

VALORIZATION OF STEEL SLAG IN ROAD CONSTRUCTION - COMPREHENSION OF MOLYBDENUM'S REPARTITION

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Abstract- Steel production in an electric arc furnace (EAF) generates a by-product called EAF slag. As a result of the presence of significant amounts of impurities, EAF slag is generally not or less recycled in a next steel production and stored in the form of a dump which takes increasingly space. Many studies have shown that slag may substitute for natural aggregate in the construction sector. In which case, the use of slag cannot expand because some slags may contain traces of leachable heavy metals, which are considered as potential threats to human health and environment. In the present study, the slag sample was collected from an historical slag dump disposed for about sixty years. We decided to investigate the repartition molybdenum (Mo), a heavy metal much used in the recent steel production and still detected in slag. In addition to the determination of main chemical and mineralogical compositions by X-ray fluorescence (XRF) and X-ray diffraction (XRD), cathodoluminescence (CL), scanning electron microscopy (SEM) and micro fluorescence (μ XRF) were used to understand the repartition of Mo in the different phases of slag. The results indicate that Mo were localized in two phases: iron silicates ($\text{Fe}_x\text{Si}_y\text{O}_4$) and melilite (solid solution of akermanite ($\text{Ca}_2\text{MgSi}_2\text{O}_7$) and gehlenite ($\text{Ca}_2\text{Al}[\text{AlSiO}_7]$)).

Index terms- EAF steel slag, leaching test, petrography.

I. INTRODUCTION

The last two decades have shown a growing interest in the use of waste materials in the road construction [1;2;3;4;5;6]. In fact their valorization allows a number of benefits such as the conservation of natural resources, the reduction of waste storage volumes, the decrease of material construction cost and transport demands and the promotion of local economy. Yet recycling waste in such an application depends not only on its aptitude to reach road specifications but also on the condition that it does not contaminate the environment and specially surface and/or underground water with toxic elements [7;8;9]. The release of elements, mainly heavy metals, by a solid waste, is related to its chemical and mineralogical composition [10;11;12]. Analyzing the distribution of a given element in the different phases of a material is also important for the development of a treatment process able to extract them. However, due to the complexity of this analysis, it is useful to develop a methodology by coupling different techniques from the macroscopic to the microscopic scale. This paper presents the analytical methodology developed and its application for the localization of a heavy metal, the molybdenum, in a steel slag.

II. DEVELOPED METHOD

A global chemical or mineralogical analysis of a mineral material allows the determination of bulk chemical and mineralogical compositions, but it

doesn't give insight into local compositional features. Therefore to determine the distribution of the molybdenum in the different phases of a steel slag,

we proceed step by step from a global and macroscopic analysis to a local and microscopic one. Special techniques have been used for each step and coupled to localize metal inclusion and identify the mineralogical phases which contain it as described in figure 1.

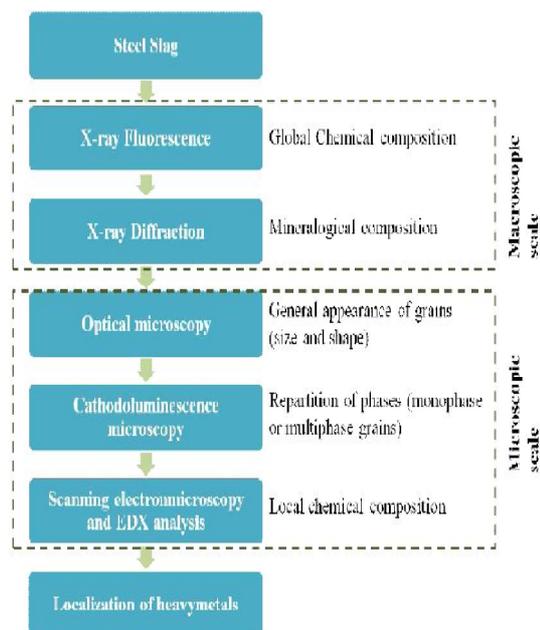


Figure 1. Description of the developed method to localize metal inclusion and identify the phase that contains it.

