Leaching Tests to Characterize Ferrous and Non-ferrous Slag Drainage Chemistry

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Abstract
Slags are important byproducts of metal mining. Some slag, especially from steel making, is used for construction purposes and in environmental applications. However, much of the slag from both ferrous and non-ferrous smelting has been deposited in waste piles. The interaction of surface water and groundwater with slag can produce metal-rich acidic to hyperalkaline drainage. Drainage chemistry depends on the physical, chemical, and mineralogical characteristics of slag. Various leaching tests have been used to estimate drainage chemistry and gain insight into the environmental behavior of slag. Single batch extraction leaching tests on ferrous slag generally resulted in alkaline to hyperalkaline leachates with potentially environmentally significant concentrations of Al (and occasionally Fe and Mn) and low concentrations of minor elements. In contrast, neutral to acidic leachates were generally produced that contained environmentally significant concentrations of Cd, Cu, and Zn (and to a lesser extent Pb) for Cu and Zn slags, and significant concentrations of Cd and Pb for Pb slag.

Key Words: steel, blast furnace, zinc, copper, lead, environment

Introduction
Non-ferrous and ferrous slags are enriched in a variety of elements compared to concentrations in many naturally-occurring soils. Slags have a wide range of uses such as road construction, roofing materials, and environmental remediation, or may be dumped on site in waste piles. In either case, slag is exposed to weathering and recent studies suggest that slag, once considered inert, may leach potentially toxic elements into the environment. In many cases, leaching tests are used to characterize slag as inert or potentially hazardous or to simulate weathering and subsequent drainage chemistry (e.g., Ettler et al. 2002, 2005, 2009, Fällman 2000, Navarro et al. 2008, Parsons et al. 2001, Piatak et al. 2004, Piatak and Seal 2010, 2012, Proctor et al. 2000, Tossavainen et al. 2007). Some leaching tests are designed to extract metals for secondary recovery, but most are aimed at characterizing slag in terms of their environmental behavior. This paper focuses on leaching tests used to characterize and better understand the environmental chemistry of ferrous and non-ferrous slag types. Ferrous slags types include those produced in a blast furnace to recover Fe and those produced in various furnace types (e.g., electric arc, basic oxygen) to make steel. The non-ferrous slag types include mostly slags produced from the smelting of sulfidic base-metal ores including Cu, Pb, and Zn. The results of standardized leaching tests, because of the comparable protocols, used on these different slag types can be compared to each other to make generalizations about slag leachate chemistry. This paper first gives a general overview of the most commonly used leaching tests on slag. Next, slag characteristics that affect leachate results are discussed. Lastly, leachate chemistries from a selected number of standardized leaching tests for each slag type are related to slag drainage chemistry and the classification of slags as hazardous or non-hazardous materials.

Types of Leaching tests
In general, leaching tests can be divided into two main types, single batch and dynamic. First, single batch (or extraction) tests are usually agitated to maintain a homogeneous mixture with the goal of reaching equilibrium or saturated conditions. Standardized tests of this type involve reducing the particle size of samples, if necessary, and then mixing with a solution at a specific ratio for a predetermined time. They commonly are used to represent a “worst-case” leaching scenario, are simplistic in design and have good reproducibility. Frequently used standardized regulatory leach tests in the United States (US) are

those developed by the US Environmental Protection Agency (USEPA) such as the toxicity characteristic leaching procedure (TCLP), which replaced the extraction procedure toxicity test (EP-tox) in 1990, and the synthetic precipitation leaching procedure (SPLP) (USEPA 2008). These tests were developed for different reasons in order to either classify a material as hazardous or non-hazardous by simulating conditions in a landfill (TCLP) or to assess the impact of the material on groundwater or surface water by simulating weathering with acid rain (SPLP). In both tests, a liquid-to-solid ratio of 20 is used on material that is < 9.5 mm in diameter with a contact time of 18 hrs. In TCLP tests, the leachant is an acetate buffer with a pH of 4.93 (less alkaline samples) or acetic acid solution with a pH of 2.88 (alkaline samples). In SPLP tests, the leachant is deionized water adjusted with a mixture of sulfuric and nitric acids to either a pH of 4.2 (eastern synthetic precipitation) or pH of 5.0 (western synthetic precipitation) depending of geographic area in the US. A standardized batch test established by the European Union (EU) to determine if a granular waste is inert, non-hazardous, or potentially hazardous (EN 12457-2, EU 2003) is also applied to slag. This standard procedure is similar to TCLP in that it is used to assess the acceptability of waste at landfills. The EN 12457-2 requires a liquid-to-solid ratio of 10 with a contact time of 24 hrs. Also, deionized water is used as the leachant and 95 percent of the material is to be less than 10 mm in diameter.

The regulatory tests such as EN-12457-2 and TCLP, used to determine if a material is hazardous or non-hazardous, should be standardized because the same test can be applied to many types of material that may end up in a landfill, whereas scientifically-driven leaching tests such as to simulate natural weathering may warrant modification to standard procedures to mimic conditions that are more specific to the purpose or the site (Wilson 1994). Standardized single batch tests have been modified in order to gain insight into slags environmental behavior. Modifications include increasing contact time (long term leaching behaviors) or periodic sampling of leachant during test (insight into rates of leaching), using leachants with modified chemistries (effect of pH or organic compounds on leaching), and modifying sample preparation procedures (effects of grain size on leaching). Also, single batch extractions have been altered to using more than one leaching solution on a single sample, each applied sequentially, and with more aggressive solutions used in each step. These sequential extraction leaching procedures target operationally defined element species or elements bound to or associated with particular phases and compounds. They are commonly used to gain insight into the mobility and bioavailability of elements. Sequential extractions have only rarely been applied to slags (Álvarez-Valero et al. 2009, Pérez-López et al. 2008).

