

Characterization and leachability of electric arc furnace dust made from remelting of stainless steel

Guylaine Laforest*, Josée Duchesne

Centre de Recherche sur les Infrastructures en Béton (CRIB), Département de géologie et de génie géologique, Université Laval, Québec, Que., Canada G1K 7P4

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Abstract

Electric arc furnace dust (EAFD) is a toxic waste product made in the remelting of scrap steel. The results of a Toxicity Characteristic Leaching Procedure (TCLP) conducted on a sample of EAFD originating from the remelting of stainless steel scrap showed that the total Cr and Cr (VI) liquor concentrations (9.7 and 6.1 mg/L, respectively) exceeded the Toxicity Characteristic Regulatory Level (TCRL). The EAFD showed a complex heterogeneous mineralogy with spinel minerals group predominance. A sequential extractions method has permitted the determination of the amount of available metals (potentially mobile component) from the EAFD as follows: Cr (3%), Ni (6%), Pb (49%) and Zn (40%). Solubility controls on Cr, Pb, Zn and Ni were identified in the EAFD. This means that the Cr, Pb, Zn and Ni concentrations in solution were controlled by the solubility of some phases from EAFD. The concentrations of Ni and Zn, which are metals not regulated by TCRL were below 0.41 and 1.3 mg/L, respectively. The solubility control on Pb was sufficient to decrease its concentration (<0.24 mg/L) to a level below the TCRL. However, the control on Cr was not sufficient to decrease its concentration (between 117 and 331 mg/L) to below the TCRL.
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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 furnaces [1]. A large quantity (10–20 kg) of electric arc furnace dust (EAFD) is generated per tonne of steel produced and around 700,000 and 50,000 tonnes 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, 200 million dollars per year are necessary to dispose EAFD in the United States [4]. Moreover, the EADF is listed hazardous waste under Resource Conservation and Recovery ACT (RCRA) in United States and under the Transportation of dangerous Goods Regulations (TDGR) in Canada. Also, high levels of several contaminants cause it to fail the Ontario Regulation 347 leachate extraction procedure [5]. Thus, the disposal of these industrial solid toxic wastes can cause environmental risk due to the mobility of toxic elements. Some heavy met-

als of EAFD like chromium are toxic and have high solubility. Chromium (VI) is particularly problematic because it must initially be reduced before being fixed in an insoluble phase.

A solubility control by a material implies that the concentration of some constituent elements in solution will be controlled by the solubility of the secondary precipitates. Reardon et al. [6] recommended conducting leaching tests on a particular waste material at least at two different water/solid ratios. They point out that if an element's concentration does not double when the water/solid ratio is halved, there must be a solid phase control on its concentration in solution.

2. Purposes

The purpose of this work were to evaluate: (1) the microtexture and the mineralogy of EAFD; (2) the contaminant-bearing phases (Cr, Ni, Zn and Pb) in the EAFD by sequential extractions; (3) the EAFD's toxicity by TCLP; (4) the mobility of the EAFD's contaminants by long-term static leaching tests in neutral environment; and (5) the solubility control by EAFD on Cr, Pb, Zn and Ni.

* Corresponding author. Tel.: +1 418 656 2131 4574; fax: +1 418 656 7339.
E-mail address: guylaine.laforest.1@ulaval.ca (G. Laforest).

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	P ₂ O ₅	LOI ^a	Total
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

^a LOI = loss on ignition.

Static leaching tests were conducted at two different liquid/solid ratios (3/1 and 6/1) as a means to distinguish elements in the leachates that have solubility control versus those that do not.

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 [7].

3. Materials

3.1. Electric arc furnace dust (EAFD)

The EAFD studied comes from Atlas Stainless Steels (Sorel, Canada) and was obtained in the summer of 2000. The EAFD result from the collection of the dust generated by the arc furnace when coal and scrap are mixed together at an approximate temperature of 1500 °C. The chemical composition of dusts varies according to the type of steel produced and the variation's range of compositions is considerable. For example, the Fe, which is the major element, can vary from 15 to 62% and represents around 43% in the EAFD from the stainless steel industry [3]. Table 1 presents the chemical composition of the major oxides of the EAFD tested. The concentrations of heavy metals are given in Table 2 along with some comparisons with data from the literature. The particle size distribution of the EAFD established by a Sedigraph particle size analyser (SediGraph 5000ET by Micromeritics) at 36 °C in an adequate liquid (density: 0.829 g/cc, viscosity: 9.14 cp) is presented in Table 3. The EAFD contains two major size fractions: a very fine-grained portion and a coarser part. Particle sizes range from less than 2.8 μm to more than 176 μm. The majority (94%) of the particles are smaller than 5.5 μm in diameter.

