The Use of Blast Furnace Slag to Decrease Heavy Metals from Electric Arc Furnace Dust Leachate: A Column Leaching Test

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Abstract

Column leaching test were performed to evaluate the leaching of electric arc furnace dusts (EAFD), a multi-elements toxic waste, amended with ground granulated blast furnace slag (GGBFS) under dynamic conditions. The aim was to find a temporary solution to metals leaching.

The use of GGBFS addition was divided into 4 categories; 1) blended with EAFD, 2) applied on the surface of EAFD to create en alkaline wetting front, 3) applied at the base of EAFD, and 4) applied both on the surface and at the base of EAFD. Columns were fed three times weakly during 1 month. The concentration of metals (Cr-Ni-Pb-Zn), pH, conductivity, and Eh potential conditions were analysed in leachates.

The results have shown that GGBFS applied at the base was the more efficient disposition. The Cr concentrations decrease according to reducing conditions and alkaline pH conditions.

1. Introduction

One of the most important problems in the secondary steel mill industry throughout the world is the disposition of dusts produced from electric arc furnace [1]. A large quantity (10 to 20 kg) of electric arc furnace dust (EAFD) is generated per ton of steel produced and around 700 000 tons and 50 000 tons of EAFD are generated each year in the United States and Canada, respectively [2,3]. In the United States, EAFD is a listed hazardous waste under the Resource Conservation and Recovery Act (RCRA). In Canada, EAFD is a listed hazardous waste under the Transportation of Dangerous Goods Regulations (TDGR) [3]. Some heavy metals of EAFD like chromium are toxic and have high solubility.

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EAFD is disposed temporary at the industry site in large porous heaps or piles. When the EAFD heaps or piles are in contact with water, a partially water-saturated environment is created. The leaching of toxic components from EAFD, mainly heavy metals, can occur. Thus, the temporary disposal of these industrial solid toxic wastes can cause environmental risk due to the mobility of toxic elements.

The purpose of this study was to find a temporary solution to decrease the concentration of heavy metals in EAFD leachate by the use of GGBFS. Column leaching test were performed to evaluate the leaching of EAFD amended with GGBFS under dynamic conditions.

2. Materials

2.1. Electric arc furnace dust (EAFD)

The EAFD was supplied by Atlas Stainless Steels (Sorel, Canada) and was obtained in the summer of 2000. EAFD is collected from dust collection of the arc furnace where coal and scrap are mixed together at an approximate temperature of 1500°C. Table 1 presents the chemical composition of the major oxides of the EAFD tested in this work. The EAFD contained some heavy metals including 10.9, 4.1, 1.4 and 5.2 % mass of Cr, Ni, Pb and Zn, respectively.

The EAFD has a bimodal size distribution. Particle sizes ranged from less than 2.8 μm to greater than 176 μm. The majority (94%) of the particles were smaller than 5.5 μm in diameter. EAFD appears as elongated grains, spherical, fine-grained and irregular particles. A predominance of spinel group minerals was identified. Magnetite was the main phase present in the EAFD, along with chromite. Most grains were identified as franklinite-magnetite-jacobsite solid solutions. A more detailed characterisation of the EAFD is presented by Laforest and Duchesne in earlier work [4].

Table 1 - Chemical composition of materials

Oxides (% mass)	CaO	SiO$_2$	MgO	Al$_2$O$_3$	MnO	Fe$_2$O$_3$	K$_2$O	TiO$_2$	Na$_2$O	LOI*	Total
GGBFS	37.31	36.77	13.91	7.77	1.02	0.85	0.43	0.36	0.31	-1.49	97.23
EAFD	6.59	5.76	4.25	0.74	5.88	39.56	0.48	0.16	1.01	3.67	68.10

*LOI= loss on ignition

2.2. Ground granulated blast furnace slag (GGBFS)

GGBFS is a waste product in the manufacture of iron composed mainly of calcium silicate and aluminosilicate. The granulated blast furnace slag is most common, wherein powerful water jets or air blasts cool and fragment the molten slag which is then plunged under water. The result is an amorphous granular material whose variable binding capacity is a function of, amongst other things, its degree of vitrification. GGBFS was provided by Algoma Steel (Sault Ste-Marie, Canada). This slag, cooled quickly, is largely glassy with a small proportion of merwinite and of solid-solution of the melilite family. The chemical composition of GGBFS is given in Table 1.

