Environmental assessment of a BOF steel slag used in road construction : The ECLAIR research program

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Abstract

Steel production generates great amounts of by-products as steel slag. Unlike blast furnace slag, the use of Basic Oxygen Furnace slag (BOF slag) has been restrained due to insufficient volume stability and to the lack of environmental regulations. This study aimed at investigating the potential release and impact of pollutants, especially Cr and V that are present in rather high concentrations in slag, from a BOF slag used in a civil engineering structure (an industrial platform), using a multi-scale approach. The one-year follow up of the experimental platform showed that concentrations of Cr and V were generally low in seepage waters, and in leachates from leaching test. Micro-analyses carried out on slag allowed us to confirm the location of these metals in rather stable ferrous mineral phases, but V was also bound to more reactive silicates. No real toxicity effect of seepage waters has been revealed from eco-toxicological tests carried out with earthworms.

Keywords: Steel slag, civil engineering, chemical analysis, hydrodynamics, environmental assessment.

Introduction

Steelmaking slag includes blast furnace iron slag, and electric arc furnace (EAF) and basic oxygen furnace (BOF) steel slag types. BOF slag production is about 10% by weight of steel output. Many uses of steelmaking slag were developed in a variety of industries, but the use of BOF slag has been restrained due to insufficient volume stability and to the lack of environmental regulations. The ECLAIR research program has been launched in order to develop a behavior model of a BOF slag used in a public works scenario. The study deals with the metallic trace elements contained in the slag mineral phases and that might be mobilized during fluid percolation through the structure, especially Cr, V and Ba (Chaurand et al., 2006). A multi-scale characterization has been carried out to evaluate the crystallo-chemical evolution of the BOF slag mineral phases and of the associated metals. These results, together with the

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evaluation of specific parameters (volume stability, hydrodynamic flows), will allow to use relevant data to develop a model characterizing the fluxes and their migration from the structure. Finally, a study of the impact of leachates on the earthworm, which is a widely used model for the evaluation of polluted soil ecotoxicological risks, has been performed. The overall model will be validated with the results obtained from the follow up of a full-scale experimental civil engineering structure (industrial platform).

Materials and methods

Studied material

The studied material is a BOF steel slag screened and treated to remove iron in 2003. The slag was dumped outside 3 years for ageing. The used mixture was made with three available granular fractions of 0-2 mm, 2-4 mm and 4-6 mm combined into equal portions in March 2007. The optimum moisture content (normal Proctor test) is 10% with a bulk density of dry material of 2.11t.m^{-3}.

Experimental site

The experimental site consists of an outside industrial platform, 10.9x6.4m and 0.52m thick, located in the southern part of France. The bottom of the work has been covered with a geomembrane and equipped with a drainage system in order to collect the stormwater percolating through the BOF slag (total mass about 70t). The platform is unpaved and there is no traffic. The dry bulk density averaged 1.9tm^{-3}. After the construction, two different types of surface appeared, one with coarse material and the other with finer material, due to surface heterogeneous compacting by work machines.

Analytical methods

The solutions were analysed, after filtration through a 0.45-µm membrane, using inductively coupled plasma optical emission spectrometry (ICP-OES) according to NF EN ISO 11885 standard method, or mass spectrometry (ICP-MS). The elemental composition of the slag was determined by ICP-OES, after alkaline fusion as regards silicon, and after aqua regia sample digestion as regards trace elements. NF EN 12457-2 leaching test was carried out to characterize the initial pollutant potential of BOF slag (single 24h-extraction with deionised water, liquid/solid ratio of 10). Bulk mineralogy of the steel slag was determined by X-ray diffraction. Optical microscopy and scanning electron microscopy (SEM) coupled with X-ray spectroscopy micro-analyses (EDS) was used to study the location of mineralogical phases in slag grains. Micro X-ray fluorescence spectroscopy (µ-XRF) helped to determine the location of trace elements within the mineral matrix using a statistical analysis (Chaurand, 2006). The oxidation state and nature of mineral phases containing iron were studied by XANES spectrometry. Fe K-edge XANES spectra were collected on LUCIA beamline of the SLS/SOLEIL, Paul Scherrer Institute, Villigen, Switzerland.

