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Investigation of stabilization/solidification for treatment of electric arc furnace dust: Dynamic leaching of monolithic specimens

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Abstract

Diffusion-controlled leaching of heavy metals (Cr, Ni, Pb and Zn) from electric arc furnace dust treated with ground granulated blast furnace slag (GGBFS) and with ordinary Portland cement (OPC) was evaluated. Monolithic specimens were evaluated under dynamic leaching conditions for 84 days with periodic leachant renewal. The influence of leaching time, nature of the leachant, binder type and the water/solid ratio of the monoliths were investigated. Results obtained showed both binders can immobilize heavy metals in the monoliths under dynamic leaching conditions, with cumulative quantity of leached metal under 0.138 mg (Cr). Alkaline leachant increased metal release from specimens and reducing the water/solid ratio of the monolith allowed for a decrease in the cumulative mass of metals leached. Chemical and mineralogical characterizations indicated that the metals were evenly distributed throughout the specimens for both binders. Decalcification was observed on the OPC monolith border following leaching. This decrease in Ca corresponded to an altered zone (20 µm), identified by scanning electron microscopy. The GGBFS sample did not show an altered zone.

Keywords: B. Microstructure; D. Granulated blast furnace slag; D. Portland cement; D. Heavy metals; E. Waste management

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]. The cost of EAFD disposal is not negligible; for example, in the United States, $200 million per year is spent on EAFD disposal [4]. In the United States, EAFD is listed as 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] and high levels of several contaminants cause it to fail the Ontario Regulation 347 leachate extraction procedure [5]. A small percentage of EAFD is recycled for zinc recovery but EAFD is mainly disposed as landfill [4]. The present study tries to find uses for this material.

One of the most popular uses of industrial by-products is in the construction industry, particularly in concrete manufacturing [4]. The addition of by-products to hydraulic binders makes recycling possible and can sometimes improve the properties of the concrete. The process of stabilization/solidification (S/S) has two general goals. Stabilization or chemical fixation refers to the immobilization of pollutants in a stable form. Solidification is a transformation of the residue into a material of low permeability, which is durable over time.

The leaching of toxic components from EAFD has been studied by others. Stegemann et al. [3] showed a significant pH influence on the leaching of heavy metals from EAFD. They utilized the Ontario Regulation leachate extraction procedure (similar to the Toxicity Characteristic Leaching Procedure (TCLP)) and other tests on many EAFD samples. Zinc and lead were found to be leached more than Cr and Ni.

Laforest [6] have suggested that the application of aggressive acidic tests to evaluate the leaching of EAFD treated by S/S is not appropriate because acidic conditions are too far from the

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Table 1
Chemical composition of materials

Oxides (% mass)	CaO	SiO_2	MgO	Al_2O_3	MnO	Fe_2O_3	K_2O	TiO_2	Na_2O	P_2O_5	LOI	Total
GGBFS	37.31	36.77	13.91	7.77	1.02	0.85	0.43	0.36	0.31	<DL	−1.49	97.23
OPC	62.49	19.75	2.62	4.41	0.05	2.92	0.89	0.17	0.28	0.23	1.90	95.71
EAFD	6.59	5.76	4.25	0.74	5.88	39.56	0.48	0.16	1.01	0.04	3.67	68.14

DL: detection limit.

Table 2
Heavy metal content of EAFD

Heavy metal	% mass
Cr	10.9
Ni	4.1
Pb	1.4
Zn	5.2

real conditions established in S/S. In fact, the pH of the S/S process is nearly 13 and the pH of the EAFD leachate is between 10 and 11. The work also compared solubility of EAFD contaminants in contact with either ground granulated blast furnace slag (GGBFS) or ordinary Portland cement (OPC) under a range of pHs (3, 5, 7, 10 and 13). Cr was soluble at pH 5, and less soluble at higher pH. Lead was not found in the leachate for pHs ranging from 5 to 10 for all mixtures. Zn and Ni concentrations decreased gradually from pH 3 to 7 and were below detection limits at pHs equal to or higher than 7. Thus, buffered leaching tests in alkaline and neutral conditions showed metals (Cr, Zn, Ni and Pb) were bound. Only zinc was soluble at low pH.

2. Purpose

The purpose of this research was to study diffusion-controlled leaching of heavy metals (Cr, Ni, Pb and Zn) from EAFD treated with GGBFS and OPC. Monoliths of mixtures of EAFD with OPC and/or GGBFS were leached by water or an alkaline solution. The influence of leaching time, binder type and water/solid ratio of the monoliths were investigated.

Within the framework of a policy of sustainable development, it is important to support re-use of the residues, rather than disposal in landfill, in order to protect natural sources. It is clear that this study is the first step in a scheme for recycling residues. Before dispersing a contaminant in the environment by using it in construction, it is necessary to analyze the life cycle of the product, including its handling and its destination after demolition.

3. Materials

The GGBFS was provided by Algoma Steel (Sault Ste-Marie, Canada). This slag, cooled quickly, is largely in a glassy form with a small proportion of merwinite and of solid-solution of the melilite family. An ordinary Type I cement was used in this study. The chemical compositions of the solid materials are given in Table 1.

