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授 与 学 位	博士（学術）
学 位 授 与 年 月 日	平成 28 年 3 月 25 日
学位授与の根拠法規	学位規則第 4 条第 1 項
研究科，専攻の名称	東北大学大学院環境科学研究科（博士課程）環境科学専攻
学 位 論 文 題 目	Recycling Technologies of Copper Smelter Slag for Iron Resource （銅製錬スラグの製鉄原料化に向けたリサイクル技術）
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博 士 論 文 要 約

1. Introduction

In recent years, the production of metal has increased and the quality of ore has degraded, and as a result, the amount of waste from the extraction process has increased. (Shen, H., et al., 2003). Huge quantities of slag, a waste solid product of pyrometallurgical operations by the metals industry are dumped continuously around the world while other methods for using them are limited. Heavy metals contained in the slag also posing a potential environmental threat to the human society. (Li, Y., et al., 2008). Considering the above situation, it become more and more severe to find a sustainable way to treating the industrial solid wastes. This research is focusing on copper slag, one of the main industrial solid waste and efforts to propose a new and a more sustainable way for recycling.

In this first chapter, an introduction of the present research was provided. Considering about the copper slag, this part of content will focus on the followings: (1). What is copper slag, and how it is produced. (2). The current situation of copper slag production and reuse. (3). A review of the current technologies considering the metal recycling and extraction from copper slag. (4). Summary and thinking.

From the review of current proposals and researches of metals extraction and recovery from copper slag, there are mainly four kinds of methods include mineral processing, hydrometallurgy, pyrometallurgy of reduction and pyrometallurgy of oxidation. All of them were conducted in the lab scale. Every method has its strong and weak points, so it is not easy to say which one is the best.

Mineral processing method is a traditional method dealing with mineral ores. In general, by using this method, copper slag is regarded as low grade copper or iron ore. Multiple stages of mineral process steps are required as illustrated in (Han, W., et al.,

2009)'s work. This might raise the cost and use vast amounts of water. Actually, only metallic copper and sulfide minerals can be floated effectively. Since the copper in slag is mainly in the form of oxides, the flotation method is not effective for recovering of them. The use of flotation in copper slag processing is therefore limited. Moreover, the iron in the copper slag is in the form of iron silicate, not in magnetite. So the magnetic separation for iron recovery is not effective as well. (Shen, H., et al., 2003)

Hydrometallurgy method has already been well developed, and there are various way in the treatment of copper slag, including leaching in sulfuric acid or ferric chloride, hydrochloric acid, ammonia, and cyanide (Prohibited due to environmental problems), to selectively extract metals such as cobalt, copper, and zinc from copper slag, with the aim of maximizing metal recovery and iron concentration. In fact, iron was regarded as the contaminant in their process which virtually adding the cost burden. What's more, the chemicals used in the process is hardly say to be safe to the environment. In addition, after the hydrometallurgy processing, the iron is usually reside in the wastes such as as ferric hydroxide, which is very difficult to be disposed and reused.

Pyrometallurgy is good option due to the large treatment capacity and fast processing speed. There are two directions in treating of copper slag whose main component is fayalite (Fe_2SiO_4). One is reduction method by remelt the slag with coal to produce metallic iron for magnetic separation. However, this method required large energy and coal input. The cost will be high and carbon dioxide cannot be avoided. The other is oxidation method by blowing the oxidizing gas into the slag for magnetite precipitation for downstream magnetic separation. This method is free of coal input. However, the reheat of copper slag also require a lot of energy. As we know, in general, high operation temperature would contribute to a high speed pyrometallurgical reaction. So, in order to increase the reaction speed, high temperature will be required, which as a result, more energy input is needed.

Considering the above problems, we proposed a controlled molten oxidation method for the recovery of copper slag. The detailed information will be provided in the next chapter.

2. Proposal

Chapter 1 provided a review of studies of iron recovery from copper slag, and suggested that pyrometallurgy method followed by magnetic separation is one of the most effective methods and suitable for the future application. 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 and also use a lot of carbon as reductant. The oxidation of fayalite to magnetite has energy and cost advantages compared with reduction to metallic iron. Based on this information, our proposal of controlled molten oxidation will be described in detailed in this chapter. Moreover, thermodynamic consideration of our proposal will be provided.

