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RESEARCH ON THE RECOVERY OF COPPER FROM METALLURGICAL SLAG

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Abstract: *Metallurgical slag is one of the most common industrial wastes. Many of these wastes are not stable over time, by reacting with water and air, continuously generating emissions of heavy metals. Metallurgical slag processing is necessary for at least two reasons: reducing pollutant emissions and broadening the raw material base. The recovery of these slags is very difficult because they are the result of metallurgical processes that aimed to fix metals considered impurities in chemical matrices as stable as possible. This paper presents the initial research on the behavior of metallurgical slags against different leaching technologies.*
Keywords: *copper, waste, matte, slag, recovery*

1. Introduction

The development of the metallurgical industry is conditioned by solving the major problems arising from the industry-nature relationship, strictly aimed at controlling pollution and at protecting natural and energy resources. The essential changes of this millennium must be related to the development of metallurgical technologies according to the requirements of industrial ecology [1]. In the metallurgical industry, the notion of waste must be abandoned, it is more correct to speak of by-products. Concern for compliance with legislative requirements on environmental protection and the need to harmonize technological processes with rational management of material and energy resources, must lead to the recovery of waste through technologies that provide the optimal solution both economically and ecologically.

Compared to the practice and trends manifested worldwide, the Romanian metallurgical industry lags, both in the fields of collection, transport and storage of all categories of waste, as well as in terms of recovery solutions through recycling and / or use [2].

The concerns pursued in the development strategies of metallurgical plants around the world are in two directions:
- development of high-performance technologies that substantially reduce emissions;
- increasing the yields of recovery and recycling of by-products to values close to 100%.

This paper tries to bring to the attention of decision makers the importance of capitalizing on these "industrial wastes" with appreciable economic and environmental implications.

2. Considerations regarding slag formation

Slag from lead metallurgy dissolves 6-15% ZnO. Ferrous oxide forms in the presence of silicon dioxide silicates with lower melting points than the two components, which pass into the slag:

$$2FeO+SiO_2= 2FeO\cdot SiO_2 \quad (1)$$

$$4FeO+3SiO_2= 4FeO\cdot 3SiO_2 \quad (2)$$

$$FeO+SiO_2 =FeO\cdot SiO_2 \quad (3)$$

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Cooper-lead mats are obtained by melting lead concentrates with more than 1% Cu. Generaly, liquid mattes from lead-reducing smelting consist of sulfides of iron, copper and zinc, containing in dissolved state small amounts of metallic iron, copper, gold, silver and Fe_3O_4. In addition to these elements, there are inclusions of slag and significant amounts of lead, because, FeS dissolves up to 30% Pb in the form of PbS and metallic lead (20-30% PbO) [3]. At a content above 1% copper a copper-lead matte is produced in the agglomerate, in the weight of 0.5-2.0%, in the form of Cu_2O, Cu_2S and silicate and is collected almost entirely in the matte in the form of Cu2S, based on the following reactions:

$$Cu_2O+FeS =[Cu_2S]+FeO \quad (4)$$

$$Cu_2O+CO = 2Cu+ CO_2 \quad (5)$$

$$2Cu+FeS =[Cu_2S]+Fe \quad (6)$$

If the charge does not contain a sufficient amount of sulfur for the sulfurization of copper, it dissolves in the lead and is to be removed during the operation of decoppering of the raw lead. Most of the iron in the agglomerate passes into the slag, and a certain amount into the lead-copper mat.

Upper iron oxides are reduced according to the reactions:

$$3Fe_2O_3+ CO = 2Fe_3O_4+CO_2 \quad (7)$$

$$Fe_3O_4+ CO = 3FeO+CO_2 \quad (8)$$

Slag is a secondary non-metallic product, resulting from the metallurgical processes of extraction and elaboration of metals and alloys, characterized by a certain chemical-mineralogical composition [4]. It is a mixture of different oxides, resulting from the melting of ore tailings, fuel ash, fluxes and the metal bath and which can form chemical compounds, solutions and eutectic mixtures. In the processes of extraction and elaboration of metals and alloys, slag must fulfill the following functions: - favoring the development of the main physico-chemical process (reduction, oxidation, etc.) characteristic of a metallurgical operation (elaboration of cast iron in furnace, non-ferrous alloys etc); - removal and capture of elements harmful to the quality of the metal or alloy produced (eg sulfur, phosphorus, arsenic, etc.); - favoring the evacuation of gases from the metal bath in the atmosphere; - preventing the penetration of gases from the atmosphere of the aggregate (for example hydrogen, nitrogen, oxygen, etc.) into the metal bath; - favoring the removal of non-metallic inclusions from the metal bath; - to regulate the heat transmission to the metal bath or vice versa, as the case may be;

In order to correspond to these functions, slag must have certain physico-chemical properties (viscosity, density, thermal and electrical conductivity, surface tension, etc.) which depend primarily on its chemical composition [5].