Table 2
Heavy metals content of EAFD

	Heavy metals (mass%)			
	Cr	Ni	Pb	Zn
Studied EAFD	10.9	4.1	1.4	5.2
Stegemann et al. [3] ^a	3.9	3.1	1.2	5.5
Al-Zaid et al. [4] ^b	–	0.01	1.31	10.7
Law et al. [12] ^c	0.015–17.7	0.014–3.34	0.025–3.81	0.14–28.0

^a Average values of the characterization of six Canadian EAFDs.

^b Average values obtained from four different EAFD samples.

^c Range of values from the characterization of 32 American EAFDs.

4. Methods

4.1. Microtexture and mineralogy

The microtexture and the mineralogy were studied by XRD and SEM analyses. The EAFD was analyzed by a Siemens D5000 X-Ray diffractometer using Cu K α radiation generated at 20 mA and 40 kV. The specimen was step-scanned as random powder mounts from 2 to 62.8° 2 θ at 0.02° 2 θ steps integrated at 1.2 s step⁻¹. XRD analysis can detect crystalline phases presented on the order of about 5 mass% or more.

4.2. Sequential extraction procedure

The sequential extraction procedure was used to operationally define heavy metals in the EAFD into different geochemical phases, in order of increasing stability. By the use of progressively reactive extractants, the sequential extraction procedure can determine to which mineral phase each of the contaminants (Cr, Ni, Zn and Pb) is linked in the EAFD sample.

The methods of sequential extraction was investigated originally by Tessier et al. [8] to furnish detailed information about the mode of occurrence, biological availability and mobilization of trace metals in sediments. To be near the type of the material studied, the method used in this work was adapted according to the procedure of Leinz et al. [9] used for the partitioning of trace metals in mine wastes. Also, this procedure is thought to be more complete than that of Tessier et al. [8] because it includes seven steps instead of five. Thus, the exchangeable fraction is now divided into two fractions: soluble and sorbed species fractions. The fraction related to Fe–Mn oxides is also divided into two fractions and allows determination of metals related to crystallised Fe oxides and amorphous Fe–Mn oxides. In this study, the nature of the material implies the adaptation of the fractions to the each step. The adapted method used and the leached fractions are presented in Table 4.

According to the sequential extraction method presented in Table 4, a sample of EAFD was subjected to seven steps of consecutive extraction with different leachate solutions. At each step, the concentration of the elements (Cr, Ni, Pb and Zn) in

Table 3
Particle size distribution of EAFD

Diameter (μm)	%
>176	0.1
176–125	4.5
62–44	1.2
5.5–3.9	28.0
3.9–2.8	38.9
<2.8	27.1

Table 4
Seven-step sequential extraction procedure

Degree of mobility	Process	Phase	Description of procedure
+++	Sorption–desorption process	(1) Soluble	0.25 g of sample with 0.25 g of silica gel added is extracted with 25 ml of water
		(2) Sorbed species	The residue is extracted with 25 ml 1 M sodium acetate for 1 h in a horizontal reciprocating shaker at ambient temperature
++	Unstable under low pH	(3) Hydroxides and carbonates	The residue from “2” is extracted in a shaker for 2 h with 25 ml 1 M sodium acetate buffered to pH 5 with acetic acid
+	Unstable under anoxic conditions (Includes Cr (III) oxides)	(4) Fe–MnO _{x,am} and silica glass	The residue from “3” is extracted with 25 ml of 0.25 M hydroxylamine hydrochloride in 0.25 M HCl for 30 min in a water bath, at 50 °C
		(5) FeO _{x,cryst}	The residue from “4” is extracted with 25 ml 4 M HCl for 30 min in a water bath at 94 °C
	Unstable under oxidizing conditions	(6) Cr (VI) oxides	Two grams of sodium chlorate are added to the residue from “5”, followed by addition of 10 ml concentrated HCl. After 45 min the aqueous phase is separated and diluted to 25 ml with deionized water. The residue is extracted for 40 min with 25 ml 4 M HNO ₃ in a boiling water bath. The two extracts are analyzed separately and the results combined
Stable species	Stable over a reasonable time span under the conditions normally encountered in nature	(7) Original stable minerals of spinel group	The residue from “6” is transferred to a Teflon beaker and is digested with 15 ml of concentrated HNO ₃ at 200 °C, to a dry bead. The dry bead is taken up in 7 ml HCl at 200 °C, to a dry bead. If there is no effervescent reaction, add 7 ml of acid fluohydric and heat at 200 °C, to a dry bead. If digestion is incomplete, add 5 ml of concentrated HNO ₃ and some concentrated hydrogen peroxide drops. Add 5 ml of concentrated hydrofluoric acid at 200 °C, to a dry bead. Add 20 ml 5% (v/v) HCL and heat slowly until dissolution. The final volume is adjusted to 25 ml with deionized water

solution is measured and gives information about the proportion of the element linked to the mineral phases attacked by the solution. Here, we have investigated seven fractions for the partitioning of heavy metals: (1) soluble; (2) sorbed species; (3) bound to carbonates and hydroxides; (4) bound to amorphous Fe–Mn oxides and silica glass; (5) bound to crystallised Fe oxides; (6) bound to Cr (VI) oxides; (7) bound to spinels.