Hydrodynamic characterization

In situ-infiltration experiments (infiltration of water in the material through a disc, under control of the water pressure at the surface) have been performed through the use of a simple ring according to the Beerkan infiltration method (Lassabatere et al., 2006). Cumulative infiltrations (total infiltrated water head versus time) were modelled to derive the water retention h(θ) and hydraulic conductivity K(θ) curves through the BEST algorithm.

Ecotoxicological approach
Ecotoxicological study has been carried out on two earthworm species, *Lumbricus terrestris* and *Eisenia fetida.* Different types of bio markers have been used: avoidance reaction, mortality, weight evolution, biochemical activity, "comet test" on earthworm coelomocyte. Earthworms have been exposed by contact to a soil contaminated by different amounts of leachates collected at the experimental platform.

Results and discussion

Chemical and mineralogical characterization
Slag was characterized by a high content of calcium (40.7% as CaO), iron (29.8% as Fe_2O_3) and silicon (16.0% as SiO_2) (Legret et al., 2008). The silicate phases (Figure 1) were mainly composed of dicalcium silicates (Ca_2SiO_4) and inverted tricalcium silicates (Ca_3SiO_5). Two types of iron oxides phases were also present, the Mg-wustite, more precisely a solid solution rich in iron and magnesium with a complex composition ((Fe, Mn, Mg, Ca)O), and dicalcium ferrite ($Ca_2Fe_2O_5$) and dicalcium aluminoferrite ($Ca_2Fe_{2-x}Al_xO_5$) (Deneele et al., 2008). Concentrations of Cr, V and Ba were as high as respectively 910, 741 and 128mgkg^{-1}. The results of micro-analyses carried out in non altered slag grains showed that chromium was mainly associated with ferrite and Mg-wustite, while vanadium was mainly located in ferrite and partially in calcium silicates. Due to weathering processes, an altered layer developed at grain rims. Silicates were dissolved, and secondary calcium silicate hydrate (CSH) phases and portlandite were formed. The partial dissolution of Mg-wustite seemed to induce the formation of brucite, of stoichiometric wustite and of a spinel-type phase (magnetite) with the trapping of Cr as impurities (Deneele et al., 2008). The determination of lime content showed that, even after 3 years of ageing, the concentration of free-lime (CaO+ $Ca(OH)_2$) was about 6%. The assessment of the potential swelling of the studied slag from the expansion test (steam test) showed a volume increase up to 20%.

Hydrodynamical characterization
Three infiltration experiments were carried out, in July 2007, November 2007 and in July 2008 (Figure 2). During the first measurement, a significant difference was observed between coarse surface and fine surface. The infiltration rate was 10 times lower for fine surface in comparison to coarse surface. During the second experiment, 6 month later, the difference between the two zones was less important and the infiltration rate was slower. This behavior was confirmed during the third measurement. It seemed that the permeability of the platform was more homogeneous and tended to decrease with time, maybe due to the reaction of slag minerals with water and atmospheric CO_2 that induced carbonation and precipitation phenomena. As regards characteristic hydrodynamic curves, the behavior of the slag could be compared to a sandy loam (Yilmaz et al., 2008).

Leaching test and experimental platform survey
Samples were collected monthly at the experimental platform from May 2007 to June 2008. Table 1 shows the result of the 12 seepage water analyses as well as the fluxes of

