

Use of Standardized Procedures to Evaluate Metal Leaching from Waste Foundry Sands

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As part of the casting process, foundries create sand molds and cores to hold the molten metal to specific dimensional tolerances. Although most of the waste foundry sands (WFSs) from this process are land filled, there is great interest in diverting them for use in agricultural and geotechnical applications. One potential limitation to their beneficial use is concern that the WFSs will leach high levels of trace metals. The aim of this study was to quantify Ag, Ba, Cd, Cr, Cu, Ni, Pb, and Zn in leaching extracts from 96 waste molding and core sands from ferrous and nonferrous foundries. The procedures used to assess leaching in the WFSs were the Extraction Procedure, the Toxicity Characteristic Leaching Procedure, and the American Society for Testing and Materials water extraction procedure. The metal extract concentrations were compared with those found in virgin silica sands and Argentinean and U.S. hazardous waste laws to determine if the WFSs met toxicity limits. Regardless of metal cast and sand binder type, the majority of the WFS extracts analyzed contained metal concentrations similar to those found in virgin sand extracts and were below levels considered hazardous. However, 4 of 28 sands that used alkyd urethane binder were deemed hazardous because Pb concentrations in these sands were found to exceed regulatory thresholds. Although other regulated metals, such as As, Hg, and Se, were not analyzed in the extracts, this dataset provides additional evidence that many WFSs have a low metal leaching potential.

FERROUS AND NONFERROUS foundries produce metal castings to supply a variety of large markets, including the automotive, mining, petroleum, and marine industries. As part of the casting process, foundries create molds and cores using sand (e.g., silica, olivine, chromite, zircon) as refractory materials. The molds are made of virgin or reclaimed sand and binding agents such as clays or organic resins. Molding sands made with calcium and/or sodium bentonite clay are called green sands, which also contain lesser quantities of bituminous coal and cellulosic materials to prevent casting defects. Core sand grains are almost exclusively bound with organic resins such as phenolic urethane, furan, and novolac (Dungan and Reeves, 2005), although natural protein-, oil-, and polysaccharide-based binders are also available (Roa, 2003; Yu et al., 2009). When assembled, molds and cores form a cavity that holds the molten metal to specific dimensional tolerances.

After the molten metal has solidified, the mold is broken to retrieve the casting. Depending on the technology used within the foundry, the sands can be reclaimed to make new molds or cores. However, a fraction of a foundry's system sand must be regularly discarded and replaced with virgin sand to avoid casting defects as a result of poor sand quality. The discarded molding and core sands, also called waste foundry sands (WFSs), are typically sent to landfills with other foundry byproducts. Because sands represent the largest volume of waste generated, their disposal in controlled landfills can be an economic burden to foundries. As a result, this has prompted research into their beneficial use in agricultural and geotechnical applications (Guney et al., 2006; Dayton et al., 2010; de Koff et al., 2010).

In Argentina, there are approximately 300 foundries, producing approximately 200,000 tons of WFS per year. According to Argentinean hazardous waste law 24.051 (AMESD, 1993), a solid waste is considered hazardous if it exhibits one of the following characteristics: ignitability, corrosivity, reactivity, or toxicity. Considering that WFSs do not possess the first three

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Abbreviations: AMESD, Argentinean Ministry of Environment and Sustainable development; ASTM, American Society for Testing and Materials; EP, Extraction Procedure; TCLP, Toxicity Characteristic Leaching Procedure; VSS, virgin silica sand; WFS, waste foundry sand.

Table 1. Regulatory levels for metals in leaching extracts.

Element	Concentration†		
	HWLA (EP)	CFR (TCLP)	ADWS
mg L ⁻¹			
Ag	5	5	0.05
As‡	1	5	0.01
Ba	100	100	–
Cd	0.5	1	0.005
Cr	5	5	0.05
Cu	100	–	1
Hg‡	0.1	0.2	0.001
Ni	1.34	–	0.02
Pb	1	5	0.05
Se‡	1	1	0.01
Zn	500	–	5

† ADWS, Argentinean Drinking Water Standards (2012); CFR, Code of Federal Regulations (2011); EP, Extraction Procedure; HWLA, Hazardous Waste Law of Argentina (AMESD, 1993); TCLP, Toxicity Characteristic Leaching Procedure.

