



KU LEUVEN

Proceedings of the
THIRD INTERNATIONAL

SLAG VALORISATION SYMPOSIUM

THE TRANSITION TO SUSTAINABLE MATERIALS MANAGEMENT

19-20 March 2013
Leuven, Belgium

Editors Annelies Malfliet, Peter Tom Jones, Koen Binnemans, Özlem Cizer, Jan Fransaer, Pengcheng Yan, Yiannis Pontikes, Muxing Guo, Bart Blanpain



REUTILISATION OF PRIMARY METALLURGICAL WASTES: COPPER SLAG AS A SOURCE OF COPPER, MOLYBDENUM, AND IRON – BRIEF REVIEW OF TEST WORK AND THE PROPOSED WAY FORWARD

Mario SANCHEZ¹, Michael SUDBURY²

¹ Universidad Andrés Bello, Santiago, Chile

² MPS Consulting, Oakville, Ontario, Canada

mario.sanchez@unab.cl, msudbury@cogeco.ca

Abstract

Metals have been produced for many millennia and in the process large quantities of waste materials were generated that have had undesirable environmental consequences. The copper industry as an example currently process ores containing less than 1% copper with discard of 99% of the weight of this material including overburden, tailings and slag from mining, flotation and smelting operations. The primary metal production industry has given much attention to the improved management of processes, use of water, control of emissions, industrial safety and hygiene and and energy efficiency. Solid waste use has received less attention. This paper reviews some of the preliminary work undertaken to explore techniques for recovering residual values (copper, molybdenum & cobalt) as well as separating and utilising the main components (iron and silica) from copper slag and further work proposed.

Introduction

Copper smelter slags have seen limited use mainly as bulk products for road construction and abrasive material for cleaning metallic surfaces¹. The work described in this paper is targeted at revenue generation by the recovery of residual base metals as well as the bulk components, iron and silica. The production of slag in the copper industry ranges from 2.0 to 5.5 ton of slag per tonne of copper produced. A proposal for work on this slag was contained in an earlier report². The initial idea was to follow the example of the iron making industry³ and to modify the composition of the slag to permit its use by the cement industry as illustrated in Figure 1. More recent work has focused primarily on oxidation of finely sized slag to form hematite thereby destroying the molybdenum spinel permitting leaching of the molybdenum.

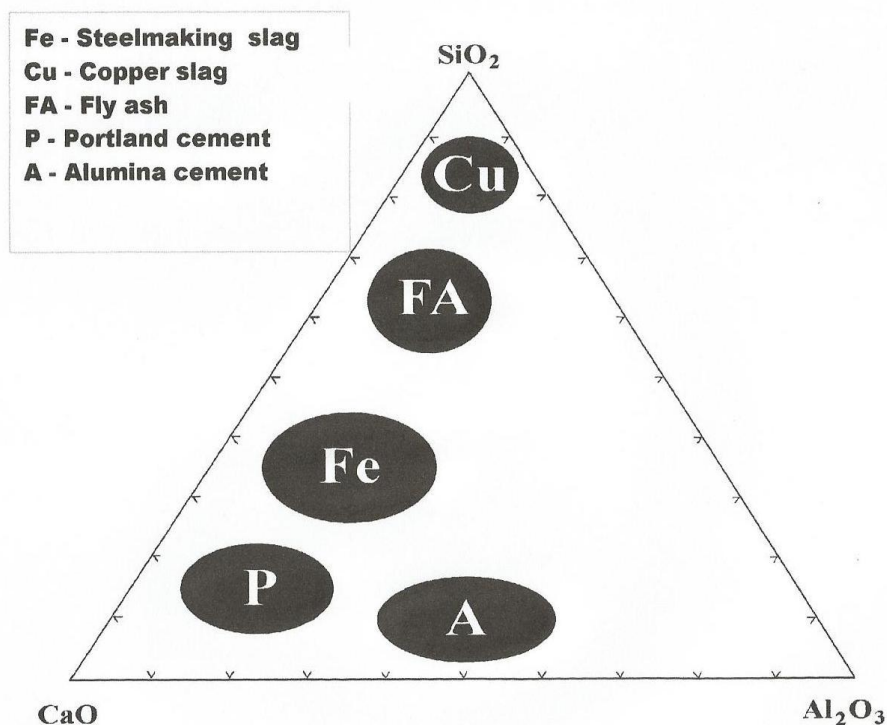


Figure 1: Comparison of Slag and Cement Composition

A more critical characterisation suggested other more interesting possibilities to increase the value of this by-product. Slag coming out of the smelter processes are currently characterised by elements of interest, particularly copper as the principal focus of recovery. Table 1 shows the content of copper, iron, molybdenum and silicon of an historically accumulated Chilean copper slag, quenched and slowly cooled⁴. Technologies used today are able to ensure a lower content of copper in the final slag (less than 0.6%), but iron and silicon existing, as iron oxides and silica, remain approximately the same. The molybdenum is high enough to make its recovery of interest.