In addition to single and sequential batch extraction tests, dynamic leaching tests such as flow-through or column tests have been conducted on slag in order to understand the kinetics of contaminant mobilization and (or) to simulate natural weathering conditions. Standardized procedures are uncommon for these types of tests and usually conducted according to laboratory, site, or sample requirements. Leachants are continuously or intermittently renewed to maintain a driving force of leaching and represent conditions far from equilibrium. They are commonly designed to simulate field conditions and may include periodic wetting and drying of the material to mimic rain events. These types of tests commonly require a longer time frame compared to batch tests and are sometimes difficult to reproduce.

Tests, such as column tests or the batch SPLP test, which are designed to simulate field conditions commonly compare leachate results to aquatic water-quality and drinking water guidelines. In contrast, tests that are designed to estimate the total amount of a contaminant released (e.g., TCLP, EN 12457-2) may have method-specific criteria that are greater than the environmental guidelines because leachates are considered more concentrated than that produced under natural conditions. Commonly, the drinking water standard is multiplied by a factor of 100 to determine a screening criterion for the later type of leaching tests (Proctor et al. 2000, Wilson 1994).

Slag Characteristics

Bulk chemistry

The bulk chemistry is one component of the environmental behavior of slags and only one of the factors that influence which elements and the amount leached. Although the compositions of slag can be highly variable even within each slag type, generalizations of their common chemical compositions were summarized in a review on the characteristics and environmental aspects of slags by Piatak et al. (*in press.*) (Table 1). The major element chemistry of non-ferrous and ferrous slags is dominated by SiO_2, CaO, FeO, Al_2O_3, and MgO. Blast furnace Fe slag is mainly CaO and SiO_2 with lesser amounts of Al_2O_3 and MgO. Steel slag has a similar composition but commonly contains less SiO_2 and more FeO. In contrast, non-ferrous slag from the production of base metals is dominated by SiO_2 and FeO with generally lesser amounts of CaO and Al_2O_3, and only minor MgO. The differences in the bulk chemistries result from the variations in ore and flux compositions and in smelter conditions (Piatak et al. *in press*). The concentrations of Al_2O_3 and FeO in some slag exceed USEPA industrial-use and residential-use soil screening levels (USEPA 2010); Al in some Zn slag and Fe slag and Fe in many steel and most non-ferrous base metal slags exceed these guidelines (Piatak et al. *in press*).

Table 1. Chemical and mineralogical characteristics of slag.

Slag type		Chemistry		Mineralogy		
		Major oxides	Minor elements	Silicates	Oxides	Other
Ferrous	Fe	CaO, SiO_2 > Al_2O_3, MgO > FeO	As, Mn	olivine, melilite, merwinite, glass, feldspar	spinel, (Ca,Fe,Mn)O	calcite, Fe metal, alabandite-oldhamite
	steel	CaO, FeO, SiO_2 > Al_2O_3, MgO	As, Cr, Mn			calcite
Non-ferrous	Cu	FeO, SiO_2 > CaO, Al_2O_3 > MgO	As, Co, Cr, Cu, Pb, Zn	olivine, melilite, pyroxene, feldspar, glass	spinel, (Fe,Zn)O	sulfides, metallic and intermetallic phases
	Pb		As, Mn, Pb, Zn			
	Zn	FeO, SiO_2, Al_2O_3 > CaO > MgO	As, Pb, Zn			

Note: Phases given were the most commonly reported ones in slag based on a literature review by Piatak et al. (*in press*) and not a comprehensive list. The chemistry of slag was also generalized from Piatak et al. (*in press*).

The minor element chemistry of slag may be more significant in terms of the leaching of elements with potentially environmentally deleterious effects. Elements that commonly exceed environmental guidelines (CCME 2007, USEPA 2010) in ferrous slag include As, Cr, Mn, and rarely Co (Table 1). Arsenic, Pb, and Zn are found in significant concentrations that exceed soil screening guidelines in non-ferrous slag (Piatak et al. *in press*). Cadmium (rarely), Co, Cr, and Cu are anomalously high in some Cu slag and Mn is anomalously high in some Pb slag (Table 1). Based on major and trace element chemistries of the various slags types, the focus in the subsequent sections on slag leachate chemistry will be on the following elements: As, Al, Co, Cr, Cu, Fe, Mn, Pb, and Zn. Note that although many samples exceed the industrial soil screening guideline of 1.6 mg/kg for As, the average concentration of As in soil in the US also exceeds this guideline (7.2 mg/kg) (Shacklette and Boerngen 1984).