3. Slag acid leaching

In this stage the slag is prepared for processing followed by its acid leaching. The preparation of the slag for leaching requires its grinding for a more intimate contact between the solid and liquid phases. Because the tested slag is extremely hard, which implies a high energy consumption, it was proposed to grind in two stages: an initial crushing, followed by an acid leaching that friable the material and in the second stage grinding in the ball mill.

Acid leaching can be performed with sulfuric acid, hydrochloric acid or nitric acid. Tests have shown that the use of sulfuric acid leads to low extraction yields and the use of hydrochloric acid leads to the formation of chlorocomplexes that behave differently in variations in the concentration of solutions. For this reason, we opted for nitric acid, which forms soluble salts with all common metals and has a very low availability to form complex combinations [6].

The following chemical reactions occur after leaching with nitric acid:

$$Fe(s) + 4HNO_3(aq) \xrightarrow{30\%} Fe(NO_3)_3(aq) + NO(g) + 2H_2O(l) \quad (9)$$

$$3Zn(s) + 8HNO_3(aq) \xrightarrow{40\%} 3Zn(NO_3)_2(aq)+ 2NO(g) + 4H_2O(l) \quad (10)$$

$$Cu(s) + 4HNO_3 (aq) \rightarrow Cu(NO_3)_2 (aq) + 2NO_2 (g) + 2H_2O(l) \quad (11)$$

$$FeO + 4HNO_3 \rightarrow Fe(NO_3)_3 + NO_2 + 2H_2O \quad (12)$$

$$2HNO_3 + ZnO \rightarrow Zn(NO_3)_2 + H_2O \quad (13)$$

$$2HNO_3 + CuO \rightarrow Cu(NO_3)_2 + H_2O \quad (14)$$

$$As + 5HNO_3 \rightarrow H_3AsO_4 + 5NO_2 + H_2O \quad (15)$$

Lead processing technology involves the pyrometallurgical processing of lead concentrates which aims to reduce lead to metal and separate it from other accompanying metals. For this purpose, various additives of fluxes form a lead slag and a mat which are made up of very stable thermodynamically eutectic, thus allowing their very efficient separation of lead.

The waste resulting from the lead processing process is therefore a mixture of solid solutions very difficult to separate. Separation tests by physical processes have led to unsatisfactory results because they have only been able to separate the different types of eutectics from each other and not the metals.

The very high stability of this waste has also been demonstrated by pyrometallurgical tests performed in order to reduce some metals, mainly lead. For this purpose, the ground waste was mixed with reducing materials and heat treated at 1100 ° C. The result was a separate melt in two phases, which did not contain reduced metal (table 1).

Table 1. Results of pyrometallurgical tests

Component	Mat treated at 1100 °C lower nacelle area	Mat treated at 1100 °C upper nacelle area
MnO	1.5487	1.3961
Fe_2O_3	41.0229	50.5215
As_2O_3	0.3292	0.2332
Sb_2O_3	0.8028	0.0000
PbO	14.0723	8.3077

There is a concentration of metals in the lower part of the nacelle, but without a separation that allows their isolation. This technology is to be further developed, using an electric arc furnace from the titanium industry. This furnace greatly streamlines the process of reducing metals in the form of oxides, being very versatile and adaptable to large variations of metal concentrations.

From a chemical point of view, both wastes – slag and mate –are very reactive to acids, with which they react partially, very energetically. Following the hydrometallurgical leaching tests, certain selectivity towards a certain metal is not observed, all of which dissolve partially, in a smaller or larger proportion. Some semimetals dissolve completely, but are minor constituents of this waste.

The resulting lye contains a significant number of solubilized metals, which involves their chemical separation. The relatively high costs of the reagents used impose the need to separate the products from the solutions into economically valuable forms. Thus, iron, soluble in any variant of acid leaching, leads to a significant consumption of acids. Under these conditions, its disposal as waste or as an oxide for the steel industry is inefficient. Consequently, the proposed technology aims to obtain high quality products with other economic destinations, such as pigments.

