Proceedings of the 9ICEG
9th International Congress on Environmental Geotechnics
25-28 June, 2023 | Chania, Greece
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https://doi.org/10.53243/ICEG2023-40

EPA LEAF Testing of a Powdered Ladle Slag (PLS) to support pH Neutralization and Stabilization/Solidification Applications

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ABSTRACT

A ladle slag from an electric arc furnace (EAF) steel mill was pulverized to enable a wide range of beneficial uses. The powdered ladle slag (PLS) was subjected to a baseline characterization and EPA 1316 and 1313 leach testing for target analyte list (TAL) metals to prequalify it for pH neutralization and stabilization/solidification (S/S) applications. Mineralogically, the PLS was dominated by merwinite (~15%), gehlenite (~6.6%) and iron magnesium oxide (6.2%) with an amorphous content of 33 to 37%. The natural pH was 12.5. EPA 1316 leaching of Resource Conservation and Recovery Act (RCRA) metals were at or below their reporting limits (RLs) for liquid to solid (L/S) ratios up to 100 except barium (Ba). For trace metals, only molybdenum (Mo) was above the RL for all L/S up to 100, whereas vanadium (V) only exceeded its RL at an L/S~40. EPA 1313 leaching with sulfuric acid instead of nitric acid generally increased the concentration of all metals except for calcium and Ba. In mid-range pH, the leached concentrations differed up to 4 and 1 order of magnitude for common soil elements and other metals, respectively. For potential S/S applications (8≤pH≤12.5), Ba, Mo, and V were the only non-common soil elements routinely detected above their respective RLs. V leaching was attributed to larnite and other silicates and peaked at pH~10.5 at 0.2 mg/L. Thereafter, V concentrations gradually became non-detectable from pH 9 to pH 7.5. Since all results corresponded to pure 100% PLS, the material was successfully pre-qualified.

Keywords: ladle slag, pH neutralization, stabilization/solidification, leaching, vanadium

1 INTRODUCTION

This paper reports on the select material properties and leaching behavior of a Powdered Ladle Slag (PLS) that originated from an electric arc furnace (EAF) steel mill ans is part of a broader study (Grubb et al in press). At a steel mill, the primary EAF produces the liquid iron (Fe) melt and conventional EAF slag. The EAF slag undergoes various crushing and screening processes to recover the metallic Fe (i.e, scrap returned to the primary furnace) and to produce slag aggregates. Further Fe purification and alloying to make steel of various grades occurs in secondary and tertiary ladle furnaces (LFs)—the LF slag evaluated in this study was taken from a secondary furnace and was pulverized (to pass No. 100 sieve) to enable innovative beneficial use purposes.

One of the main challenges for EAF steel mills is that they are usually placed on very compact sites, which limits the amount of processed EAF slag aggregates that may be stockpiled on site for a range of beneficial uses (Proctor et al 2000; National Slag Association, 2022). A typical premier EAF slag product is Department of Transportation (DOT) approved asphalt chips for high rutting resistant hot mix asphalt (HMA) surface courses that may yield a price of $20 to $30/ton freight on board (FOB). Traditionally, the shipping of EAF slags as an aggregate, fill or earthwork material is effectively limited to an effective range of 50 to 100 miles (80 to 160 km) due to transportation costs. More recently however, small trailer-mounted milling systems are capable of pulverizing slags (of any type) at rates of 2,000 to 5,000 tons/month and preparing them for pneumatic storage and delivery, thus enabling slags to be beneficiated as powders. This achieves two goals: 1) leverages the geochemical, and cementitious

properties of slags for upselling into water, wastewater, and environmental treatment applications and/or the reagent substitute markets, and 2) earns higher FOB prices to support the added processing cost and upselling at greater distances.
For example, the strong alkaline nature of slags and their residual lime/portlandite contents make them ideal for a range of agricultural lime, soil fertilization, pH neutralization, carbon sequestration, metals immobilization and stabilization/solidification (S/S) activities as long as their geochemistry is suitable, which often reduces to consideration of their trace metal content and leaching. Specifically, the mobile milling and pneumatic delivery of PLS media also offers seamless upselling into large scale cement-based applications (concrete, block, pavers, S/S) where the PLS media can be a substitute for Portland Cement (PC) that reduces the overall carbon footprint. In large urban settings, PLS can be well matched with a variety of uses based on its volume and environmental profile. For example, consider the New York City metro area where the stabilized dredged material (SDM) from the Port Authority of New York and New Jersey (PANYNJ) designated for upland disposal or beneficial use (daily cover, mine reclamation, fill projects, brownfields) requires 10 to 15 wt% Portland Cement (PC) addition on more than 100,000 CY annually. Hence, a 2.5 to 5 wt% dose of PLS in combination 5% to 10% PC likely satisfies the cementitious demand for most SDM and environmental S/S projects.