Moreover, some phases of GGBFS seem to be able to exert a solubility control on chromium [5-7]. This is particularly interesting considering the high chromium content of the EAFD. This is the main reason of the use of the GGBFS in this study aiming at reducing the metal content leached from EAFD.

3. Methods – Column leaching test

EAFD were amended with GGBFS at a ratio by mass of 2:1 (600g of EAFD : 300g of GGBFS). Five columns were set up to study the different types of disposition of GGBFS to limit heavy metal generation from EAFD. Fig. 1 presents the column leaching test experimental setting. The labels (in bold) and descriptions of the columns are described below:

Co-disposition: **GGBFS+EAFD**: a column with 600 g of EAFD and 300 g of GGBFS completely mixes up;
Cover: **GGBFS/EADF**: a layer of GGBFS applied on the surface overlying a layer of EAFD to create an alkaline wetting front;
Liner: **EAFD/GGBFS**: a layer of EAFD overlying a layer of GGBFS applied at the base;
Cover and liner: **GGBFS/EAFD/GGBFS**: a layer of EAFD taken between two layers of GGBFS (one at the top and one below at the base);
Control column: **CONTROL**: reference column composed only of a layer of EAFD.

Samples were placed into polycarbonate columns (8.5 cm diameter, 40 cm height) open to the atmosphere at the top, and closed at the bottom with two filters (paper filter (whatman 42) and nylon filter (100 mesh (150μm), respectively) and a drain for sample collection (Fig. 2). To avoid preferential flow, a layer of Ottawa sand (ASTM-190) was disposed above the materials. In the same way, a layer of sand was placed under the

materials in order to prevent the obstruction of the drains. Ottawa sand was selected because it is an inert material composed mainly of silicon dioxide (>99%). The material was compacted in 3 layers (200g each) using 3 knocks of compactor at each layer. The compactor had a mass of 1 386 g and a height of fall of 42 cm. Columns was fed from the top with 500 ml of deionized water three times weekly during 33 days.

Distilled water
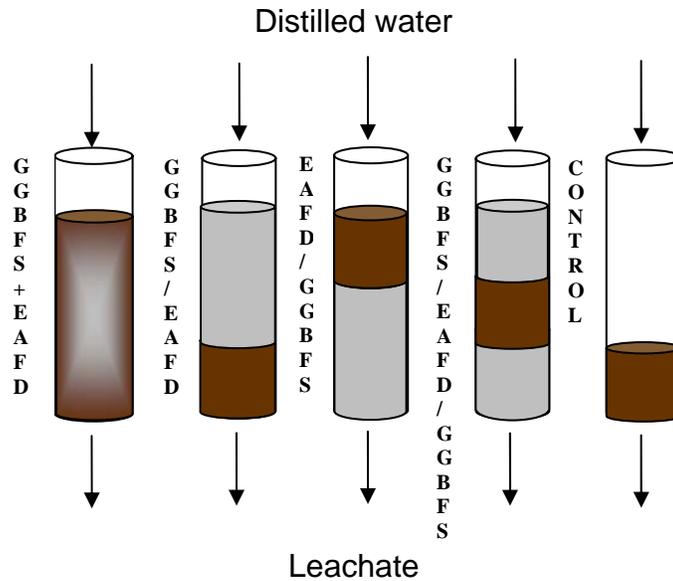
Fig. 1. Schema of the experimental column settings.
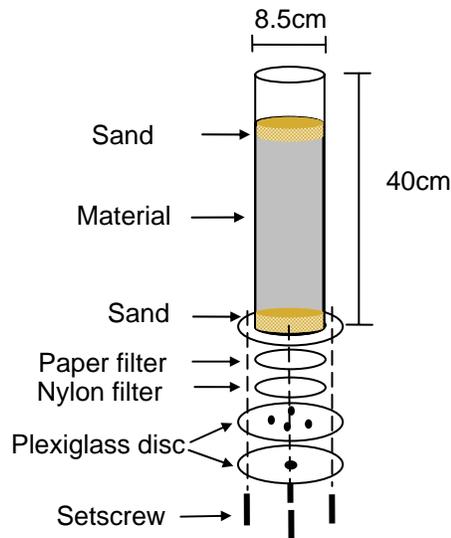
Fig 2. Column components.

