Physicochemical characterization of copper slag and alternatives of friendly environmental management

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Abstract: Copper slags are usually considered a waste and characterized only by the final copper content. Large and increasing quantities are being produced and disposed of by stockpiling near the metallurgical plants. This paper stresses the importance of physico-chemical characterization when considering uses for slags and the possibility of recovering the valuable metals still remaining in this phase. The purpose of this work is to support and encourage a change in the classical perception of slag from a 'waste' to a 'resource'; promote the development of new technologies for treatment to recover residual values and encourage a search for new uses; with the ultimate objective of eliminating slag stockpiles thereby diminishing the environmental impact of smelting operations. Some of the results of experimental laboratory work done by the authors and examples of commercial applications will be shown. A promising future for valorization and utilization of slags is expected and will provide an example when considering the use of all the other large quantities of wastes generated by the mining industry.

Keywords: Copper smelting, residual metal recovery, stockpile elimination, by-product recovery.

1. Introduction

Ferrous and non ferrous slags have been the subject of research for some time seeking uses in a wide spectrum of possible applications [1]. Most of the copper produced in the world (80% - 90%) is coming from sulphide ores that require oxidation at high temperatures requiring pyrometallurgy treatment. However, pyrometallurgical processes produce large quantities of slag, and this constitutes one of the main by-products of the metal extraction industry [2]. The average composition of primary copper slag corresponds to 30–40 % iron, 35-40% silica, less than 10 % of alumina and calcium oxide and copper content is around 1%Cu, similar to the ore mined. Cleaning of the primary slag is often economically justified and techniques including slow cooling and flotation, or pyrometallurgical or hydrometallurgical process are economical and have been adopted. Additionally as the amount of slag stockpiled near the smelter increases and smelter throughput is increased the cost of transport and disposal tends to increase.

Recycling slags has been a success in the iron and steel industry, so, mining and metallurgical plants are looking to the slag as resource of new products and materials in order to optimise their economical and environmental balance. The frequent presence of minor amounts of zinc, molybdenum and noble metals such as gold and silver as well as residual copper after conventional slag cleaning offer a potential additional target for slag reprocessing. Extraction of these residual metals also has the attraction of making the iron silicate phase more acceptable in a range of present or potential commercial applications. Finally in some circumstances copper slags may be viewed as a source of iron and silica. Future shortages of minor metals is expected to encourage research for techniques to permit economic recovery of these residual values converting slag from a waste to a resource.

The quantity of slag generated by each ton of blister copper produced varies from one operation to another and depends on mineral composition of the concentrate treated and type of process used [3]. Chile has seven smelters dealing with copper concentrates pyrometallurgical processes:

Chuquicamata (CODELCO, in Calama),
Altonorte (Xstrata, in Antofagasta),
Potrerillos (CODELCO, in El Salvador),
Hernan Videla Lira (Enami, in Copiapo),
Chagres (Anglo American, in Catemu),
Ventanas (CODELCO, in Puchuncavı) and
Caletones (CODELCO, in Rancagua).

The average of slag production in Chile is 2.2 ton per ton of blister copper produced, but this figure could cover approximatly a range from 2 to 5 ton of slag/ton of blister copper in other smelters of the world.

Physico-chemical characterization plays an important role in understanding the behaviour of slags during smelting processes and hence it is important to have a comprehensive knowledge about its management. In this way, there are some systems that could be used as representative to follow different steps during smelting and converting, for both metal and oxide phases. In the case of copper minerals and sulfide concentrates, the quinary system Cu-Fe-S-O-SiO_2, shown in Figure 1, accomplishes quite well this purpose [4, 5].

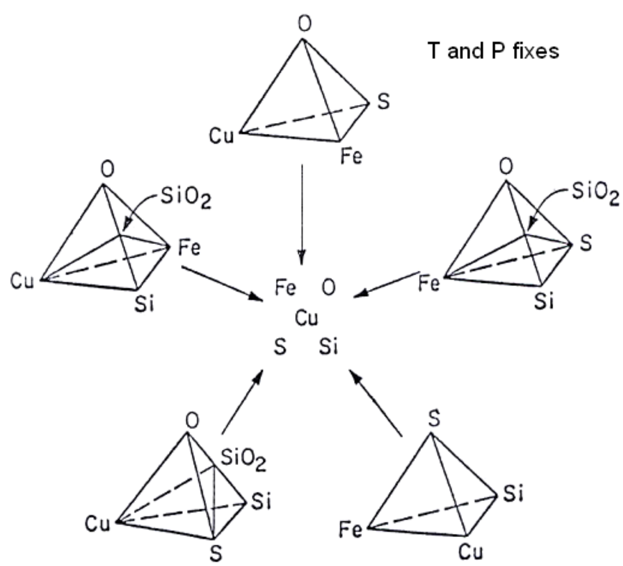


Fig. 1. Quinary system Cu-Fe-S-O-SiO_2, T and P fixes.