Acid leaching tests showed partial solubilisation of this waste. The results of these tests are presented tables 2, 3, 4 and 5. By treatment with acids, regardless of their nature, silicic acid is released which has the effect of gelling the solution. For this reason, after the acid attack it is necessary to immediately dilute the mixture with water and separate the lye by sedimentation in sludge thickeners. If it is desired to re-treat the residue with acid, it is necessary to remove the silica with sodium hydroxide solution, when a soluble sodium silicate (glass water) is obtained, which can be used in the construction materials industry.

Table 2. Matte HCl leaching extraction

Compound	Solubilisation [%]	Metal extraction
Al_2O_3	0.2001	72.66
SiO_2	1.6108	57.68
SO_3	3.5095	31.38
CaO	1.5044	88.53
MnO	0.9859	95.12
Fe_2O_3	18.9646	70.51
NiO	0.0878	100.00
CuO	15.3770	42.20
ZnO	2.1061	58.09
As_2O_3	0.7982	55.56
Sb_2O_3	0.5521	100.00
PbO	7.2490	57.47

Table 3. Slag HCl leaching extraction

Compound	Solubilisation [%]	Metal extraction
Al_2O_3	0.2896	73.96
SiO_2	4.5899	79.10
SO_3	2.8803	57.04
CaO	3.9155	93.05
MnO	0.8749	89.36
Fe_2O_3	42.2442	85.95
NiO	0.0538	100.00
CuO	2.5025	37.87
ZnO	9.3813	82.81
As_2O_3	0.5976	100.00
Sb_2O_3	0.5560	100.00
PbO	11.7388	81.86

Table 4. Matte H_2SO_4 leaching extraction

Compound	Solubilisation [%]	Metal extraction
Al_2O_3	0.1984	72.05
SiO_2	0.0000	0.00
SO_3	1.8082	16.17
CaO	1.0257	60.36
MnO	0.9755	94.12
Fe_2O_3	19.4673	72.38
NiO	0.0878	100.00
CuO	2.3429	6.43
ZnO	1.7293	47.70
As_2O_3	0.5214	36.29
Sb_2O_3	0.2623	47.51
PbO	0.0000	0.00

Table 5. Slag H_2SO_4leaching extraction

Compound	Solubilisation [%]	Metal extraction
Al_2O_3	0.2793	71.35
SiO_2	0.0000	0.00
SO_3	0.0000	0.00
CaO	0.8601	20.44
MnO	0.8400	85.80
Fe_2O_3	43.6050	88.72
NiO	0.0284	52.81
CuO	2.8787	43.56
ZnO	9.5849	84.61
As_2O_3	0.3529	59.05
Sb_2O_3	0.0000	0.00
PbO	0,0000	0,00

Although sulphuric acid does not dissolve lead, tests have always shown that the extraction of other metals is also deficient, so that, despite all expectations, the use of this acid did not lead to a selective leaching of copper from lead (figure 1).