The sequential extraction procedure allows the determination of the proportion of contaminant, which is mobile and that which is linked to stable phases. The metals bound to spinels require an acid digestion and are thus related to a stable phase where the metals are part of the mineral structure. The six other steps are subject to sequential release of metals according to the conditions of solubility, pH and Eh. Step 1 (soluble) concerns the ionic composition subject to the solubility of the phase. Step 2 (sorbed species) concerns the sorption–desorption process. Step 3 (bound to carbonates and hydroxides) is related to the decrease of pH values. Steps 4–6 (bound to Fe–Mn oxides and silica glass, Fe oxides and to Cr (VI) oxides) concern a decrease of the Eh values. It is very important to view the sequential extraction procedure as a tool to determine the degree of facility of metals released from the material tested via successive leaching steps, which become more aggressive.

The sequential extraction procedure is a test subject to many experimental errors due to the numerous leaching steps and multiple handlings on the same initial solid sample. Thus, the results will be regarded as an approximation of the relative proportions of metals associated with each phase. For this reason, the extraction results have been rounded off to the nearest one percent.

4.3. Leaching tests

4.3.1. Toxicity characteristic leaching procedure (TCLP)

The Toxicity Characteristic Leaching Procedure (TCLP) (U.S. EPA (Method 1311)) [10] is the standard leaching test used to determine the degree of toxicity of waste. TCLP was run on the EAFD sample.

4.3.2. Static leaching test

The static leaching test is used to measure the quantity of metals available at long term (365 days) from the EAFD. The presence or absence of a solubility control was investigated.

A series of batch leaching experiments were performed at 3/1 (45 g liquid/15 g solid) and 6/1 (45 g liquid/7.5 g solid) liquid/solid ratios in 60 ml high-density polyethylene containers. The containers were mounted horizontally on a Plexiglass carousel that was suspended in a temperature bath maintained to within 0.5 °C at 25 °C. The carousel was rotated between 10 and 20 rpm for 7, 56, 84 and 365 days. The leaching solution was distilled water. Cation analyses were done on solution samples obtained at time set intervals (7, 56, 84 and 365 days).

4.4. Method for chemical analyses

Solution samples were filtered through 0.22 µm membrane filters and acidified with HCl for cation analyses (Cr, Ni, Pb and Zn) on a Perkin-Elmer Analyst 100 Atomic Absorption Spectrophotometer (AAS). The AAS detection limits for Cr, Ni, Pb and Zn are 0.078, 0.14, 0.19 and 0.018 mg/L, respectively. All solutions were kept at 4 °C until analysis.

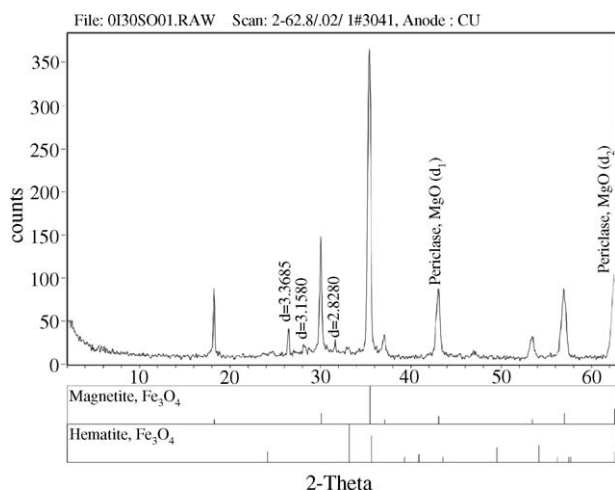


Fig. 1. XRD results for EAFD ($\lambda = 0.154184$ nm Cu $K\alpha$).

5. Results and discussion

5.1. Microtexture and mineralogy

The result of the mineralogical investigation of the EAFD conducted by XRD is presented in Fig. 1. The main phases observed were magnetite (Fe_3O_4) and hematite (Fe_2O_3) (phases also identified by Bruckard et al. [11]). The two main lines of the periclase (MgO) are also presented along with three unknown lines ($d = 0.33685$ nm, $d = 0.31580$ nm, and $d = 0.28280$ nm).

The EAFD was also observed under a JEOL LSM-840A Scanning Electron Microscope equipped with an energy dispersive X-ray analysis system (EDXA). For SEM observations, two types of samples were prepared. For the first sample, the specimen was observed intact on double-sided adhesive tape to obtain some understanding of the sample texture. Then, the coarser fraction obtained from wet sieving in a ultrasonic bath (sieve $20\ \mu\text{m}$) was observed. The portion remaining on the sieve was recovered and mounted in epoxy on a polished thin section. This last preparation permitted an appreciation of the internal structure of the EAFD particles and the density contrast of some phases. Samples were coated with a thin alloy of Au–Pd.