This system contains practically all phases existing during the pyrometallurgical processes to obtain copper, in the temperature range 1100-1350ºC and oxygen pressure in the range 10^{-16}-1 atm. Particularly it contains slag phases ocurred during smelting, converting and pyrorefining.

Traditionally slags have been considered as material for road construction and as abrasive media useful for cleaning metallic surfaces. However, the idea of this presentation is to discuss the possibility of extracting valuable materials, as metals and compounds, to increase economical value of the industrial operation and hence, increasing economical balance of the production plant [6, 7]. In this way, iron contained into slag, using an adequate treatment to separate it, could be used for the iron industry and steel fabrication. Silica could be used for ceramics and glass wool fabrication. Both materials constitute more than 50% of this phase, so the impact in diminishing the amount of this waste is very clear.

2. Markets and Commercialization

The marketing of slag is seen increasingly by industries employing smelting furnaces to produce metal as an integral part of the scope of operations to generate revenue rather than incurring the expense of impoundment of slag in a local stockpile or delivery to a waste disposal site. It is the case of the slags produced by the iron and steel, the copper and nickel sulphide, and the nickel laterite industries. Attention must be paid to the global quantities currently produced, the size of historical stockpiles, the preparation required, the quality standards, and the marketing challenges and opportunities. The benefit is emphasized of National and International Associations to interface with regulatory authorities, facilitate investigations, set and publicize standards [1].

Statistics on smelter slag production are not routinely published. Global statistics on metal production are more readily available from various publications including the US Geological Survey (USGS) statistical tables, International Study groups for the various non-ferrous metals and mining and similar trade associations. An estimate of annual production of iron and steel slag used the USGS factor while base metal and PGM smelter slag was developed from metal production statistics as shown in Table 1 [1].

Table 1. Estimates of Global Smelter Slag Tonnage

Smelter Type	Metal via Smelter kt	Recovery Factor %	Smelter Metal Input kt	Smelter Feed Grade %	Smelter Input kt	Factor Slag/Feed Wt Ratio	Slag Tonnage kt
Copper	12,000	95	12,600	27	47,000	0.8	37,000
Nickel	450	95	470	10	4,700	1	4,700
Fe-Ni	300	95	320	2	16,000	1	16,000
PGM	0.3	85	0.35	0.015	2,300	1	2,300
Iron*	860,000	-	-	-	860,000	0.3	260,000
Steel*	860,000	-	-	-	860,000	0.2	170,000
Cement							2,700,000

* Metal output

The main observations from Table 1 are that:

- The combined quantity of iron and steel slag produced is only about 15% of the tonnage of its principal present and prospective market in the cement industry.
- The combined quantity of non-ferrous slag is about 20% of the combined iron and steel production, smaller but still significant.

The approximate annual global production of major metals (2009/2010) is given in Table 2, with an estimate of the gross market value of this production and the corresponding estimated slag quantities. The global tonnage of cement production is provided for reference together with the corresponding value. The gross tonnage and value of global steel production are recorded but since steel slag originates predominantly from the refining of pig iron the net production and a value added figure is used for evaluation. Ferro-nickel and iron and steel are produced under strongly reducing conditions giving high recovery. Thus a discussion of slag cleaning is only relevant to sulphide smelters [8, 9]. Two cleaning techniques are in common use in sulphide smelters, electric furnace processing under reducing conditions and slow cooling and flotation. Metals recovered include copper, gold, nickel, cobalt and PGM's [10, 11].