Conductivity, oxidation-reduction potential (Eh) and pH conditions were measured on the leachates on a pH/Eh/conductivity meter accumet model 20. Eh values were measured relative to a silver-silver chloride electrode, and are reported as Eh values relative to the standard hydrogen electrode. A another part of the leachate samples was filtered through 0.22 µm membrane filters and was acidified with HCl for cation analyses (Cr, Ni, Pb and Zn) in a Perkin Elmer Aanalyst 100 Atomic Absorption Spectrophotometer (AAS). All solutions were kept at 4°C until analysis. The AAS detection limits for Cr, Ni, Pb and Zn are 0.078, 0.14, 0.19 and 0.018 mg/L, respectively. The Cr(VI) concentrations were obtained by a chromic acid titration method using ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) as titrating solution and barium 4-(phenylamino) benzenesulfonate as colorimetric indicator. This method was described by Laforest and Duchesne [8].

In this study, iron was not the subject of a particular follow-up despite its high content in the EAFD (28%). In fact, iron is not considered a toxic element but rather an undesirable element. Chromium, Ni, Pb and Zn were studied due to their relatively high levels in the EAFD and also because these metals appear on the list of toxic metals, metals regulated by federal or state agencies in the United States [9].

4. Results and Discussion

4.1. pH conditions

The pH values of the leachates recovered from columns are presented in Fig.3. All pH measured were alkaline with values over 10. The pH values for the CONTROL column and the column GGBFS/EAFD were slightly less basic (10.5 after 33 days) than the others columns (around 11.5 after 33 days).

Thus, GGBFS cover (GGBFS/EAFD) did not create an alkaline wetting front as suggested previously. This column behaves as the control concerning the pH of the leachate. In the other hand, the column with a layer of GGBFS at the base ((EAFD/GGBFS) and (GGBFS/EAFD/GGBFS)) were more efficient to maintain alkaline pH conditions over the experimental period. The pH of the blended column (GGBFS+EAFD) was neutral at the beginning of the experiment and reached alkaline values after few supplying.

The results show that the more effective way of preserving alkaline conditions is to use the GGBFS as a liner. This configuration is also the simplest to set up in a scenario of temporary storage.
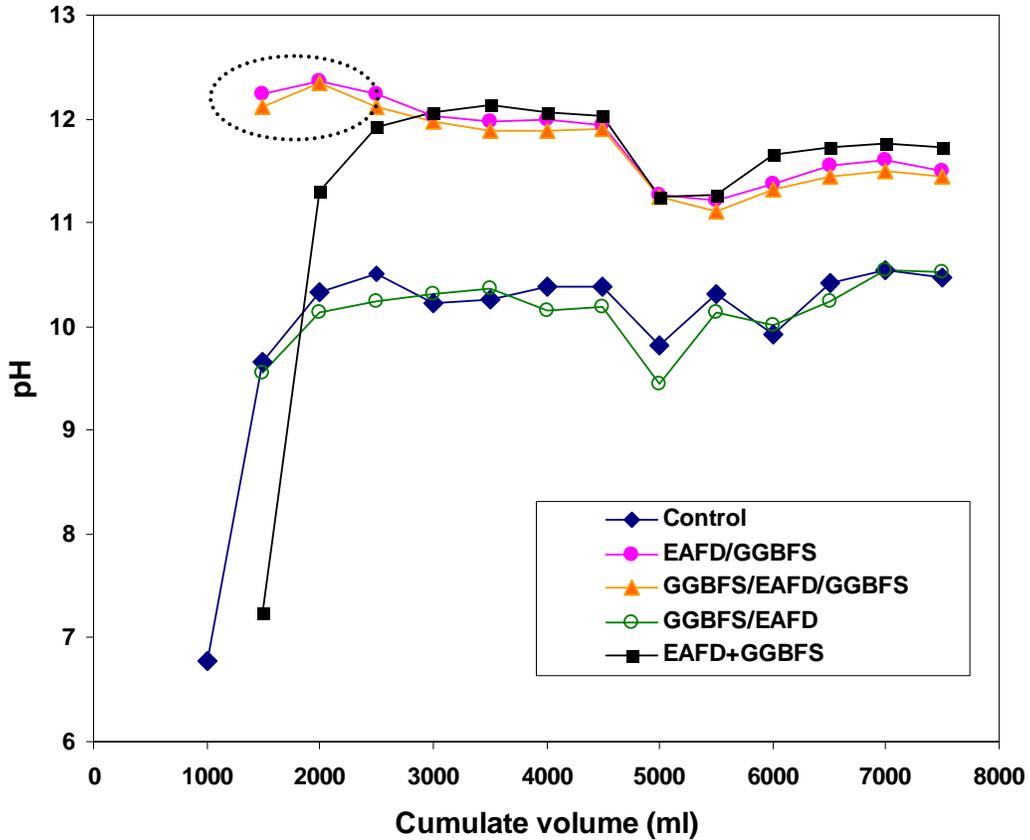
Fig.3. Evolution of pH conditions of leachates recovered from columns.

