Environmental assessment of the behavior of a BOF steel slag used in road construction : the PRECODD-ECLAIR research program

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Abstract

Steel production generate great amounts of by-products as steel slags. The use of Basic Oxygen Furnace slags (BOF slags) has been restrained due to insufficient volume stability, and due to the lack of environmental regulations. The purpose of the PRECODD-ECLAIR research program is to develop a behavior model based on a multi-scale physico-chemical, mechanical, hydrodynamic and ecotoxicological characterizations of a BOF slag used in a public works scenario. This paper aims at presenting the overall ECLAIR research program, the equipped experimental platform constructed using a BOF steel slag, and the first results of the slag characterization.

Keywords: Steel slag, civil engineering, chemical analysis, hydrodynamics, environment.

1. Introduction

Steel production generates great amounts of by-products as steel slags (2.2 million tons in France in 2004). Conversely to blast furnace slags which have been extensively used in cement industry, building trade and road construction, the use of Basic Oxygen Furnace slags (BOF slags) has been restrained due to insufficient volume stability, and due to the lack of environmental regulations. Ageing processes have been developed in order to control the volume instability and the use of this product is developing in civil engineering to save natural resources.

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Mainly composed of tricalcium and dicalcium silicates (Ca_2SiO4), dicalcium ferrite (Ca_2Fe2O5) and solid solutions containing iron and manganese oxides ((Fe, Mn,Mg,Ca)O) (Goldring and Juckes, 1997), steel slags also contain free lime (CaO) and periclase (MgO) coming respectively from the additions during ore reduction and from the refractory wall of the oven. Leaching tests carried out on steel slags have shown that the pH of leachates could reach high values (10-13) and trace elements could be released from some slags (Motz and Geiseler, 2001; Chaurand et al., 2006). Besides, weathering promotes the hydration and carbonation of BOF-slags inducing a modification of the mineralogical assemblage and of the trace element speciation (Chaurand, 2006).

Few studies deal with the transfer of contaminants from the by-product layer to the underlying soil, or with the evaluation of the potential impact on the ecosystems at the pilot or work scale. They essentially concern the municipal solid waste incineration bottom ashes (Freyssinet et al., 2002) or electric arc furnace slags (Lind et al., 2001). A study about the human health and ecological risks posed by the uses of steel-industry slags has shown that direct risk for human is low, but on site evaluation is necessary as regards the environment (Proctor et al., 2002).

The aim of the PRECODD-ECLAIR project is to develop a behavior model based on the physico-chemical, mechanical, hydrodynamic and ecotoxicological characterizations of a BOF steel slag used in a public works scenario, within the frame of a research approach integrated in the comprehensive problems of the better knowledge about steel slag behavior.

This paper aims at presenting the overall ECLAIR research program, the equipped experimental platform constructed using a BOF steel slag, and the first results of the slag characterization. The geochemical characterization of the slag is presented elsewhere (Deneele et al., 2008).

2. Presentation of the PRECODD-ECLAIR research program

In 2006, the PRECODD-ECLAIR research program has been launched for three years 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. A multi-scale characterization (macro, micro and molecular) will be carried out to evaluate the crystallo-chemical evolution of the BOF slag mineral phases and of the associated metals. These results, together with the 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 on the earthworm, which is a widely used model for the evaluation of polluted soil ecotoxicological risks, will be performed. The overall model will be validated with the results obtained from the follow up of a full-scale experimental civil engineering structure.

The project comprises seven different steps:

Step 1: Follow up of an experimental civil engineering structure constructed using a BOF steel slag. The quality of water percolating through the structure will be monitored for at least one year in order to evaluate the fluxes of elements originating from the slag.
Step 2: The understanding of geochemical mechanisms of metal release from the slags needs the knowledge of the metal speciation and of the mineral matrix evolution. Initial material and materials resulting from weathering in situ at the experimental site, or coming from a lysimeter and from laboratory leaching tests, will be studied. Multi-scale structural techniques will be used, including X-ray diffraction and electron microscopy. Microscopic synchrotron radiation tools will also be used to characterize metals in slags, especially as regards valence and speciation.
Step 3: A first step of modeling will be performed to simulate the weathering and transport phenomena observed during leaching reactions. It will allow to model the evolution of the mineral matrix for major constituents as well as for contaminants carrying phases. The CHESS/HYTEC model coupling chemistry and transport will be used.
Step 4:The hydraulic characterization of steel slags is necessary for the modeling of pollutant transport. The hydrodynamic characteristic curves, suction versus water content ($h(\theta)$) and hydraulic conductivity versus water content ($K(\theta)$), will be determined.
Step 5: The modeling of pollutant transfer in the soil under a civil engineering structure will be carried out using the PHREEQC model and the data from the previous steps.
Step 6: The toxicity of leachate from the steel slags will be evaluated on the earthworm thanks to a set of not very specific or non-specific biomarkers, including genotoxicity, biochemistry, physiology or behavior of worms.
Step 7: This last step will be dedicated to the proposal of a conceptual model to simulate the long term behavior of pollutants at the work scale, depending on the implemented scenario (work structure and size, mechanical and environmental conditions…).

3. Materials and methods

3.1 Studied material

The studied material is a BOF steel slag screened and treated to remove iron in 2003. The slag was dumped outside in a 3 m heap from 2004 to 2006 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. Figure 1 shows the result of the grain size analysis of the slag mixture. The optimum moisture content (normal Proctor test) is 10% with a bulk density of dry material of 2.11 $t.m^{-3}$.

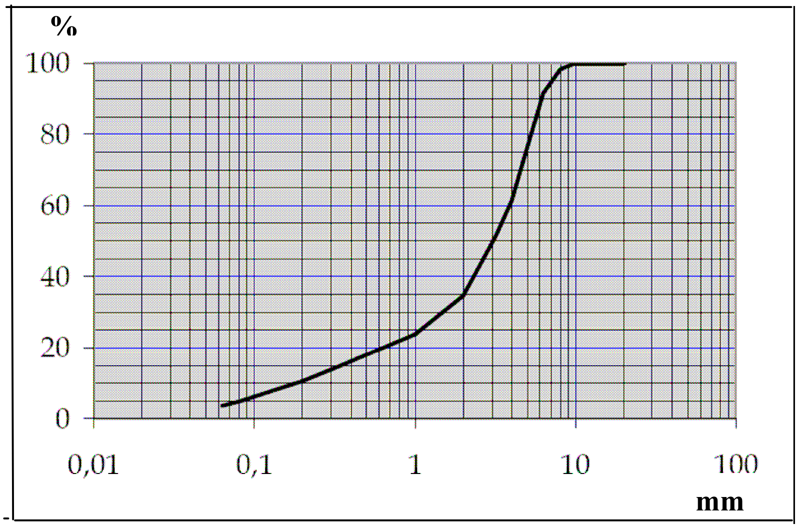

Figure 1. Grain size analysis of the studied material

3.2 Experimental site

The experimental site consists of an outside industrial platform, 10.9 x 6.4 m and 0.52 m 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 slags. Two 0.26 m-thick layers of slags have been dumped in the platform and compacted (total mass about 70t). The bearing capacity of each layer was about 50 Mpa after compaction (plate-bearing test). The platform is unpaved and there is no traffic. The level of the water table is generally below 2 m at the site. The dry bulk density average 1.88 t m^{-3}, which is not so far from the optimum proctor bulk density.

Figure 2. View of the experimental platform

In addition to the platform, a 2-m^3 lysimeter has been installed outside and filled with the same compacted BOF slag. This approach will allow a multi-scale comparison of the results regarding potential pollutant release from the slags and the fitting and validation of predictive models.

3.3 Hydrodynamic characterization

One of the purposes of this research program is to develop a specific laboratory setup that affords a complete hydrodynamic characterization. In addition, in situ infiltration experiments (infiltration of water in the material through a disc, under control of the water pressure at the surface) have already been performed through the use of a simple ring and SW 080 infiltrometer. Cumulative infiltrations (total infiltrated water head versus time) were modelled to derive the water retention $h(\theta)$ and hydraulic conductivity $K(\theta)$ curves.