Fig. 2 shows secondary electron (SE) images of a random dispersed sample of EAFD. The images show some elongated grains, spherical, fine-grained and irregular particles. The SE images show also some spherical particles composed of

Fe–Cr–Mn oxide (Fig. 2A), probably a variation of magnetite and a chromium carbonate, which appears in the form of an elongated particle (Fig. 2B).

Fig. 3 presents SEM images in backscattered electrons (BSE) and SE mode for the coarser fraction ($>20\ \mu\text{m}$) of EAFD mounted on a polished thin section. The images reveal the zonation in the spherical particles where the inner part of a spherical grain is composed of Fe–Cr–Ni–O (magnetite with some variation in standard formulae) and the grain is covered with a crust of different composition (silica glass composed of Cr–Si–Fe–O). Fig. 3A illustrates this zoning of composition with emphasis on the density contrast existing between the layers. The BSE mode makes it possible to appreciate more clearly the difference between the core of the particle, composed of a denser Fe–Ni oxide, and the border composed of Fe–Cr oxide, probably chromite (FeCr_2O_4). Some exsolution phenomena were observed and an example is presented in Fig. 3B. Spheres with internal holes probably resulting from the degassing during the formation were also observed (Fig. 3C).

These SEM data confirms the predominance of spinel group minerals. The presence of magnetite was confirmed and observed as spheres (Figs. 2A and 3A) and as octahedral shape. Magnetite is the main phase presents in the EAFD and presents a variable formula $(\text{Fe}, \text{Mn}, \text{Mg}, \text{Zn}, \text{Ni})^{2+}[(\text{Fe}, \text{Al}, \text{Cr}, \text{Mn}, \text{V})_2^{3+}]_2\text{O}_4$. Chromite (FeCr_2O_4) is also a common phase and occurs as a spherical external layer around particles with an inner part composed of Fe–Ni oxide (magnetite) (Fig. 3A). The spherical phases containing Mn are probably jacobsonite (MnFe_2O_4) (Fig. 2A). Most grains are probably franklinite–magnetite–jacobsonite solid solutions. Franklinite (ZnFe_2O_4) is a phase not observed here but confirmed by Hagni et al. [1], Stegemann et al. [3] and Bruckard et al. [11]. No phase containing Zn or Pb was observed. The Ni also occurs like an intrusion in magnetite particles. Some phases contain Ca and Si and indicate some high temperature reactions (Fig. 2A).

Given the heterogeneity of the EAFD and the complexity of the phases often inside the same particle, characterization of this material is essential for each source of EAFD. Differences in the chemical composition are mainly due to the type and amount of scrap material used in the electric arc furnace [4], but for the same type of steel, the variation in composition is small due to the use of standard steel-making materials and the stability of the process [4].

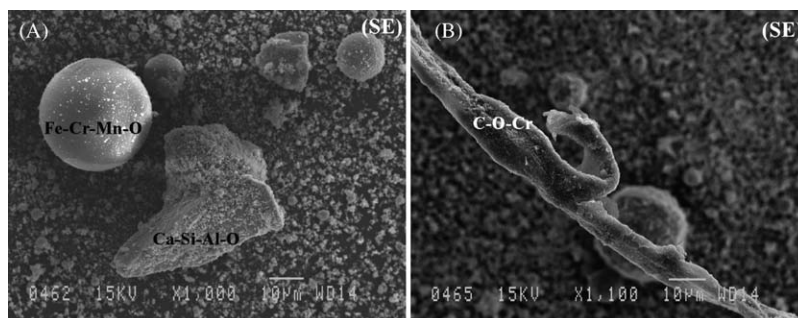


Fig. 2. SEM pictures in secondary electrons (SE) mode of a random dispersed samples of EAFD.