First, the global quantitative chemical composition of the mineral material is determined by x-ray fluorescence and the global qualitative mineralogical composition is obtained by x-ray diffraction. Then, optical techniques are used on a sample of the mineral material fixed on a resin substrate.

Optical microscopy under reflected light allowed the exploration of the minerals that compose the material by the difference of light reflected intensities. Thus, metal inclusions were distinguished thanks to their reflection contrast against their host mineral. Different monophasic and polyphasic grains were selected and numbered.

A color sorting was afterward undertaken on the basis of the mineralogical composition of the grains by using cathodoluminescence microscopy. This technique is able to differentiate a number of minerals according to their composition and reflected angle. For example, the red color is generally attributed to the presence of calcite [13]. The feldspar silicates are blue and the plagioclase silicates are green [14]. Finally, each color group was analyzed by scanning electron microscopy coupled with EDS probe which provides local chemical composition. As a result the phase containing the metal inclusion is identified.

III. RESULTS: APPLICATION TO MOLYBDENUM

3.1 Material

The molybdenum-bearing mineralogical phases are investigated in a steel slag produced by an electric arc furnace (EAF-S). Its gap-grading analysis according to EN 933-1 European standard [15], shows that it can be assimilated to a 0/1mm sand.

3.2 Analytical techniques and sample preparation

The different analytical techniques used are described in this part.

3.2.1 X-ray fluorescence

The analysis of major and trace elements in EAF-S by x-ray fluorescence was undertaken using Bruker SRS 3400 spectrometer.

The sample split is grounded into a fine powder (<100 μ m). Then 10 grams of the powder is mixed with 3 grams of a reagent for tableting (wax micopowder C₃₈H₇₆N₂O₂) and compacted using Sodemi press at a pressure of 20 tons per cm² maintained for 30 seconds.

3.2.2 X-ray diffraction

The average bulk mineralogical composition was obtained by powder x-ray diffraction using a Siemens D5000 diffractometer with Bragg-Brentano geometry. The diffractometer is equipped with a copper anti-cathode (40 kV, 40 mA) that the CuK α radiation is equal to 1.54056 Å.

The EAF-S is dried and grounded into fine powder (<100 μ m). A sample of 200 grams were analyzed and data was collected at 2 θ from ~5° to 70° (path equal to 0.03° every 5 seconds).

3.2.3 Optical microscopy using reflected light

The petrographical analysis was made using Nikon Eclipse LV 100 POL microscope equipped with 5 megapixel resolution camera (Leica DFC 420) and image acquisition software (Leica Application Suite V3).

In order to facilitate observation, the same slide made of dried EAF-S fixed with epoxy resin (fig. 2) was used for all microscopy observations (optical, cathodoluminescence and SEM/EDS).

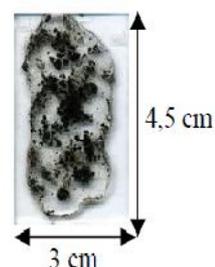


Figure 2. Image of the slide used for optical observations and analyses

3.2.4 Optical cathodoluminescence microscopy (CLM)

Mico-morphological analyses were made on the previously prepared slide (fig.2) using CITL 8200MK3 cold cathode luminescence (CL) instrument with an accelerating voltage of 20 kV of electron energy and a beam current of 400 μ A. CL images were recorded using a Leica digital camera mounted on Olympus BX40 microscope.

3.2.5 Scanning electron microscopy (SEM)

The slide (fig.2) was covered with a thin layer of spray-on carbon, which acted as a conductor. Micrographs were obtained using a JEOL JSM 6400 microscope equipped with an EDS system (energy dispersive spectroscopy). The beam of electrons is accelerated with electric current of which the potential difference is 15 kV. This set-up enabled determining the atomic composition of a sample during observation.