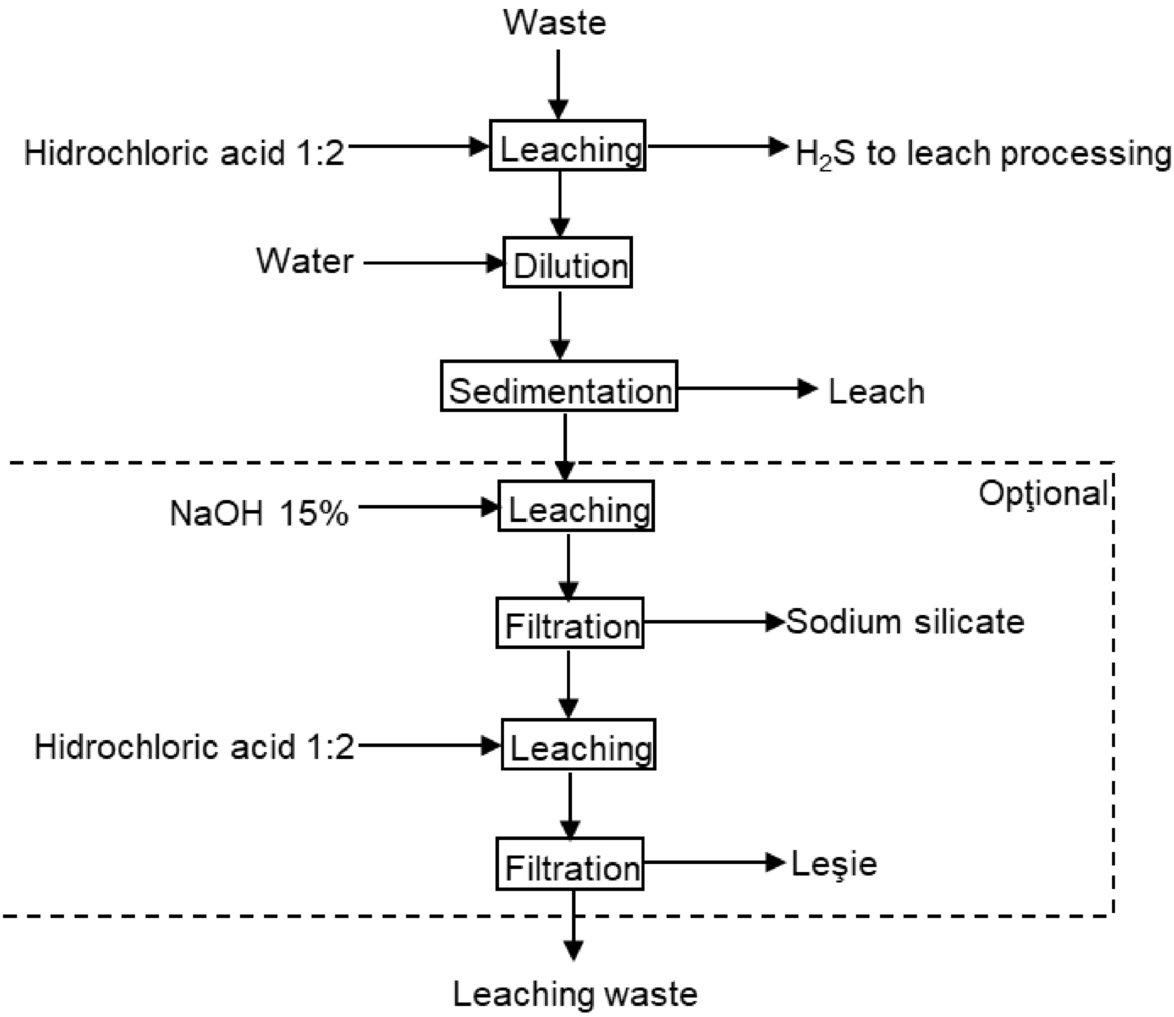

Figure 1. Slag leaching proposed flow sheet

NH_3 leaching is very effective and selective (table 6). The disadvantage is the low saturation concentration of the cupro-ammoniacal complex solution, which implies the need to circulate large volumes of solution. Copper is extracted very easily by cementation. The result is not final, the extraction can be continued. It is estimated that extraction can be efficient.

Table 6. Slag ammonium leaching extraction

Compound	Initial	NH_3 leaching residue	Metal extraction [%]
Al_2O_3	0.915	0.4814	0.00
SiO2	5.8025	6.2858	0.00
SO_3	5.0495	2.9851	43.90
CaO	4.208	4.9029	0.00
MnO	0.979	1.2074	0.00
Fe_2O_3	49.1481	51.8075	0.00
NiO	0.0538	0.0589	0.00
CuO	6.6084	3.3605	51.74
ZnO	11.3287	11.4026	4.48
As_2O_3	0.5976	0.4329	31.25
Sb_2O_3	0.556	0.5697	2.76
PbO	14.3405	14.9694	0.94

4. Conclusions

Experimental research on the leaching of matte and slag resulting from the metallurgical process of obtaining copper focused on the solubilisation of these two by-products with hydrochloric acid, sulfuric acid and ammonia. The metal extractions obtained revealed that ammonia leaching is the most efficient and selective, obtaining a metal extraction of 51.74%.

Following the theoretical and experimental studies performed, it was concluded that this slag and ash waste can be used as raw materials or as additives in various fields.

The proposed project can be considered an environmental objective because it will significantly accelerate the closure of slag and ash dumps and their greening, by capitalizing on the materials resulting from the works performed on the dump.

The recovery of slag and ash resulting from ore processing has a great advantage for the environment by reducing pollution in their waste dumps.

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