EVALUATION OF THE USE OF SLAG FROM THE MINING OF Au AND Ag AS A REPLACEMENT OF THE SAND IN CEMENT MORTARS

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***Abstract*— To the benefit of gold minerals, extraction processes are generally applied by carrying out cyanidation and subsequent smelting to obtain dore thereby generating slags. The properties of the slag obtained vary depending on the origin of the mineral and on the type of load flux used. However, in the Pyrometallurgy literature the reuse of the slag generated at this stage of the process has not been analyzed.**

Therefore, the present research is focused on studying the characteristics of slags of minerals from San Juan province in Argentina, obtained at a laboratory scale, analyzing the possibility of recycling in case they present appropriate physical and chemical properties.

Slag characterization (description) was made by using different techniques such as: chemical analysis with acid digestion and subsequent determination with ICP, structural study by applying optical microscopy techniques in white light mode and polarized light. Observation and semi-quantitative chemical analysis of the samples is completed by using an ESEM scanning electron microscope and analysis with the EDS technique. Finally, analyses about the physical properties obtained are carried out for subsequent use of the slag as cement.

***Keywords*— Slag; Gold; Recycling, Cement**

I. INTRODUCTION

Extractive and metallurgical processes involved in mining activities generate large amount of residues. Among them are those produced by pyrometallurgical processes such as potentially recoverable slag. At present, there is a worldwide trend to search and study new ways to make efficient use of these residues. Some of the reasons that have led to the emergence of this trend are the exhaustion of favorable areas for mineral disposal, the slag dump increased cost and also restrictive regulations as far as waste production is concerned (Lovera Dávila *et al*., 2004; Leon *et al.,* 2009).

A number of studies have been made at an international level to find new uses for slags produced by pyrometallurgical processes such as those generated by steel working in which re-utilization has been focused on Portland cement. The use of copper slags at the same level has also been studied but to a lesser degree. Only few studies have been made about the use of slags from pyrometallurgical processes of gold ores due to the small tonnes generated in this kind of process (Yi *et al*., 2012; Parra and Sanchez, 2010; National Clean, 2011; Orizola, 2006).

However, due to the high content of silica present in slag from gold ores, it is found relevant to study gold pyrometallurgical processing phases and the chemical properties of slags in order to determine their further re-utilization either in cement, glass or in any silicate-based product.

According to their silicate matrix, there are two types of slag, ferrous slag and blast furnace or non-ferrous slag. Copper slags and those from gold and silver ores are included in the second category. The main difference between both types of slag is their CaO content, which is much greater in steel slags. This accounts for differentiation in the cementitious properties of both materials since ferrous or blast furnace slag has inherent binding properties which are either not found or negligible in copper slag (Batic *et al*., 2006).

Compared to Portland cement, slag cement, which is obtained by adding slags to a Portland cement clinker, has proved to have advantageous properties such as lower hydration heat, higher chemical strength, and consequently higher durability, as well as high long-term mechanical strength. This is possible because lime generated during the forging process (harmful for concrete chemical strength) is combined with slags, thus forming hydraulic substances that improve concrete mechanical and chemical strength.

Because the demand for Portland cement increases with the population growth worldwide, which leads to greater power requirements and consequently to higher levels of contaminant emissions associated with the cement industry, pyrometallurgical residues might be used to partially substitute Portland cement (Orizola, 2006).

Practices related to obtain ecological cement might bring about both technical and economic profits by making use of materials with no other purpose whatsoever and which on many occasions constitute environmental liabilities (Batic *et al*., 2006).

II. METHODS

First, a chemical and structural characterization is carried out of three slag samples that were obtained from precious metal deposits currently in production in San Juan province from Argentina, which have different mineralogical characteristics. In addition, a chemical characterization was made of the cement to be used in order to mix it with the slag dosing.

A. Structural characterization

Mineralogical analysis

To characterize the 3 slag samples, were designated M1, M2 and M3. A structural study is carried out by applying optical microscopy techniques in white and polarized light mode. In this case, an Olympus GX 51 microscope is used with a Leco IA 32 image analyzer. In addition to the observation and semi-quantitative chemical analysis of the samples with a (FEI Quanta 200) scanning electronic microscope SEM which allows analysis to be made by means of the EDS technique, X-ray diffraction testing is also made to identify the phases present in each of the samples.

Granulometric analysis

An analysis of particle size was carried out to determine the material retained on the IRAM 74 µm sieve, which responds to the 1503 IRAM Standard: Ordinary Portland cement – physical requirements lower than 15% (IRAM 1504, 1997). The analysis was carried out on three slag samples in a wet system, using 177 µm, 149µm, 88 µm and 74 µm sieves.