Table 2. Smelting Industry Product Value and Slag Cleaning Targets

Industrial Sector	Metal Prod'n kt/y	Price $/t Metal	Metal Revenue Million $/y	Slag kt/y	Slag Cleaning Targets
Copper	12,000	10,000	120,000	37,000	Cu & Au
Nickel	450	20,000	9,000	4,700	Ni & Co
Ferro-nickel	300	20,000	6,000	16,000	-
PGM	0.3	$50,000,000	15,000	2,300	Ni-Cu PGM,Cr
Blast Fce Iron	860,000	500	430,000	260,000	-
Steel (via pig)	860,000	200 added	172,000	170,000	-
Notes:					
Steel*(Total)	1,100,000	700	770,000	-	-
Cement	2,700,000	100	270,000	2,700,000	-

*Includes scrap recycling and DRI

3. Non Ferrous slags

3.1 Physico chemical antecedents

Figure 2 explains the behaviour of the $FeO-Fe_2O_3-SiO_2$ ternary system, which best represents acid slag associated to copper extraction. It is possible to appreciate a liquid region inside these components, which is in fact the region of industrial operation to ensure easy management of oxide phases. This diagram is contained inside the quinary diagram shown in Figure 1 and permits following the changes in slag composition during oxidation at high temperatures [4, 5].

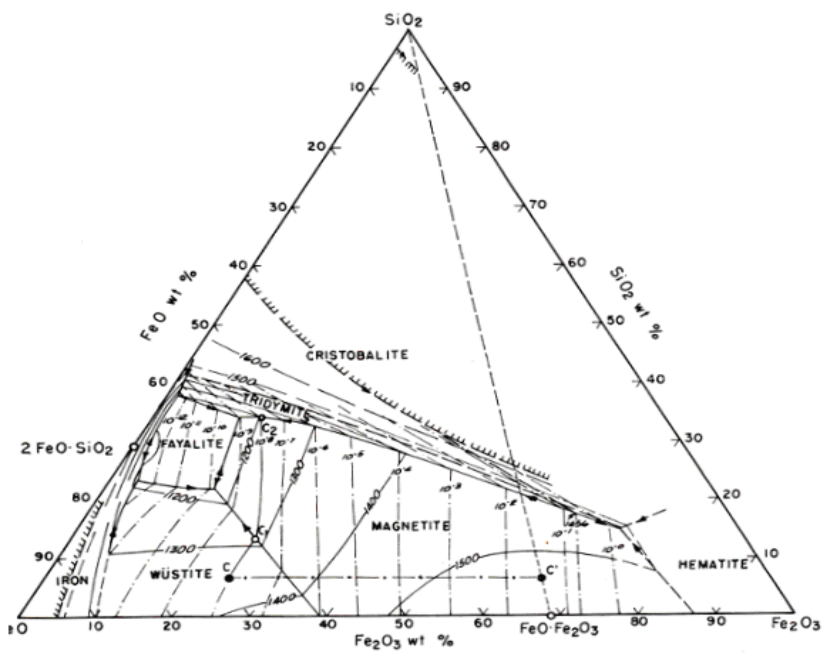


Figure 2. $FeO-Fe_2O_3-SiO_2$ ternary system.

In case of use of basic slag, in processes such as the Mitsubishi smelter, the liquid region is extended to the right side of the diagram, given the possibility to operate at higher oxygen pressures than using silica. This fact is shown in Figure 3 where both situations are presented, that is, FeO-Fe_2O_3-SiO_2 and FeO-Fe_2O_3-CaO phase diagrams, explaining how the use of CaO can improve use of higher oxidation levels during slag formation [12].

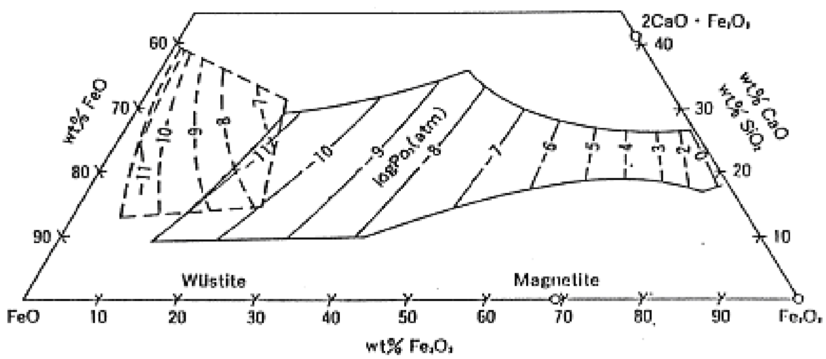


Figure 3. Isotherm at 1300 ºC and isobars of oxygen potentials for ternary systems $FeO–Fe_2O_3–SiO_2$ and $FeO–Fe_2O_3–CaO$.