Mineralogy

Although phases found in slag are not naturally-occurring minerals, mineralogical terminology is used for the sake of clarity. The primary mineralogy, mineral chemistry, and amount of crystalline versus amorphous phases influence the leaching of elements from slag. If cooled at a slow enough rate to allow crystallization, the minerals in the various slag types are a reflection of the bulk chemistry that in turn is dependent on the chemistry of the furnace melt and efficiency in metal recovery. Ferrous slag contains

significant Ca silicates with olivine-group phases commonly falling between larnite (Ca_2SiO_4) and monticellite ($CaMgSiO_4$) in composition (Piatak et al. *in press*) (Table 1). Melilite ($(Ca,Na)_2(Mg, Fe^{2+}, Al, Si)_3O_7$) is nearly as common as olivine in crystalline ferrous slag samples with other Ca silicates including merwinite ($Ca_3Mg(SiO_4)_2$), pyroxene ($ABSi_2O_6$), plagioclase ($(Ca,Na)(Si,Al)_4O_8$), bredigite ($Ca_7Mg(SiO_4)_4$), and others reported less frequently. Oxides such as periclase (MgO), wüstite (FeO), and spinel-series phases are common with the Fe-bearing oxides more frequently found in steel slag compared to Fe slag. Quartz (SiO_2), calcite ($CaCO_3$), Fe metal, and alabandite-oldhamite (MnS-CaS) have also been repeatedly found in ferrous slag (Table 1). Glass is likely ubiquitous to all slag samples (although not always reported).

Non-ferrous slag, which is generally Fe-rich, commonly contains Fe-bearing silicates such as fayalite (Fe_2SiO_4), melilite, and pyroxene (commonly hedenbergite), among others (Piatak et al. *in press*). Feldspars and spinel-series phases (mostly magnetite- Fe_3O_4) are not uncommon among many other oxide and silicate phases. A wide variety of sulfides, metallic phases, and intermetallic compounds are also reported in non-ferrous slag in contrast to the more limited amount of these phases in ferrous slag (Table 1). Calcite was not found in non-ferrous slag; glass is likely ubiquitous.

The partitioning of the major and trace elements into the crystalline or amorphous phases in slag may affect the potential for these elements to be leached depending on how susceptible the phase is to weathering or degradation by the leaching solution. Of the elements previously discussed that exceed environmental guidelines in slag, Al, Fe, and Mn are commonly found in crystalline silicates or siliceous glass. Piatak and Seal (2012) discussed the partitioning of these elements within the phases in pre-1900 blast furnace Fe slag and reported the following: Al and Mn partitioned into glass generally more than into crystalline silicates, which was generally more than their partitioning into oxides; Fe was partitioned into metals with somewhat subequal and varying proportions into glass, crystalline silicates, and oxides. De Windt et al. (2011) reported Fe in silicate and oxide phases in steel slag (without mention of glass). Calcium was present in crystalline Ca silicates and glass and, in ferrous slag especially, in Ca oxides and Ca carbonates. In terms of minor elements, Cr was commonly found in oxides such as chromite (De Windt et al. 2011, Fällman 2000). Zinc was incorporated into silicates, oxides, or sulfides, whereas Cu and Pb were more often reported in the sulfides, intermetallic compounds, and glass (Parsons et al. 2001, Piatak and Seal 2012). Some As minerals have been reported as well as As metal (Costagliola et al. 2008). Glass may be the primary host of a variety of elements including Cd (Parsons et al. 2001).

Leachate Chemistry by Slag Type

Despite the various types of leaching tests used, each slag type has a characteristic leachate chemistry. This section focuses on the results of three types of standardized single batch extraction tests on various slag types from recent publications or unpublished data from the authors. Studies include the following:

1. SPLP results on steel slag from the Chicago area (Illinois and Indiana, US) (Piatak & Seal *unpublished*), pre-1900 Fe slag from the Hopewell Furnace (Pennsylvania, US) (Piatak and Seal 2012), Zn slag (from sphalerite (ZnS)-rich ores) from the Hegeler smelter (Illinois, US) (Piatak and Seal 2010), Cu slag (from chalcopyrite ($CuFeS_2$)-rich ore) from the Vermont Cu belt (Vermont, US) and Ducktown mining district (Tennessee, US) and Pb-Ag slag (from galena (PbS)- and tetrahedrite ($(Cu,Fe,Ag,Zn)_{12}Sb_4S_{13}$)-rich ores) from the Clayton smelter (Idaho, US) (Piatak et al. 2004), and Cu slag (from chalcopyrite-rich ore) from the Penn mine (California, US) (Parsons et al. 2001). Tests performed in Piatak et al. (2004) used a modified procedure with a 1-minute agitation and contact time of 24 hrs, instead of end-over-end agitation for 18 hrs. Also, the < 2 mm size-fraction was used for tests in Piatak and Seal (*unpublished*, 2010, 2012) and in Piatak et al. (2004), instead of < 9.5 mm. An eastern synthetic precipitation solution with an initial pH of 4.2 was used as the leachant in all studies except Parsons et al. (2001) in which a western synthetic precipitation solution with a pH of 5.0 was used.

2. TCLP results on Cu slag from the Penn mine (Parsons et al. 2001), Fe and steel slag from 58 furnaces throughout the US (Proctor et al. 2000), Cu and Cu-Pb slag (from chalcocite (Cu_2S)-, enargite (Cu_3AsS_4)-, galena-, and sphalerite-rich ores) from the Tsumeb smelter (Namibia) (Ettler et al. 2009), and steel slag from Mingo Junction (Ohio, US) (Ziemkiewicz and Skousen 1999). The concentrations of elements in Proctor et al. (2000) were reported as minimum, maximum and average; the range in values is used in this report. Also, both Ettler et al. (2009) and Ziemkiewicz and Skousen (1999) performed tests on finer-size fractions (< 0.1 mm and < 3.2 mm, respectively) than stated in the TCLP protocol (< 9.5 mm).