Table 1: Composition of a Chilean Copper Smelter Slag

Slag Treatment	Composition (wt%)			
	Cu	Mo	Fe	Si
Quenched	0.9	0.3	41.2	14.0
Slowly cooled	1.1	0.3	43.4	14.4

An estimate of the gross value of base metals in ore and slag (Table 2) gives some indication of the economic incentive for reprocessing the present discard slag.

Table 2: Gross value of base metal content of typical Chilean smelter slag

Product	Copper (wt%)	Molybdenum (wt%)	Gross Value \$/tonne*
Cu-Mo ore	0.6	0.03	41
Cu-Mo Slag	0.6	0.3	90

*Gross Value = metal content x market price (Cu = \$6/kg; Mo = \$18/kg)

Additional potential production of bulk commodities from one tonne of fayalite slag containing 40% iron and 30% silica, after oxidation is 0.47 tonnes hematite and 0.30 tonnes silica. The value of these products would be dependent on the recovery and physical form (size shape and hardness) and chemical quality (purity) of material that results from commercial separation techniques. This is at present unknown pending pilot scale investigation of potential treatment schemes and market development.

Main Metals Recovery

Copper Recovery

Copper smelters are focused on copper recovery in Chile as elsewhere. Some experiences on recovery of products contained in slag have been developed in Chile as well as worldwide. Chilean smelters use pyrometallurgical techniques or slag flotation techniques to recover additional copper from slag⁵.

Slag cleaning by coal reduction

The Teniente Converter slag is transferred to a slag cleaning furnace (HLE), pulverised coal is injected and the slag temperature maintained with oxygen-fuel burners. The coal reduces the

content of magnetite in the bath, decreasing slag viscosity, and copper particles are released to form a rich copper matte (>70% Cu) which is returned to the Peirce Smith Converter⁶.

Slag cleaning in an electrical furnace

The current technology uses an AC electrical furnace with supplementary coke addition to heat and reduce the slag⁷. Copper is recovered by direct electrical reduction of magnetite, releasing the suspended inclusions while oxides are reduced by the graphite electrodes. Reduction of magnetite by carbon generates a gas film separating liquid slag from the coal. Magnetite and cuprous oxide are reduced by the carbon monoxide at the gas/slag interface while at the coal/gas interface the Boudouard reaction takes place. The gas generated produces bubbles that ascend and react with oxides in the slag phase forming a metallic phase that is treated in another furnace to obtain Blister Copper.

Slag flotation

This slag cleaning process requires slow cooling, crushing grinding and flotation of smelter slag with copper metal and sulphide particles reporting to the flotation concentrate. This process was widely used in the past by small miners because it is a very simple and effective way to recover copper. The slag flotation has become less important recently due to the decrease of copper content in final slag, a result of new optimisation methods in smelting processes. In Chile, the Xstrata smelter at Altonorte, still uses the flotation process for slag treatment.

Molybdenum Recovery

Typical copper slag show that the molybdenum is dispersed throughout the iron oxide phase and, at the copper-making step the molybdenum is highly oxidised and associated to the magnetite structure as shown in Figure 2 corresponding to the stability diagram of Cu-O-S, Fe-O-S and Mo-O-S systems at 1300°C.

Molybdenum when present in a copper ore is usually separated as a separate flotation product in the concentrator. This separation is imperfect and some molybdenite is present in the copper smelter feed. The molybdenum sulphide oxidises readily and most of the molybdenum reports in the smelter slag. The molybdenum in slag is reported to be bound in an insoluble spinel which belongs to the $2\text{FeO} \cdot \text{MoO}_2\text{-Fe}_3\text{O}_4$ series⁸. In the molten state, the slag is chemically homogenous with the exception of some copper and copper sulphides which are entrained in the liquid, and it retains a homogenous state when it is rapidly cooled. When the slag is slowly cooled, at least two solid phases may form; a ferrous silicate and oxides phases.