The quaternary system $Cu–Fe–O–SiO_2$ is shown in Figure 4, and it is used to analyse the relevant phase relations when taking into account the physicochemical behaviour of the slags. Also, they are of great importance in copper production when using pyrometallurgical methods. This quaternary system is made up of six binary systems: Cu–Fe, Cu–O, Fe–O, $Cu–SiO_2$, $Fe–SiO_2$ and $O–SiO_2$, four ternary systems: Cu–Fe–O, $Cu–Fe–SiO_2$, $Fe–O–SiO_2$ and $Cu–O–SiO_2$, and the quaternary system itself. All of these systems have been extensively analysed [13, 14, 15, 16].

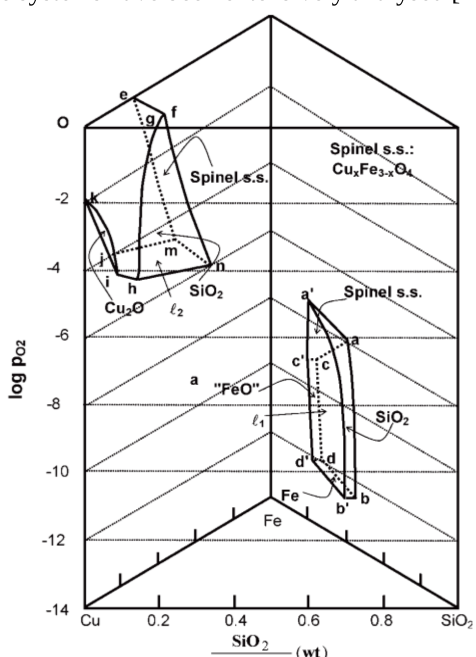


Figure 4. Stability diagrams of quaternary system $Cu–Fe–O–SiO_2$: stability areas at 1200ºC.

Copper and molybdenum are two metals found in present slags that offer the best potential for economic recovery. The copper analysis remaining after conventional slag cleaning can be close to 1% while molybdenum is sometime found in a range of 0.2 to 0.4%, depending on kind of mineral treated and technology used. These concentrations are higher in some cases than the analysis of the original ore and thus may warrant recovery by retreatment.

Figure 5 shows some important aspect related to recover of copper and molybdenum from a slag [17]. Selective recovery of copper metal requires an oxygen potential below 10^{-6} atm. In the case of copper, increasing of oxygen potential must ensure to obtain the metal at around 10^{-6} atm, but at this level, also iron will largely present as magnetite. Molybdenum metal recovery requires much more reducing conditions close to that for iron reduction to metal resulting in formation of a ferro- molybdenum phase. This alloy must be broken down before the molybdenum can be recovered as a separate phase [18].

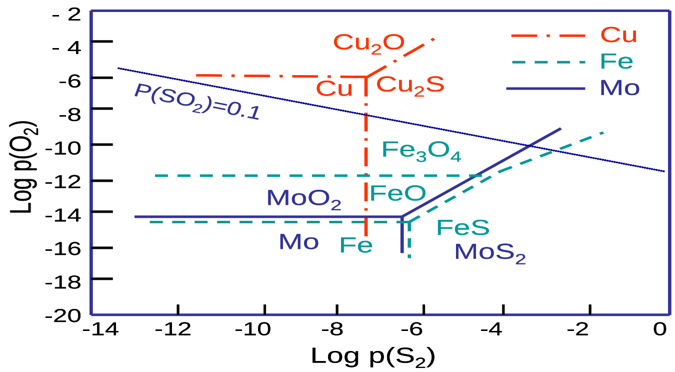
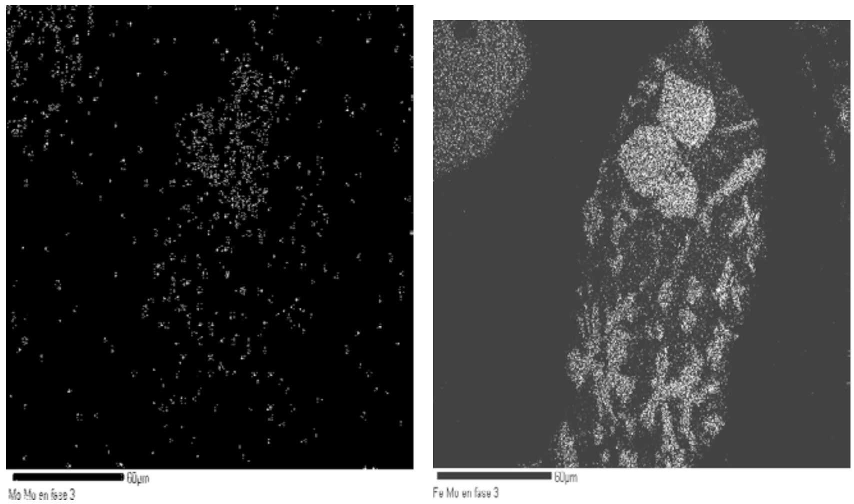