The EAFD was supplied by Atlas Stainless Steels (Sorel, Canada) and was obtained in the summer of 2000. EAFD is collected from arc furnaces where coal and scrap are mixed together at an approximate temperature of 1500 °C. The chemical composition of the dust varies according to the type of steel produced, with the variations in composition being considerable. For example, Fe, which is a major component, can vary from 15 to 62% and represents around 43% in EAFD from the stainless steel industry [3]. Table 1 presents the chemical composition of the major oxides of the EAFD tested in this work. The concentrations of heavy metals are given in Table 2. 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.

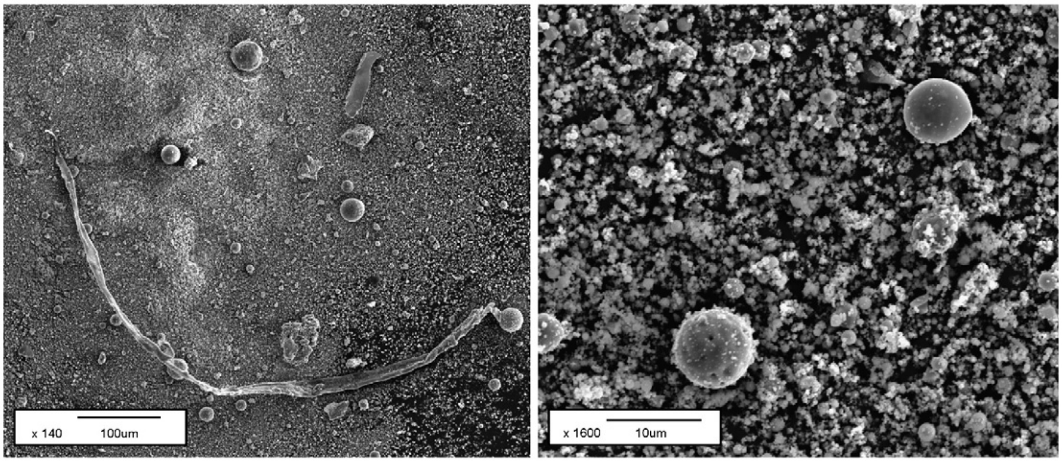

Fig. 1. Scanning electron microscope (SEM) micrographs in secondary electron (SE) mode of a random disposed sample of EAFD.

Table 3
Mixture characteristics of monolithic specimens

Monolithic specimen	% GGBFS	% OPC	% EAFD
GGBFS + EAFD	75	0	25
(GGBFS/OPC)+EAFD	37.5	37.5	25
OPC + EAFD	0	75	25
EAFD	0	0	100

EAFD particles have the form of elongated grains and spherical, fine-grained and irregular particles (Fig. 1). 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 characterization of EAFD is presented by Laforest and Duchesne in earlier work [7].

4. Methods

4.1. Specimen preparation

The treated residues (solidified materials) were pastes containing GGBFS and/or OPC incorporating 25% EAFD (GGBFS+