A series of five different slag, slowly (S) and rapidly (R) cooled were used and their chemical characterisation is shown Table 3.

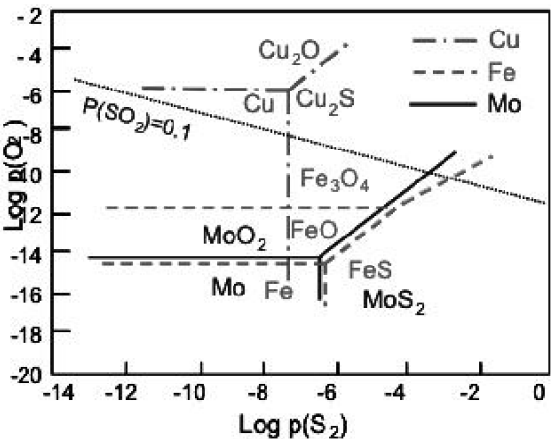


Figure 2: Stability diagram of Cu-O-S, Fe-O-S and Mo-O-S systems at 1300°C

Table 3: Composition and magnetite content of slowly and rapidly cooled slag

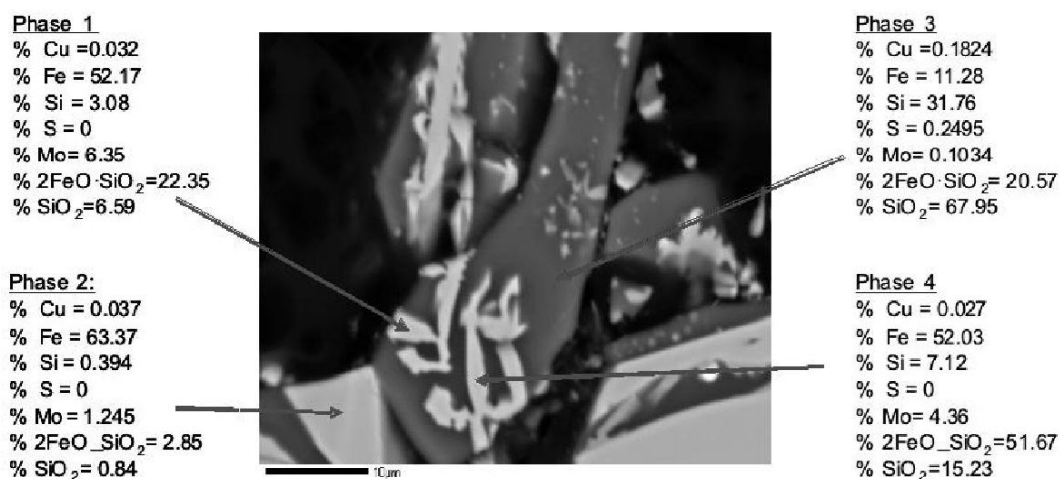
Slag	Fe ₃ O ₄ (%)	Cu(%)	Fe(%)	Mo(%)
Slag 1-S	23.4	1.21	42.2	0.27
Slag 1-R	1.4	0.85	48.4	0.30
Slag 2-S	14.1	1.32	50.7	0.20
Slag 3-S*	7.9	1.19	45.7	0.40
Slag 3-R	13.4	0.77	43.0	0.40

* anomalous

An SEM characterisation (Figure 3) was made and microprobe analyses (Figure 4) were carried out. The SEM image shows complex precipitated oxides and silicates, where the molybdenum formed separate phases of Fe-Mo-O type, with iron content between 52.03 and 63.57% and molybdenum content in the range of 1.25 and 6.35%. See phases 1, 2 and 4 in Figure 3. Also these phases have low silica content suggesting that iron could be present in a spinel structure of magnetite type, such as FeO-MoO₂-Fe₃O₄. Phase 3 shows a glassy iron silicate type silica rich solution with low content of molybdenum.

The electronic microprobe analysis in Figure 4 shows the distribution of iron (a) and molybdenum (b) and it is possible to appreciate the association between both elements in the slag.

Table 4 shows extraction of iron and molybdenum from slag, using an acid leaching⁹. Note the high molybdenum extraction when the magnetite content in the slag is low (magnetite formation suppressed by rapid cooling).