Figure 5. Stability diagram for copper and molybdenum in Cu-Mo-Fe system, 1300ºC.

Association between iron and molybdenum is shown in Figure 6 obtained by SEM analysis, so confirming previous statement. Note strong association between iron and molybdenum.



(a) (b)

Figure 6. SEM analysis for molybdenum (a) and iron (b) distribution in slags.

3.2 Recovery of metals/materials and Laboratory works

The opportunities to market slags are influenced by both composition and method of cooling. Electric furnace slag cleaning produces a molten product that can be cast or granulated depending on market demands. Molten slags in Europe have been cast into blocks for use a sea defences to take advantage of their high specific gravity and inertness. Granulated fayalite slags are widely used for abrasive cleaning of steel in ships and bridges. Granulated forsterite slags are used as mould sand in producing aluminium castings. Finely ground granulated slag has been found to have pozzolanic properties and has been used for consolidation of mine backfill. Slag cleaning also offers the opportunity to add additional fluxes following cleaning, such as lime and alumina, to modify final slag properties to enhance pozzolanic properties or permit production of slag wool [1, 19, 20].

In the case of copper slags, work have been done in order to understand how materials with an high value could be recovered, thereby increasing the economic value of the main metal production. In addition to recovering copper still remaining in the slag phase by flotation or pyrometallurgical cleaning, the attention has been paid to molybdenum and iron recovery [21, 22]

Figure 7 shows the different associations between copper, iron, silica and molybdenum into slag [21] and we can appreciate that, as established in Figure 6, molybdenum is quite associated to iron, and in some phases concentration of molybdenum is quite high depending on association with iron.

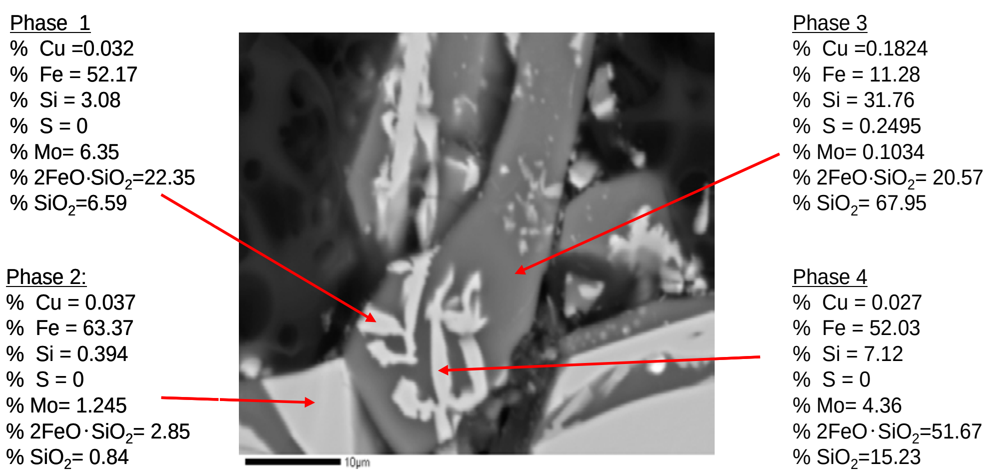


Figure 7. SEM characterization of a copper slag.

Figure 8 shows how extraction of molybdenum could be incresed when content of magnetite diminish in the slag phase, that is, when iron-molybdenum compounds are broken and, by this way, molybdenum will come liberated [21].

