved. The optimized parameters for leaching 20 g of copper smelter slag are as follows: sulfuric acid leachant 17.6 g, sodium chlorate oxidant 2.5 g, reaction time 3 h, temperature 95°C. During the neutralization step, 4.3 g of calcium hydroxide were added slowly to the pulp to maintain the pH of the leaching solution at around pH 2.0 for at least 1 h, with constant monitoring throughout the process.¹⁰⁾

Banza et al.²⁹⁾ used different oxidants, including hydrogen peroxide, potassium dichromate, chlorine, and ferric chloride, for oxidative acid leaching. By controlling the acidity, iron co-extraction was decreased as a result of the oxidation of soluble ferrous iron to hydrolyzable ferric iron. However, the extractions of base metals were not sufficiently high because of the slow kinetics. The residue is still not environmentally safe.²⁹⁾

2 · 1 · 3 Physical beneficiation Barnes et al.¹⁴⁾ described an industrial flotation process for copper slag at Mount Isa Mines Limited in Australia. The slag is ground prior to flotation. Using sodium s-butyl xanthate as a collector, methyl isobutyl carbinol as a frother, and hydroxyethylcellulose as a magnetite depressant, the process produces a concentrate grade of 42.54 mass% copper, with 82 % recovery from a slag of 3.7 mass% Cu. However, most of the cobalt is in the flotation tailings. Similar results were reported by Rao and Nayak³⁰⁾. In the flotation experiment, a converter slag (3.7 mass% copper, cooled in a refractory-lined pit) with potassium amyl xanthate as a collector and pine oil as a frother, at pH 8–9, gave a concentrate containing 44 mass% copper, with 96% recovery. Cobalt and nickel were also reported in the tailings.

Based on the mineral properties of copper slags, attempts were made by Han et al.⁶⁾ to explore the recovery of copper and iron using mineral beneficiation technology. As shown in Fig. 7, in the grinding and beneficiation stages, a copper recovery of 48.8% and a copper concentrate grade of 14.26 mass% were achieved; an iron concentrate grade of 54.76 mass% and iron recovery of 65.81% were also obtained.⁶⁾

Actually, copper slag flotation is the same as sulfide ore flotation. This means that only metallic copper and sulfide minerals can be floated effectively. Since the copper in slags is mainly in the form of oxides, and cobalt and nickel are usually

Fig.7 Flow diagram of mineral beneficiation of copper slag⁶⁾.

in the form of oxides (cobalt is homogeneously distributed), the flotation method is not effective for recovering cobalt, nickel, and copper oxides. The use of flotation in copper slag processing is therefore limited.

2 · 2 Iron recovery technology

2 · 2 · 1 Oxidation methods for magnetic separation

One of the methods of processing copper slags is based on oxidation followed by magnetic separation, yielding an iron-rich concentrate as the raw material for blast-furnace iron-smelting.

A copper slag generated from a copper smelter in China has been investigated by Liu et al.³¹⁾ for the recovery of iron. The iron content of this waste copper slag is generally higher than 40 mass%. The majority of the iron is present as fayalite (Fe_2SiO_4) and magnetite (Fe_3O_4), which are difficult to use directly. The fayalite iron can be changed to a magnetite phase by high-temperature molten oxidation of the copper slag. The copper slag melting point is 1200°C . An oxidizing atmosphere was formed by blasting oxidizing gases into the furnace hearth above 1200°C for oxidation of fayalite. Finally, the iron was recovered by magnetic separation. The grade of the iron concentrate was more than 61 mass%. This fully satisfies the requirements of raw materials for blast-furnace iron smelting. An oxidation temperature of 1350°C , a duration of 60 min, and injection of O_2 into the slag at 0.3 L/min for 7 min, gave an iron concentrate with 62.8 mass% iron and 79.3% recovery, after grinding of the oxidized sample to 0.074 mm for magnetic separation at a magnetic field intensity of 10000 A/m.³¹⁾