**Figure 3:** SEM image of copper slag showing phase composition

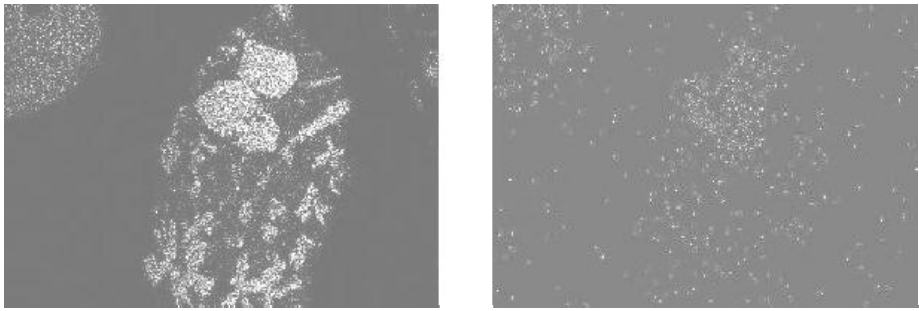


Figure 4: Microprobe Analysis of Copper Slag showing iron (a) and molybdenum (b)

Table 4: Acid leaching of slag showing link between molybdenum solubility and magnetite content

Slag	Fe ₃ O ₄ (%)	Extraction of Fe (%)	Extraction of Mo (%)
Slag 1-S	23.4	82	22
Slag 1-R	1.4	65	95
Slag 2-S	14.1	57	30
Slag 3-S*	7.9	77	18
Slag 3-R	13.4	47	30

*anomalous

Magnetite content can also be reduced by roasting under oxidising conditions. The whole results of molybdenum extraction for different residual magnetite content in slag when roasted under oxidising conditions prior to leaching is shown in Figure 5. Note that molybdenum recovery increases with the decreasing of magnetite content.

Iron Recovery

Flash smelting operations with recycle of converter and fire refining slag produce high matte grades and the resulting furnace slag is high in copper. These slag are