3. EN 12457-2 results from Cu and Cu-Pb slag from the Tsumeb smelter (Ettler et al. 2009) and steel slag (Sweden) (Tossavainen et al. 2007). Ettler et al. (2009) performed tests on a finer-size fraction (< 0.1 mm) than stated in the EN 12457-2 protocol (< 4 mm).

The results of these three types of leaching tests cannot be compared directly to each other because each protocol has different leachate parameters. Comparisons can be made for results from the same test protocols considering modifications; results from all tests can compared to gain insight into how slag reacts to various leaching environments and which elements are consistently released. For comparison purposes, the element concentrations in the leachates were converted to an amount released from the solid by multiplying leachate concentrations (mg/L) by the liquid-to-solid ratio and are reported as milligrams per kilogram (mg/kg).

Overall, the leachate signature of ferrous slag was very different to that of non-ferrous slag. Based on non-static pH SPLP tests (Fig. 1), the pH and alkalinity of ferrous slag leachate were significantly higher than those of non-ferrous slag leachate from base metal extraction. In particular, steel slag from the Chicago region produced leachate that was alkaline to hyperalkaline with pH values reaching 12 and alkalinity reaching nearly 9,000 mg $CaCO_3$ per kg of slag (or 427 mg $CaCO_3$/L in leachate). The dominant cation released from the steel slag was Ca (up to 4,540 mg/kg) presumably from the breakdown of Ca silicates, with Si being the next most abundantly released cation (up to 414 mg/kg) (Fig. 2). These SPLP leachate results on steel slag from the Chicago area were consistent with modified EN 12457-2 leaching tests on steel slag from France for which Ca and Si were released in the greatest amounts, followed by lesser amounts of Al, Fe, and Mg (De Windt et al. 2011). In general for steel slay, Al was released more than Mg, which was released more than Fe (Fig. 2). As shown in Figure 2, Fe was commonly released in lower concentrations in steel slag compared to Fe and non-ferrous slags using both SPLP and EN-12457-2 leachate protocols, whereas the concentrations of Al and Mg were variable among the slag types. The formation of Al hydroxides may be controlling Al, brucite may be controlling Mg, and Fe (oxy) hydroxides or Fe oxides may be controlling Fe (Bayless and Schulz 2003, De Windt et al. 2011). The concentrations of many minor elements were consistently low in steel slag leachate including Cd, Co, Cu, and Pb (Fig. 3). Under the likely alkaline conditions of steel slag leachate, the concentrations of many of these elements were probably limited by precipitation of or sorption onto secondary phases or by mineral solubility kinetics. The concentrations of some elements, such as Cr, Mn, and Zn, were highly variable in the steel slag leachates (Figs. 2 and 3). Chromium may be controlled by secondary $Ba(S,Cr)O_4$ depending on leachate chemistry (Fällman 2000), whereas Mn and Zn may be controlled by other secondary phases.

The leachate chemistries of pre-1900 Fe slag (Piatak and Seal, 2012) and modern Fe slag (Proctor et al. 2000) were similar to those of the leachate chemistries of steel slag with some variations. Both the pre-1900 Fe and Chicago steel slags produced a hyperalkaline leachate with Ca as the major cation, although the amount of Ca released was significantly lower from the Fe slag (up to 958 mg/kg) (Figs. 1 and 2). Based on the pre-1900 Fe slag, the next most abundant cation released was Si followed by Mg, followed by Al, and then Fe. This trend was slightly different than that found for steel slag but was based on only one Fe slag study (major element chemistry was not reported by Proctor et al. 2000). Alkalinity was consistently lower in the pre-1900 Fe slag leachate compared to steel slag leachate with many

concentrations below detection (Fig. 1). Sulfate was the next most abundant anion in the SPLP leachates on ferrous slag; concentrations ranged from 2 to 64 mg/L sulfate and include 2 to 5 mg/L sulfate present in leachant. Similar to steel slag, the amounts of As, Cd, Co, Cu, and Pb were consistently low and the amounts of Cr, Mn, and Zn were variable based on both SPLP and TCPL leaching tests (Figs. 2 and 3). Due to their similar mineralogy and chemistry, the mineralogy that controls the concentrations of elements in the steel slag leachates are likely similar to the ones that control concentrations in the Fe slag leachates.

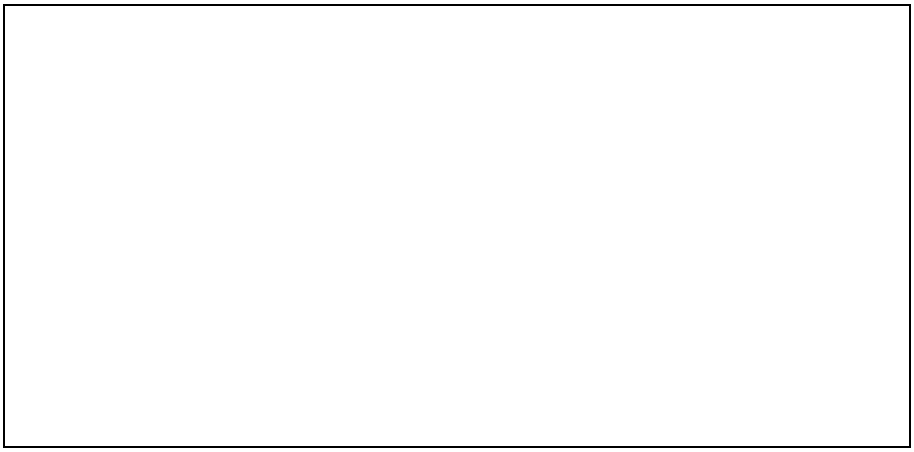

Figure 1. pH and alkalinity in slag leachates produced using modified SPLP protocols. Alkalinity (mg $CaCO_3$ released per kg of slag) is shown as open symbols if at the detection limit of the method.