4.2. Eh conditions

The Eh values of the leachates recovered from columns are shown in Fig.4. The control column is the column showing the more oxidizing conditions. The influence of GGBFS addition can be seen on the Eh values which are reduced. In fact, as mentioned previously, GGBFS has a reducing potential that creates an environment where the Eh values (-200 to -400 mV) will be low.

The reducing conditions are established in columns where the base is composed of GGBFS. For the blended column (GGBFS+EAFD) and the column with GGBFS as a cover (GGBFS/EAFD) the Eh values are reduced compared to the control column but in a lesser extent than columns with GGBFS at the base. The reducing conditions can be

important in presence of chromium, mainly for the reduction of Cr(VI) to Cr(III), which is less toxic and more easily fix in cementitious matrix.
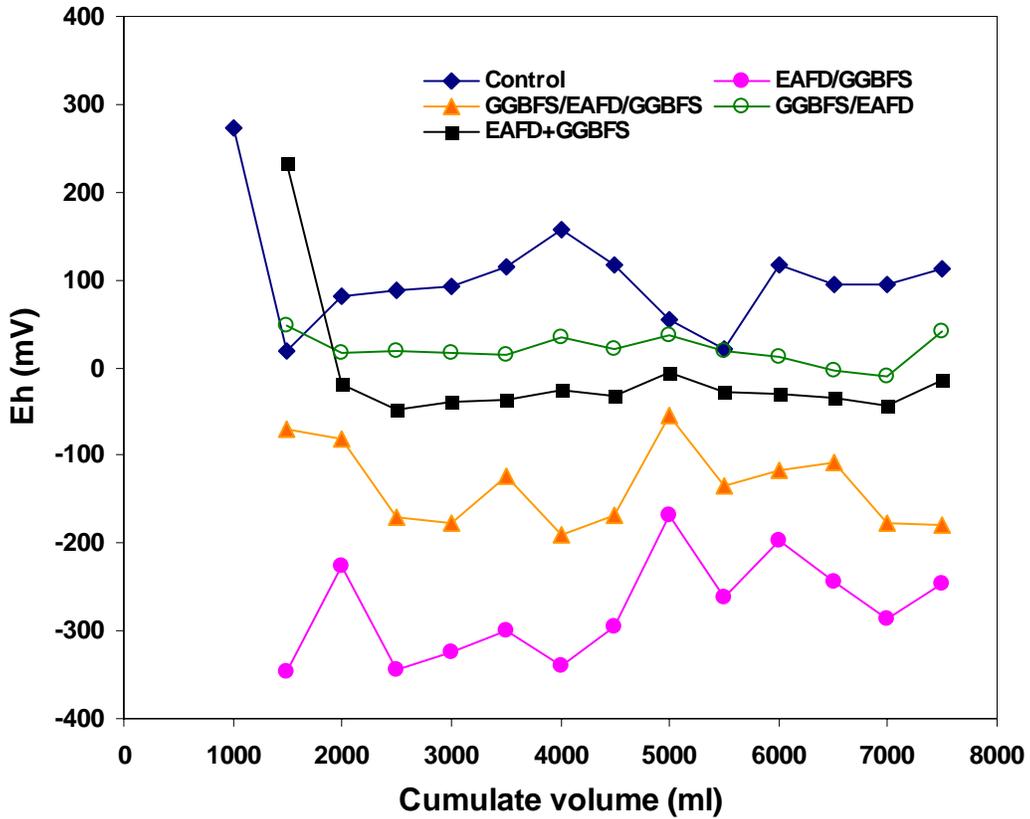
Fig.4. Evolution of Eh conditions of leachates recovered from columns.