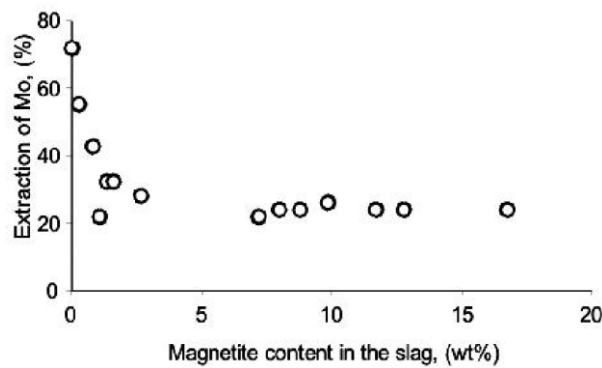


Figure 5: Link between magnetite content of slag and molybdenum solubility

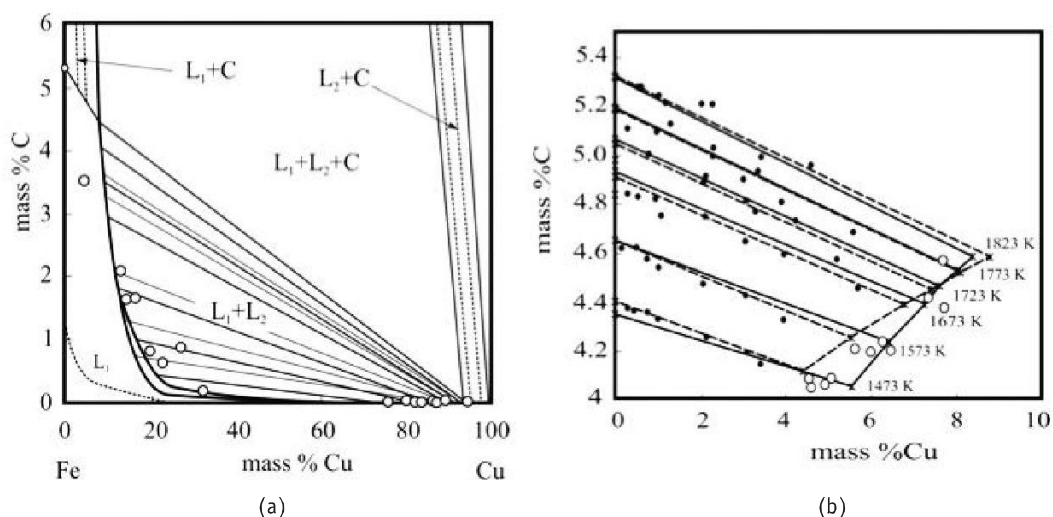


Figure 6: Immiscibility gap in the Cu-Fe-C system

cleaned in an electric furnace using coke as a reductant^{10, 11}. Iron is a major element in the final slag and can be recovered as metal in an additional reducing step. The solubility of carbon in the Fe-Cu-C system as a function of (a) copper content at 1723 K and (b) copper content at given temperature is shown in Figure 6¹². When an excess of carbon is present reduction of slag results in the formation of an Fe-Cu-C alloy. Since the solubility of carbon in copper is negligible, while the melt rich in iron dissolves copper and carbon, solubility of copper decreases with the increasing of carbon content, as shown in Figure 6 (a). Also this figure shows the miscibility gap between copper and iron rich melts. In Figure 6 (b) the effect of temperature on the copper solubility of carbon saturated iron melts is shown, and it can be observed that the copper concentration increases with temperature up to about 9% at 1823 K.

Iron reduction investigation

Analyses, both chemical and mineralogical, of flash furnace slag used in these experiments are shown in Table 5. Details on experiments can be obtained from the reference cited¹⁰.

Table 5: Analysis of slag uses for iron reduction investigation

Compound	Cu ₂ O	Cu ₂ S	FeS	FeO	Fe ₃ O ₄	SiO ₂	Al ₂ O ₃	CaO	Other
Wt%	0.76	2.00	1.17	40.61	12.38	33.00	2.12	0.69	7.27
Element	Cu	Fe	S	Si	Al	Ca	As	mg/kg	
Wt%	2.27	41.3	0.83	15.4	1.60	0.49	74		

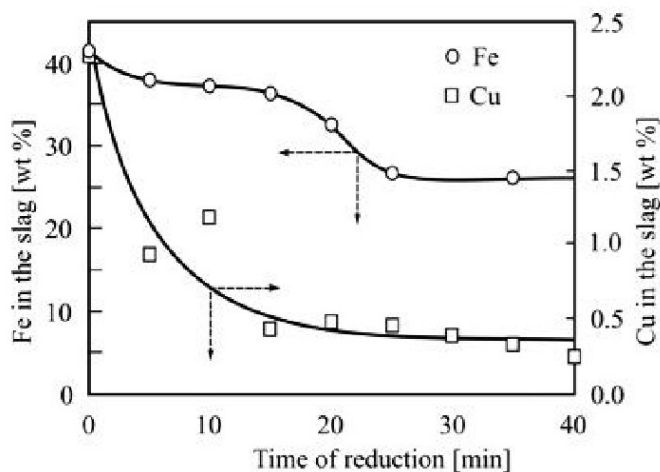


Figure 7: Preferential removal of copper during slag reduction

The reduction kinetic of copper oxide and magnetite was studied by using graphite rod as reducing agent at 1450 °C and a CaO/SiO₂ ratio of 60/40 in the CaO-SiO₂-FeO system. Results are shown in Figure 7 where the concentration of copper and iron in function of time are shown.

Results for composition of the phases obtained during copper and iron selective reduction are shown in Table 6. The microstructure of metal and final slag phases are shown in Figure 8, for (a) lower part of the metallic alloy, (b) central part of the metallic alloy, (c) upper part of the metallic alloy in contact with the slag phase, and, (d) final slag phase.

Table 6: Phase composition during the selective reduction of slag

Carbon addition wt%	1 st . Step: selective copper reduction					2 nd . Step: reduction to metallic iron				
	First slag rich in iron			Metallic phase		Final slag			Iron Alloy	
	%Cu	%Fe	%S	%Cu	%Fe	%Cu	%Fe	%S	%Cu	%Fe
100	0.32	24.6	0.5	51.0	48.2	0.02	3.8	0.26	1.36	98.0
150	0.20	30.1	0.45	12.2	87.0	0.24	4.2	0.25	0.84	98.9

During the first stage, both copper and iron are reduced and a copper rich metallic alloy is obtained, and, in the second stage, a rich iron alloy is obtained, The copper content decreases to 0.24% in the final stage, and to 0.84% in the final metallic alloy. The iron alloy obtained by using 150% of carbon addition was micro-analysed in order to observe the copper-iron interaction, and the result is shown in Figure 9 as a micrograph of the iron alloy containing 98.9% iron.