‡ Not quantified in this study.

characteristics, they are subjected to the Extraction Procedure (EP) (SW-846 method 1310B) (USEPA, 2004) to determine if they meet the toxicity characteristic. A solid waste exhibits the characteristic of EP toxicity if the extract contains any of the listed constituents at concentrations equal to or greater than the respective values listed in Table 1. Although the EP method was replaced by the Toxicity Characteristic Leaching Procedure (TCLP) (SW-846 method 1311) (USEPA, 1992), both methods have been used to assess the stability of foundry sands for beneficial use applications (Fahnlne and Regan, 1995; Deng and Tikalsky, 2008; Siddique et al., 2010).

In addition to the EP and TCLP procedures, several studies have also examined the leaching behavior of WFS metals using the “standard test method for shake extraction of solid waste with water” (method D 3987) (ASTM International, 2004) and the Synthetic Precipitation Leaching Procedure (SPLP) (SW-846 method 1312) (USEPA, 1994). Overall, the variety of leaching methods and subsequent results indicate that the majority of waste sands from iron, steel, and aluminum foundries have a low metal leaching potential. However, waste sands from brass and copper foundries have been reported to contain relatively high concentrations of Cu, Pb, and Zn in leaching extracts (Kendall, 2003; Deng, 2009), likely making them unsuitable for beneficial use applications.

Although existing datasets demonstrate that most WFSs are not hazardous, regulatory agencies in many countries will not consider issuing beneficial use permits unless country-specific data are generated. Because data are limited in South America, the aim of this study was to quantify metals (i.e., Ag, Ba, Cd, Cr, Cu, Ni, Pb, and Zn) in EP, TCLP, and American Society for Testing and Materials (ASTM) extracts after performing the procedures on a variety of waste molding and core sands from ferrous and nonferrous Argentinean foundries. To determine if the WFSs met the toxicity characteristic, EP and TCLP extract concentrations were compared with their respective contaminant concentrations as specified by hazardous waste law 24.051 (AMESD, 1993) and Title 40, Part 261.24 (Code of Federal Regulations, 2011). To gauge metal leachability under the less aggressive conditions of the EP and TCLP, the WFSs were also subjected to the ASTM water extraction procedure. In addition, all WFS results were compared with extracts obtained from virgin silica sands (VSSs) to provide more information regarding the chemical properties of the molding and core sands.

Materials and Methods

Foundry Sands

A total of 96 waste molding and core sands, as well as 14 VSSs, were collected from iron, steel, aluminum, and bronze foundries located in the province of Buenos Aires, Argentina. The binder systems associated with the WFSs are presented in Table 2. Samples were collected from WFS piles at the point of disposal at the foundries and then reduced in size using a quartering method. In brief, approximately 200 kg of sand was initially obtained, which was crushed to break the aggregates and then mechanically mixed. Afterward, the sand was spread over an area not exceeding 3 m², with one half being collected with a clean shovel. After mixing the subsample, the procedure was repeated until a final sample size of 0.1 kg was obtained. The samples were shipped in 60-mL polypropylene containers to the Northwest Irrigation & Soils Research Laboratory in Kimberly, Idaho, for processing as described below.

Leaching Procedures

The EP and TCLP were conducted according to SW-846 methods 1310B and 1311, respectively (USEPA, 1992, 2004). The water leaching procedure was conducted according to method D 3897 (ASTM International, 2004). Table 3 provides a list of operational criteria for the leaching procedures.

Table 2. Binder systems associated with the waste foundry sands analyzed in this study.

System	Binder components	Sand		Binder	No. of samples
		% (w/w)			
Alkyd urethane	Linseed oil-based alkyd urethane. Some components contain trace quantities of Pb and Co salts.	98–99.2		0.8–2	28
Phenolic	Phenolic-containing resins included the resole and furan.	98.5–98.8		1.2–1.5	23†
Shell	Phenol-formaldehyde based resin consisting of novolac oligomers.	97–98		2–3	17
Green sand	A mixture of sodium and/or calcium bentonite is used as the binder. Additional additives include bituminous coal, cellulose, and water.	85–90		10–15	14
Natural binders	Aqueous emulsion with a mixture of soybean oil, polysaccharides, reducing sugars, and water.	97		3	9
Unknown	Miscellaneous comingled waste sands.	–		–	5

† Only 2 of 23 sands were furan based.