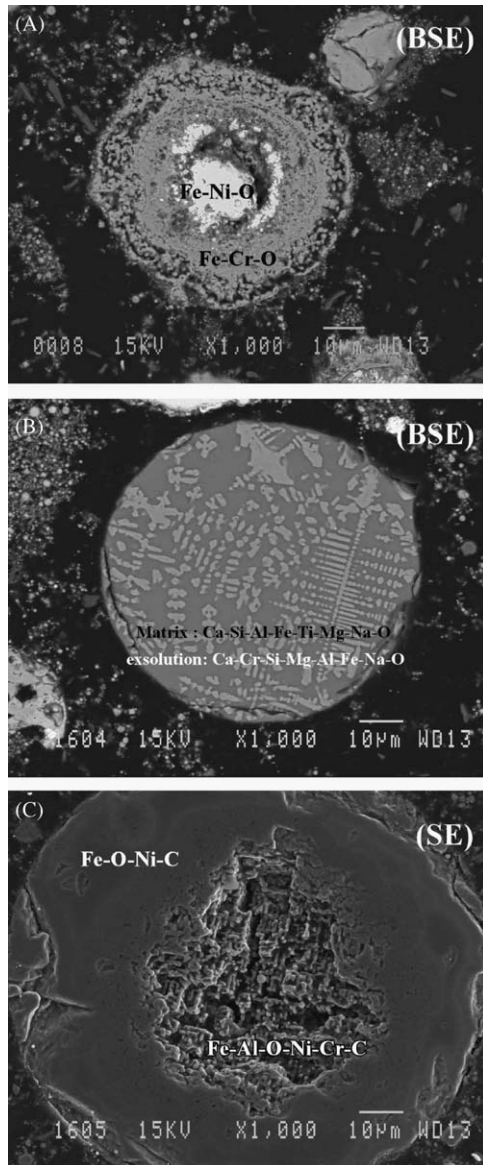


Fig. 3. SEM pictures in backscattered electron (BSE) and secondary electron (SE) modes of the coarse fraction (>20 µm) of EAFD mounted on a polished thin section.

5.2. Sequential extraction results

The sequential extraction exposes the sample to increasingly rigorous chemical treatments. This provides a means for evaluating the availability and potential mobility of metals extracted from the various phases.

Results from the sequential extraction procedure are presented in Table 5. The concentrations of heavy metals measured in solution after each step are expressed in µg/g-EAFD. The results of the sequential extraction procedure are consistent with the chemical analysis of the EAFD head presented in Table 2. For example, Cr resulting from the sequential extraction accounts for approximately 8% of the EAFD comparatively with 10.9% Cr for the chemical analysis. This difference between the values is acceptable considering the number of steps and analyses in the sequential extraction procedure. In the EAFD, chromium

Table 5
Sequential extraction results for EAFD sample

Element	Fraction	µg/g	%
Cr	Soluble	600	1
	Sorbed species	300	0
	Bound to carbonates and hydroxides	1900	2
	Bound to Fe-MnO _x am and silica glass	1500	2
	Bound to crystallised Fe oxides	17200	21
	Bound to Cr (VI) oxides	3500	4
	Bound to spinel	55700	69
Total		80700	100
Ni	Soluble	0	0
	Sorbed species	0	0
	Bound to carbonates and hydroxides	1100	6
	Bound to Fe-MnO _x am and silica glass	0	0
	Bound to crystallised Fe oxides	10000	55
	Bound to Cr (VI) oxides	2200	12
Bound to spinel	4800	26	
Total		18100	100
Pb	Soluble	0	0
	Sorbed species	0	0
	Bound to carbonates and hydroxides	5900	49
	Bound to Fe-MnO _x am and silica glass	4400	36
	Bound to crystallised Fe oxides	1600	14
	Bound to Cr (VI) oxides	0	0
Bound to spinel	0	0	
Total		11900	100
Zn	Soluble	0	0
	Sorbed species	400	1
	Bound to carbonates and hydroxides	11700	39
	Bound to Fe-MnO _x am and silica glass	3100	11
	Bound to crystallised Fe oxides	9700	33
	Bound to Cr (VI) oxides	400	1
Bound to spinel	4400	15	
Total		29700	100

is the most abundant contaminant extracted by the sequential procedure with total content of 80,700 µg/g which accounts for 8% followed by Zn with content of 29,700 µg/g (3%), Ni 18,100 µg/g (2%) and Pb with 11,900 µg/g (1%). From Table 2 the head assay values for Zn, Ni and Pb are 5.2, 4.1 and 1.4%, respectively.

The results (Table 5) show that Cr and Ni are tightly bound to stable phases extracted mainly between the fifth and the seventh steps (FeO_xcryst, Cr (VI) oxides and spinel group). The association of Cr and Ni was confirmed by the analysis of intact EAFD particles by SEM using the EDXA technique. Chromium and Nickel (with iron and oxygen) mainly form the heart of the spherical particles shown in Fig. 4. These spherical particles, like those mentioned in Section 5.1, are minerals of the group of the spinels, probably magnetite with some variation in the standard formulae. These particles are covered with a less dense silica glass crust with some variation in composition [Cr-Si-Fe-O, Al-O-Fe-Cr-C-Cl-Si (Fig. 4 (2)) and Ca-Cr-Al-Si-O (Fig. 4 (3))]. Rims of silicate glass around a metallic heart were also observed by Hagni et al. [1].