3.3 Molybdenum distribution

Chemical characterization of EAF-S shows (table 1) that it is composed of 70% by weight of siliceous oxides of silicium, calcium, aluminum and iron. It also contains metals (copper (Cu), nickel (Ni), chromium (Cr), molybdenum (Mo), vanadium (V), zinc (Zn)...).

Table 1. Chemical composition of EAF-S by x-ray fluorescence

Elements	Units	EAF-S
SiO ₂	% by weight	32.9
TiO ₂	% by weight	0.4
Al ₂ O ₃	% by weight	8.1
Fe ₂ O ₃	% by weight	14.1
MnO	% by weight	1.5
MgO	% by weight	3.9
CaO	% by weight	15.8
Na ₂ O	% by weight	0.2
K ₂ O	% by weight	0.8
P ₂ O ₅	% by weight	0.2

The study of the mineralogical composition by x-ray diffraction (fig.3) shows that EAF-S is a crystalline material mainly composed of quartz, calcite and silicates and Ca-Al silicates.

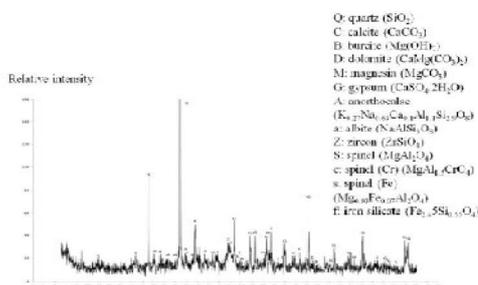


Figure 3: X-ray diagram of the EAF-S

The localization of molybdenum (Mo) inclusions in EAF-S and the determination of the chemical compositions of their host minerals were undertaken as follow: first Mo inclusions were observed in the slide (previously prepared using EAF-S sample and a resin) with optical microscopy under reflected light and the grains that contain them were selected and numbered.

The observation of the slide (fig. 4a) showed that the minerals that compose EAF-S range in size from 50µm to 1mm. These minerals were homogenous grains that could be silicates, carbonates and heterogenous grains difficult to be analyzed by this technique.

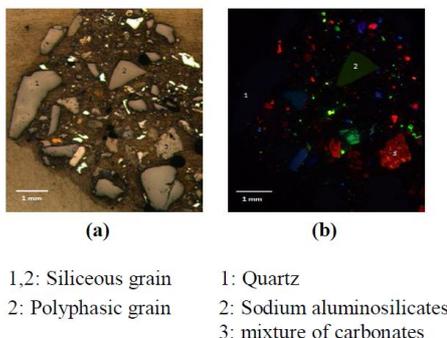


Figure 4. Optical observations of EAF-S: mineral identification and selection (a: reflecting light; b: CLM)

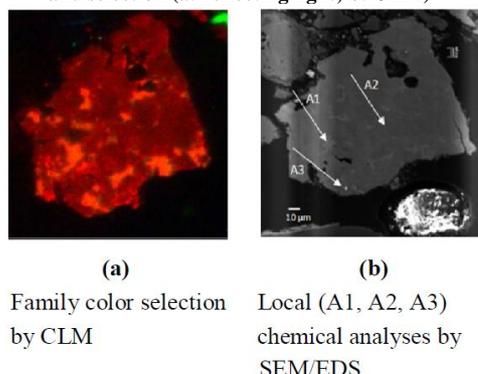


Figure 5. Optical analyses of EAF-S: selection of "family color" and analysis by SEM/EDS

Optical cathodoluminescence microscopy was thus

used to differentiate (by color) mineral phases that could contains Mo inclusions. Different "color families" were observed (fig. 4b) and selected (fig.5a) and analyzed by SEM coupled with EDS (fig.5b). The results in table 2 showed that chemical composition of the selected grain could be attributed to melilite $(CaNa)_2(Mg,Fe,Al)[(Al,Si)SiO_7]$.