Table 3. Operational criteria for the leaching procedures.

Criteria	EP†	TCLP‡	ASTM§
Extraction fluid	deionized water	acetic acid solution	reagent water
pH of extraction fluid	maintain pH 5 ± 0.2 with 0.5 mol L ⁻¹ acetic acid	4.93 ± 0.05 (nonalkaline materials); 2.88 ± 0.05 (alkaline materials)	N/A¶
Particle size reduction	<9.5 mm	<9.5 mm	not required
Liquid-to-solid ratio	16:1	20:1	20:1
Extraction method	rotary agitation at 30 rpm	rotary agitation at 30 rpm	rotary agitation at 29 rpm
Extraction period	24 h	18 ± 2 h	18 ± 0.25 h
Leachate solid separation	0.45-µm pore size filter	0.6–0.8 µm pore size glass fiber filter	0.45-µm pore size filter

† Extraction Procedure.

‡ Toxicity Characteristic Leaching Procedure.

§ American Society for Testing and Materials, method D 3897.

¶ pH of the deionized water was 4.87 before initiation of the extraction procedure.

To increase the number of samples that could be processed at one time, the leaching procedures were modified by reducing the total sample mass to 2 g. The samples were placed into 50-mL polyethylene centrifuge tubes (cat. no. 06-443-20; Fisher Scientific) to which extraction fluid was added. The tubes were then capped and tumbled at 30 rpm at room temperature on a rotary shaker (Appropriate Technical Resources, Inc.). Afterward, the tubes were centrifuged for 10 min at 4000 × *g*, and the ASTM and EP extracts were filtered through 0.45-µm pore size polypropylene syringe filters (Whatman International Ltd.); TCLP extracts were filtered through a 0.7-µm pore size glass fiber filters (cat. no. 09-804-142H, Fisher Scientific). After filtration, the TCLP and ASTM filtrates were acidified with HNO₃ to pH <2. All filtrates were stored in 15-mL polypropylene tubes (Corning) at 4°C until analyzed by inductively coupled plasma–atomic emission spectroscopy according to SW-846 method 6010C (USEPA, 2007). Quality control operations included the analysis of blanks and duplicate samples.

Results and Discussion

The pH of the extraction fluid is one of the most important factors that controls the leaching of metals. The final pH values of the extracts according to the sand binder system are presented in Table 4. On average, the pH ranged from 5.0 to 5.4 in the EP extracts. Unlike the TCLP, the EP extraction fluid (i.e., deionized water) is not buffered, and additions of acetic acid are made during the procedure to maintain the pH at 5.0 ± 0.2. Because the pH of the WFSs was determined to be >5 (data not shown), extraction fluid no. 1 was used for the TCLP (USEPA, 2004). The final pH values of the TCLP extracts were similar to the initial pH of 4.9. In the case of the ASTM extraction procedure, the final pH values ranged from 6.7 in the VSS extracts to 8.4 in waste sands containing phenolic-based resins. The pH of the sands is the dominant factor controlling the final pH of the ASTM extracts because the procedure does not call for pH control of the deionized water. In a study of ferrous and nonferrous WFSs (*n* = 594), Deng (2009) found that the mean final pH of ASTM and TCLP extracts was 8.3 (median, 8.9) and 6.5 (median, 5.1), respectively.

The metal concentrations in the leaching extracts from the foundry sands, irrespective of the binder system used, are

presented in Table 5. Of the eight metals analyzed, only Ag and Ni were not detected above their respective detection limits in the VSS and WFS extracts; Cd, Cr, and Pb were also not detected above detection limits in the VSS extracts. The mean concentrations in the WFS extracts from the EP, TCLP, and ASTM procedures were very similar to those from the VSSs, except in the case of Ba (TCLP only), Pb, and Zn. In the WFS extracts, the Pb and Zn concentrations were up to two orders of magnitude greater than VSS concentrations. The greatest concentrations were associated with the EP and TCLP, which are considered to be more aggressive than the ASTM procedure (Baba and Kaya, 2004). In general, the ASTM and TCLP results from this study were found to be similar to results obtained by Dungan and Dees (2009) and Deng (2009).

