NEW RESOURCES: STUDIES ON SLAG REPROCESSING AND UTILISATION IN CHILE

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Introduction

Currently, a large family of slags is produced in industrial processes, and it can be classified according to their physicochemical properties in three different groups: non-ferrous slag, ferrous slag and incineration slag. The most important, in terms of production, are copper and ferrous slags, and a large amount of them is produced and dumped worldwide every year. However, copper slags contain valuable metals susceptible to be reprocessed for recovering Fe, Cu and Mo. Also, iron and steel making slags can be reutilised in the construction industry, agriculture and regeneration of anaerobic water lake. Therefore, this paper summarises the application of slags, and discusses methods for metals recovery, including hydrometallurgical and pyrometallurgical processes, and reutilisation of steel slags.

Copper slags

Copper in Chile is produced by processing sulphide concentrate in seven smelters, and 4.5 million tons of slags are generated every year. A portion of these slags has been used in asphalt stabilisation for filling roads, manufacture of mineral wool for insulation, refractory materials and abrasive for jet cleaning of metal surfaces.[1]

The molten slags are either dumped near the smelter site or granulated under a water jet. In the first case, slow cooling yields a dense and hard crystalline product, and a glassy and amorphous material in the second case. However, for rapid cooled slags, valuable metals cannot be recovered by traditional methods.[2]

The main components in the copper slags are Fe and SiO_2, and the slag also contains a considerable amount of Cu. Depending on their origins, some slags contain Mo at attractive levels for recovering and utilisation. The composition and mineralogical characterisation of a typical copper slag is shown in Table 1.

Table 1: Characterisation of a typical smelting copper slag[1]

Compound	Cu_2O	Cu_2S	FeS	FeO	Fe_3O_4	SiO_2	Al_2O_3	CaO
wt%	0.76	2.00	1.17	40.61	12.38	33.00	2.12	0.69
Element	Cu	Fe	S	Si	Al	Ca	Mo	As [mg/kg]
wt%	2.27	41.3	0.83	15.4	1.60	0.49	0.3	74

The iron in copper slag shows content between 30 and 45%, higher grade than an ordinary iron ore. Therefore, copper slag is an attractive option as new iron resource, and several methods have been proposed for recovering iron from copper slag.[3-5]

Thermodynamic considerations

The stability of components in the Fe-Si-O, Cu-O and Mo-O systems are shown as function of the oxygen potential and temperature in Figure 1. The operating conditions of copper converting and slag cleaning processes are also represented in the stability area.

The slag making oxides, SiO_2, Al_2O_3 and CaO, are stable up to 1650°C, therefore, at lower temperature, the direct reduction and separation of valuable metals such as iron, copper and molybdenum can be done by carbon, in solid or liquid states, in a wide temperature range as shown in Figure 1.

Carbonaceous materials are conventionally used as reducing agents for bath smelting processes, and the overall reduction reaction of waste copper slag by carbon can be illustrated simply by the following equation:

Copper slag + Carbon + Fluxes = Fe-rich alloy + Cu-rich alloy + Slag + Gas (1)

Although the bath smelting process for reducing copper slags consumes a higher energy than other methods[6], it produces an iron rich alloy, recovering valuable metals dissolved in the alloy, and a secondary slag suitable for the ceramic or cement industries.

When Mo oxide is present, it is also reduced and dissolved into the Fe-C alloy along with copper and small amounts of silicon. However, silicon needs to be kept in a low activity, because it decreases the carbon solubility in molten iron, and in order to maintain the lowest possible copper content, it is necessary to increase the carbon content in molten iron.

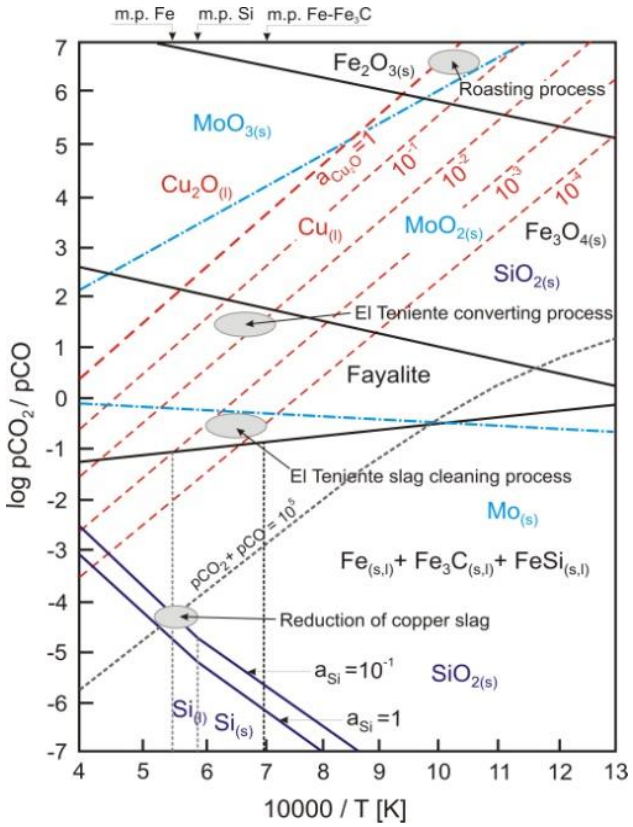

Figure 1: Stability diagram for the Fe-Si-O, Cu-O and Mo-O systems including the copper converting, slag cleaning processes and oxidation roasting and reduction condition

The molybdenum contained in the slag is associated to iron oxides such as the $2FeO{\cdot}MoO_2$-Fe_3O_4 spinel series. Thus, by roasting in oxidative processes at 700-750°C as shown in Figure 1, the molybdenum bound in the iron oxide spinel could be liberated in the soluble form of molybdenum trioxide, as follows

$$Fe_xO_y{\cdot}MoO_2 + (0.75x-0.5y+0.5)O_2 = 0.5xFe_2O_3 + MoO_3 \quad (2)$$

Therefore, molybdenum can be recovered by selective leaching from the iron oxides and silica.

Steel slag

Steel plants produce slags in larger quantities than the non-ferrous industry, but they are consumed as supplementary cement kiln feed, and accumulation does not appear to be a concern. However, some studies have been conducted on controlling eutrophication in enclosed water bodies as well as for water pollution treatment.[7,8]

Electric furnace slag was used for environmental remediation in a lake impacted by the aquaculture activity in southern Chile. The study was conducted *in-situ* by

RioClaro Ltd. Project Group.[9] In a twelve months run, 48 ton of EAF slags were distributed in nine stations to control the parameters for preventing anaerobic conditions at the bottom of the lake. The main results were: removal of 89% of total accumulated organic materials (TOM), increasing dissolved oxygen (DO) from 8.96 to 12.1 mg/L, more than 100% of the required increasing of 2.5 mg/L from the base line, and remove accumulatively 115% and 135% of total phosphorus (TP) and total nitrogen (TN) respectively. These results are relative to the base line taken at the beginning of the experimental run and higher than 100% due to the reloaded of the organic materials in the lake during the raining season.

Final Remarks

Copper slags have a number of well-defined markets. However, they still have a potential for increasing industrial applications, such as, molybdenum recovery and provide a more environmentally acceptable by-product.

Steel slags have been used successfully in engineering applications focused on water pollution treatment and remediation of organically-enriched sediments suppressing nutrient fluxes in enclosed water bodies.

Adding value to the slags is important not only in an economical point of view for saving metal resources, but also for protecting the environment and contributing for a circular economy settlement.

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