Carbothermal reduction of copper smelter slag for recycling into pig iron and glass

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ABSTRACT

Slags produced from copper smelting are siliceous and often contain valuable metals such as copper and iron as well as deleterious elements such as arsenic and lead. A copper slag was obtained from the former Anaconda smelter site, USA and characterized by SEM-EDS, XRD, TG-DTA and ICP-OES. A recovery process was developed to separate the valuables from the silicates thereby producing value-added products and simultaneously reducing environmental concerns. Results show that the major phase was an amorphous iron-calcium-aluminosilicate of variable composition with copper sulfide prills. Thermodynamic calculations and carbothermal reduction experiments indicate that most of the copper and iron can be recovered as pig iron from the initial slag using minor amounts of lime and alumina and treating at 1350 °C/1623 K or higher for 30–90 min. The resulting secondary slag can also be recycled as a glass to the glass and ceramic industry. Statistically designed experiments were conducted on the slag to identify the most favored regime to optimize the recovery of pig iron as well as the hardness and density of the secondary slag.

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1. Introduction

Pyrometallurgical treatment of metalliferous ores leaves behind the undesirable but unavoidable slag phase following the recovery of metal values. With environmental constraints becoming more and more stringent and availability of space for storing the slag becoming increasingly difficult to find, the metallurgical and mining industry is faced with a steep challenge of recycling the slag. It is also of importance that the slag contains some recoverable metal values and innovative processing of the slag may lead to some of its utilization. If the processing can be performed to recover some of the metal values and complete utilization of the remainder after recovery, it is likely to be very useful to the metallurgical industry. Not only will this remove the slag and generate valuable products, it can return the affected site to its previous natural state and thereby help sustain the industry even more. The present work was undertaken with a view to the above.

Increased demand of copper in the last few decades resulted in the generation of a large amount of smelter slag. About 80% of the world's copper to date was produced from sulfide ores by concentrating followed by the pyrometallurgical operations such as smelting and refining (Heimlich et al., 2010; Fan et al., 2014).

While slag from blast furnace in iron making has found extensive utilization in cement industries, the utilization of the smelter slag from the copper industry has not been explored in depth. Various researchers (Peyronnard and Benzaazoua, 2011; Tariq and Yanful, 2013) studied the utilization potential of copper smelter slag in low strength binder application in mine backfilling. They identified the phases that are responsible for binding strength generation in view of their high iron and aluminum content. However, they require large amount of lime addition to compensate for their low calcium content. Also, copper smelter slags lay in the higher end of the energy requirement spectra among many other industrial byproducts studied in view of the drying and milling treatment needed for processing the copper slag (Peyronnard and Benzaazoua, 2011). While blast furnace slag was found to possess excellent cementitious property, the base metal slags were reported to have limited binding properties (Tariq and Yanful, 2013). Lime and gypsum both may be added to the copper smelter slag to enhance its pozzolanic property for use as a binder in mine backfilling.

Smelting of copper ore implies oxidizing the sulfide and iron content within. Copper can be lost to the slag as sulfide if oxidation is incomplete or as oxide or silicate if oxidation is excessive. To reduce the copper loss, smelting usually involves controlled oxidation to prevent all of the iron sulfide from getting oxidized. A silica bearing flux is added to aid the formation of the slag. Thus, a

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mixture of copper sulfide and iron sulfide, known as matte, and oxide-silicate slag result (Gyurov et al., 2010). The matte is further oxidized in a separate step known as converting in which the sulfide matte is converted to blister copper and an oxide slag. Smelting is performed commonly using one of the four relevant technologies: reverberatory furnace, electric arc furnace, flash smelting and Noranda Process. Roasting, smelting and converting are completed in a single furnace in the Noranda Process. The bath smelting in reverbaratory furnace involves oxidation of the molten bath. This technology is obsolete today. On the other hand, flash melting technology involves oxidation of the airborne particles in the molten state using pure oxygen or oxygen enrichment. Clearly, the nature and composition of the slag generated in each of these processes will be different. The SO_2 content of the reverb flue gas is much less and copper losses to the slag is low. On the other hand, the copper losses in flash melting is high and the SO_2 content of the flue gas is also high so that the recovery of the sulfur in the acid plant is more efficient.

It is estimated that 2.2–3 tons of smelter slag is generated per ton of copper produced (Das et al., 2010; Gonzalez et al., 2005). These molten copper slags are managed near the smelter site. It is usually allowed to cool slowly under air forming a dense, hard crystalline product. However, sometimes it is quenched with water resulting in a glassy, granulated, amorphous material. Copper smelter slag typically contains about 1% copper and 40% iron depending upon the initial ore quality and the furnace type. Significant amounts of silica and minor amounts of other elements (e.g., zinc, molybdenum, lead and arsenic) are also associated with this slag. Some of these minor elements can be deleterious to the environment. The copper content of the flash smelter slag is usually higher than that of the reverb furnace. Oxidizing conditions are maintained in the smelter. Therefore, most of the species are likely to be in the oxide form. However, due to incomplete mass transport at the matte/slag interface, some sulfides may also be present in the slag phase. Some of these may be associated with the silicate phase or may form an independent phase. All the phases in the slag are chemically stable. Thus, the copper slag does have significant valuable content which can be recovered by recycling the slag, hence mitigating its negative impact by producing economic benefits and returning the affected site to its near-natural setting after the slag is removed.