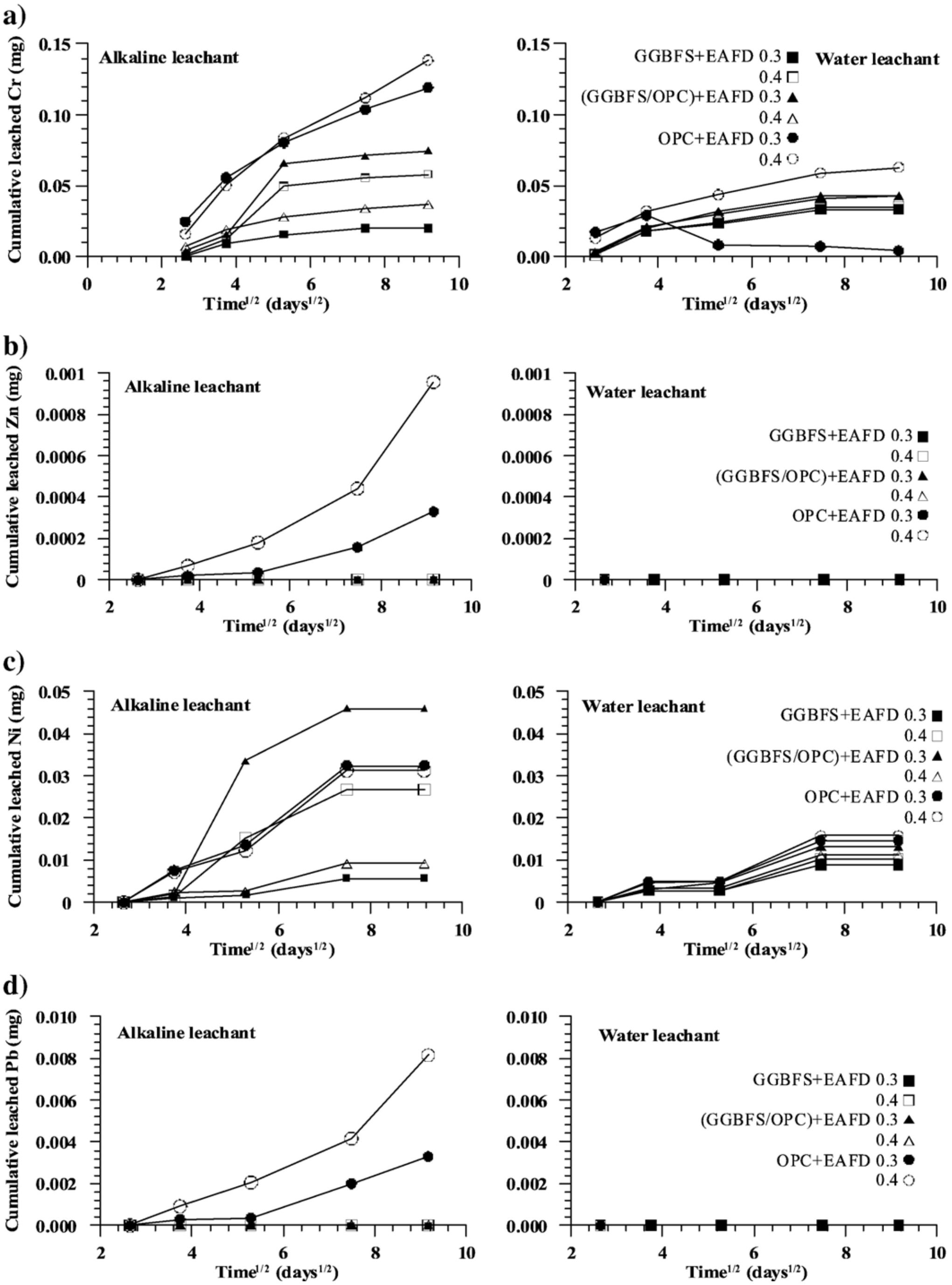

Fig. 2. Cumulative mass of contaminant leached according to the square root of time for Cr, Pb, Zn and Ni for monoliths leached by water or an alkaline solution.

Table 4
Maximum leaching concentrations measured during leaching test

Contaminant	Concentrations (mg/L)
Cr	1.00
Pb	0.26
Zn	0.25
Ni	0.48

EAFD, OPC+EAFD and (GGBFS/OPC)+EAFD) with water/solid ratios of 0.3 or 0.4. Mixture characteristics are presented in Table 3. A specimen containing only EAFD was also prepared.

4.2. Leaching test

A dynamic leaching test was conducted according to the ANSI/ANS 16.1 procedure [8]. The pastes were cast in sealed plastic containers to form cylindrical monoliths (diameter 1.4 cm, height 2.5 cm), kept in an environment maintained at 100% relative humidity. After hydration for 56 days, the solid samples were suspended in containers filled with a leachant (distilled water or alkaline solution (1 g/L $Ca(OH)_2$+0.24 g/L NaOH+0.45 g/L KOH)) at a liquid/solid mass ratio of 10/1. The leachants were renewed after 7, 14, 28, 56 and 84 days of reaction. After each renewal, the leachate was analyzed for pH and was filtered using a 0.22 μm membrane. The filtrate was analyzed for cation (total Cr, Zn, Pb, Ni) concentrations by Atomic Absorption Spectrometry (AAS).

4.3. Characterization of chemical and mineralogical modifications

In order to examine the microtexture of the monoliths and the degradation of the sample, the specimens were observed under a JEOL JSM-840A Scanning Electron Microscope (SEM) equipped with an energy dispersive X-ray analysis system (EDXA). The samples were cast in epoxy, polished and coated with a thin alloy of Au–Pd prior to observation.

Chemical alterations of the specimens were analyzed by a CAMECA SX 100 electron microprobe (EPMA) at an accelerating voltage of 15 kV, a current strength of 20 nA and a beam scanning area of $1000 \times 1000\ \mu m^2$. The measurements were performed on polished sections from the border to the center of the specimen (about 1-mm depth). The content of Ca, Cr, Zn and Ni was analyzed. Lead could not be analyzed due to sample contamination by the polishing device.

Table 5
Maximum concentration of contaminants for toxicity characteristic and safe drinking water, U.S. Environmental Protection Agency

	Toxicity characteristic	Safe drinking water	
Contaminant	Regulatory level (TCRL) (mg/L)	MCLs [a] (mg/L)	NSDWRs [b] (mg/L)
Cr	5.0	0.1	
Pb	5.0	0.015	
Zn			0.3

[a] Maximum Concentration Level.

[b] National Secondary Drinking Water Regulations.

These analyses were performed on two specimens; OPC+EAFD and GGBFS+EAFD after 84 days of leaching in distilled water.