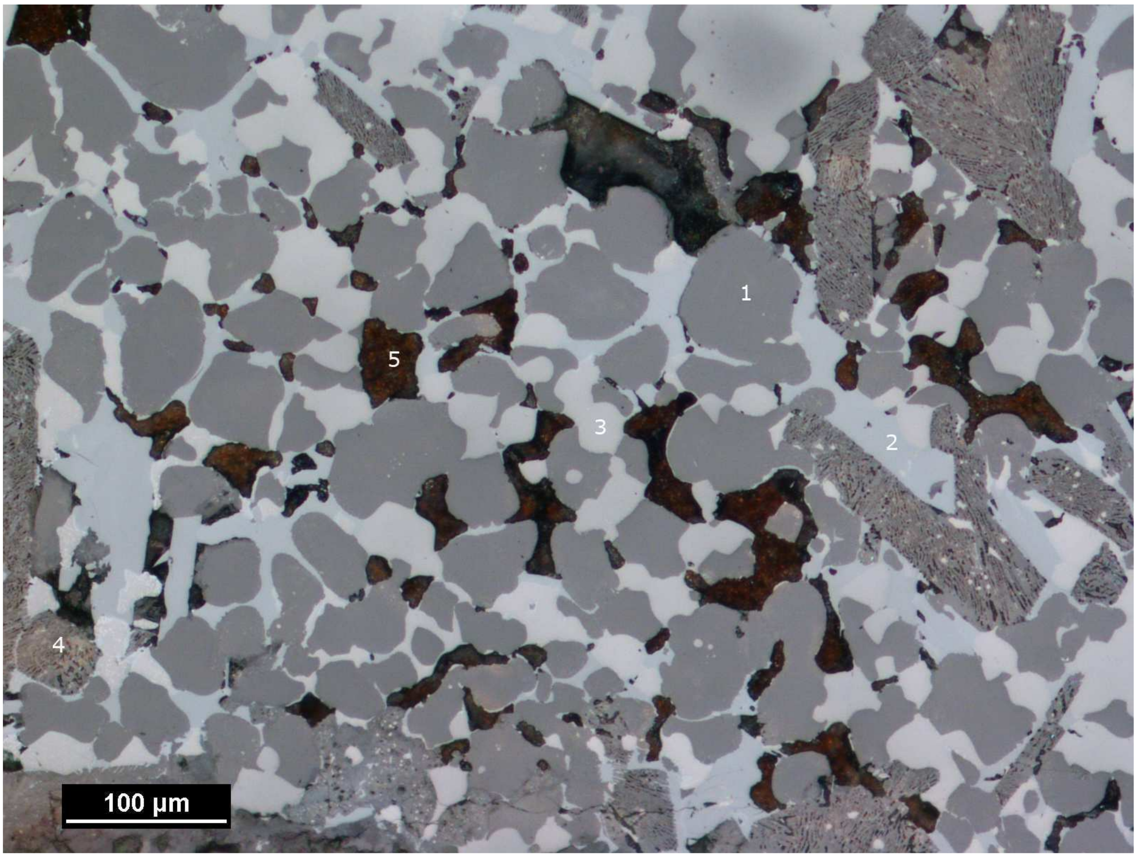

Figure 1: Optical microscopy micrograph of the mineralogical assemblage of the BOF steel slag

(1: dicalcium silicate (Ca_2SiO_4); 2: dicalcium aluminoferrite ($Ca_2Fe_{2-x}Al_xO_5$); 3: Mg-wustite, ((Mg, Fe, Mn, Ca)O); 4: inverted tricalcium silicates (Ca_3SiO_5); 5: lime (CaO))

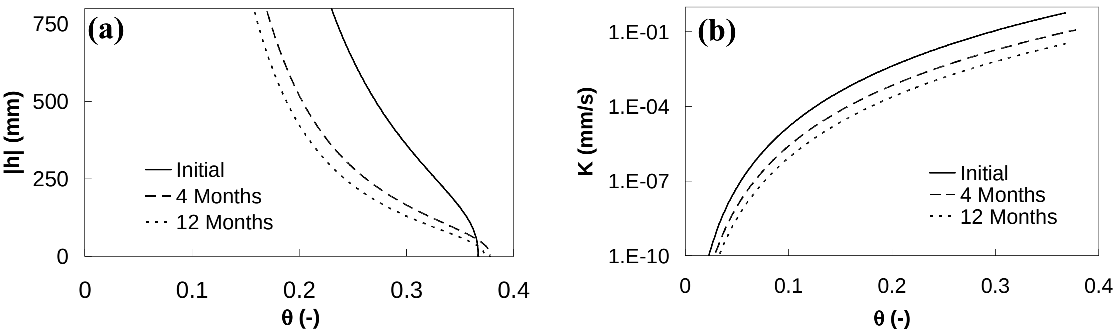

Figure 2. Site-averaged water retention curves *h(θ)* (a) and hydraulic conductivity curves *K(θ)* (b) vs. time