4.3. Conductivity measurements

The conductivity measurements are an indicator of ions diffusion. The conductivity values of the leachates recovered from columns are presented in Fig.5. This figure shows a rapid decrease in the ionic charge in solution. The first flushes were the more concentrated. It is interesting to see that the columns containing GGBFS presented higher conductivity values at the first measurement than the control. After the passage of approximately 3 litres of water through the columns, a steady-state is established.
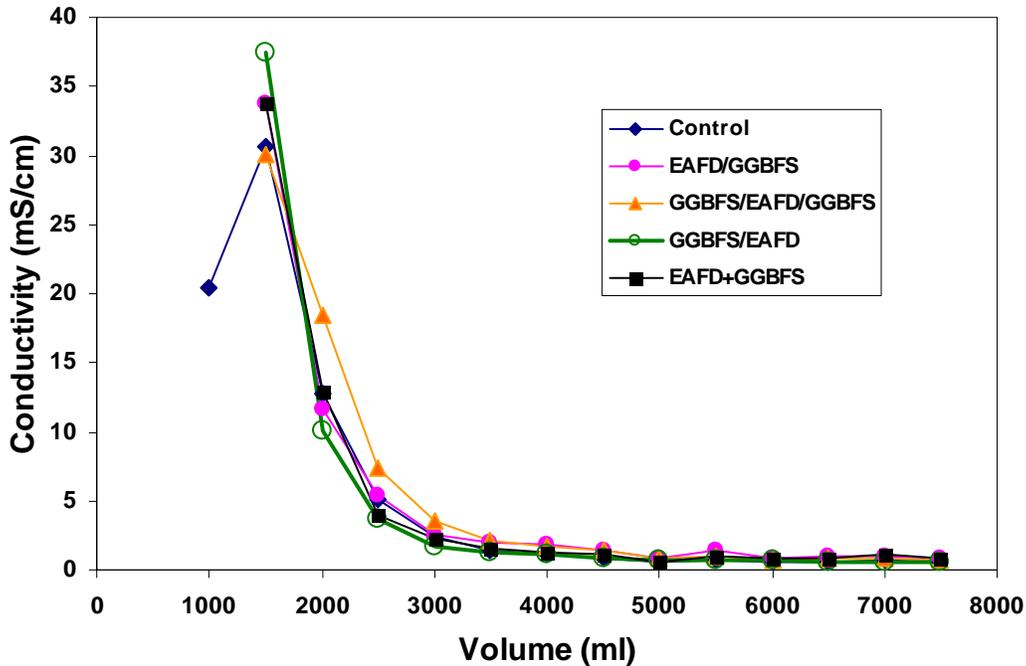
Fig.5. Conductivity of leachates in function of alimentation.

4.4. Chemical composition of the leachates

The cumulative mass of Cr in leachates is presented in Fig. 6 as a function of the cumulative volume of water passing through the columns. The control column has leached 441mg of Cr after the passage of 7500 ml of leachate. The cumulative mass of chromium leached was decreased in the presence of GGBFS. This is especially true for the columns where GGBFS was placed at the base under the EAFD (EAFD/GGBFS and GGBFS/EAFD/GGBFS)).