3.4 Analytical methods

The total trace metal concentration in slags was measured using HNO_3/HCl (aqua regia) sample digestion. The solutions were analysed, after filtration through a 0.45-µm membrane, using inductively coupled plasma atomic emission spectroscopy (ICP-AES or ICP-MS) according to NF EN ISO 11885 standard method. The major elemental composition of the slag was determined by ICP-AES, after alkaline fusion as regards silicon. Chloride, fluoride, sulphate and phosphate were determined using ionic chromatography according to NF EN ISO 10304 standard method. Various characteristics such as pH, total Carbon, loss of ignition were also determined. NF EN 12 457-2 leaching test has been carried out in order to characterize the initial pollutant potential of each fraction of BOF slag (single 24h-extraction with deionised water, liquid/solid ratio of 10). Bulk mineralogy of the steel slags was determined by X-ray diffraction. Thin sections were prepared for microscopic analysis. Optical microscopy and scanning electron microscopy (SEM) coupled with X-ray spectroscopy micro-analyses (EDS) was used to study the localization of mineralogical phases in slag grains. More details are given in Deneele (2008).

4. Results and discussion

4.1 Chemical characterization

Table 1 shows the results of the chemical analysis of the three fractions of steel slags and of the studied mixture. The pH-H_2O, loss of ignition (LoI) at 550°C, Carbon content, major element and trace element contents have been determined. As compared to other data (Chaurand, 2006), the composition of the studied BOF steel slag was representative of the worldwide production, as regards major element content. Slags were characterized by a high content of calcium, iron and silicon. The composition was quite homogeneous whatever the grain size fraction. The chemical composition of steel slags depends on the production source, ores and nature of added materials during production process. So, trace element contents vary very much (Chaurand, 2006; Proctor et al., 2002). Nevertheless, results in table 1 confirmed the presence of vanadium, chromium, barium and boron in steel slags. Besides, the content of chromium, vanadium and barium seemed to increase with the grain size.

The results of leaching test performed on each slag fraction are shown in table 2.

Table 1.Chemical analysis of BOF steel slag fractions

Parameter	Unit	0-2 mm	2-4 mm	4-6 mm	0-6 mm
pH-H_2O		12.7	12.8	12.1	12.7
LoI 550°C	%	4	1.0	1.0	3.0
C	%	1.78	0.63	0.97	1.46
Al_2O_3	%	2.77	1.69	3.54	2.1
SiO_2	%	14.52	14.86	12.4	15.97
TiO_2	%	0.58	0.47	0.39	0.48
CaO	%	42.02	43.85	44.75	40.7
MgO	%	7.45	6.52	7.16	6.46
Na_2O	%	0.06	0.06	0.05	0.07
P_2O_5	%	1.62	1.43	1.14	1.4
K_2O	%	0.04	0.05	0.03	0.06
Mn_3O_4	%	2.95	2.54	2.15	2.59
Fe_2O_3	%	28.46	27.84	27.47	29.82
As	mg/kg	<2	<2	2.87	<2
Ba	mg/kg	96.7	124	137	128
B	mg/kg	113	135	124	118
Cd	mg/kg	<1	<1	<1	<1
Cr	mg/kg	782	877	917	910
Co	mg/kg	5.59	6.68	7.51	7.86
Cu	mg/kg	4.21	2.49	<2	2.7
Mo	mg/kg	4.03	3.45	4.01	4.02
Ni	mg/kg	7.44	5.35	4.78	4.04
Pb	mg/kg	6.83	5.75	6.54	5.74
V	mg/kg	596	740	777	741
Zn	mg/kg	9.13	<6	<6	<6
Hg	mg/kg	<0.2	<0.2	<0.2	<0.2

Table 2. Results of the leaching tests

Parameter	Unit	0-2 mm	2-4 mm	4-6 mm
Dry residue	mg/kg	18680	18700	13200
Conductivity	µS/cm	8250	8100	7490
pH	-	12.6	12.5	11.4
Organic C	mg/kg	15.32	15.09	31.99
Sulfates	mg/kg	22.4	14.2	17.9
As	mg/kg	<0.1	<0.1	<0.1
Ba	mg/kg	5.18	5.52	3.16
Ca	mg/kg	7520	7578	7040
Cd	mg/kg	<0.05	<0.05	<0.05
Cr	mg/kg	<0.1	<0.1	<0.1
Pb	mg/kg	1.16	0.63	0.38
V	mg/kg	<0.1	<0.1	<0.1
Hg	mg/kg	<0.01	<0.01	<0.01