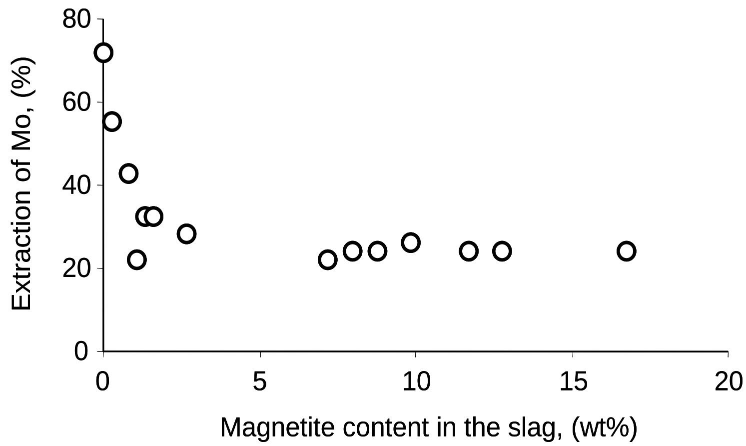


Figure 8. Extraction of molybdenum related to magnetite content.

Various experiments were undertaken aimed at recovering iron for direct use in the iron industry, or to obtain an iron-molybdenum alloy to be used in the steel industry. The results of direct reduction are shown in Figure 9 [21]. The copper content of the slag decreases rapidly while iron content remains almost constant during this period of time, indicating a selective reduction of copper giving a final slag containing 0.3% copper. Separate reduction of this clean slag would yield an iron product analyzing about 1% copper still too high for most uses of the iron.

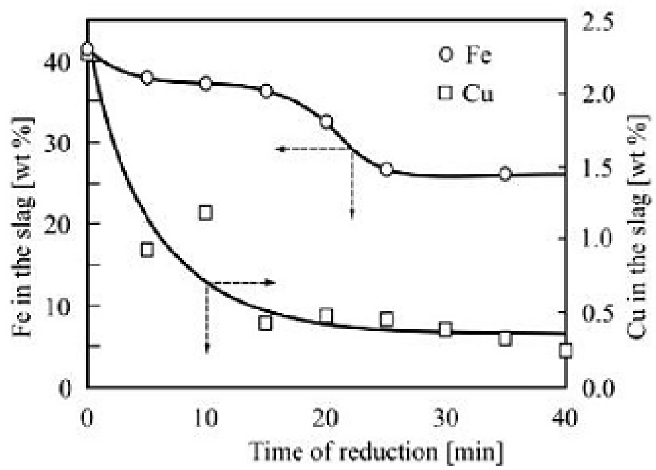


Figure 9. Concentration of copper and iron as function of time.

The needs for an efficient utilization for the iron industry is less than this figure. Further experience developed in two reduction stages allows to obtain copper content in the final slag about 0.24% and 0.84% in the final alloy. This was still not considered acceptable.

The alternative of producing an iron-molybdenum alloy from clean copper slag was studied with the first results shown in the Figure 10. Even when the alloy is obtained, the copper content is still high so it is not possible its directly utilization the iron-molybdenum alloy. Further research is required to obtain the desirable final content for being used in the steel industry.

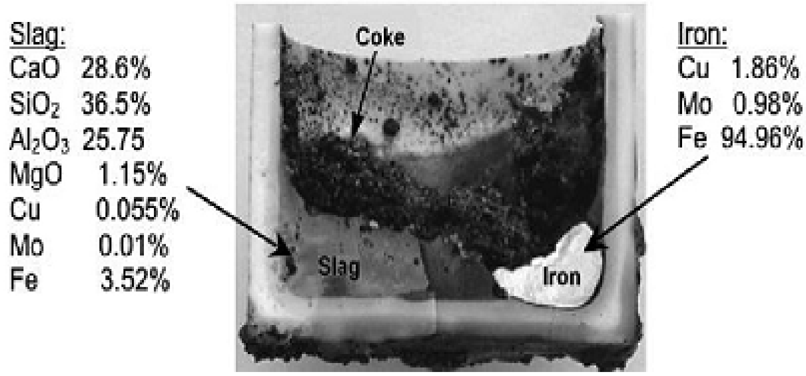


Figure 10. Slag and iron-rich alloy obtained at 1460ºC in an alumina crucible.

