EVOLUTION OF CHEMICAL, MINERALOGICAL AND MAGNETIC PROPERTIES OF ELECTRIC ARC FURNACE SLAG OVER WEATHERING

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Introduction

Management of steel-making slag stored on production site is an important environmental issue. Our study deals with Electric Arc Furnace (EAF) steel slag accumulated during several decades on the site of Châteauneuf steelmaking plant (Loire, France). The very important volume (> 200 000 m^3) and the high chromium contents (> 2%) prevent the off-site transportation and the recycling in classic slag applications. In this context, in-situ options are explored such as phyto-management. This work proposes to investigate the long-term behaviour of this slag and more specifically metal elements mobility during weathering processes. Fast chemical and magnetic analysis methods are used at the field scale and results are compared with laboratory analyses performed on taken samples (chemical characterisation and qualitative mineralogy). Coupling chemical and magnetic data aims to determine if certain metallic elements are associated with Fe bearing minerals, *i.e.* to potentially high magnetic susceptibility minerals. Thus, magnetic susceptibility could be used as a proxy for heavy metals pollution as it has been presented in different studies[1,2]. Then, first leaching experiments are conducted regarding metallic elements mobility.

Measurements and experiments protocols

Material characterisation

In this study, the priority has been given to the chemical and magnetic properties characterisations of the slagheap surface which is more vulnerable to chemical weathering processes (leaching, oxidation, hydration/dehydration, dissolution). This is also the part which is the most important to study in the perspective of phytostabilisation. Detection and mapping of metallic elements abundance were performed with a large data set of field measurements according to a grid with 276 points 10 meters apart. Chemical analyses were performed on the slagheap surface with a pXRF instrument (Olympus Vanta serie M) and magnetic susceptibility

was measured using a Bartington MS3 meter equipped with a field loop. For each grid point, measurements were done on the roughly homogenised and flattened surface. Thirty-one samples of 500 cm^3 representative of the surface 0-5 cm layer were then collected through the previous grid for laboratory analysis. Magnetic susceptibility was measured with Agico MKF1-FA Kappabridge, chemical analyses were realised with the pXRF analyser (Olympus Vanta serie M) on finely ground and compacted slag (< 250 µm). This grinding step allows to realise chemical analyses on bulk material, whereas on the field, only grain surface analyses can be done. Principal Components Analyses (PCA) enable to combine field and laboratory data and to see correlations between parameters. Correlations observed are interpreted as elements associations in minerals.

Leaching tests

Leaching tests were conducted with deionised water on slag samples, with a L/S ratio of 10. Slag grains (grain size ranging from 0.40 to 1.25 mm) were introduced in autoclaves during 24 h, 7 days and 30 days at temperatures of 40°C, 60°C and 110°C in order to increase kinetics and to simulate weathering processes occurring over several decades. Leachates were analysed by ICP-AES and ICP-MS. Metal extraction rates are calculated according to initial contents in solid samples, liquid and solid weights and leachates concentrations. Temperatures higher than 60°C might appear as unrealistic weathering conditions, but it is much lower than crystallisation temperatures of the slag minerals and it stays in their stability range.[3] Thus, observed mineralogical transformations are attributed to alteration processes.

Results and discussion

Field and laboratory results comparison

Field and laboratory analyses of slag give different chemical compositions (Figure 1). It suggests that the surface of the slag grains has a different chemical composition compared to the bulk material. The core of the grains would be richer in Fe and other metals than the peripheral part. This is consistent with a preferential weathering of the edge of the grain which would be consequently richer in hydrated phases and alteration minerals such as portlandite ($Ca(OH)_2$) and calcite ($CaCO_3$).[4]

The correlation circles obtained with PCA are given in Figure 2. Field study shows a correlation between Fe and magnetic susceptibility, which is quite intuitive, and another correlation between Cr and Mn contents (Figure 2a). No significant correlation appears between Si, Al and other elements. Laboratory study shows a global correlation between Fe, Cr and Mn contents and magnetic susceptibility (Figure 2b). Ca and Si contents are clearly anti-correlated.