Cao et al.³²⁾ studied the precipitation of iron components in the copper slag from a copper smelter using a high-temperature oxidation method. The enrichment, precipitation, and growth of the iron components in the slag could be improved by prolonging the oxidation time and increasing the O_2 flow rate and the temperature. The optimal conditions were a temperature of 1380°C , an O_2 flow rate of 7 L/min, and an oxidation time of 6 min; the grain size increased from 20 to 80 mm, the volume fraction increased from 20 % to 50 %, and an iron concentrate with 54 mass% at a 90 % recovery rate was obtained by magnetic separation.³²⁾

2 · 2 · 2 Smelting reduction methods for magnetic separation The objective of reduction technology is to convert the metals in copper slags into desired forms, which can be separated from the slags. One method is molten reduction or roasting, in which metals in various forms in the slag are reduced to free metals. Then magnetic separation, flotation, or leaching is used for separation of the metals from the slag.

A granulated slag from Sterlite Industries India Limited was used to recover iron in a 50 kVA furnace. Iron recovery of 85 % was obtained from a charge of 10 kg of granulated copper slag mixed with 2.5 kg of lime and 600 g of graphite powder, smelted for 1 h using 45 kWh.³⁾

In order to recycle iron from copper slags with a total iron content of ≈ 40 mass%, a technique involving lignite-based direct reduction followed by magnetic separation has been investigated by Yang et al.⁸⁾ After analysis of the chemical composition and crystalline phase, based on the experimental mechanism, tests for studying the effects of different parameters on iron recovery were carried out. The results show that the optimum parameters are as follows: a mass ratio of copper slag/lignite/CaO of 100:30:10, a reduction temperature of 1250°C , a time of 50 min, and a particle size of 85 % of the roasted product of less than 43 mm; under these conditions, direct reduction gave iron powder with a total iron content of 92.05 mass% and an iron recovery rate of 81.01%. After reduction, the fayalite and magnetite in the copper slag were reduced to metallic iron. The metallic iron particles, whose sizes were mainly larger than 30 mm, were loosely supported on the surfaces of the slag particles. Monomer dissociation of metallic iron particles was therefore easily achieved by grinding, and then the dissociated metallic iron particles were recovered via magnetic separation.⁸⁾

Li et al.⁷⁾ studied the process of molten reduction iron-making from copper slag, based on the smelting reduction mechanism. The effects of slag basicity, holding temperature, holding time, and CaF_2 addition (mass ratio of CaF_2 to CaO) on the iron yield and sulfur and phosphorus removal efficiency from the molten iron were examined. In a N_2 atmosphere, an iron yield of 89.28 %, a sulfur content in the hot metal of 0.039 mass%, and a phosphorus content of 0.087 mass% were obtained under the following conditions: basicity 1.6, holding time 30 min at 1575°C , and $\text{CaF}_2/\text{CaO} = 0.1$. This study solved the problem of high sulfur contents in iron from smelting reduction.⁷⁾

3. Thermodynamic Considerations and Proposed Treatment Process

A review of studies of iron recovery from copper slag suggested that magnetic separation is one of the most effective methods. It is preferable to convert fayalite to magnetite rather than metallic iron because the reduction of iron oxides to metallic iron is an endothermic reaction. The oxidation of fayalite to magnetite, shown in eq. (2), has an energy cost advantage compared with reduction to metallic iron. Also, an additive flux such as CaO can react with SiO_2 to form a calcium silicate, which may promote the separation of SiO_2 from the formed magnetite phase, as shown in eq. (3).

Fig.8 Flow diagram of smelting reduction method⁸⁾. Fig.9 Potential diagram of Fe-Si-O system³³⁾.

Fig. 9 shows the potential diagram of Fe-Si-O for different temperatures and O₂ partial pressures. The figure was produced using the FactSage database³³⁾. In the figure, we can see a co-existence region of Fe₃O₄ and SiO₂, which means that the fayalite (Fe₂SiO₄) can thermodynamically separate into Fe₃O₄(s) and SiO₂(s), as shown in eq. (2). Fig. 10 shows the effect of CaO addition to the Fe-Si-O system³³⁾. The figure shows that addition of CaO increased the stable Fe₃O₄ region by the formation of calcium silicate (CaSiO₃) and calcium iron silicates (Ca₃Fe₂Si₃O₁₂, Ca₂FeSi₂O₇). These thermodynamic results suggest the possibility of phase separation of Fe₃O₄ from fayalite slag using an oxidation treatment.