Figure 11 shows a flow sheet proposed for recovery valuable metals and materials from non ferrous copper slags, This flowsheet was developed from laboratory testwork to recover copper, molybdenum and iron from copper slag. Information about experiments and the results obtained could be gotten from the literature [17, 21, 22].

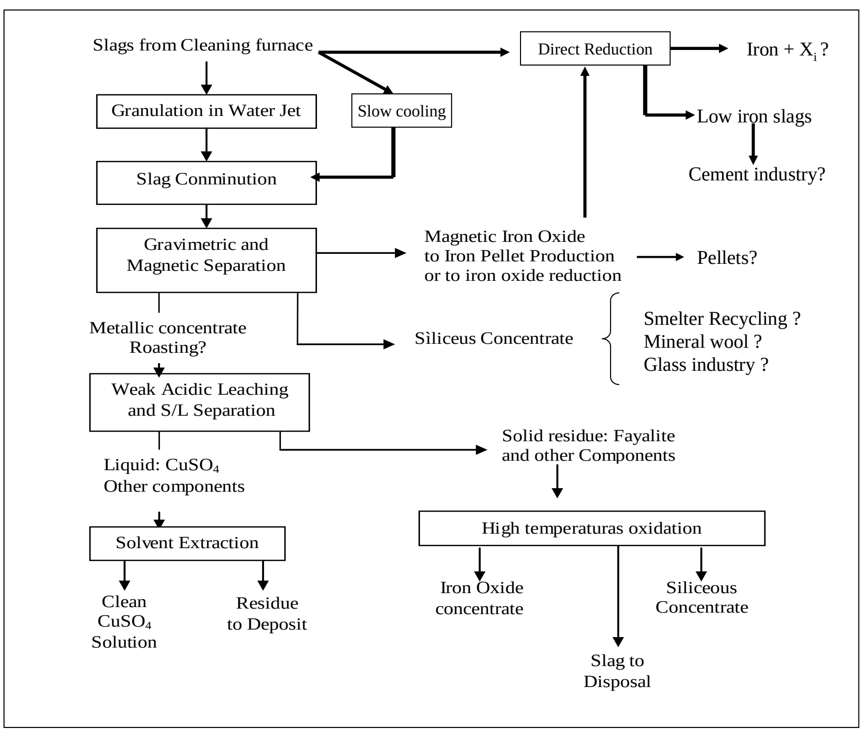


Figure 11. Flowsheet proposed for metal/material extraction from non ferrous slags.

4. Conclusions

An examination of the non-ferrous smelting industry suggests that there is merit in cleaning slags both for additional metal recovery and to provide a more attractive slag product for marketing. The quantity of non-ferrous slag produced annually is substantial and much of it is still stockpiled. The historical accumulations slags were estimated and the non-ferrous tonnage is also substantial. Iron and steel slags are produced in larger quantities than the non-ferrous industry but are increasing consumed by the cement industry as supplementary cement or cement kiln feed and accumulation does not appear to be a concern.

Iron and steel slags have good value added applications in the cement industry and accumulation does not appear a concern. Clean non-ferrous slags have a number of well defined markets but the revenue generation seldom justifies the freight cost from remote smelters and until larger and more profitable slag applications are developed stock-piling is expected to continue although increasing application of slag cleaning is providing a more environmentally acceptable product.

A concerted and cooperative effort to explore new slag applications by the industry is needed to fund and coordinate investigation of new slag applications. Investigation into ways to chemically activate the pozzolanic properties of granulated non-ferrous slags or adding fluxes to clean molten slag to enhance pozzolanic properties is an interesting approach since it provides a binder for backfill in nearby mines.

Iron and steel slags have an interesting history of successful cooperative development of uses. Non ferrous and particularly copper slags have at present limited uses and markets. Efforts to develop new uses to broaden markets is just beginning. The possibility of recovering minor metals from slags is also under investigation, specifically molybdenum for some copper slags and vanadium from selected steel slags. Both could prove a useful source of supplementary reveue for the main operation and in addition would make the bulk slag product more attractive by removing elements of environmental concern from the bulk slag product. The possibility of turning non-ferrous slag into a profitable commodity rather than incurring the expense of accumulating unsightly piles around smelters is an attractive prospect that deserves greater industry attention.

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