Table 6 presents the metal concentrations in the leaching extracts for the WFSs as categorized by binder type. Barium, Cr, Cu, and Zn were above detection limits for all binder types when extracted with all three procedures. In general, Ba, Cr, and Cu concentrations were greatest in the TCLP extracts, whereas the Zn concentrations were greatest in the EP extracts. A comparison of the metal leaching data (Tables 5 and 6) with the regulatory levels in Table 1 demonstrates that the majority of the WFSs, regardless of binder type, did not meet the toxicity characteristic for Ag, Ba, Cd, Cr, Cu, Ni, and Zn under the Argentinean and U.S. hazardous waste laws. However, 4 of 96 WFSs failed due to excessive Pb because concentrations exceeded the respective EP and TCLP regulatory thresholds of 1 and 5 mg L⁻¹. All four of these waste sands were originally manufactured with

Table 4. pH value of the extractants from the foundry sands as measured after the extraction period.

Foundry sand	EP†	TCLP‡	ASTM§
Virgin silica sand	5.1 ± 0.3¶	4.8 ± 0.1	6.7 ± 0.6
Alkyd urethane	5.3 ± 0.4	4.8 ± 0.1	7.3 ± 1.2
Green sand	5.2 ± 0.2	4.9 ± 0.1	7.9 ± 0.8
Natural binders	5.4 ± 0.4	4.8 ± 0.1	7.1 ± 1.2
Phenolic urethane	5.0 ± 0.2	4.9 ± 0.1	8.4 ± 1.3
Shell	5.2 ± 0.3	4.9 ± 0.1	7.4 ± 0.9
Unknown binders	5.0 ± 0.3	4.8 ± 0.1	7.0 ± 0.4

† Extraction Procedure.

‡ Toxicity Characteristic Leaching Procedure.

§ American Society for Testing and Materials, method D 3897.

¶ Values are mean ± SD.

Table 5. Summary of metal concentrations in the virgin silica sand and waste foundry sand leaching extracts.

Element	Sand†	Concentration								
		Minimum			Maximum			Mean#		
		EP‡	TCLP§	ASTM¶	EP	TCLP	ASTM	EP	TCLP	ASTM
mg L ⁻¹										
Ag	VSS	<0.007	<0.007	<0.007	-††	-	-	-	-	-
	WFS	<0.007	<0.007	<0.007	-	-	-	-	-	-
Ba	VSS	0.009	0.068	<0.004	0.041	0.159	0.007	0.019	0.111	-
	WFS	<0.004	<0.004	<0.004	0.151	0.748	0.171	0.027	0.069	0.014
Cd	VSS	<0.003	<0.003	<0.003	-	-	-	-	-	-
	WFS	<0.003	<0.003	<0.003	-	-	0.004	-	-	-
Cr	VSS	<0.007	<0.007	<0.007	-	-	-	-	-	-
	WFS	<0.007	<0.007	<0.007	0.087	0.085	0.009	-	0.007	-
Cu	VSS	<0.005	<0.005	<0.005	-	-	0.011	-	-	0.007
	WFS	<0.005	<0.005	<0.005	0.015	0.370	0.028	-	0.017	-
Ni	VSS	<0.020	<0.020	<0.020	-	-	-	-	-	-
	WFS	<0.020	<0.020	<0.020	-	-	-	-	-	-
Pb	VSS	<0.042	<0.042	<0.042	-	-	-	-	-	-
	WFS	<0.042	<0.042	<0.042	7.78	11.04	0.539	0.219	0.757	0.065
Zn	VSS	<0.006	<0.006	<0.006	0.048	0.038	0.028	0.009	0.012	0.007
	WFS	<0.006	<0.006	<0.006	1.90	3.79	0.367	0.129	0.104	0.057

† VSS, virgin silica sand; WFS, waste foundry sand.

‡ Extraction Procedure.

§ Toxicity Characteristic Leaching Procedure.

¶ American Society for Testing and Materials, method D 3897.

Calculations based on setting sample concentrations less than the method detection limit to one half the method detection limit.