The composition difference between A1 and A2 analyses shows that it could be a mix of akermanite $Ca_2MgSi_2O_7$ and gehlenite $Ca_2Al[AlSiO_7]$. Furthermore, different metal inclusions (Mo, Fe) have been also revealed by A3 analysis.

Table 2. Chemical composition at A1, A2 and A3 points of selected color (red) by SEM/EDS

	A1		A2		A3	
	% by weight	At%	% by weight	At%	% by weight	At%
Si	34.57	41.36	36.26	38.07	29.62	33.77
Ca	36.49	30.59	24.52	18.04	24.36	19.46
Mg	10.77	14.87	8.52	10.33	24.07	31.70
Al	7.48	9.32	30.69	33.56	6.98	8.29
Mn	4.42	1.55			8.12	2.71
Fe					2.29	1.31
					1.60	0.93

Further analyses by SEM/EDS (fig. 6 and table 3) showed that the grain analyzed was composed by iron silicates (A2 analysis). It also contained Mo (A1 analysis) with an important atomic percentage (14.6%).

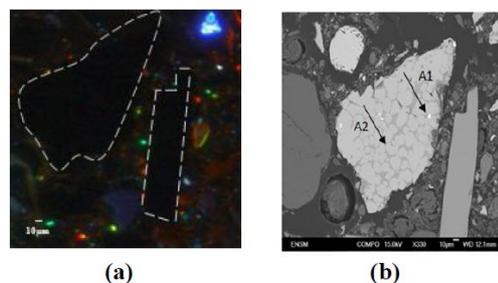


Figure 6. Optical analyses of EAF-S: selection of "family color" and analysis by SEM/EDS

Table 3. Chemical composition at A1 and A2 points of selected grain by SEM/EDS

Element	A1		A2	
	% by weight	At%	% by weight	At%
Si	5.12	11.4	8.43	15.48
Fe	29.37	33.29	91.57	84.52
Mo	22.14	14.6		

Knowing that the detection of the K-alpha emission line (17,4 keV) of molybdenum is not possible with existing SEM/EDS because it requires an electric

current with potential difference above 30 kV, we studied the L-alpha emission line (2,29 keV) that it is near to the K-alpha emission line of sulfur (2,31 keV). To resolve this problem, we confirmed results with another technique which is the micro fluorescence X. This technique is not equipped with efficient camera like the SEM but allows to exert a potential difference of 40 kV and to obtain a mapping of the areas of the slide containing molybdenum. When different areas of the slide containing molybdenum were identified, we made chemical analysis of the phases present in these areas with the SEM/EDS.

To conclude Mo inclusions were localized into two types of mineralogical phases: iron-rich phases such as iron silicates ($\text{Fe}_x\text{Si}_y\text{O}_4$) and calcium and/or magnesium aluminosilicates phases like akermanite $\text{Ca}_2\text{MgSi}_2\text{O}_7$ and gehlenite $\text{Ca}_2\text{Al}[\text{AlSiO}_7]$.

CONCLUSION

In this paper, we presented the methodology developed for the analysis of a mineral waste material in order to understand the localization of heavy metals. The methodology allows passing from macroscopic scale to microscopic scale by coupling different techniques until the identification of phases containing metal inclusions becomes possible.

The application of the methodology to identify the phases containing Mo inclusions in a steel slag demonstrated two types of phases: iron-bearing phases such as iron silicates ($\text{Fe}_x\text{Si}_y\text{O}_4$) and calcium and/or magnesium aluminosilicates phases like akermanite $\text{Ca}_2\text{MgSi}_2\text{O}_7$ and gehlenite $\text{Ca}_2\text{Al}[\text{AlSiO}_7]$.

The methodology of characterization established in this study can be used to characterize other mineral waste materials. Furthermore, the identification of the phases containing metal inclusion could help the development of metal extraction techniques and therefore open new perspectives for waste valorization.

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