5. Results and discussion

5.1. Leaching test results

5.1.1. Effect of leaching time

The results of the dynamic leaching test are presented in Fig. 2. This figure shows the calculations of cumulative mass leached of each metal as a function of the square root of time for both leachants (distilled water or alkaline solution). The cumulative mass leached increases with time and values obtained after 84 days of experiment are low, with cumulative values near 0.001 mg Zn, 0.046 mg Ni, 0.008 mg Pb and 0.138 mg Cr. The maximum concentrations measured during leaching tests (Table 4) are compared with the maximum concentration of contaminants for toxicity characteristic and safe drinking water level of the U.S. Environmental Protection Agency (Table 5). This attempt to compare the concentrations measured in the dynamic leaching test to regulatory limits is not

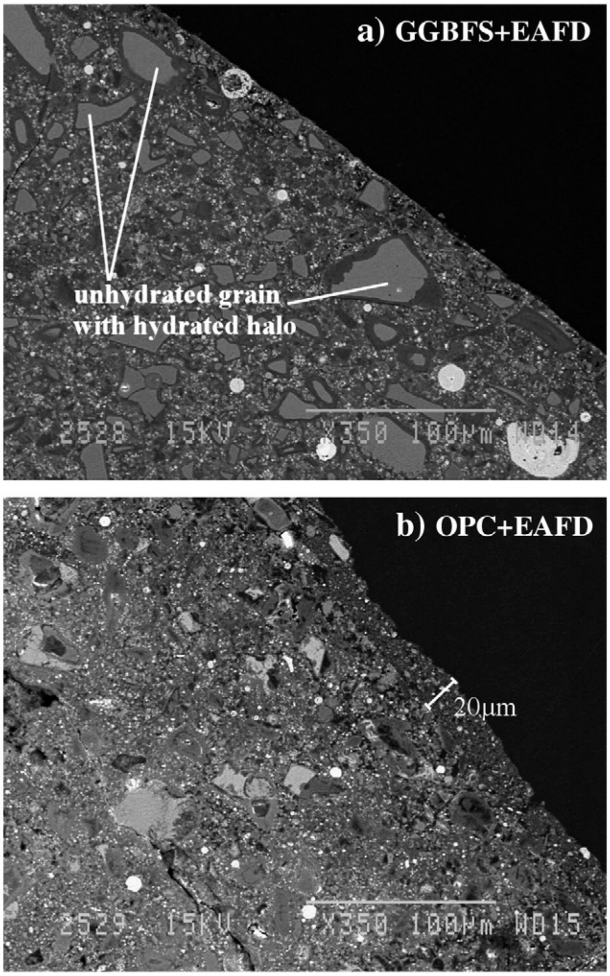

Fig. 3. SEM micrographs in backscattered electron (BSE) mode of the border of the monolith samples after 84 days of dynamic leaching test; a) GGBFS+EAFD and b) OPC+EAFD.

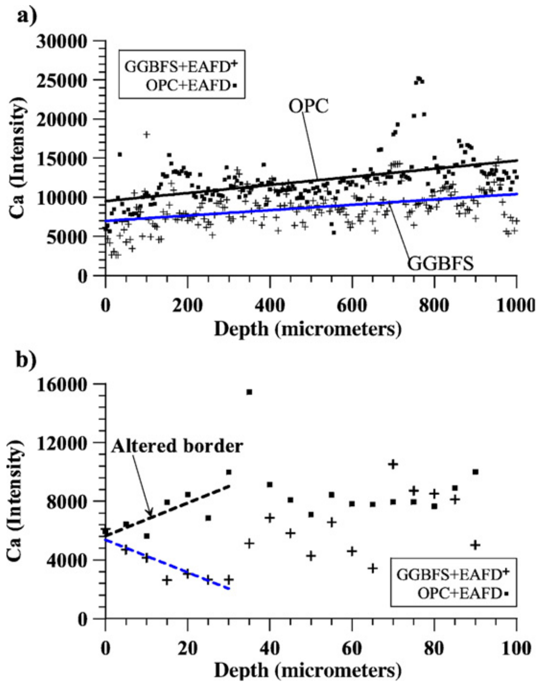

Fig. 4. Calcium concentration measured by EPMA according to depth on monolith samples (GGBFS+EAFD and OPC+EAFD) leached for 84 days; a) profiles from the border up to 1000 μm, b) zoom of profiles a: from the border up to 100 μm (zoom on the border area).

intended to be normative but rather to see whether the measured concentrations are comparable with those of a toxic substance or drinking water. For Cr and Pb levels, the maximum concentrations measured were under the Toxicity Characteristic Regulatory Level. Zn maximum concentration measured was under the National Secondary Drinking Water Regulations (NSDWR). The maximum Ni concentration measured was 0.48 mg/L.

5.1.2. Effect of leaching solution type

Fig. 2 shows that the nature of the leachant has an influence on the cumulative amount of metals leached during the experiment. For Pb and Ni, both metals show cumulative mass leached as almost null for monoliths leached by distilled water. Cumulative mass of Cr or Ni leached were halved in distilled water compared to the alkaline solution. The pH values measured in the alkaline solution were between 12.5 and 13, while those in water varied from 11.3 to 12.5. The high pH measured in the water leaching solution is mainly an indication of the buffer capacity of the samples.

5.1.3. Effect of water/solid ratio of monoliths

According to Fig. 2, most of the monoliths with 0.3 water/solid ratio presented lower cumulative mass of metals leached than those with 0.4. This is explained by the decrease in the paste porosity as liquid/solid ratio decreased. This physical mechanism is important for metal retention in monolithic samples where leaching rates are diffusion-controlled.