B. Chemical characterization

In order to determine both the slags and cement chemical composition, acid attack decomposition was carried out along with volumetric and gravimetric determination. Subsequently, an ICP reading was made by using a 7300 DV Perkin Elmer ICP-OES equipment (optical emission spectrometer) in order to determine minor elements.

Once characterization was made, the required dosing has to be analyzed in order to obtain the corresponding mixture of cement-slags.

Probes are then developed which are aimed at assessing the cement-slags physical properties by means of compression strength tests, tensile strength tests, hydration heat and elastic modulus determination through ultrasound speed. All the above-mentioned properties were evaluated at 7, 28 and 60 days.

III. RESULTS AND DISCUSSION

A. Structural characterization.

Mineralogical analysis

The results showed that the samples are made up of very large particles with angled morphology, vitreous and homogeneous in appearance (Fig. 1). The EDS analyses confirm that most of the samples are silicate phases, a fact eventually verified with DRX.

Grain size analysis.

From the grain size analysis carried out (Fig. 2), it may be inferred that the material retained in the 74 µm IRAM (Argentine Standards Institute) sieve (equivalent to 200-mesh sieve) is smaller in size than the maximum value of 15% specified in the 1503 IRAM Standard.

B. Chemical characterization.

Chemical analysis of slags

Table 1 shows the results of chemical characterization of slag. From these results, it may be inferred that, according to both the IRAM 1504 (1997) Standard and the IRAM 50000 (2010) Standard; the slags analyzed can be used in cement manufacturing since they have an insoluble residue (R.I) of < 1%; SO3<2.5%; MgO <5%; Calcination Loss (PPC)< 3%, specified by the standards above

From the concentrations obtained, it may be determined if the slag is basic, meaning that it meets both certain basicity index values (Eq. 1) and hydraulicity indexes (Eq. 2).

These indexes have a value much higher than the simple chemical composition of the slag. The slag behavior and value also depend on its minor components

$$Ib = \frac{CaO}{SiO_2} \quad (1)$$

$$Ih = \frac{CaO + MgO + Al_2O_3}{SiO_2} \quad (2)$$

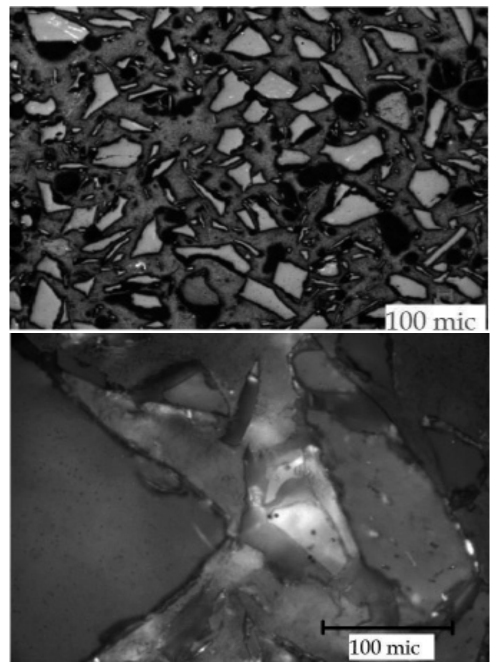

Figure 1. (a) Sample 1. Vitreous particles in detail, (b) Sample 1. Vitreous particles in detail.

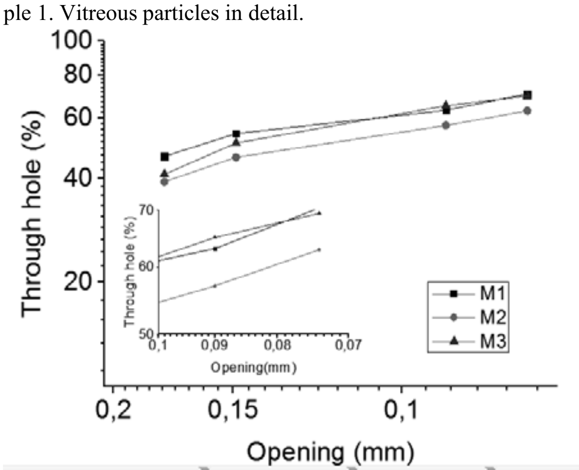

Figure 2: Grain Size analysis.