According to the sequential extraction test, Cr and Ni released at the fifth step come from the (spherical) magnetite, proba-

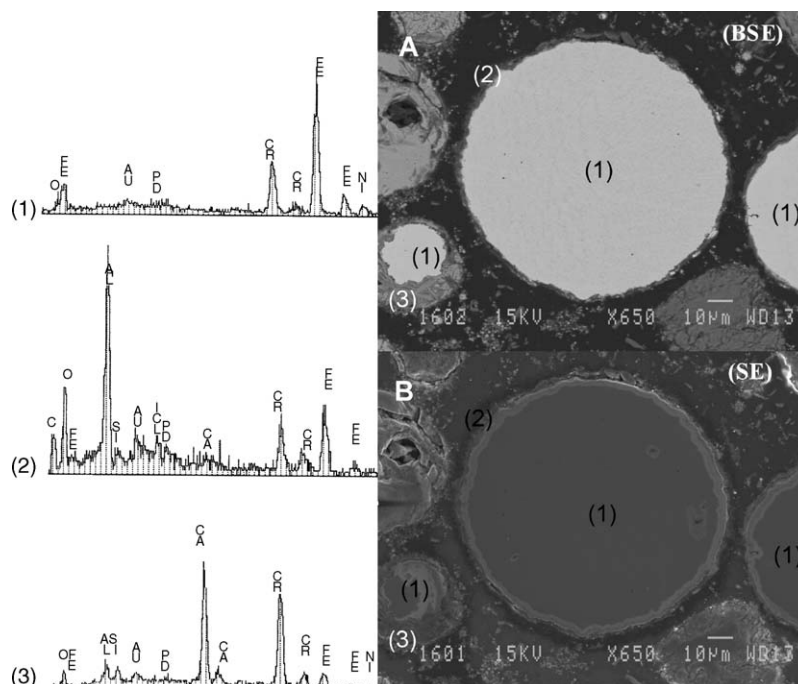


Fig. 4. SEM pictures in backscattered electron (BSE) and secondary electron (SE) modes showing Cr and Ni association in EAFD particles.

bly from the finest fraction ($<20\ \mu\text{m}$) of EAFD. The Cr and Ni released at the seventh step probably come from the same type of spherical particle that may be more stable, as observed in Fig. 4. A part of Cr release at the fifth step comes from chromium carbonate ($\text{Cr}(\text{Fe}, \text{Ca})\text{CO}_3$) (Fig. 2B).

Lead and zinc are less stably bound than Cr and Ni and are extracted starting from the 3rd step to the 5th one (hydroxides and carbonates, $\text{Fe-MnO}_{x\text{am}}$ and silica glass and $\text{FeO}_{x\text{cryst}}$). These elements were not observed by SEM and no phase with Pb and/or Zn was detected by XRD. This implies that these metals are probably in the finer part of EAFD. Law et al. [12] have observed the tendency of Zn and Pb to be more concentrated in the least dense fraction, which contains the greatest quantity of the finest particles.

To summarize the data, chromium is mainly related to the fractions bound to original stable spinel minerals (69%) and to crystallised Fe oxides (21%). Nickel is related in majority to the fractions bound to crystalline Fe oxides (55%) and to original stable spinel minerals (26%). Lead is principally bound to hydroxides and carbonates (49%) and also bound to amorphous Fe–Mn oxides and silica glass (36%). Finally, zinc is principally bound to carbonates and hydroxides (39%) and to crystallised Fe oxides (33%).

About 1% of all extracted metals are soluble and sorbed species and this represents $900\ \mu\text{g/g}$ of Cr and $400\ \mu\text{g/g}$ of Zn which is mobile when in contact with water without any change to the pH or Eh. The fraction bound to carbonates and to hydroxides can be considered mobile at slightly lower pH and can be added to the water soluble and sorbed species fractions to give a global value of 16% for heavy metals bound to mobile phases. A large percentage (46%) of metals was incorporated in the mineralogical structure, probably in some type of spinel such

as chromite or magnetite. The spinels are refractory phases and their structure is attacked only in the last step of the sequential procedure.

From Table 5, it is possible to estimate the amount of heavy metals, which may be available (fractions 1–3) from EAFD. The following values represent the percentages and the amounts of metals, which can be mobile: 3% ($2800\ \mu\text{g/g}$) of Cr, 6% ($1100\ \mu\text{g/g}$) of Ni, 49% ($5900\ \mu\text{g/g}$) of Pb, and 40% ($12,100\ \mu\text{g/g}$) of Zn.

We should keep in mind that the increasing chemical strength of the sequentially applied method provides a basis for judging metal availability; water-soluble metals being most available and spinel-bound metals being the least available. Some others factors influence the results. The particle complexity is a major factor to consider in the interpretation of the results. The zonation and exsolution phenomena also influence the results because the rims around the particle must disaggregate before allowing solubilization of the heart of the particle. This implies that phases may probably dissolve in a subsequent step.