Table 1: Results of leaching test and seepage water analyses

Parameter	Leaching test NF EN 12457-2 (L/S=10)	Seepage water fluxes (L/S=0.11)	Inert waste threshold 12/31/04 Decree	Seepage water	Drinking water 2001-1220 Decree
	mgkg-1	mgkg-1	mgkg-1	mgL-1	mgL-1
Cond. µScm-1	7388	-	-	5330-9540	1000
pH	12.2	-	-	12.3-13.0	6.5-8.5
Dry residue	14520	220	4000	1074-4428	-
Organic C	29.7	3.5	500	14.9-55.6	-
Sulfates	19.2	0.27	-	0.49-6.4	250
As	<0.1	<0.0011	0.5	<0.01	0.01
Ba	3.3	0.21	20	1.3-2.25	0.7
Ca	6950	82	-	429-1074	-
Cd	<0.05	<0.0007	0.04	<0.005	0.005
Cr	<0.1	<0.0012	0.5	0.01-0.02	0.05
Fe	<0.3	<0.0033	-	<0.03	0.3
Pb	0.58	<0.0011	0.5	<0.01	0.01
Si	1.54	<0.02	-	<0.03-1.5	-
V	<0.1	<0.0015	-	<0.01-0.03	-
Hg	<0.01	<0.000012	0.01	<0.0006	0.001

chemicals contained in the percolating waters. Results of the leaching test are also shown as well as reference values of the French Decree on drinking water (surface fresh water for drinking water production) and inert waste threshold values for leaching test (NF EN 12457-2).

Results of leaching test indicated that the conductivity and dry residue of leachate were high, and the pH was very alkaline, more than 12, due to the high content of free-lime in slag. In the conditions of the leaching test, the release of Fe and of trace elements was generally low, less than 0.1mgkg^{-1} for Cr and V. Analysis of seepage waters showed that the pH was very alkaline, more than 12, and the conductivity was rather high. The concentrations of Organic Carbon and sulfates were quite low. Except for Ba, the concentrations of trace elements were low, less than 0.02mgL^{-1} for Cr, and less than 0.03mgL^{-1} for V (U.S.EPA action level for drinking water 0.05mgL^{-1}, recommend notification level 0.015mgL^{-1} (OEHHA, 2000)), as well as concentrations of Fe (less than 0.03mgL^{-1}). Fluxes of elements from the experimental platform after one year were also very low, lower than that measured from leaching test. As showed above, Cr in slag is located in the ferrous minerals, ferrite, wustite and spinel-type magnetite, which proved to be very stable as confirmed by the low release of Fe in leachates. Vanadium was also bound to ferrite, but also to calcium silicates which reactivity with water is higher. Nevertheless, the release of Si in water was weak, probably due to the high content of lime in slag inducing a high concentration of dissolved Ca (Drissen, 2007). Long term behavior of V might be affected by carbonation and partial dissolution of silicates (Huijgen and Comans, 2006).

Ecotoxicological study

Habitat modification, especially as regards soil pH, appeared weak and without significant effect. No mortality and effect on weight evolution of earthworms were noticed. Some differences have been found as regards biochemical markers for the most polluted leachate and, an avoidance reaction has been observed with the higher contamination rate tested. No genotoxicity effect has been noticed, and more generally, no real toxicity effect has been pointed out with the tested leachates.

Conclusion

A multidisciplinary approach for the assessment of environmental behavior of BOF slag used in road construction has been implemented. Seepage waters from an experimental platform have been analysed for one year. Concentrations of Cr and V were generally low in seepage waters and leachates from leaching test. Micro-analyses carried out on slag allowed us to confirm the location of these metals in rather stable ferrous mineral phases, but V was also bound to more reactive silicates. No real toxicity effect of seepage waters has been revealed. Further analyses are in progress as regards the geochemical evolution of slag mineral phases and chemical speciation of Cr and V due to natural weathering, as well as modeling approach for metal release and transport.

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Acknowledgment

The ECLAIR project is partly financed by the French Agence Nationale de la Recherche (ANR) within the frame of the PRECODD program.