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Recovery of metal values from copper slag and reuse of residual secondary slag

Prince Sarfo[a], Avimanyu Das[a], Gary Wyss[b], Courtney Young[a,*]

[a] Metallurgical and Materials Engineering, Montana Tech, Butte, MT 59701, United States
[b] Center for Advanced Mineral & Metallurgical Processing, Montana Tech, Butte, MT 59701, United States

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ABSTRACT

Resource and environmental factors have become major forces in mining and metallurgy sectors driving research for sustainability purposes. The concept of zero-waste processing has been gaining ground readily. The scant availability of high quality raw materials has forced the researchers to shift their focus to recycling while the exceedingly stringent environmental regulations have forced researchers to explore new frontiers of minimizing/eliminating waste generation. The present work is aimed at addressing both aspects by employing recycling to generate wealth from copper slag and producing utilizable materials at the same time thus restoring the ecosystem. Copper slag was characterized and processed. The pyrometallurgical processing prospects to generate utilizable materials were arrived at through rigorous thermodynamic analysis. Carbothermal reduction at elevated temperature (near 1440 °C) helped recover a majority of the metal values (e.g., Fe, Cu and Mo) into the iron-rich alloy product which can be a feed material for steel making. On the other hand, the non-metallic residue, the secondary slag, can be used in the glass and ceramic industries. Reduction time and temperature and carbon content were shown to be the most important process variables for the reaction which were optimized to identify the most favored operating regime that maximizes the metal recovery and simultaneously maximizes the hardness of the secondary slag and minimizes its density, the two major criteria for the secondary slag product to be utilizable. The flux addition level was shown to have relatively less impact on the process performance if these are maintained at an adequate level. The work established that the copper slag, a waste material, can be successfully processed to generate reusable products through pyrometallurgical processing.

1. Introduction

Waste management is one of the biggest challenges of the mining and processing industries and one such waste material is copper slag. Copper slag is generated from the pyrometallurgical production of copper. It is estimated that 2.2–3 tons of copper slags are generated per ton of copper produced and this waste is mostly managed near the smelter site (Fan et al., 2013; Gyurov et al., 2011; Das et al., 2010). Typically, copper slag contains about 1% Cu and 40% Fe with the balance being predominantly SiO_2 but also minor amounts of other elements (e.g., Zn, Mo, Pb and As). Availability of space for long-term managing of the copper slag is also a major concern to the industry.

To recover the valuables as well as address the space availability issue, many types of research with the aim of recycling and reusing these slags have been conducted in the past few decades including physical, hydrometallurgical, pyrometallurgical separations or their combination to treat these waste materials have been proposed and examined (Banza et al., 2002; Busolic et al., 2011). One of such methods employs crushing and oxidation followed by the application of physical processing technologies such as magnetic separation, eddy current separation and flotation, as well as leaching, thereby separating and recovering iron and other metal values from the copper slag (Kim et al., 2013). Also, because of the mechanical properties of the slags, they have been used as aggregates in road construction and concrete (Gbor et al., 2000; Mihailova and Mehandjiev, 2010; Gorai et al., 2003). Utilization of copper slag as binder in mine backfilling was studied by Peyronnard and Benzaazoua (2011) and Tariq and Yanful (2013). It was identified that drying and milling of the slag would be required for such application. Also, lime and gypsum may need to be added to enhance the binding property of the copper slag.

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* Corresponding author.
E-mail address: cyoung@mtech.edu (C. Young).

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Heo et al. (2016), proposed an aluminothermic smelting reduction process for simultaneous recovery of iron and removal of hazardous material from the copper slag. In this process, iron oxide in molten slag is reduced by solid aluminum to form elemental iron.

$$3(\mathrm{FeO}) + 2\mathrm{Al}(\mathrm{s}) = 3\mathrm{Fe}(\mathrm{l}) + \mathrm{Al_2O_3}(\mathrm{s}) \quad (1)$$

They observed that iron recovery was maximum at Al/FeO molar ratio of 0.53 at which nearly 60% iron could be recovered. Significant volatilization of the hazardous elements were noted while part of them were transferred to the iron ingot leaving the product slag much depleted in these elements. The authors indicated that the product slag could be used as cleaner functional material. Carbothermic reduction of copper slag was studied by Li et al. (2013). They used coke powder to reduce the iron oxide followed by grinding of the cooled reduction products and subjecting it to magnetic separation to recover the iron. The optimum conditions for the steps were identified and the authors concluded that 14 wt% coke powder would be optimum at which 86% iron could be recovered with a product grade of nearly 90% Fe. However, the work was focused on iron recovery and would involve cooling and milling of the product.

Recovery of copper from copper slag by physical beneficiation using froth flotation was studied by Sarrafi et al. (2004). They used mercaptobenzothiazole (MBT) collector to recover the copper from the ground copper slag and indicated that a slow-cooled slag would be more favorable for better copper recovery. Flotation of ground copper slag was also studied by Bruckard et al. (2004). According to them, using a two-stage flotation process, 80–87% Cu can be recovered from the copper slag. Using additives with ground copper slag, Guo et al. (2016) performed re-melting followed by flotation and magnetic separation to recover Cu and Fe. They indicated that a slow cooling of the molten product helped in enhancing metal recoveries. A slow cooling rate allows adequate diffusion and grain growth and ensures perfect crystalline formation of the solidified material which helps in the subsequent processing stages. On the other hand, a fast cooling rate generates amorphous fine grained structure which is detrimental to the physical separation methods. However, despite significant utilization, the amount of slag generated is far more than the amount that is being utilized currently.