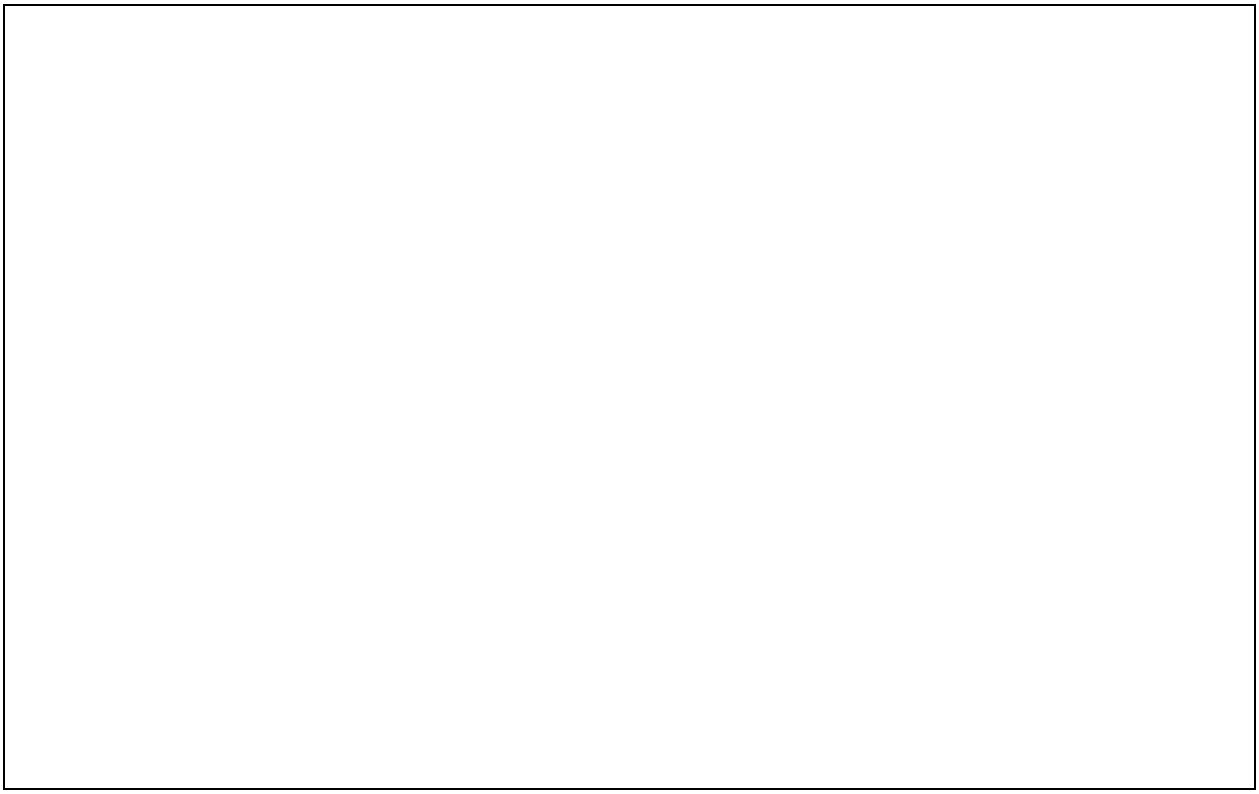

Figure 2. Amounts of As, Ca, Fe, Mg, and Mn released during SPLP (blue symbols), TCLP (green symbols), and EN-12457-2 (red symbols) leaching tests on slag. Concentrations are in mg released per kg of slag. Open symbols indicate concentrations not detected at the detection limit of the method.