In general, the addition of GGBFS was effective in the reduction of the Cr leached except for the column GGBFS/EAFD. Indeed, this column has leached a greater quantity of Cr at each measurement period than the control. A total of 477mg of Cr was leached that represents an increased of 7.5% compared to the column control. In the GGBFS/EAFD column, the water passes through the GGBFS prior to the EAFD. As seen previously, the Eh and pH conditions of that column were similar to those of the control column and the metal leached by the EAFD was not fixed in the matrix.
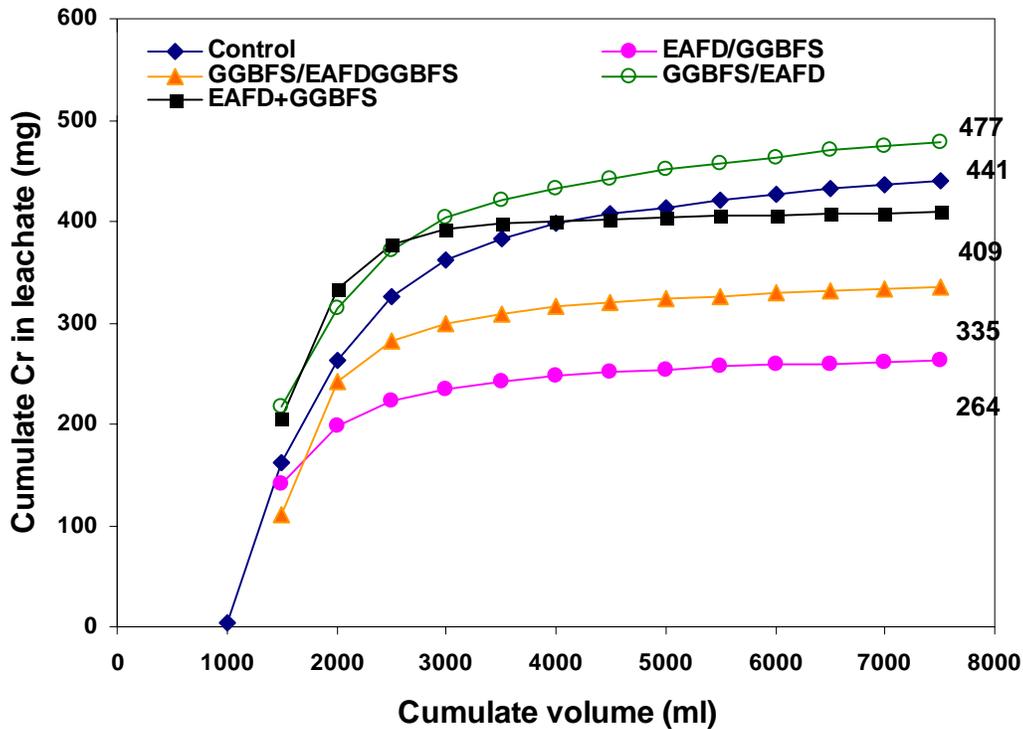
Fig. 6. Cumulative mass of Cr in the leachate

Fig. 7 presents the concentrations of Cr (VI) and Cr (total) for the control sample. It is clear, that Cr (VI) is the predominant chromium species in the EAFD's leachate. In fact, chromium can be found in 3 valency states: +2, +3 and +6. At low levels, chromium is an essential element for animal metabolism, but at levels close to 0.1 mg/g of the body weight, it can be lethal [10]. Chromium (III) and Cr (VI) are the more frequent states. The Cr(VI) is a severe toxic contaminant of natural waters, sediments and soils. Chromium (VI) is acidic, forming chromates $(CrO_4)^{2-}$ and dichromates $(Cr_2O_7)^{2-}$, the other valences are basic.

The concentrations of Pb, Zn and Ni measured in the leachates were in low concentrations. After 33 days of experiment, the cumulative quantities of metal leached in the control column were 0.73, 0.76 and 34.07 mg for Ni, Pb and Zn, respectively.
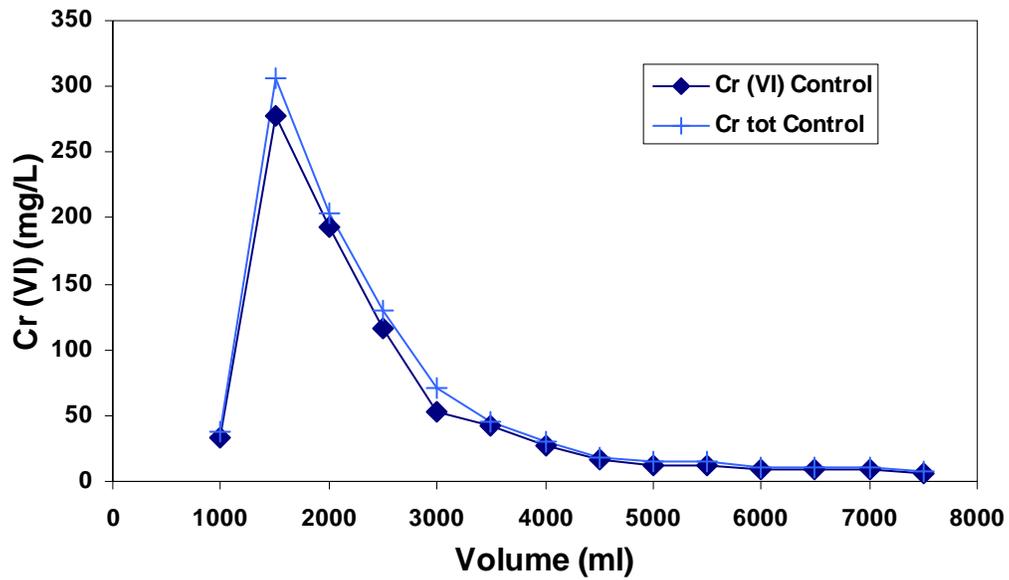
Fig. 7. Cr total and Cr (VI) concentrations in leachate as a function of the leachate volume for the control column (EAFD only).