5.1.4. Effect of binder type

Results obtained show that both binders can immobilize heavy metals in the monoliths under dynamic leaching conditions. In general, monoliths made with OPC present higher cumulative mass of metals leached than those with GGBFS. The mixtures containing both binders (GGBFS/OPC) present an intermediate behaviour. This behaviour is highlighted for Cr and Pb which show an increase in solubility with high pH, while taking into account that OPC generates more alkaline solutions than GGBFS. These data show that GGBFS is more effective than OPC in retaining metals in the monolithic samples.

5.2. Chemical and mineralogical characterization

5.2.1. Altered depths

SEM micrographs of the two types of hardened bonder pastes with EAFD (OPC+EAFD and GGBFS+EAFD) in backscattered electron (BSE) mode (Fig. 3) present the microtexture and the density contrast of the monoliths. The GGBFS paste is less hydrated with more unhydrated grains.

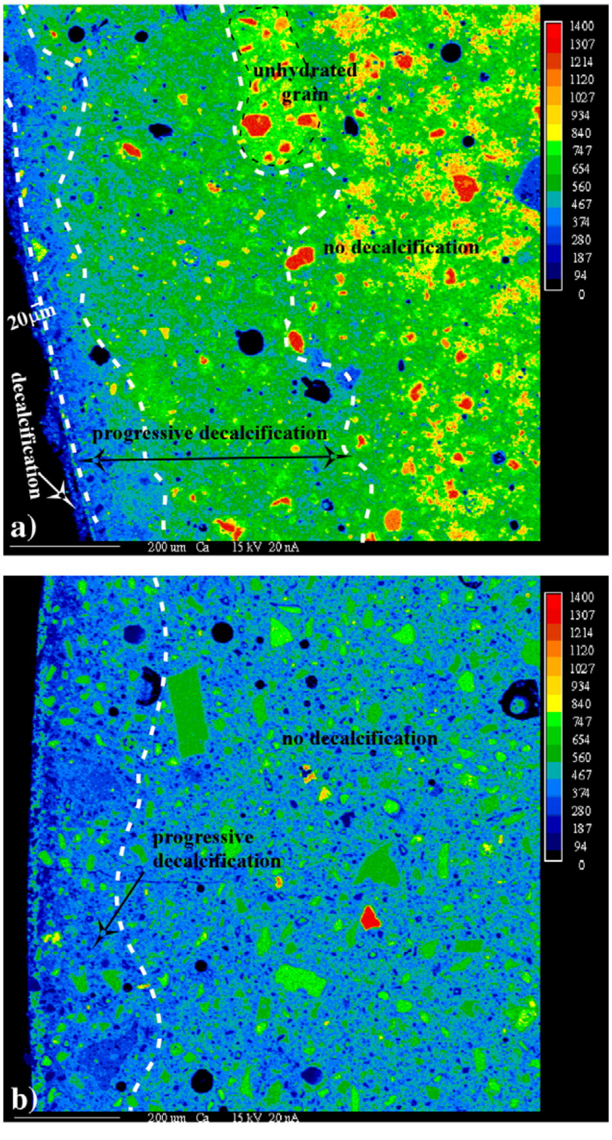

Fig. 5. Ca mapping measured by EPMA on sample leached for 84 days: area (1×1 mm^2) near the border of the paste samples.

Table 6
Leaching concentrations measured after seven days of leaching

Leachant	Mixture	Water/ binder ratio	[Cr] (mg/L)	[Ni] (mg/L)	[Pb] (mg/L)	[Zn] (mg/L)
Alkaline	EFAD	0.3	20.8	<DL	6.5	1.4
		0.4	16.3	<DL	4.7	1.8
Water		0.3	25.8	<DL	<DL	<DL
		0.4	No data	<DL	<DL	<DL
Alkaline	GGBFS+ EAFD	0.3	<DL	<DL	<DL	0.05
		0.4	0.03	<DL	<DL	0.64
Water		0.3	<DL	<DL	<DL	0.64
		0.4	0.02	<DL	<DL	0.18
Alkaline	OPC+EFAD	0.3	0.08	<DL	<DL	0.06
		0.4	0.15	<DL	0.26	0.25
Water		0.3	0.04	<DL	<DL	<DL
		0.4	0.06	<DL	<DL	0.02
Alkaline	(GGGFS/OPC)+ EFAD	0.3	0.49	<DL	0.21	0.14
		0.4	0.31	<DL	<DL	0.07
Water		0.3	0.04	<DL	<DL	0.01
		0.4	0.06	<DL	<DL	0.02

DL: detection limit.

There is no clearly visible altered border for GGBFS sample. The OPC sample clearly shows an altered border. The depth of the altered zone was around 20 μm.