Table 1: Chemical characterization of the slags

Y (ug/g)	Sample 1	Sample 2	Sample 3
Cu	286,3	655,8	44,69
Fe	27910	26590	3518
Cr	109,9	158,7	205,1
Al	23850	17480	5453
Pb	301800	256800	272100
Sn	2276	66,83	1,601
Si	4735	3101	2262
K	4150	9080	3217
Mo	4,974	8,645	7,832
Ni	30,8	45,84	81
Ag	40,25	8,428	9,824
Ti	2608	850,8	164,7
V	621,9	32,66	10,08
Mn	1223	2760	281,7
Ca	5875	7705	1292
Mg	1079	1364	312,5
Zn	3669	2329	170,6
Ba	357,8	258,4	45,17
As	156	245,1	14,7
Re	30,69	30,61	29,49
S	5248	4351	787
Co	13,86	12,24	6,031
Li	29,82	37,48	44,16
Sr	56,01	70,26	14,5
Cd	7,601	7,001	0,657
RI (%)	0.75	0.63	0.82
PPC(%)	1.67	1.43	1.12

Table 2: Basicity and hydraulicity index

Sample	**Basicity Index**	**Hydraulicity Index**
M1	1,10	7.34
M2	1,63	6.96
M3	1,25	3.49

The indexes calculated in Table 2 show that basicity and hydraulicity indexes of the samples are higher than the unity; therefore they may be used in cement manufacturing.

The results obtained from the structural and chemical characterization of the samples help to confirm that the slags studied are apt to be used in the cement manufacturing process since their chemical composition approximates to that of a Portland cement clinker.

Values higher than one of the indices of basicity and hydraulicity, shown in Table 2, indicate that the slags studied have a basic character and a latent hydraulic capacity, that is to say, they have the ability to forge and harden by themselves.

The basic components of calcium and magnesium generally favor hydraulicity, while aluminum contributes specifically to the improvement of the behavior of basic slags.

Chemical Analysis of cement

To determine the slag dosage for cement, a chemical characterization of the slag is required, as shown in table 3.

C. Analysis of physical properties.

Mortar dosing

The amount of slag in slag cement can be determined by knowing the content of the major constituents (expressed as oxides: CaO, Al_2O_3 y SiO_2). This can be made by using in 3, according Duriez and Houlnick (1950).

$$\%SLAG = \frac{c-k}{e-k}100 \qquad (3)$$

where c is the CaO weight percentage of the main cement component, e is the CaO weight percentage of the slag and k is that of the clinker.

Therefore, to determine the slag percentage, the values used were the following:

c = 39.07 %OCa

k = 44 %OCa

e = 11.42 %OCa (sample 1), 11.49 %OCa (sample 2), 11.25 % OCa (sample 3).

For comparative purposes a compound is performed by standard 100% cement and 0% slag.

Compression strength analysis

The tests to determine the mortars compression strength were carried out at 7, 28 and 60 days according to the IRAM 1622 (2006) Standard.

Figure 3 shows the results of the comparison test tube (Standard) as well as those of the slag dosing test tubes corresponding to samples 1, 2 and 3, tested at 7, 28 and 60 days:

The graph shows that, the compressive strength values, given in megapascals (MPa), increased with age in all of the test tubes, the comparison test-tube contour being that with the highest values at different times. The mortars as a whole meet the requirements of the IRAM standards from the Argentine Institute of Standardization and Certification.

It should be noted that the three test tubes with slags have a low initial mechanical strength but they managed to develop long-term higher mechanical strengths.

Table 3: Chemical characterization of Portland cement.

Name	Cement (%)
Na_2O	0,14
K_2O	0,18
Pb	0,02
Fe_2O_3	3,2
CaO	39,07
MgO	0,79
RI	1,0
SO_3	2,43
SiO_2	0,66
R_2O_3	7,29
Cl	0,024
PPC	1,14

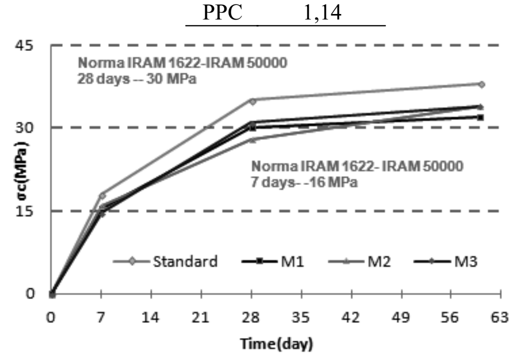

Figure 3: Compressive strength test.

Table 4. Compressive strength and ultrasound speed values.

Sample	RCU(Mpa)	vus(Km/s)
7 days Sample		
M1	16	3,16
M2	16	2,88
M3	15	2,77
Standard	18	3,60
60 days Sample		
M3	34	3,73
M2	34	4,48
M1	32	4,10
Standard	38	4,46

The compressive strength determined that the slag cement study is within the limits specified in the requirements of IRAM 1622 (2006) and IRAM 50000 (2010) mechanical requirements

Compressive strength and ultrasound speed Analysis
Interestingly enough, the Ultrasound Pulses Propagation Speed could be related with the cement Compressive Strength. To this end, results are shown in Table 4.