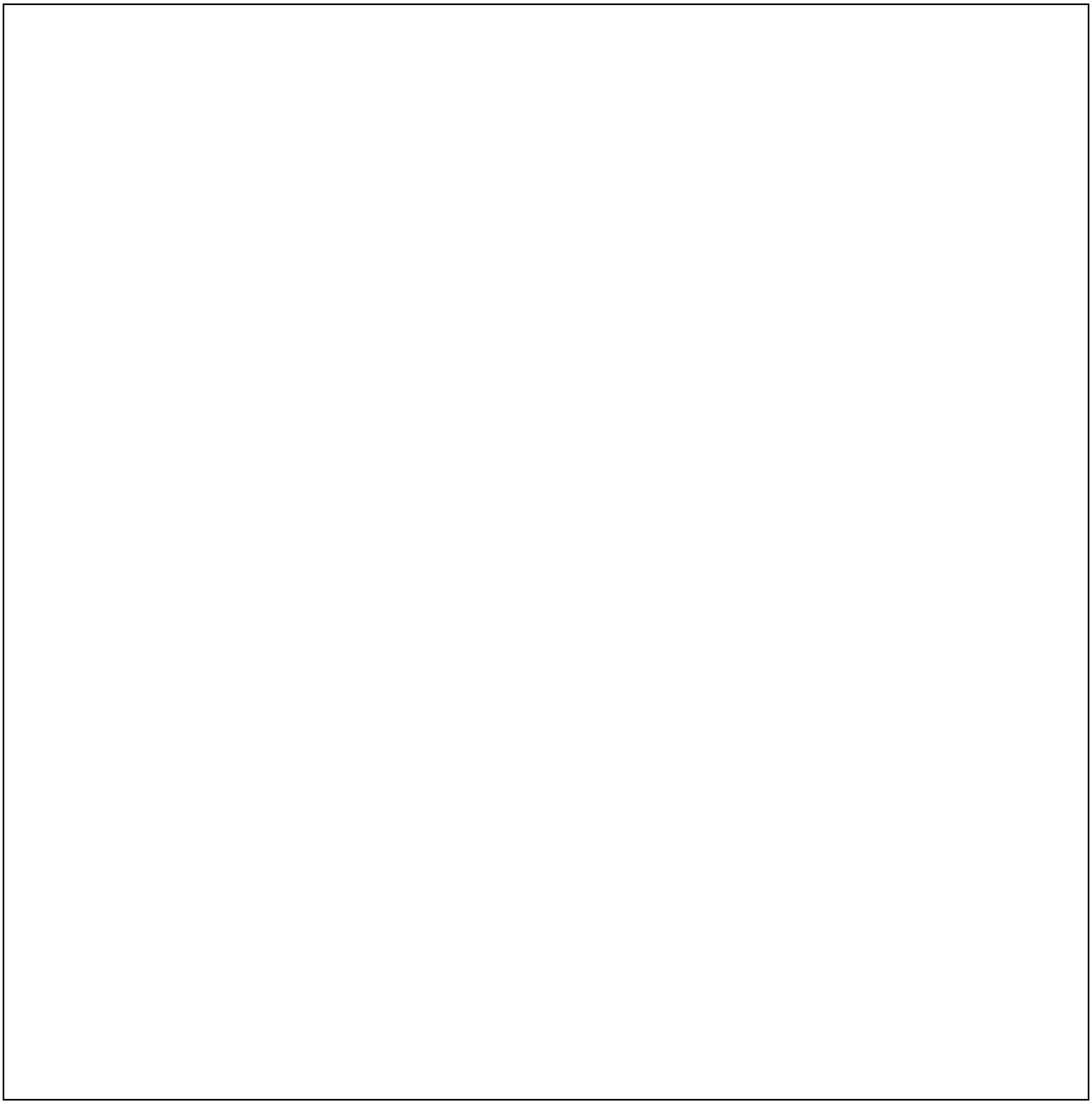

Figure 3. Amounts of As, Co, Cr, Cu, Pb, and Zn released during SPLP (blue symbols), TCLP (green symbols), and EN-12457-2 (red symbols) leaching tests on slag. Concentrations are given in mg released per kg of slag. Open symbols indicate concentrations not detected at the detection limit of the method. Within a slag type, symbols that are the same but different colors represent two types of leaching tests conducted on the same samples.

The pH and alkalinity of leachates produced by non-ferrous slags were commonly less than those produced by ferrous slags (Fig. 1). The non-static pH SPLP leach tests on Zn, Cu, and Pb-Ag slags resulted in acidic to near neutral pH (4.2 to 7.0) leachates with alkalinities reaching only a few mg $CaCO_3$ per liter (~60 mg or less $CaCO_3$ per kg of slag). Similar to ferrous slag, the major cations released most appreciably were Ca and Si (Fig. 2). Unlike ferrous slag, Fe was released in significant concentrations,

commonly in amounts greater than those of Al or Mg (Fig. 2). Concentrations of some trace elements were released from non-ferrous slags in significant amounts. For example, the concentrations of Cu were similar or higher than concentrations of Ca in SPLP leachates from Vermont Cu slag (Figs. 2 and 3). Non-ferrous slag generally released higher amounts of many elements such as As, Cd, Co, Cu, Pb, and Zn when compared to ferrous slag (Fig. 3). In contrast, the amounts of Al, Cr, and Mn leached from non-ferrous slag do not reach maximum values leached from ferrous slag (Figs. 2 and 3). Aluminum concentrations in leachate were suggested to be limited by saturation with respect to Al hydroxides based on numerous non-ferrous slag studies (e.g., Ettler et al. 2002, Parsons et al. 2001, Piatak et al. 2004); this was similar to results for steel slag (De Windt et al. 2011). Also, the concentration of Fe was suggested to be controlled by Fe hydroxides, oxides, or hydroxysulfates (e.g., Ettler et al. 2002, Navarro et al. 2008, Piatak et al. 2004). These Al and Fe phases likely control the concentration of other minor elements by sorption or coprecipitation (Ettler et al. 2002, 2005).

Unlike the consistent finding for Al and Fe, the concentrations of some other elements in non-ferrous slag leachate have been suggested to be controlled by a variety of phases depending on the study. For example, leachates from Cu and Pb slags have been suggested to be oversaturated with respect to Cu-Pb arsenates, controlling the concentrations of As, Cu, and Pb in solution (Ettler et al. 2009). Phases such as Cu oxides and amorphous Zn silicates have been suggested as secondary phases that limit concentrations of Cu and Zn in Cu slag (Parsons et al. 2001). In Ettler et al. (2002), Pb was suggested to be controlled by precipitation of Pb carbonate and Zn by precipitation of Zn hydroxide or Zn oxides in Pb-Zn slags. The phases that control the concentrations of minor elements in leachate are variable depending on the composition of the slag and the aqueous environment created by the particular leaching test method. Despite the phases or mechanisms controlling their concentrations, many minor elements were released in greater amounts from non-ferrous slag when compared to ferrous slag likely due to bulk chemical and leachate composition (e.g., lower pH) differences.