Our proposal of molten oxidation process with crushing magnetic selection method which seems a more sustainable approach based on directly blowing oxidizing gas onto or into molten slag after smelting process.

In general, molten copper slag dumped out from the flash smelter is water quenched for a fast solidification. In our proposal, by transferring the molten slag to another container or furnace, a further processing will be performed at the molten state of copper slag. Through directly blowing an oxidizing gas onto or into the molten copper smelting slag, most nonmagnetic iron-containing components are designed to be transformed into magnetite, which has strong magnetism and large crystal size for the downstream magnetic separation. Importantly, because of this oxidation process is exothermic reaction, it required relevant less energy input to maintain the furnace operation. After the magnetite precipitation, the slag would permit the selective recovery of magnetite and non-magnetic slag constituents by magnetic separation for future reuse. The iron concentrate from magnetic separation has high iron grade would be suitable to steel mill for the iron and steel production. The solid residue, mainly silica, would be suitable for future use as flux for copper smelter or in the production of ceramic materials.

Through this proposal, copper slag was hypothesized to be fully used with as low cost as possible. Moreover, the molten oxidation process is the underlying processes and can be developed by additional operations. For example: an additive flux such as lime can react with silica to form a calcium silicate, which may promote the separation of silica from the formed magnetite phase.

Reduce, reuse and recycle (R3) are the three essential components of environmentally responsible behavior when we considering about a new process. R3 is sometimes called the waste hierarchy, the evaluation of processes that protect the environment alongside resource and energy consumption in the most advantageous actions. (Hansen, W., et al., 2002). Our proposal is based on R3 principle and carried out “an integrated approach” to solve the sever situation of copper slag.

REUSE - elements of the discarded item are used again.

Although iron in copper slag occupied nearly 40 mass%, research on iron recovery has rarely been reported. The main reason is that the iron is present as fayalite, not as magnetite or metallic iron. A further treatment is necessary for iron recovery from the slag. Our proposal of molten oxidation, through converting the fayalite into magnetite, can effectively separate the iron-bearing and non-iron-bearing slag constituents for specific purposes. Importantly, other valuable metals such as copper, zinc, and lead .etc would distribute for the future extraction.

REDUCE - to buy less and use less (energy or additives).

Our proposal of molten oxidation is hypothesized to be a more sustainable process by directly dealing with molten copper slag which saved the reheat energy. In addition, due to the exothermic reaction of oxidation, less energy input during the process is achieved. Moreover, the reducing carbon addition is free of charging compared with reduction method. Importantly, the injected oxidizing gas is cheap and easy obtained within the copper smelter factory.

RECYCLE - discards are separated into materials that may be incorporated into

new products.

The final product from our proposal is the iron-bearing constituents collected from magnetic separation are mainly magnetite which has high iron grade. This product could be use as iron concentrate which would be suitable to steel mill for the iron and steel production. Moreover, the solid residue, mainly silica, would be suitable for future use as flux for copper smelter or in the production of ceramic materials.

3. TTT & CCT Oxidation (Air)

In general, there are two cooling processes adopted into the slag treatment, one is an air-cooling process and the other is a water quenching process. However, this slag cooling processes does not utilize the sensible and the latent heat related to high temperature melt when the slags are exhausted. So for that reason, it is important to develop a slag treatment process that is able to produce the value-added slags by not only the effective utilization of the sensible and the latent heat but also the positive control of microstructure of slag. For this purpose, it emphasized the importance of TTT and CCT diagram. With them, the property of the final slag could be estimated by the designed cooling path. Furthermore, it could be possible or easier to recover the sensible and the latent heat through a given cooling path. (Kashiwaya, Y., et al., 2007). In the present chapter, using an infrared furnace, crystallization behavior concerned with TTT and CCT of copper smelter slag were measured and clarified by all kinds of experimental analysis.

Glassy iron silicate $[(\text{Fe}, \text{Ca}, \text{Al}, \text{Mg})_x\text{SiO}_y]$ was the main component of the water-granulated copper slag, and was the base and background of slag matrix in the SEM images. There were relevant amounts of matte suspension, and the precipitation of fayalite and magnetite may have resulted from the matte smelting process or water cooling. The magnetite content was 7.5 mass% in the original water-granulated slag analyzed using the chemical titration method. In addition, there is no hematite exist in the slag. Heavy and toxic metals are also present such as copper, zinc, lead, arsenic, and chromium etc.