As a control to verify the applicability of the sequential extraction method to EAFD, the residual solids of the steps 3–6 were studied by SEM and EDXA techniques. The observations confirm the presence of magnetite composed of Cr, Fe, Mn, and O after each step studied and the presence of the original spinel minerals at the last step. For the first time in this study, Zn and Ni were observed. These two elements appear disseminated in the sample after an exposure of the EAFD at the fourth step. This small quantity of the Zn and Ni is probably a relic of the third step (carbonates and hydroxides) where the released of these two elements was more important. This observation confirms that a part of Zn and Ni was bound to carbonates and hydroxides. Silicon was less associated to metals and become less abundant after the

Table 6
TCLP results for EAFD (liquor analysis)

Element	mg/L
Crtotal	9.7
Cr (VI)	6.1
Ni	2.3
Pb	0.4
Zn	93.9

fourth step. This implies that the silica glass is probably attacked in the step as Fe–Mn oxides. The sixth step shows mainly spherical magnetite composed of Cr, Fe, Mn, O and some secondary precipitates with Cl and/or Na resulting from the lixiviant. Thus, the low amount of metals extracted by the sixth step was bound to spinel. The oxidizing conditions permit the extraction of some chromium and nickel bound to chromate oxides.

5.3. Leaching test results

5.3.1. TCLP results

The TCLP results presented in Table 6 show that the EAFD is a toxic waste. The total Cr (9.7 mg/L) and the Cr (VI) (6.1 mg/L) liquor concentrations after leaching are over the value of Toxicity Characteristic Regulatory Level (Table 7). The Pb concentration is under the regulatory level. The Ni and Zn concentrations are not regulated by the TCLP but it is important to note the high Zn concentration reached (93.9 mg/L). The EAFD is a toxic waste according to its high Cr concentration and must be treated. Stabilization/solidification (S/S) processes could be used to treat EAFD. This will be the subject of further research. The following section tries to evaluate the long-term leaching behaviour of EAFD in a neutral initial environment.

5.3.2. Static leaching test results

5.3.2.1. pH. The pH values measured over 365 days at two different liquid/solid ratios are presented in Fig. 5. The solution pH values indicate a variation from pH 9.8 to 11.5. The basic values of pH imposed by EAFD probably prevent the calcium carbonates, metal hydroxides and metal oxides solubilization.

5.3.2.2. Nickel and lead. The Ni and Pb concentrations in the water/EAFD leachates are presented in Figs. 6 and 7, respec-

Table 7
Maximum concentration of contaminants for toxicity characteristic and safe drinking water, U.S. Environmental Protection Agency

Contaminant	Toxicity characteristic regulatory level	Safe drinking water	
	(TCRL) (mg/L)	MCLs (mg/L) ^a	NSDWRs (mg/L) ^b
Cr	5.0	0.1	n.a.
Pb	5.0	0.015	n.a.
Zn	n.a.	n.a.	0.3

n.a.: Not available.

^a Maximum concentration level.

^b National secondary drinking water regulations.

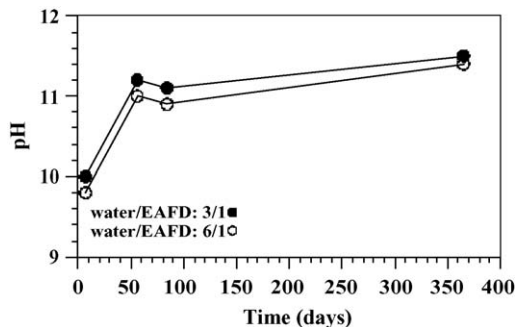


Fig. 5. Solution pH values for water/EAFD leachates over 365 days.

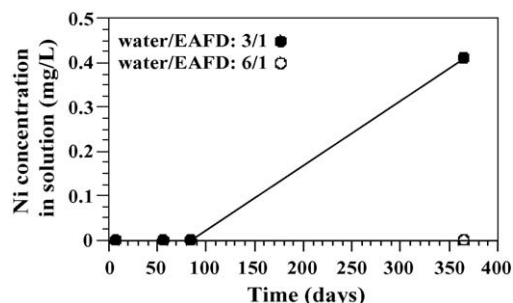


Fig. 6. Concentration of Ni in water/EAFD leachates over 365 days.

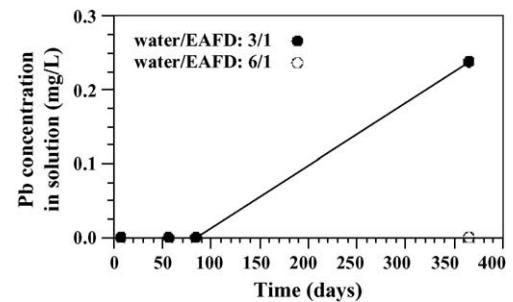


Fig. 7. Concentration of Pb in water/EAFD leachates over 365 days.

tively. A solubility control exists on both metals studied. The Ni and Pb concentrations with water/EFAD ratio of 6/1 are practically zero. This means that the Ni and Pb are insoluble during 365 days when EAFD reacts with six times as much water. The Pb concentrations are under the TCRL limit for the testing period.