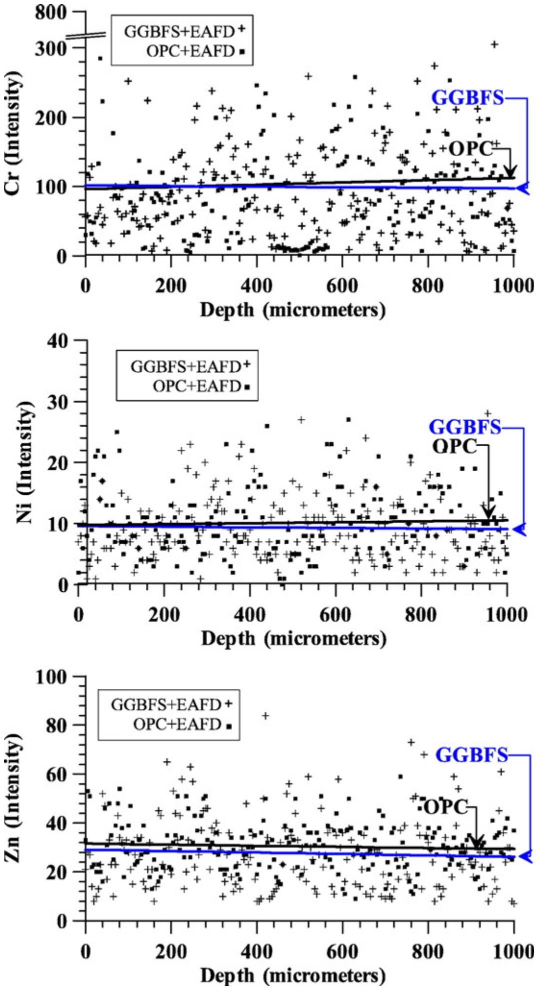

Fig. 6. Cr, Ni and Zn analysis measured on paste samples by EPMA according to depth (after 84 days of leaching).

The profiles (up to 1-mm depth from border) of Ca content following leaching by distilled water obtained by EPMA are presented in Fig. 4a. For the OPC sample, the Ca content decreases from the core of the monolith to the border (20 to 0 μm) (Fig. 4b). The Ca decrease corresponds to the altered zone identified by SEM. Decalcification of the monolith surface in contact with the water leachant is a probable cause of OPC paste degradation [9]. The GGBFS paste does not show the same characteristics. The increase of Ca content towards the border (Fig. 4b) may mark the beginning of Ca transfer into solution.

Fig. 5 shows Ca mapping of the same specimens of OPC+ EAFD and GGBFS+EAFD, respectively, analyzed by EPMA after 84 days of leaching. The area studied measured 1 × 1 mm^2 and was located near the borders of the hardened pastes. These maps present greater detail on Ca distribution and one can establish different stages of decalcification according to Ca content. An altered border where Ca content was very low

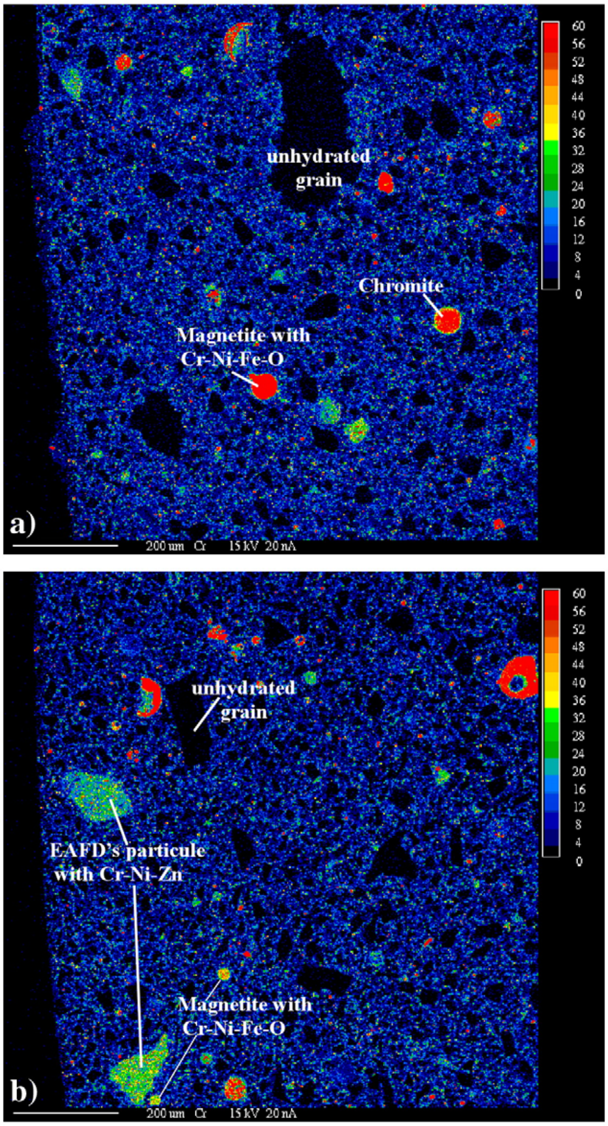

Fig. 7. Cr mapping measured by EPMA: area (1 × 1 mm^2) near the border of paste samples (after 84 days of leaching).