The conductivity of leachate was high and the pH was very alkaline due to the high content of lime and carbonates in slags. In the conditions of the leaching test, the release of trace elements was generally low, concentrations of chromium and vanadium were below the detection limit in leachates. The leaching of elements was lower in the 4-6 mm fraction, probably due to a grain size effect.

4.2 Hydrodynamic characterization

The infiltrations were performed at both initial stage (August 2007) and 6 months later over smooth-like and coarse-like zones. The presence of these different zones may result from the emplacement of the material. During the first campaign (initial stage, figure 3) the infiltration differed according to the kind of zones, the coarser zone being more conductive. Six months later, infiltrations were reduced for both zones. Clearly, hydrodynamic behaviour was inhomogeneous at the initial stage and then became more homogeneous with a reduction of the hydraulic conductivity of both zones. Such a reduction could be attributed to the chemical evolution of the material: clogging of the porosity due to precipitation of certain phases.

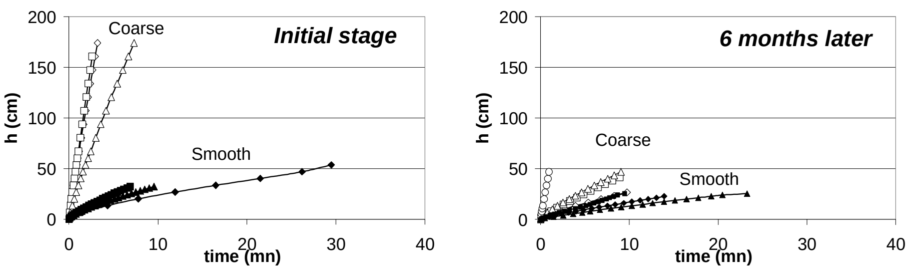

Figure 3. Results of the in situ infiltration experiments

4.3 Experimental platform survey

The experimental platform has been in operation since May 2007.

Table 3. Results of the analysis of the seepage water from the experimental site

Parameter	Unit	06/19/2007	10/29/2007	12/17/2007
Dry residue	mg/L	1670	4428	1810
Conductivity	µS/cm	7830	6190	5960
pH	-	12.9	12.6	12.9
Organic C	mg/L	55.6	53.5	41.1
Sulfates	mg/L	2.45	<1	<1
As	mg/L	<0.01	0.01	<0.01
Ba	mg/L	2.14	1.75	1.79
Ca	mg/L	490	429	1074
Cd	mg/L	<0.005	<0.005	<0.005
Cr	mg/L	0.01	0.01	0.02
Pb	mg/L	0.01	<0.01	<0.01
V	mg/L	<0.01	<0.01	<0.01
Hg	µg/L	<0.1	0.6	<0.1

Due to the rather low precipitation depth at the experimental site during the study period and to the high water retention capacity of the slags, only three samples of seepage water have been collected and analysed. Table 3 presents the results of the analysis of the water samples collected in June (1360 L), October (120 L) and December (650 L) 2007. The pH of seepage waters was very alkaline, more than 12, and the conductivity was rather high. The concentrations of Total Organic Carbon and sulphates were quite low. The calcium content was very high and, except for barium, the concentrations of trace elements were low, below or close to the detection limit.

5. Conclusion

The ECLAIR-PRECODD project has been launched for 3 years in 2006. The purpose of the project is to develop an integrated approach to assess the environmental behavior of a BOF steel slag used in a civil engineering scenario. An experimental platform has been constructed and equipped to collect seepage water. Hydrodynamic characterization pointed out the heterogeneity of the slag layer and the effect of weathering inducing a decrease of the hydrodynamic conductivity. Results of the chemical characterization revealed the presence of Cr and V in steel slags, but leaching test and first results of seepage water analysis seemed to show a very low release of trace elements in water.

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