5.3.2.3. Chromium and zinc. The Cr and Zn concentrations in the water/EAFD leachates are presented in Figs. 8 and 9, respec-

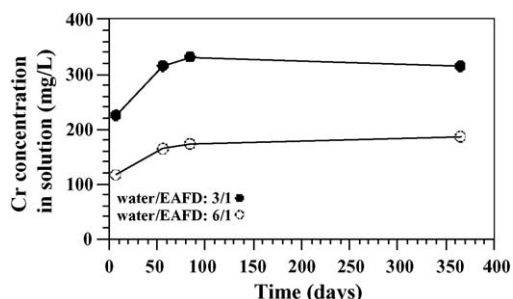


Fig. 8. Concentration of Cr in water/EAFD leachates over 365 days.

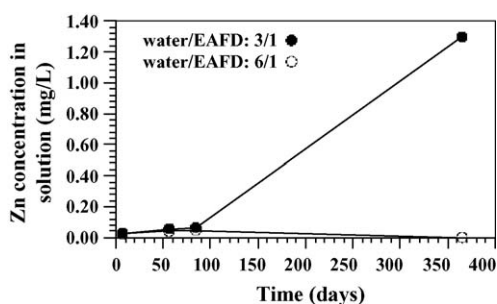


Fig. 9. Concentration of Zn in water/EAFD leachates over 365 days.

Table 8
Amount (in percentage) of metal extracted from EAFD

Liquid/solid	Time (days)	Amount of metal extracted (%)			
		Cr	Ni	Pb	Zn
3/1	7	0.6185	0.0000	0.0000	0.0002
3/1	56	0.8679	0.0000	0.0000	0.0003
3/1	84	0.9115	0.0000	0.0000	0.0004
3/1	365	0.8674	0.0030	0.0051	0.0075
6/1	7	0.6414	0.0000	0.0000	0.0002
6/1	56	0.9010	0.0000	0.0000	0.0005
6/1	84	0.9508	0.0000	0.0000	0.0005
6/1	365	1.0246	0.0000	0.0000	0.0000

tively. These data indicate a solubility control on Cr and Zn. This means that doubling the mass of EAFD to the mass of water did not result in a doubling of the solution concentrations. The Zn concentrations were very low and near to the NSDWRs limit. This limit is only presented as comparison and does not effect the possible disposition in landfill. However, the solubility control established by EAFD is not sufficient to decrease the Cr concentration under the regulatory level for landfill (TCRL). It is thus important to stabilize the material in order to reduce the quantities of chromium in the leachates.

The most notable feature was that all metals were subjected to a solubility control by phases present in EAFD for pH varying from 9.8 to 11.5. The amount of metal extracted presented in Table 8 show that the percentage of metal extracted is low but the concentration, particularly for Cr is not negligible.

6. Discussion

The static leaching test results show that the solubility of Cr and/or Cr-bearing phases is specially influenced by pH. The concentrations of Cr in solution were many-times larger for the static leaching tests than those obtained in the TCLP test. The final pH value for TCLP is 4.3. The static tests show final pH values varying from 9.8 to 11.5. This is significant in that the evaluation for EAFD landfill disposal must be evaluated by TCLP. The EAFD studied does not pass the TCLP limit (TCRL) but the liquor concentration obtained (9.7 mg/L) is not representative of concentrations obtained by static leaching test (117–331 mg/L). The behaviour for Zn is opposite. The Zn concentrations of static leaching test (<1.30 mg/L) were many times lower than those obtained in the TCLP test (93.9 mg/L). A knowledge of

the nature and complexity of phases present in EAFD are very important in anticipating leaching performance in landfill. The buffering capacity of waste must be considered because acidic conditions due to co disposition with organic matters are not always present.

7. Conclusions

The EAFD particles appear as elongated grains, spherical, fine-grained and irregular particles. The predominance of spinel group minerals was determined. Magnetite is the main phase present in the EAFD together with chromite. Most grains are franklinite–magnetite–jacobsonite solid solutions. No phase containing Zn or Pb was observed, but the hydroxides, carbonates and iron release Pb and Zn according to the sequential extraction results. These results revealed evidence of Zn in iron oxides. The Ni was found in Fe–Ni oxides (magnetite). The chromium appears both in chromium carbonate and chromite (spinel mineral). Many EAFD particles present different textures (zonation, exsolution and degassing phenomena). The EAFD is a toxic waste. The total Cr and Cr (VI) concentrations (9.7 and 6.1 mg/L, respectively) exceeded the Toxicity Characteristic Regulatory Level. A solubility control on Cr, Pb, Zn and Ni was identified in the EAFD. However, this control was not sufficient to decrease the Cr concentration to below the regulatory level. Future works may include analysis of leachates from the different granular sizes-fraction of EAFD.

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