Physical separation of copper from copper smelter slag through froth flotation has been studied extensively (Sarrafi et al., 2004; Bruckard et al., 2004; Guo et al., 2016). Sarrafi et al. (2004) found that 72% copper recovery could be achieved using mercaptobenzothiazole (MBT) as collector from a reverbaratory smelter slag containing a total copper of 1.15%. They also concluded that slow cooling of the slag leads to better recovery (up to 85%) of copper using flotation. Bruckard et al. (2004) studied the flotation of copper from various copper slags generated in a pilot plant smelter. The copper content in the slags varied from 5.2% to 15.1% and the nature of the slags also varied from very oxidized to very reduced. Metallic copper was the dominant copper form in the slags. About 80–87% recovery of copper values were reported by them from most of the slags using a rougher-scavenger circuit. Significant amount of iron exists in the fayalite form but cannot be recovered by magnetic separation of the flotation tailings. Guo et al. (2016) modified the crystal phases and grain growth by using additives with the ground slag, re-melting and slow cooling of the molten slag. Through a combination of flotation and magnetic separation, subsequent copper and iron recoveries were 72% and nearly 64%, respectively. Undoubtedly, physical separations remain a feasible route of valuable recovery; however, they require cooling of the molten slag which leads to a loss of the heat value contained in the molten slag. Milling costs for comminution are also added in this case. Moreover, the concentrates need to be processed again at

high temperature for refining. On the other hand, processing in the molten condition to recover the valuables is more energy efficient.

Metal recovery from the initial copper slag in this study was done at a high temperature with carbon (graphite) as a reducing agent and some fluxes (alumina and lime) to adjust the secondary slag properties. Based on their thermodynamic stability, the resulting carbothermal reduction is able to produce a copper-bearing, iron-rich alloy as a pig iron as well as a usable secondary slag (glass).

The carbothermic reduction, being a high temperature process, will be able to utilize the heat content in the slag. The temperature may have to be raised in some cases (flash smelter slag) and minor variations in the carbothermal process parameters may have to be incorporated. But the basic principle of iron and secondary recovery will remain the same in all cases and the recovery of pig iron and secondary slag can be carried out in much the same way as discussed in the present paper. When utilizing legacy slags, the temperature of the raw materials will have to be raised from ambient temperature to the reduction temperature which will involve energy input. However, the slags of an operating plant can be treated in a downstream process where the heat content of the slag will be fully utilized. In the latter case, costs will be minimal involving the procurement of fluxes and raising their temperature as well. Of course, the energy expenses in maintaining the slag at reduction temperature in another furnace will remain.

2. Thermodynamic considerations

The work was initiated with thermodynamic calculations of chemical reactions involving an in-depth study of binary phase diagrams of Cu-Fe-C-Si-Mo-As systems and the CaO-SiO_2-Al_2O_3 ternary phase diagram using a typical slag composition. It was noted that many of the metallic elements in the initial slag can be recovered by carbothermal reduction of the silicate oxide and sulfide-rich slag using some fluxes at elevated temperature. A generic equation for the reduction may be stated as follows:

Copper slag + Carbon + Fluxes = Pig iron + Secondary Slag + Gas
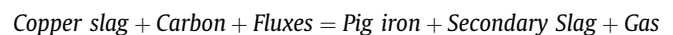
Fluxes such as CaO, Al_2O_3 and Na_2O are required to be added to the system in order to improve the recovery of metal as well as create the conditions to obtain the desired properties of the metal and secondary slag phases. In the reduction process, the oxides (and sulfides) of iron and copper would be reduced to form pig iron. Some of the other oxides would also be reduced and dissolved into the pig iron along with small amounts of silica while other oxides would remain as such and will report to the slag phase. Carbon is typically saturated in the molten iron-based alloy, while zinc and lead oxides in initial slag would be mostly vaporized. If desired, the copper can be recovered before or after making the pig iron by treatment with aluminum sulfide-ferrous sulfide flux and thereby producing a copper matte phase (Cohen and Blander, 1996; Shimpo et al., 1997). However, this aspect was not explored in this study but, rather, is reserved for a future study.

Fig. 1 shows that the phase diagram of Fe-Cu as well as copper content variation with temperature in Fe-Cu-C system. It indicates that ~10% copper can be dissolved in the γ-iron phase at 1300 °C/1573 K (Fig. 1a). Solubility of copper increases with lower carbon content and increasing temperature (Fig. 1b). Since it is inevitable that much of the copper present in the original slag will be reporting to the pig iron, the solubility of copper in iron along with the influence of carbon content of the pig iron becomes significant. Because the pig iron will be saturated with carbon, it will be easy to remove the copper by sulfide treatment as indicated above. Silicon and molten iron at high temperature are miscible but silicon can decrease the solubility of carbon in molten iron (Gyurov