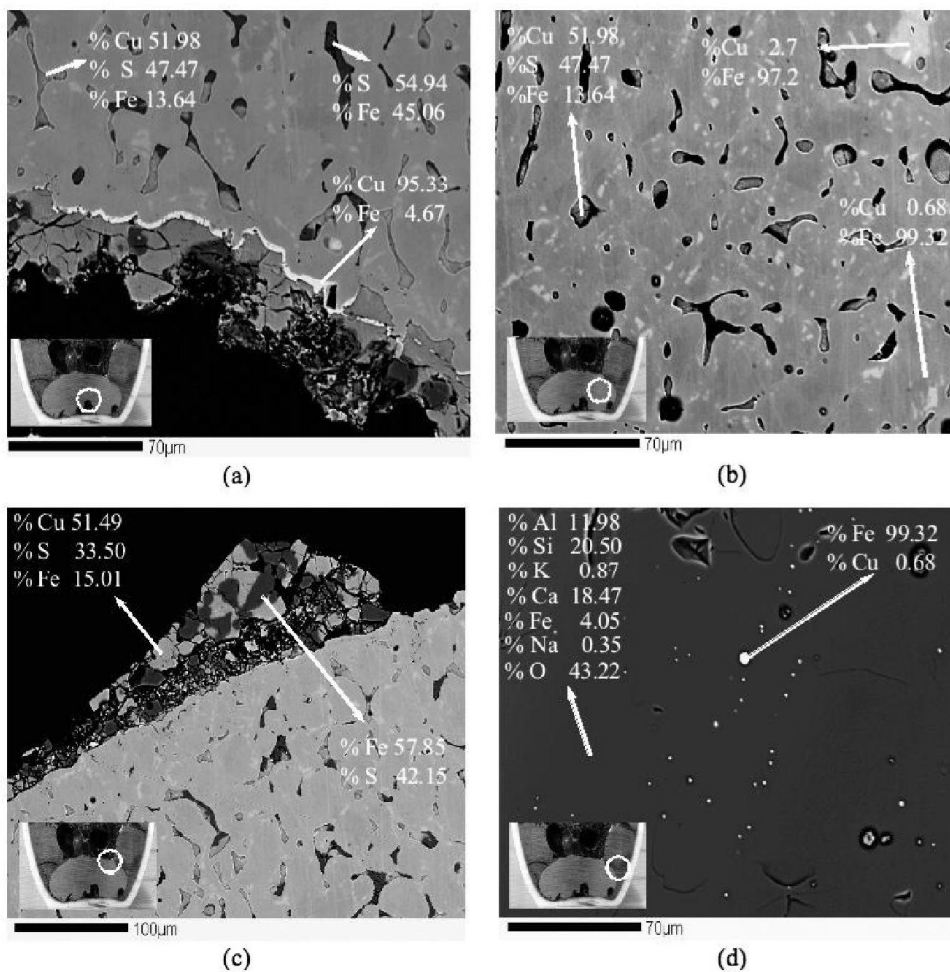


Figure 8: The microstructure of metal and final slag phases for (a) lower part of the metallic alloy, (b) central part of the metallic alloy, (c) upper part of the metallic alloy in contact with the slag phase, and, (d) final slag phase

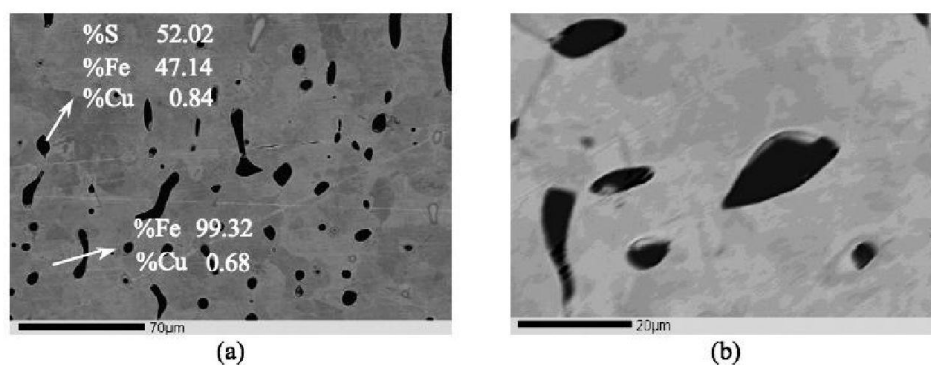


Figure 9: Micrograph of the iron alloy containing 98.9% iron at two magnifications