Overall, there are many types of leaching test procedures that vary according to sample preparation, leachant composition, method of contact, solid to solution ratio, leachant renewal, leachate separation, temperature, and contact time. Many studies, a few of which are discussed below, have focused on the influence these parameters have on the release of elements from slag. For example, the composition of the leachant will influence the amount of an element released, at times more strongly than the bulk chemical composition of the slag (Ettler et al. 2002, Robbins et al. 1983). The use of organic acids in the leaching solution has been shown to release greater quantities of some elements, particularly Pb, compared to other leachate procedures (Parsons et al. 2001, Robbins et al. 1983). Ettler et al. (2009) tested the same Cu and Pb-Cu slags using TCLP and EN 12457-2 protocols and Parsons et al. (2001) tested the same Cu slag using both TCLP and SPLP protocols. The finding were consistent between both studies in that the TCLP protocol released higher amounts of minor elements (As, Cr, Cd, Cu, Pb, and Zn) compared to the other tests that did not use an extraction solution containing acetic acid (Fig. 3). This was likely due to the lower pH of the buffered TCLP solution and enhanced extraction by acetic acid (Ettler et al. 2009, Parsons et al. 2001). The maximum amounts of As, Cd, Cr, Cu, Pb, and Zn for both ferrous and non-ferrous slag types were released when acetic acid is used in the extraction solution (Fig. 3, TCLP protocol).

Another factor that influences the release of elements from slag is particle size. The leaching of minor elements generally increases with decreasing particle size as found by Vitkova et al. (2011) for Cu, Co, and Zn in Cu slag. Likewise, the proportion of glass, which is dependent on how fast the slag cooled, also influences which and how much elements are released. Iron and steel slags that were remelted and cooled rapidly, resulting in higher glass content, leached higher amounts of Si, lower amounts of Al, and similar amounts for many minor elements compared to air cooled samples (Tossavainen et al. 2007). Although findings were not always consistent, studies by Johnson et al. (1982) and Robbins et al. (1983) suggest some minor elements, such as As, Cu, Pb, and Zn, in non-ferrous slags may be leached more from glassy granulated slag compared to slow cooled crystalline slag.

Leachate and Slag Drainage Chemistry and Potential Environmental Impact

Although the batch leaching tests are designed to reach equilibrium condition, the reaction time may not always be long enough to represent a "worst-case" leaching scenario or the leaching environment may not mimic field conditions and end up overestimating leaching. However, the leaching tests can be used to gain insight into slag drainage chemistry and potential environmental impacts from slag weathering. For ferrous slag, the only major element that may be of environmental concern based on leachate chemistry is Al with concentrations in many of the SPLP leachates that exceeded USEPA aquatic life criteria and secondary drinking water guidelines for both steel and Fe slag; the concentrations of Fe and Mn periodically exceeded secondary drinking water guidelines for Fe slag and did not exceed aquatic life criteria for ferrous slag in SPLP leachates (USEPA 2009a, b). In addition, Cr, Mn, and Zn concentrations were variable, whereas other minor elements were consistently low in ferrous slag leachates. Despite the range in concentrations found in the leachates for Cr, Mn, and Zn, all fell below either aquatic life criteria or drinking water guidelines for the SPLP leachate results or below the hazardous waste criteria for TCLP and EN 12457-2 for the studies included in this report. Therefore, the environmental impact from the release of potentially toxic elements from ferrous slag is likely minimal.

A comparison of the leachate chemistry to slag-impacted waters at two sites supports the minimal environmental impact from ferrous slag. First, the chemistries of groundwaters collected within and beneath steel slag piles in the Chicago area were generally consistent with the SPLP leachate chemistries such that the alkaline groundwater had pH values as high as 12.8 and contained significant Ca (Roadcap et al. 2005). The relative abundance of other major elements such as Al, Fe, Mg, and Si and the low concentrations of minor elements such as As, Cd, Co, Cu, Pb, and Zn in the groundwater chemistry reported by Roadcap et al. (2005) were also consistent with Chicago steel slag leachates (Piatak and Seal *unpublished*). Roadcap et al. (2005) reported secondary calcite precipitates containing elements such as Cd, Cr, Cu, Pb, and Zn where slag-impacted groundwater came to the surface in the Chicago region. Similarly, Bayless and Schulz (2003) found secondary calcite containing Fe, Mn, and S, and clay minerals and Fe oxides in aquifers beneath slag in the Chicago region. Under these high pH conditions, many elements, including potentially toxic elements (e.g., Cu, Pb, Zn) are removed from solution by coprecipitation with and sorption onto other secondary minerals (Roadcap et al. 2005). Similar to findings for Chicago steel slag, slag-impacted groundwater and surface water chemistries at the Hopewell blast furnace slag site were generally consistent with SPLP leachate results in that many minor element concentrations were low and nearly all were below USEPA drinking water and aquatic life criteria (USEPA 2009a, 2009b). The exception is Cu in some of the SPLP leachates, which exceeded USEPA hardness-based aquatic life criteria; a stream sediment sample downstream of the slag also contained Cu in excess of sediment criteria (Piatak and Seal 2012, Sloto and Reif 2011).