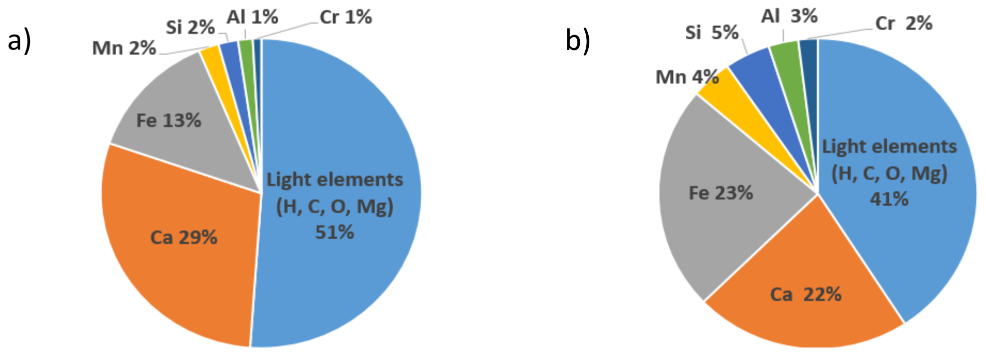

Figure 1: Mean chemical composition of slag from field (a) and laboratory (b) analyses

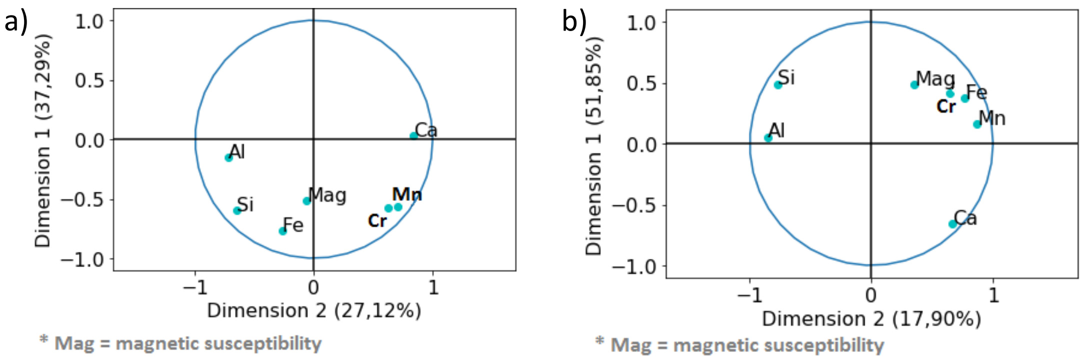

Figure 2: Correlations circle obtained with field data (a) and with laboratory data (b)

Future XRD and SEM studies will help to explain differences between field and laboratory results. A better knowledge of the mineral composition of the material, and more specifically of Cr speciation, is necessary to know if magnetic susceptibility can be used as a proxy for this element. According to previous studies on the same material[4] and on other EAF slag[5], Cr is mainly found in magnesiochromite ($(Mg,Fe)(Al,Cr)_2O_4$), in brownmillerite ($Ca_2(Al,Fe,Cr)_2O_5$), in a lesser extent in wustite (Fe,Mn,Mg,Cr)O and more scarcely in calcium chromite ($CaCr_2O_4$).

Leaching tests

Elements concentrations were very low in leaching solutions. Significant concentrations were obtained only for Ca (30 to 40 ppm) and Cr (1 to 8 ppm). It is consistent with previous studies[4,5] which suggested that only Cr present in Ca bearing minerals (brownmillerite and calcium chromite) is able to be mobilised during meteoric alteration. However, extraction rates are very low, between 0.13 and 0.19% for Ca, and between 0.09 and 0.33% for Cr (Figure 3).

At 40°C and 60°C the Ca extraction rate appears to be constant regardless of time, while the Cr extraction rate increases with time and temperature. At 110°C the extraction rates decrease with time for both Ca and Cr, indicating that a phenomenon of precipitation might have occurred after a first extraction due to alteration.

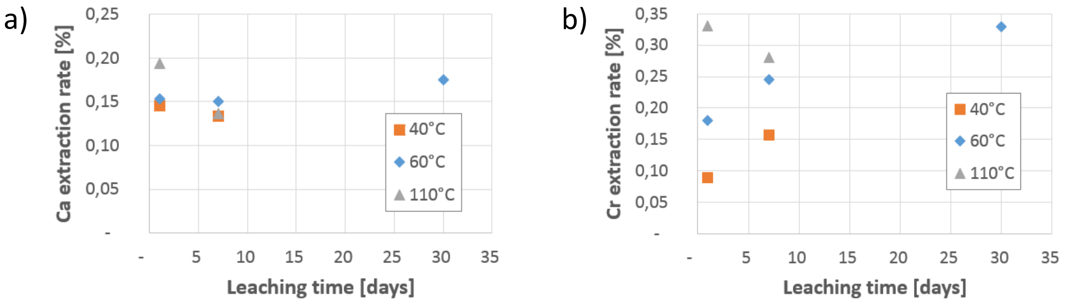

Figure 3: Ca (a) and Cr (b) extraction rates depending on leaching time and temperature

Conclusions

Coupled chemical and magnetic measurements enable a quick reconnaissance on the field; beyond chemical information, we obtain an idea of mineral composition of the material. Leaching tests show an expected behaviour of Cr and Ca. Further mineralogical analyses and leaching experiments will permit to discuss about mineral transformations throughout weathering at the grain scale.

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