Recovery of Other Components

Some processes using hydrometallurgical techniques have also been developed. For example a bioleaching process add treated non-iron metallic sulphides and refractory minerals containing gold and silver, by using a non-expensive bacterial process for pre-treatment of auriferous pyrites, followed by cyanidation to recover precious metals. Further, liquor is treated by solvent extraction (SX) and electrowinning (EW), to obtain pure metal¹³. Additionally, a study on the recovery of copper, cobalt, nickel and zinc contained in slag using hydrometallurgical treatment, was reported. This process includes a roasting pre-treatment and a subsequent leaching with sulphuric acid¹⁴. In Turkey, a process for treatment of ancient copper smelting slag has been proposed. In this process, copper and cobalt are recovered in metallic form and/or as compounds, whereas iron is recovered as magnetic oxide or pigment, and abrasive material is produced using final reduced slag. The process stages include carbothermal reduction in a DC arc furnace, granulation, leaching, chemical precipitation, selective sulphidising roasting and product preparations¹⁵. In Japan, researchers aiming to reuse some wastes such as municipal ones, slag and sludge, in order to recover nonferrous metals such as cobalt and copper, have been also conducted¹⁶.

Summary & Perspectives

Public & regulatory attitudes to mine wastes have been undergoing a progressive change over time, from the perspective of something of no value to be discarded to that of a potential resource. Other factors bearing on this new view include a desire to conserve resources, minimise mine foot-print, avoid air and water contamination, reduce closure and decommissioning costs and eliminate the need for perpetual maintenance of sites. Social pressures and economic factors both encourage a search for economic ways to turn wastes into useful commodities.

Smelter slag is one class of waste that is a prime target for investigation. A primary objective of recent investigations has been to find ways of separating residual pay metals from the bulk of the slag (a magnetite - Fe_3O_4 /fayalite - Fe_2SiO_4 matrix) and more particularly from copper smelter slag that contain molybdenum in addition to copper.

Copper smelter slag are usually subject to a cleaning operation commonly involving holding the molten slag at temperature in a furnace under mildly reducing conditions allowing time for reduction of dissolved copper oxide and some magnetite and for coalescence and settling of metal and sulphide droplets. An alternative approach is to cool the slag slowly, grind finely and then recover solid copper metal or sulphide

inclusions to be recovered by flotation. Neither technique recovers cobalt or molybdenum if present. Furnacing under more strongly reducing conditions allows recovery of cobalt and molybdenum in an iron alloy for granulation and chemical treatment by chemical dissolution. Large amounts of iron are dissolved and require expensive processing prior to use or disposal.

Oxidation of slag to hematite has been tested in a tube furnace with slag ground through 400 mesh. Copper, molybdenum can all be selectively recovered from the hematite calcine using mild acid leaching. The conditions for commercial operation have not been established but are thought to involve production of a fine (250 mesh) water granulated slag for charging to and oxidation in a fluid bed furnace operated with supplementary fossil fuel to maintain a bed temperature in the 500°C-750°C range and a bed residence time of 5-10 hours. Magnetite and forsterite oxidation involves migration of iron ions through the oxide matrix^{17, 18} – a fairly slow process at modest temperatures although possibly faster in the glassy phase associated with rapid cooling of molten slag by water granulation. Volatilisation of molybdenum trioxide is expected to limit the operation temperature ($p\text{MoO}_3 = 1 \text{ atm}$ at around 1000°C).

Leaching of slag without a preliminary thermal treatment does not appear promising as dissolution of the iron matrix also occurs.

The authors preference for a possible future pilot scale investigation is fluid bed oxidation with modest fossil fuel addition for temperature control.