†† Maximum or mean data less than the method detection limit.

alkyd urethane resin, where octanoates used to accelerate the curing time contained Pb (personal communication, foundry employees). Based on the amount of resin used by the foundries, the Pb concentration in the sands was calculated to range from 60 to 290 mg kg⁻¹ (dry weight).

Because the original purpose of the EP and TCLP was to assess leaching of inorganic and organic analytes in a municipal landfill, the use of these tests to determine the suitability of beneficially using WFSs in geotechnical and agricultural applications is not necessarily warranted. Regardless, state regulatory agencies are currently using the TCLP and ASTM procedures to qualify WFSs for use as a raw material in manufacturing products such as cement, asphalt, and soil blends (USEPA, 2002; Wisconsin DNR, 2010). In these cases, the leachate thresholds for metals are often set much lower than the TCLP regulatory thresholds, sometimes by as much as several thousand times. The extracts in this study were not analyzed for As, Hg, and Se; therefore, it is possible that additional sands could have met the toxicity characteristic for these regulated metals. However, in a recent study of 594 WFSs, it was reported that 95th percentile concentrations for As, Hg, and Se in TCLP extracts were well below toxicity thresholds (Deng, 2009). In a study of waste sands from 52 foundries, maximum TCLP extract concentrations for the same metals were below toxicity thresholds at 1.22, 0.10, and 0.83 mg L⁻¹, respectively (Fahnline and Regan, 1995).

Our results confirm that the EP and TCLP are more aggressive than the ASTM procedure in solubilizing metals from foundry sands, which can largely be attributed to the low pH of the EP and TCLP extractants. A comparison of

the WFS extract concentrations to those obtained from VSSs demonstrates that the metals were likely derived from the components (e.g., clays, coal, and resins), which are added to the molds and cores. Based on the test conditions applied in this study, 96% of the WFSs were determined to be nonhazardous waste, with failed sands only being attributed to the use of Pb in alkyd urethane resin. If these particular foundries are interested in using these sands in various beneficial applications outside of the foundry, then alternative binder components without Pb should be considered. Sands that exceed the toxicity thresholds for Pb and other regulated metals should be examined more carefully before being considered for beneficial uses or should not be used at all, especially in the case of unencapsulated applications. Despite the presence of high Pb in a few sand extracts, our dataset provides additional evidence that many WFSs have a very low metal leaching potential. The beneficial use of low-contaminant WFSs should be encouraged where applicable because it can decrease disposal costs, extend the useful life of landfills, and alleviate the environmental burdens associated with the mining of virgin sands.

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Table 6. Comparison of minimum, maximum, and mean metal concentrations in leaching extracts from the virgin silica and waste foundry sands by binder type.