The melting temperature of the copper slag used in the present study was about 1593 K. The isothermal transformation procedures were carried out at different incubation temperatures of 1493, 1393, 1193, 1093, and 993 K to study the crystallization behaviors. From the XRD analysis, it can be concluded that although fayalite and magnetite already existed in the original copper slag, their amounts changed with the holding time. In addition, after a certain holding time, hematite was precipitated. The apparent activation energy of magnetite precipitation from the oxidation of fayalite under the present experimental conditions is 15.5 kJ/mol. From the TTT diagram, it can be clearly understood that magnetite was precipitated before hematite under isothermal transformation. The initiation time of crystallization increased with decrease in holding temperature.

Under air isothermal transformation treatment, a short time of exposure to air did

not lead to a major change in the microstructure of the sample. With increase in the holding time, the nucleation of magnetite began and the quantity of magnetite increased with time. With the continuation of the heating, the magnetite nuclei increased in size and occupied the entire background. After an elongated time of heating, the nuclei continued to germinate and bonded together to yield large magnetite particles. Simultaneously, silica separated out of fayalite, which is seen as black dots. This phenomenon suggests that the fayalite in glass or crystal phase changed to magnetite by the reaction with oxygen. Moreover, there is transformation structure from magnetite to hematite appeared as small crosses. The TTT reaction mechanism is proposed. When the sample was in contact with air, oxygen can be expected to break the strongly bonded silicate anions. Hence, magnetite was precipitated first and silica separated out of fayalite. With the continuing oxidation, hematite was precipitated from magnetite. Heavy metals such as chromium, zinc, and arsenic were found to show a higher likelihood to exist in magnetite, while copper showed the reverse behavior. Silica, which was seen as small black dots, were usually attached to magnetite and showed a distinctive peak in counts per second (cps) of iron and silicon.

During the CCT treatment under the current experimental, magnetite is directly precipitated from the remelted copper slag instantly contacting with air. Concerned about hematite, it takes relevant short time for an appearance of peaks in the XRD patterns. Moreover, the hematite peak intensity is increase along with the increase of time duration of oxygen by air. There is no magnetite CCT curve because of the instant growth of magnetite in the copper slag when contacting with air, while a hematite CCT curve does exist. However, due to the very short time of the hematite XRD peak appearances under air atmosphere, the hematite CCT curve will be very close to the original melting point at tens of seconds in scales. What could be confirmed is the precipitation of hematite is behind the magnetite after tens of seconds of exposure to air.

4. Molten Oxidation

In the present study, the simulation of our proposal, i.e., directly blowing oxidizing gas onto molten slag for magnetite precipitation, was implemented using an infrared furnace. The crystallization behaviors were studied, with the variation of the magnetite and hematite content during molten oxidation showing a trade-off relationship. It was concluded that a lower oxygen partial pressure was beneficial to the precipitation of magnetite. In particular, the use of 1 vol% oxygen resulted in a selective oxidation tendency for magnetite precipitation. Moreover, the crystal morphology of the iron oxides and the distribution of impurities were investigated. It was observed that chromium and zinc exhibited likelihood to be tracked with iron, which emigrated and transformed into precipitated iron oxide during molten oxidation, whereas copper exhibited the reverse behavior. In addition, an attempt was made to describe the reaction mechanism considering the molten oxidation processes based on

current knowledge. The ion diffusion, which is assumed to be the mobility of O^{2-} , was relatively weak in the early stage and was enhanced as the oxidation progressed. The gas diffusion was assumed to dominate the “controlling step” during the later stage of the reaction.

From the present study, it was found that selective precipitation of magnetite from copper slag could be realized by easily controlling the oxygen partial pressure, which set the foundation for the future high efficient magnetic separation of iron-bearing and non-iron-bearing slag constituents for specific purposes.

5. Magnetite Liberation & Magnetic Separation

Our proposal of controlled molten oxidation process which would contributed to the selective magnetite precipitation from copper smelter slag for iron recovery was implemented in the present study with mineral liberation via high-voltage (HV) electrical pulses and magnetic separation.