References

1. B. Gorai, R.K. Jana and Premchand, "Characteristics and utilisation of copper slag—a review", *Resources, Conservation and Recycling*, **39** (4) 299-313 (2003).
2. M. Sanchez, F. Parada, R. Parra, F. Marquez, R. Jara, J.C. Carrasco and J. Palacios, "Management of copper pyrometallurgical slags: giving additional value to the copper mining industry", in *Proceedings of VII International Conference on Molten Slags Fluxes and Salts*, 543-550, The South African Institute of Mining and Metallurgy, Cape town, South Africa, 2004.
3. J. Davené and J. Herberson, "To Make the Most of Steelmaking Slag" In *Recycling and Waste Treatment in Mineral and Metal Processing: Technical and Economy Aspects* (TMS fall 2002 Extraction and Processing Division Meeting), vol. 1, 243-255, GTC print AB, Lulea, Sweden, 16-20 June, 2002.
4. C. Gonzalez, R. Parra, A. Klenovcanova, I. Imris and M. Sanchez, "Reduction of Chilean copper slags: a case of waste management project", *Scandinavian Journal of Metallurgy*, **35** 1-7 (2005).
5. S. Demetrio, J. Ahumada, M.A. Duran, E. Mast, U. Rojas, J. Sanhueza, P. Reyes and E. Morales, "Slag cleaning: the Chilean copper smelter experience", *JOM*, **52** (8) 20–25 (2000).
6. I. Imris, S. Rebolledo, M. Sanchez, S. Castro, G. Achurra and F. Hernandez, "The copper losses in the slags from El Teniente process", *Acta Metallurgica Slovaca*, **4** (3) 69-78 (1998).

7. I. Imris, S. Rebolledo, M. Sanchez, S. Castro, G. Achurra and F. Hernandez, "The copper losses in the slag from the El Teniente process", *Canadian Metallurgical Quarterly*, **39** (3) 281-289 (2000).
8. J. Lotens and A. Van Del Giesen, "Method for the non Leachable immobilisation of molybdenum compounds in a slag", *International Patent WO 00/29071*, 2000.
9. D. Busolic *et al*, "Recovery of molybdenum from roasted copper slag", in *Proceedings of VIII International Conference Molten 2009*, 1281-1287, Edited by M. Sanchez, R. Parra, G. Riveros, C. Díaz, ISBN 978-956-8504-20-5, Santiago, Chile, January 18-21, 2009.
10. D. Busolic, F. Parada, R. Parra, E. Urdy, J. Palacios, M. Hino, F. Cox, A. Sanchez and M. Sanchez, "Recovery of Iron from copper flash smelting slag", in *Proceedings of VIII International Conference Molten2009*, 621-628, Edited by M. Sanchez, R. Parra, G. Riveros, C. Díaz, ISBN 978-956-8504-20-5, Santiago, Chile, January 18-21, 2009.
11. T.J. Kim, "Flash smelting in Korea", in *Copper smelting - An update*, 33-39, Edited by D.B. George, J.C. Taylor, AIME, New York, 1981.
12. M. Hino, "Lecture on Pyrometallurgical Process for Chilean Slags", FONDEF Project D021159, August 2004.
13. A. Mazuelos, F. Carranza, I. Palencia and R. Romero, "High efficiency reactor for the biooxidation of ferrous iron", *Hydrometallurgy*, **58** (3) 269-275 (2000).
14. H.S. Altundogan and F. Tumen, "Metal recovery from copper converter slag by roasting with ferric sulphate", *Hydrometallurgy* (Netherlands), **44** (1-2) 261-267 (1997).
15. B. Derin, F. Cinar, O. Yusel, E. Acmar and O. Addemir, "A Process designed for the ancient copper smelting slag", *Yazawa International Symposium on Metallurgical and materials processing: Principles and technologies* 471-482, San Diego, USA, 2003.
16. M. Maeda, T. Nakamura and Y. Nishimura, "Copper recycling project in Japan: super smelter and super dust concept" in *Proceedings of 3rd International Symposium on Recycling of Metals and Engineered Materials*, 215-221, Minerals, Metals and Materials Society/AIME, Point-Clear, Alabama, USA, 1995.
17. D. Papanastassiou and G. Bitsianes, "Mechanisms and kinetics underlying the oxidation of magnetite in the induration of iron ore pellets", *Met Trans*, **4** (2) 487-496 (1973).
18. S.J. Maxwell, "Oxidation kinetics of fayalite (Fe_2SiO_4)", *Phys. Chem. Minerals*, **19** 220-228 (1992).