Element	Sand†	Concentration											
		Minimum			Maximum			Mean#			SD		
		EP‡	TCLPS	ASTM¶	EP	TCLP	ASTM	EP	TCLP	ASTM	EP	TCLP	ASTM
		mg L ⁻¹											
Ba	VSS	0.009	0.068	<0.004	0.041	0.159	0.007	0.019	0.111	-††	0.010	0.030	-
	AU	<0.004	<0.004	<0.004	0.082	0.437	0.020	0.027	0.051	0.006	0.015	0.083	0.004
	PHL	<0.004	<0.004	<0.004	0.151	0.743	0.027	0.029	0.105	0.007	0.035	0.169	0.006
	SHL	<0.004	<0.004	<0.004	0.030	0.313	0.029	0.011	0.044	0.006	0.008	0.074	0.007
	GS	0.012	<0.004	<0.004	0.090	0.213	0.171	0.036	0.031	0.052	0.021	0.065	0.044
	NAT	<0.004	<0.004	<0.004	0.063	0.749	0.009	0.017	0.111	0.005	0.019	0.242	0.003
	UKN	0.018	<0.004	0.050	0.113	0.334	0.067	0.056	0.122	0.024	0.035	0.136	0.025
Cd	VSS	<0.003	<0.003	<0.003	-	-	-	-	-	-	-	-	-
	AU	<0.003	<0.003	<0.003	-	-	-	-	-	-	-	-	-
	PHL	<0.003	<0.003	<0.003	-	-	0.004	-	-	-	-	-	-
	SHL	<0.003	<0.003	<0.003	-	-	-	-	-	-	-	-	-
	GS	<0.003	<0.003	<0.003	-	-	0.004	-	-	-	-	-	-
	NAT	<0.003	<0.003	<0.003	-	-	0.004	-	-	-	-	-	-
	UKN	<0.003	<0.003	<0.003	-	-	-	-	-	-	-	-	-
Cr	VSS	<0.007	<0.007	<0.007	-	-	-	-	-	-	-	-	-
	AU	<0.007	<0.007	<0.007	0.008	0.010	-	-	-	-	-	-	-
	PHL	<0.007	<0.007	<0.007	0.008	0.022	0.009	-	-	-	-	-	-
	SHL	<0.007	<0.007	<0.007	0.009	0.085	0.007	-	0.014	-	-	0.021	-
	GS	<0.007	<0.007	<0.007	-	-	-	-	-	-	-	-	-
	NAT	<0.007	<0.007	<0.007	0.008	0.018	0.007	-	-	-	-	-	-
	UKN	<0.007	<0.007	<0.007	-	0.076	0.007	-	0.022	-	-	0.031	-
Cu	VSS	<0.005	<0.005	<0.005	-	-	0.011	-	-	0.007	-	-	0.002
	AU	<0.005	<0.005	<0.005	0.008	0.370	0.007	-	0.029	-	-	0.073	-
	PHL	<0.005	<0.005	<0.005	0.015	0.046	0.008	0.006	0.011	-	0.004	0.012	-
	SHL	<0.005	<0.005	<0.005	0.013	0.042	0.005	-	0.013	-	-	0.010	-
	GS	<0.005	<0.005	<0.005	0.008	0.023	0.028	-	0.007	0.009	-	0.005	0.008
	NAT	<0.005	<0.005	<0.005	0.006	0.031	0.006	-	0.014	-	-	0.009	-
	UKN	<0.005	<0.005	<0.005	-	0.101	0.006	-	0.029	-	-	0.041	-
Pb	VSS	<0.042	<0.042	<0.042	-	-	-	-	-	-	-	-	-
	AU	<0.042	0.393	<0.042	7.78	11.04	0.539	0.701	2.50	0.160	1.62	2.53	0.139
	PHL	<0.042	<0.042	<0.042	-	-	-	-	-	-	-	-	-
	SHL	<0.042	<0.042	<0.042	-	0.140	-	-	-	-	-	-	-
	GS	<0.042	<0.042	<0.042	-	-	-	-	-	-	-	-	-
	NAT	<0.042	<0.042	<0.042	-	0.331	-	-	0.073	-	-	0.103	-
	UKN	<0.042	<0.042	<0.042	-	0.583	0.372	-	0.133	0.091	-	0.251	0.157
Zn	VSS	<0.006	<0.006	<0.006	0.048	0.038	0.028	0.009	0.012	0.007	0.013	0.011	0.008
	AU	<0.006	<0.006	<0.006	1.90	3.79	0.180	0.149	0.218	0.036	0.370	0.720	0.050
	PHL	<0.006	<0.006	<0.006	0.308	0.290	0.174	0.116	0.053	0.026	0.100	0.064	0.046
	SHL	<0.006	<0.006	<0.006	0.388	0.076	0.367	0.131	0.027	0.118	0.136	0.021	0.115
	GS	<0.006	<0.006	0.007	0.381	0.224	0.166	0.097	0.050	0.068	0.111	0.062	0.049
	NAT	<0.006	0.009	<0.006	0.482	0.230	0.022	0.133	0.094	0.008	0.165	0.082	0.006
	UKN	0.016	<0.006	0.105	0.416	0.469	0.339	0.157	0.140	0.190	0.167	0.188	0.090

† AU, alkylid urethane; GS, green sand; NAT, natural binders; PHL, phenolic urethane; SHL, shell; UKN, unknown; VSS, virgin silica sand.

‡ Extraction Procedure.

§ Toxicity Characteristic Leaching Procedure.

¶ American Society for Testing and Materials, method D 3897.

Calculations based on setting sample concentrations < method detection limit to one half the method detection limit.

†† Maximum and mean data less than the method detection limit.

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