10 hours of molten oxidation at 1 vol% oxygen atmosphere would lead to approximately 40-50 mass% magnetite content in 100 g copper slag in which the magnetite particle size is larger than approximately 50 μm .

Through HV electrical pulses breakage, mineral liberation was performed to the magnetite precipitated copper slag. With the use of laser microscope and its corresponding image software, mineral distribution was complemented and depicted the 100 μm under sieve product has a large percentage of the liberated minerals.

Through 50 μm under sieve crushing product feeding to magnetic separation, iron grade in concentrate would reach to approximately 60 mass% with a recovery of approximately 60 % at magnetic field intensity of 100 mT. During this whole recycling process, chromium and zinc revealed to be more likely tracking with iron into the concentrate, while copper, arsenic, and lead signified reverse behaviors resided in the tailing.

6. Conclusions

In this chapter - conclusions, a summary of the present research work will be provided to review the scattered chapters as a whole. Feasibility analysis will be considered focusing on the future application. Of course, there are many problems raised due to the preliminary research of our innovative proposal. In this last discussion, the future research will be considered focusing on the problems and actual.

A summary of the present research work will be provided to review the all

chapters as a whole mainly focusing on the followings.

In the first chapter, a review of current proposals and researches of metals extraction and recovery from copper slag was provided. There are mainly four kinds of methods include mineral processing, hydrometallurgy, pyrometallurgy of reduction and pyrometallurgy of oxidation. Every method has its strong and weak points, so it is not easy to say which one is the best.

Considering the above information, we proposed a recycling process to directly oxidizing the molten state copper slag for magnetite precipitation in the second chapter. This proposal saves the reheat energy input and cost.

There are two cooling processes adopted into the slag treatment in the copper smelter, one is an air-cooling process and the other is a water quenching process. However, these slag cooling processes does not positively control of microstructure of slag which results the limitation in the downstream utilization. For this purpose, it emphasized the importance of TTT and CCT oxidation process of molten copper slag. With the study of them, the property of the final slag could be estimated by the designed cooling path. Furthermore, it could be possible or easier to recover the heat through a designed cooling path.

The TTT procedures were carried out at different incubation temperatures to study the crystallization behaviors. It can be concluded that although fayalite and magnetite already existed in the original copper slag, their amounts changed with the holding time. In addition, after a certain holding time, hematite was precipitated. From the TTT diagram, it can be clearly understood that magnetite was precipitated before hematite under isothermal transformation. The initiation time of crystallization increased with decrease in holding temperature. During the CCT treatment under the current experimental, magnetite is directly precipitated from the remelted copper slag instantly contacting with air. Concerned about hematite, it takes relevant short time at tens of seconds in scales for an appearance of peaks in the XRD patterns. Moreover, the hematite peak intensity is increase along with the increase of time duration of oxygen by air.

However, there are some obvious flaws when adopting the TTT and CCT to copper slag in air.

TTT process is actually not widely used because of its complex operations. Moreover, from the study, the initiation time of crystallization decreased with increase in holding temperature which suggesting that higher temperature provide strong reaction driving force for magnetite or hematite precipitation in copper slag. It would take relative longer time for the precipitation of all iron into magnetite or hematite by TTT process compared with molten oxidation. In addition, during the process, hematite was also precipitated. Well actually, the magnetite was preferred because of its intensive ferromagnetism and large crystal size. The hematite appearance would affect the downstream magnetic separation process.

CCT is more famous than TTT process. From the study, it suggested that magnetite is directly precipitated from the remelted copper slag instantly contacting with air, and the lower cooling rate providing more effective magnetite precipitation. However, even at the cooling rate of 1.4 K/s for very long time, it is not sufficient for

oxidizing all the iron in copper slag into magnetite or hematite. Moreover, same as TTT process, hematite was also precipitated.

From the above information, the controlled molten oxidation method comes naturally to us.

In the forth chapter, the simulation of our proposal, i.e., directly blowing oxidizing gas (pure oxygen, air, and 1 vol% oxygen) onto molten slag for magnetite precipitation was implemented. The crystallization behaviors were studied, with the variation of the magnetite and hematite content during molten oxidation showing a trade-off relationship.