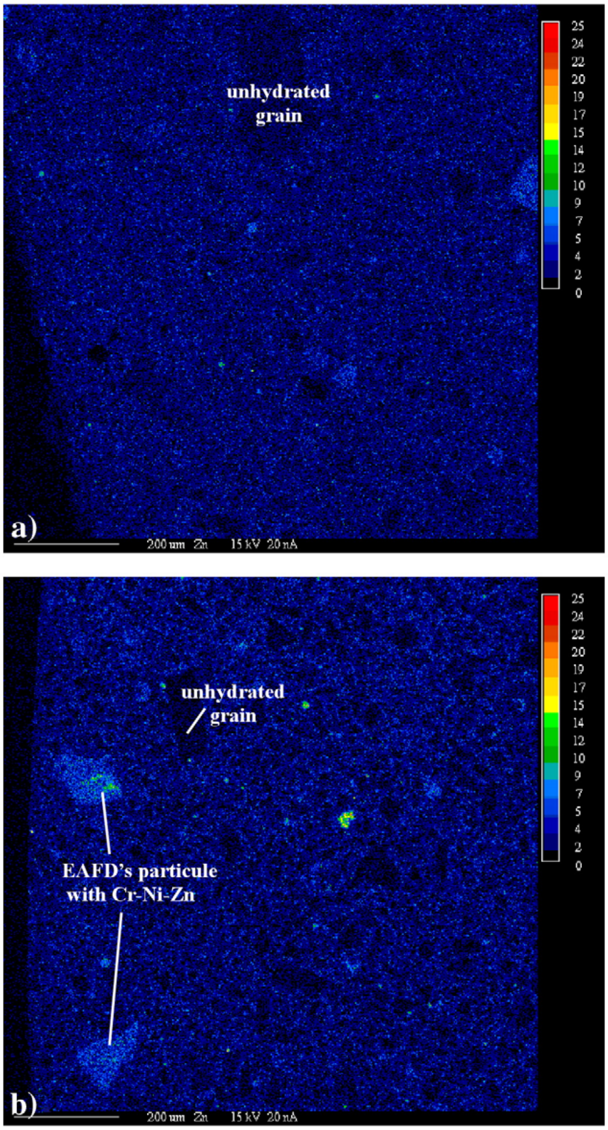

Fig. 8. Zn mapping measured by EPMA: area (1 × 1 mm^2) near the border of paste samples (after 84 days of leaching).

appeared only on the OPC sample (Fig. 5a). This is a decalcification phenomena similar to that observed by Bertron et al. [9]. The depth of the zone where decalcification occurred was identified from Fig. 5a at around 20 μm. This depth is the same as that previously identified by SEM observations (Fig. 3) and EPMA Ca profiles. (Fig. 4b) The subsequent 70 μm towards the monolith core has been affected by leaching and illustrates further intense decalcification. The next 410 μm indicates a further decalcification state of lower intensity. The monolith core has not been subjected to leaching or decalcification. The GGBFS sample presents only two decalcification steps (Fig. 5b). The first decalcification step corresponding to an altered border is not evident. Two steps were identified for the GGBFS sample; progressive decalcification to a depth of monolith border and a monolith core unaffected by decalcification. Progressive decalcification of the GGBFS sample was less evident than in the OPC sample. The difference in Ca distribution is more subtle in the GGBFS sample due to its lower Ca content (37.31% CaO) than for OPC (62.49% CaO).

5.2.2. Heavy metal leaching

Table 6 presents the leaching concentrations measured after 7 days of leaching. The EAFD monoliths had not solidified after 7 days, explaining the absence of long-term measurements. The EAFD imposed a relatively high pH environment. At 7 days, the pH value of water in contact with EAFD monolith was approximately 10.8. The leachates from the alkaline solution maintained pH values around 12. The alkaline pH does not favour solubility control as indicated by the Pb and Zn concentrations, which are higher under the alkaline leaching environment. Ni does not leach whereas Cr release is more important with concentration values between 16 and 26 mg/L after 7 days of leaching. The metal concentrations leached from the monoliths treated with GGBFS and/or OPC are much weaker. In fact, at 7 days, the maximum concentrations obtained