Fig. 8 presents the pH as a function of the Eh conditions for all measurements. The columns with GGBFS at the base (EAFD/GGBFS and GGBFS/EAFD/GGBFS) are those presenting the higher pH conditions and the more reducing environment. These columns are the most effective in reducing the amount of metals leached mainly chromium.
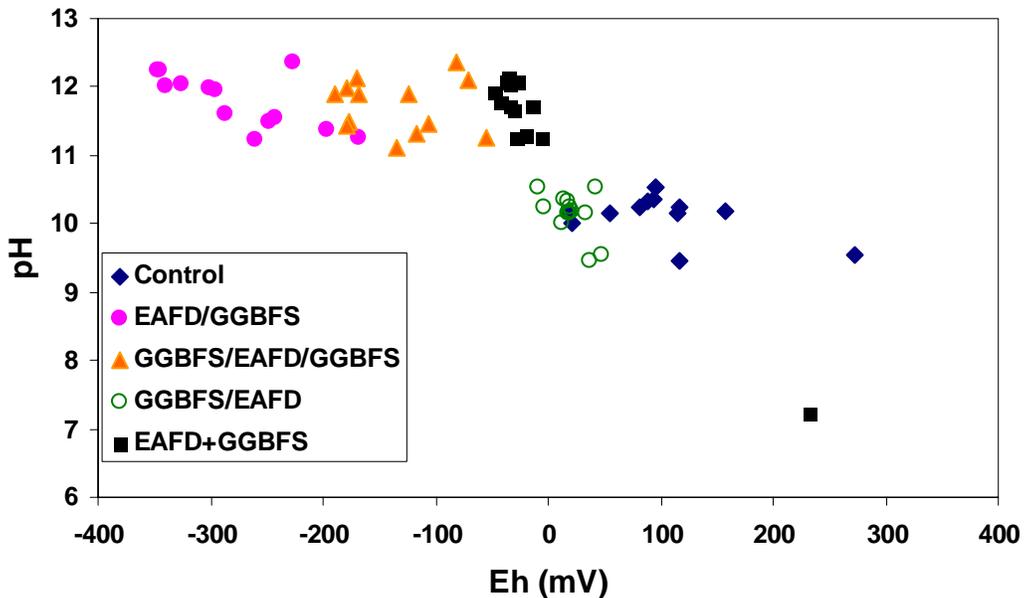
Fig. 8. pH and Eh conditions of leachates

5. Conclusions

In this study, column leaching test were performed to evaluate the leaching of EAFD, a multi-elements toxic waste, amended with GGBFS under dynamic conditions. The aim was to find a temporary solution to metals leaching.

The results have shown that the use of GGBFS can decrease the amount of heavy metals leached from EAFD, mainly chromium. The concentrations of other metals (Ni, Pb, and Zn) were almost null. In general, columns with GGBFS at the base present lower cumulative mass of metals leached than those with GGBFS throughout mixed or with GGBFS placed as a cover. A liner of GGBFS is the most efficient disposition to decrease metal concentrations. The Cr concentrations decrease according to reducing conditions and alkaline pH conditions.

This study has shown that GGBFS is an interesting binder for waste containment. This binder can generate conditions able to reduce Cr(VI), a problematic toxic element leached by EAFD. Using of GGBFS is doubly interesting considering that the GGBFS is itself a by-product of the iron industry.

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