It was concluded that a lower oxygen partial pressure was beneficial to the precipitation of magnetite. In particular, the use of 1 vol% oxygen resulted in a selective oxidation tendency for magnetite precipitation. From this study, it was found that selective precipitation of magnetite from copper slag could be realized by easily controlling the oxygen partial pressure, which set the foundation for the future high efficient magnetic separation of iron-bearing and non-iron-bearing slag constituents for specific purposes. The crystal morphology of the iron oxides and the distribution of impurities were also investigated. It was observed that chromium and zinc exhibited likelihood to be tracked with iron, which emigrated and transformed into precipitated iron oxide during molten oxidation, whereas copper exhibited the reverse behavior. An attempt was also made to describe the reaction mechanism considering the molten oxidation processes based on current knowledge. The ion diffusion, which is assumed to be the mobility of O^{2-} , was relatively weak in the early stage and was enhanced as the oxidation progressed. The gas diffusion was assumed to dominate the “controlling step” during the later stage of the reaction.

The above study was conducted on mill-gram scale experiments using an infrared furnace. Generally, the study on mineral liberation and separation require gram-scale slag sample due to the experimental operation. In the fifth chapter, gram scale slag sample was prepared by an electric furnace. Molten oxidation at 1 vol% oxygen atmosphere was performed for magnetite precipitation. The magnetite precipitated copper slag would be used for mineral liberation and separation. 10 hours of molten oxidation at 1 vol% oxygen atmosphere would lead to approximately 40-50 mass% magnetite content in 100 g copper slag in which the magnetite particle size is larger than approximately 50 μm .

A new specific mineral liberation technology - High-voltage (HV) electrical pulses was implemented for an attempt to the liberation of precipitated magnetite in copper slag, which capable of producing of the high percentage of the monomineral particles at disintegration of mineral aggregates. (Andres, U., 2010). With the use of laser microscope and its corresponding image software, mineral distribution was complemented and depicted the 100 μm under sieve product has a large percentage of the liberated minerals.

Through 50 μm under sieve crushing product feeding to magnetic separation, iron grade in concentrate would reach to approximately 60 mass% with a recovery of approximately 60 % at magnetic field intensity of 100 mT. There is a trade-off relationship between iron grade and the recovery rate. Higher magnetic intensity

would contribute to lower Fe grade in the concentrate, while the improving of recovery rate would result in lower Fe grade in the concentrate. During this whole recycling process, chromium and zinc revealed to be more likely tracking with iron into the concentrate, while copper, arsenic, and lead signified reverse behaviors resided in the tailing.

The total investment of our proposal is mainly a furnace system. The Outotec™ Ausmelt TSL furnace technology is a good option.

The Ausmelt TSL process employs a lance to inject fuel or gas into the furnace bath. This causes intense mixing, promoting rapid reaction within the bath. The process is suited to a wide range of metals and waste materials, and is also in wide commercial use. This furnace could be specifically designed to suit an individual application of processing including feeding, gas injection, and off-gas procedures. The below figure shows the simulation of actual production with Ausmelt TSL furnace. (Brochure of Outotec Ausmelt TSL Process, 2011)

Molten slag could be directly added into the furnace from the feed system. 1 vol% oxygen are injected into the furnace bath via a lance. This serves to oxidize the iron in the slag for magnetite precipitation. The huge current of gas leads to the stirring of the molten slag for a uniform reaction. The intense mixing promotes rapid reaction kinetics. The final magnetite precipitated copper slag could be removed with batch tapping or continuously via a weir.

The gas collection system of Ausmelt TSL furnace was shown in the below figure. 1 vol% oxygen could be easily achieved by mixing the air and nitrogen gas flowing into the lance. The off-gas collection could be achieved with the stationary vessel, port sealing and operation under suction enables efficient capture of the gases and dusts.

All of the above information enables our proposal to be realized and have advantage over other processes which is low energy and free carbon input.

Problems and Future researches:

1. Magnetite precipitation inadequacy and hematite appearance during CCT process.
2. Magnetite enlargement (size and speed) during molten oxidation or cooling.
3. Heavy metals reduce or recollection method.