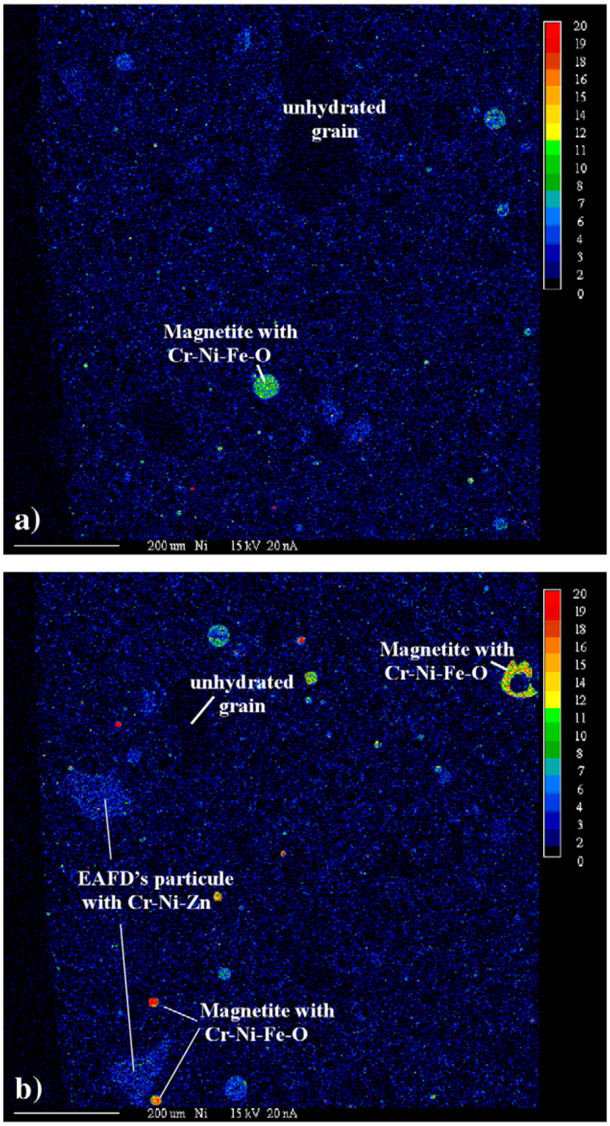

Fig. 9. Ni mapping measured by EPMA: area (1 × 1 mm^2) near the border of paste samples (after 84 days of leaching).

were: 0.49, 0.26 and 0.64 mg/L for Cr, Pb and Zn, respectively. The Ni concentrations were under the detection limit. These data show that the treatments of EAFD with both binders were effective in decreasing metal concentrations in the leachates. The binders, GGBFS and OPC, were able to fix the metals in the solid matrix by coprecipitation and by sorption.

Fig. 6 presents in-situ Cr, Zn and Ni contents measured by EPMA. Concentrations were measured from the border to the center of the monoliths. The profiles of these heavy metal concentrations present no variation according to depth, and the linear regression slopes are not pronounced. Differences between linear regressions calculated for GGBFS and OPC samples are not significant, with the influence of binder on metal leaching not detectable at this scale. No evidence of metal leaching progression near the border of the monoliths was identified.

Similarly, mapping of Cr, Zn and Ni contents by EPMA on samples leached for 84 days (Figs. 7–9, respectively) showed no evidence of leaching. The areas studied correspond to 1×1 mm^2 sections near the border of the hardened pastes. Fig. 7 shows that Cr content is predominantly evenly distributed across each sample (OPC + EAFD and GGBFS + EAFD). The Cr content was higher at isolated points throughout the sample corresponding to chromite ($FeCr_2O_4$) and magnetite ($FeFe_2O_4$) particles (from the original EAFD). In EAFD, magnetite particles are impure with substitutions of Fe by Ni and Cr. Some EADF particles containing Cr, Ni and Zn were also identified. Fig. 8 shows that Zn content is evenly distributed across both samples with some EAFD particles rich in Cr–Ni–Zn. Ni was also evenly distributed (Fig. 9) with some higher Ni concentration particles corresponding to magnetite. The evidence of unhydrated binder grains appears in Figs. 5, 7–9. These unhydrated grains are important for the long-term integrity of the samples because they can react with water to produce C–S–H, which can contribute both to monolith strength and to contaminant retention.

6. Conclusions

This study has shown that both OPC and GGBFS binders can fix heavy metals (Cr, Ni, Pb and Zn) as monoliths under dynamic flow leaching. In general, monoliths made with ordinary Portland cement (OPC) present higher cumulative mass of metals leached than those with ground granulated blast furnace slag (GGBFS). The nature of the leaching solution has an influence on metals leached during the experiment. For Pb and Ni, both metals show cumulative mass leached as almost null for monoliths leached by distilled water. Cumulative mass of Cr or Ni leached was halved in distilled water compared to the alkaline solution. The effect of the water/solid ratio is clear. In fact, monoliths with 0.3 water/solid ratio presented lower mass of metals leached than those with 0.4. This is explained by the decrease in the paste porosity as liquid/solid ratio decreased.

The EPMA mappings of Cr, Ni and Zn content are useful for indicating the distribution of these metals in the stabilized waste matrix. Chemical and mineralogical characterizations showed the metals are evenly distributed within the stabilized matrix for both binders. If a metal is uniformly dispersed throughout the waste matrix after 84 days under a dynamic leach test (a diffusion-controlled test), it is an indication that the metal is not trapped in the pores of the material or absorbed on the grain surface. If such were the case, the edge would contain less Ni, Zn, Cr than the core of the samples.

Decalcification was observed on the OPC monolith border. The Ca decrease corresponded to an altered zone as identified by SEM. Decalcification in contact with water as a leachant is a probable cause of OPC paste degradation. The GGBFS sample did not show an altered border. With both binders, unhydrated grains were observed which can contribute in the long term to monolith strength and contaminant retention. This study has shown that GGBFS is a promising binder for waste containment. This binder shows a high resistance to leaching with no decalcification in contact with water. Use of GGBFS is doubly interesting considering that GGBFS is itself a by-product of the iron industry.

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