This work was aimed at recovering the metal values from copper slag through a pyrometallurgical technique while simultaneously generating a secondary reusable slag. The authors present the experimental data obtained from laboratory experiments performed to recover the maximum amount of metal in the form of iron-rich alloy at high temperature with graphite as a reductant and some fluxes to adjust the slag properties with the goal of making a secondary slag with maximum hardness and minimum density which can be used in the glass and ceramic industries.

2. Theoretical background

Slags from a copper smelter can vary widely in terms of the composition which is strongly dependent on the ore quality and operating conditions of the smelter. Recovery of various metallic elements may be accomplished by similar process steps. The performance of these recovery processes will be dependent upon, apart from the process conditions, the exact composition of the slag. Carbothermic reduction of the metal-oxide phases in the presence of fluxes at high temperature has long been known as a useful technique for the recovery. In fact, slag cleaning has been in practice in many plants to recover valuable metals such as Co and Mo. Iron oxide and silicates are almost always important constituents of the copper slags. Therefore, the reduced metallic phase is usually rich in iron and is commonly referred to as iron-rich alloy. The iron-rich alloy (metal phase) will have other dissolved metallic elements depending upon the oxidized percentage of the initial slag prior to carbothermic reduction. Of course, silica does not get reduced and the silicate rich slag obtained from the carbothermic reduction process may have important applications in glass and ceramic industries. For simplicity purposes, this secondary slag is simply referred to as “secondary slag” in the present work. Thus, the carbothermic reduction process will lead to the generation of a metal-rich phase and a secondary slag phase apart from the gas phase which will escape the system. Fluxes such as CaO and $\mathrm{Al_2O_3}$ must be added to the system so that reduction efficiency is improved and favorable properties of the metal-rich and secondary slag phases are obtained.

The metal phase is likely to be saturated with C and the copper content will be dictated by the Fe-Cu phase equilibrium diagram as well as the carbon content. Of course, copper needs to be removed from the iron-rich alloy before it can be used. Since, this metal-rich phase (iron-rich alloy) is usually saturated with carbon, it is relatively easy to treat it with an aluminum sulfide-ferrous sulfide flux for the removal of copper (Cohen and Blander, 1996; Shimpo et al., 1997). Some abrasion-resistant cast irons are also known to contain significant amounts of copper. The zinc, if present in the starting slag, will be reduced to its metallic state but will also evaporate at the elevated working temperature. Mo will be recovered into the iron-rich alloy phase as determined by the binary phase diagrams. The metal phase composition will, in turn, determine the secondary slag phase composition and its properties. Two of the major properties for the secondary slag to be utilizable in glass and ceramic industries are that the hardness should be high enough and the density must be as low as possible.

Most slag systems are described using the ternary phase diagram of CaO-$\mathrm{SiO_2}$-$\mathrm{Al_2O_3}$ system (Levin and McMurdie, 1975) which is shown in Fig. 1. This figure shows the chemical composition of the original copper slag sample being investigated in the present work along with two different compositions; however, in this case, Glass I and II would refer to Secondary Slag I and II, respectively. The reason for choosing these compositions is that both have a reasonably low melting point which is less than 1300 °C. In addition, at these temperatures, the Si content of the iron-rich alloy will be somewhat higher as given by the Fe-Si binary phase diagram which will enhance the fluidity of the metal phase.

It may be noted that the starting copper slag will have significant S content in the form of sulfides part of which will invariably remain in the metal phase as inclusions. The basicity of the Secondary Slag I phase in the region is relatively low. This is likely to lead to a low degree of desulphurization and the refractory lining will also remain vulnerable to corrosion. The relationship can be seen from Young’s model (Young et al., 1992) which correlates the degree of desulfurization (C_s) with the Optical Basicity (B) for $B < 0.8$ at a temperature T (K):

$$\begin{aligned}\log \mathrm{Cs} = &-13.913 + 42.84\mathrm{B} - 23.82\mathrm{B}^2 - 11710/\mathrm{T}\\ &- 0.02223(\%\mathrm{SiO2}) - 0.02275(\%\mathrm{Al2O3}) \quad (2)\end{aligned}$$

Evidently, the lower the basicity the lower will be the desulfurization. Also, a lower basicity signifies an acidic nature of the slag which would facilitate corrosion of the basic refractory lining.

On the other hand, Secondary Slag II will have a much higher basicity and might be favorable for the removal of impurities from the iron-rich alloy. Also, a higher alumina content is likely to lead to a higher strength of the secondary slag.

A study of the phase diagrams of Cu-Fe-C-Si-Mo-As systems and the CaO-$\mathrm{SiO_2}$-$\mathrm{Al_2O_3}$ ternary phase diagram using a typical slag composition reveal that variation in temperature change the Cu content in Fe-Cu-C system (Moffatt, 1987; Burgo, 1999; Turchanin et al., 2001). It indicates that ~10% copper can be

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