The ultrasound speed compressive strength data were obtained in order to determine the material homogeneity. The test consists in transmitting longitudinal waves by means of ultrasound compression and then measuring the time it takes for the waves to pass through the test tube.

It is clear that changes in the ultrasound propagation speed are proportional to the cavities content, pore structure, cracking and micro cracking in the test tubes.

During the forging process, there is a rapid increase in such speed while the mortar gains mechanical strength. In general terms, it may be concluded that the faster ultrasound speed of the mortars studied, the greater their mechanical strength.

The ultrasound tests show that as the specimens age, both the speed of ultrasound and the elastic modulus increase.

In Table 4, it can be observed that the resistance to compression of samples made with addition of slag is low in 7 days and increases in 60 days, which implies that the addition of slag does not contribute to the increase of resistance to compression during the curing period, only helped to decrease porosity, durability and improved the compaction, behaving as an aggregate

Tensile strength analysis
The results from the tensile strength tests are shown in Fig. 4, in which the data are lower than those obtained from the compressive strength tests in a ratio ranging from 5 to 10. However, the ratio obtained is consistent with the values according the 50000 IRAM (2010) Standards; which range from 8.6 for a one-month mortar to 10.6 for 12-month mortars.

Heat of hydration analysis.
In order to determine the heat of hydration (q), a calorimeter was used with which the test-tube initial temperature was first measured and then, it was measured at 7 and 28 days, respectively, in accordance with the IRAM 1617 (2010) Standard.

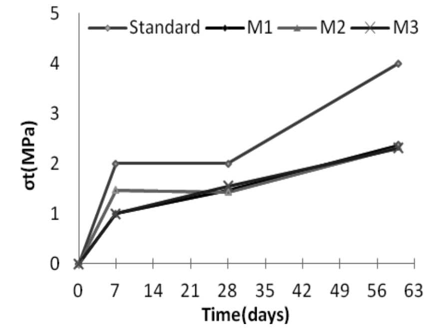

Figure 4: Tensile Strength Test.

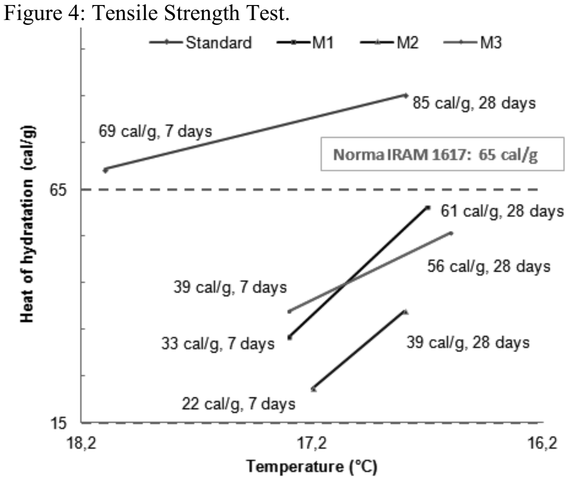

Figure 5: Hydration Heat.

The values obtained are shown in Fig. 5 from which it may be concluded that the slag-bearing mortars developed a hydration heat below the lower limit according to the IRAM 1617 (2010) Standard for 7 and 28 days, respectively, whereas the contrast mortar develops a greater heat of hydration.

Generally a Portland cement of low heat of hydration is not economical if it is done with “pure” cement (Portland cement) because it requires a special composition of Portland clinker. Therefore the use of slag cement produces less heat of hydration than a Portland cement, which is why low values of heat of hydration in calories / gram were obtained with mortars slags in comparison with the standard mortar.

Slag-bearing mortars were found to have lower hydration heat than the comparison mortar at 7 and 28 days respectively. For this reason, using slag cements in warm or hot zones such as our province is found advisable in order to help prevent the risks of thermal cracking.

IV. CONCLUSIONS

The following are some of the advantages of using substitute cementitious material partially composed of slags from gold smelting processes (as compared to Portland-based cement):

- Similar mechanical properties.

- The hydraulicity index is in direct proportion to the RCU (see Table 4) and in inverse proportion to the resistance to compression (Fig. 3)
- The long term mechanical mortars slag (60 days) resistances are higher due to a complete hydration of the cementitious material. Besides, porosity is lower, durability and compaction are higher.
- Cement production capacity may be expanded when substituted by a slag in a percentage of 11%.
- Because no additional thermal processing is required (leads to energy saving and less contamination)
- Waste accumulation in slagheap or fills is lower.

From the energy saving standpoint, there are good prospects for slag cement since 1 ton of Portland cement requires 1,5 t of raw material and 850 kcal for its processing whereas 1 ton of slag cement, which contains 65% of slag and 15% moisture, requires only 0.5 t of raw material and 400 kcal.

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