In contrast to ferrous slag, several minor elements, some periodically and some consistently, either exceeded drinking water guidelines and aquatic life criteria in SPLP leachates or hazardous waste criteria in TCLP and EN 12457-2 leachates from non-ferrous slag. First, As exceeded the drinking water guideline in a SPLP leachate from a Pb-Ag slag from Idaho (Piatak et al. 2004) and was released in concentrations high enough to exceed hazardous waste criteria for a Cu slag (based EN 12457-2) and a Pb-Cu slag (based on TCLP) from Namibia (Ettler et al. 2009). These were the only exceedances noted for As. Some elements such as Cd, Cu, and Zn consistently exceeded drinking water or aquatic life criteria in SPLP leachates but were only rarely considered hazardous based on TCLP or EN 12457-2 leachates. For example, Cd, Cu, and Zn commonly exceeded aquatic life criteria and periodically exceed drinking water guidelines in SPLP leachate from Cu, Zn, and Pb slag with the exception of Cu from Pb slag (Parsons et al. 2004, Piatak et al. 2004, Piatak and Seal 2010). In contrast, EN 12457-2 leachates from Cu and Pb-Cu slag did not contain enough Cd, Cu or Zn to be considered hazardous despite the slag having a smaller particle size than required by the protocol (Ettler et al. 2009). Cadmium did leach from a Cu slag (Parsons et al. 2001) and a Pb-Cu slag (Ettler et al. 2009) in concentrations that exceeded the hazardous criteria in TCLP leachates; TCLP criteria have not been established for Cu and Zn. Lead only

periodically exceeded the aquatic life criteria and drinking water guideline in Zn-, Cu-, and Pb-slag SPLP leachates (Piatak et al. 2004, Piatak and Seal 2010). Copper and Pb-Cu slags were considered non-hazardous for Pb based on EN 12457-2 but considered hazardous based on TCLP likely due to the affinity of acetic acid in the leachant for Pb (Ettler et al. 2009, Parsons et al. 2001). Cobalt leached from Zn and Cu slags in amounts that exceeded the chronic aquatic life criterion but not the acute criterion (Piatak et al. 2004, Piatak and Seal 2010). Overall based on the various leaching tests, Cd, Cu, and Zn, and to a lesser extent Pb, are potential environmental contaminants released from Cu and Zn slags, whereas Cd and Pb may be a concern for Pb slags.

A comparison of leachate chemistry to slag-impacted waters at non-ferrous slag sites can also be used to gain insight into their overall environmental impact. Although, surface water and groundwater collected adjacent to the slag dump at the Hegeler Zn smelter (USA) generally contained higher concentrations of some elements such as Al, Ca, Fe, sulfate, and Zn and lower pH values compared to SPLP leachates on slag from the site, the concentrations of some elements such as Cd, Co, Cu, and Pb were similar in site waters to the leachates (Kay et al. 2009, Piatak and Seal 2010). In contrast to the SPLP tests on Hegeler Zn slag, column leaching tests that are generally designed to simulate field conditions were found to contain higher concentrations of some elements such as As, Cu, Ni, and Sb compared to groundwater at Pb and Ag smelters in Spain (Navarro et al. 2008). Navarro et al. (2008) attributed this difference in chemistries to attenuation processes in the aquifer.

Overall, SPLP leaching tests were shown to be chemically similar to surface waters and or groundwater at two ferrous slag sites and one non-ferrous slag site. Some inconsistency did occur between leachate chemistry and natural slag drainage chemistry possibly due to longer or shorter reaction times in the field versus the laboratory, differences between synthetic leachant composition versus natural site water composition, or physical differences of slag used in the laboratory test (e.g., crushing, sieving) compared to undisturbed slag at the site.

Conclusions

Leaching tests applied to slag include single batch extraction, sequential batch extraction, and dynamic leaching tests, with single batch being the most commonly performed. A comparison of the results from several types of standardized single batch extraction tests indicates a common chemistry for leachates from ferrous slag or from non-ferrous slag types. Ferrous slag tests generally resulted in alkaline to hyperalkaline leachates with environmentally significant concentrations of Al (and occasionally Fe and Mn) and low concentrations of other elements. For non-ferrous slag types, near-neutral to acidic leachates were commonly produced that contained environmentally significant concentrations of Cd, Cu, and Zn (and to a lesser extent Pb) for Cu and Zn slag and significant concentrations of Cd and Pb for Pb slag. In any leaching tests, the crushing or grinding of slag increases the surface area available to react with the leachant, which may increase the amounts of elements released. Also, the leachant composition, such as some organic solutions, may preferentially leach particular elements such as Pb. These and other components of leachate protocols may overestimate or underestimate the leaching of elements when compared to natural slag drainage chemistry. Nonetheless, leaching tests on slag can be used to gain insight into slag drainage chemistry and environmental impacts of slag weathering.

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Acronyms

CCME	Canadian Council of Ministers of the Environment
EP-tox	Extraction Procedure Toxicity Test
EU	European Union
SPLP	Synthetic Precipitation Leaching Procedure
TCLP	Toxicity Characteristic Leaching Procedure
US	United States
USEPA	US Environmental Protection Agency
USGS	US Geological Survey