In the use of iron resources from copper slags in steel-mills, copper is the main impurity in steel production. Chlorination of the copper in the slag is one candidate for copper removal from the slag. The chlorinated copper can be separated by vaporization or aqueous leaching. Fig. 11 shows the potential diagram of Cu-Ca-Si-Cl-O at 1073 K³³⁾. In the calculation, the activity of Cu₂O(s) was fixed at 10⁻³, which was roughly estimated from the FactSage database³³⁾, using the flash smelter slag composition shown in Table 2. We can see a co-existence region of CuCl, CaSiO₃, and SiO₂ in the figure. This means that CaCl₂, which is one of the most commonly used chlorination agents, can thermodynamically chlorinate the copper in the slag according to eq. (4).

We propose a new copper slag treatment flow consisting of magnetite formation by oxidation, copper removal by

Fig.10 Potential diagram of Fe-Ca-Si-O system³³⁾. Fig.11 Potential diagram of Cu-Ca-Si-O system at 1073 K³³⁾.

chlorination, and grinding and magnetic separation steps, as shown in Fig. 12. This treatment sequence might be realistic and relatively low-cost for future commercial scale-up. However, we must investigate the following topics before developing pilot-scale and commercial-scale processes.

1. Mechanisms of precipitation of magnetite phase in copper slag by oxidation
(Effects of fluxes such as CaO, O₂ partial pressure, temperature, and treatment time)
2. Mechanisms of chlorination of impurities in copper slags
(Effects of chlorination agents such as CaCl₂, O₂ partial pressure, temperature, and treatment time)
3. Optimization of grinding and magnetic separation for recovery of precipitated magnetite phase from copper slags
(Determination of high recovery conditions such as grinding and magnetic separation methods)

4. Conclusion

A review of studies of iron recovery from copper slags suggested that in order to recover iron effectively, fayalite should

Fig.12 Flow diagram of proposed process for copper slag treatment for iron recovery.

be converted to metallic iron or magnetite. One of the methods for processing copper slags is based on magnetite formation by oxidation, followed by magnetic separation, yielding an iron-rich concentrate as the raw material for blast-furnace iron-smelting. Another method is a reduction process that converts iron oxide into metallic iron in copper slags, which can be separated from the slag. Then magnetic separation, flotation, or leaching is used for separation of the metals from the slag.

During pyrometallurgical processing of non-ferrous metals, smelting residues such as smelter slag and flue gas dusts containing valuable metals and harmful substances are inevitably generated as secondary products. In order to reduce environmental loading and to recover valuable metals, such materials require appropriate treatment, with the aim of maximizing metal recovery and iron resource purity.

Thermodynamic considerations regarding the conversion of fayalite to a magnetic iron phase such as magnetite and

the chlorination of copper impurities using CaCl_2 were also discussed in this review. Based on the results of previous research and thermodynamic considerations, we proposed a copper slag treatment process for iron recovery and the removal of impurities such as copper.

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銅スラグのクリーニングと鉄源回収*

樊 湧 柴 田 悦 郎
飯 塚 淳 中 村 崇

銅マット熔錬で発生するスラグ中には鉄がファイヤライト (Fe_2SiO_4) の形態で含有されている。銅スラグは、その物理的特性により、コンクリート骨材やバラスト、研磨材等に利用されているが、日本のような先進国では需要が年々減少しつつある。また、最近では、高品位鉄鉱石は枯渇傾向にあることから、金属製錬残渣等のリサイクル原料からの鉄源回収の要求が高まっている。本総説では、乾式処理、湿式処理、物理分離等の技術を利用した銅スラグからの鉄源回収ならびにクリーニング技術に関して、海外の研究開発情報を中心に解説している。さらに著者らは、得られ

た情報を踏まえて、熱力学計算とともに、銅スラグからの鉄源回収と銅等の不純物除去プロセスフローの提案を行っている。

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1. 東北大学大学院 環境科学研究科
2. 正会員 東北大学 多元物質科学研究所 准教授
3. 正会員 東北大学 多元物質科学研究所 助教
4. 正会員 東北大学 多元物質科学研究所 教授
5. 北京科技大学

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