Many environmental S/S projects are in older major metro areas such as New York, Philadelphia, Northern New Jersey, Chicago, Detroit, Baltimore, etc., that would enable 100% local utilization of PLS (and maybe even powder EAF slag) while lowering the overall CO_2 footprint of projects. The first step in evaluating these or similar applications is to screen and/or prequalify the PLS media against the regional environmental regulations or site-specific acceptance criteria for the end use sites. Accordingly, the PLS media was subjected to various characterization tests to understand its base properties, mineralogy and leaching behavior for potential use in S/S projects. Specifically, pH-dependent leaching of the PLS media was assessed by EPA 1313 using nitric acid (per method) and sulfuric acid (method modification) because of its frequent use in industrial processes and occurrence in wastes (acids, acid tar pits, mine drainage, sewers, etc.). New Jersey (USA) was selected as the reference basis for this analysis because of the numerous environmental S/S projects and SDM processing that occurs in the New York metro area.

2 BASELINE MATERIAL CHARACTERIZATION

2.1 Source material and chemistry

The LF slag was freshly produced and subsequently air-cooled immediately prior to size reduction. LF slag aggregates with particle sizes ranging from an approximately 1/16- to 1-inch (1.6 to 25.4 mm) diameter were fed into a proprietary milling device operating at ambient conditions with 12 tons per hour throughput. TMS International LLC provided Jacobs with one sealable 5-gallon bucket of the resulting PLS media (for testing). Unified Soil Classification System (USCS) and specific gravity testing on the PLS media using ASTM International (ASTM) Methods D2487 and D854, respectively. The moisture content (MC) and grain size distribution were determined using ASTM D2216 and D6913, respectively.

Mineralogical testing included quantitative X-ray powder diffraction (QXRD) using the Rietveld method to determine the mineralogical composition of the PLS media. The corresponding elemental composition was determined using X-ray Florescence (XRF), infrared (IR), and inductively coupled plasma (ICP) (oxygen excluded). Carbon (C) and sulfur (S) were analyzed using an induction furnace with IR detectors. Loss on ignition (LOI) was reported at 1,000 °C by ASTM C114-11b.

Duplicate subsamples of the homogenized PLS media were also analyzed for Target Analyte List (TAL) metals content (dry milligram per kilogram [mg/kg] basis) by EPA Methods 3050B/6010D. Mercury (Hg) was not tested, because it is rarely detected in and/or leachable from iron- and steel-making slags (Proctor et al., 2000), and silicon (Si) was added because of its importance in cement chemistry and the leaching of iron/steel impurities from slags.

2.2 EPA 1316 Testing Suite

EPA 1316 is a batch leaching test (using deionized water, or DIW) to evaluate how liquid-solid partitioning varies as a function of the L/S and was conducted in duplicate (USEPA 2017b). The method specifies five L/S ratios (0.5, 1, 2, 5, and 10); however, three additional extractions at L/S 20, 50, and

100 were performed to gauge the effects of large dilution ratios on PLS leaching such as may be required for the pH adjustment of cooling ponds, lagoons, and similar. With all the PLS media less than 0.3 millimeter (mm), a 24-hour equilibration period using “end-over-end” tumbling was used in accordance with the method. The pH of the final extract solution were recorded prior to the separation of the solid and liquid phases by vacuum- or pressure-assisted filtration through a 0.45-micrometer (µm) membrane for chemical analysis. All extractions were performed in plastic containers to avoid Si contamination from glassware. Extractions were also performed in near-zero headspace conditions to limit interaction with atmospheric carbon dioxide (CO_2).

2.3 EPA 1313 Testing Suite

EPA 1313 is a pH-dependent leaching test consisting of 9 to 10 parallel batch extractions at targeted pH values between 2 and 13 at a constant L/S of 10 (USEPA 2017a). For each parallel extraction, different volumes of acid or base are combined with DIW to achieve the requisite pH target for the same L/S 10, accounting for the initial water content of the media. A tenth extract was performed without acid/base addition to determine the natural or self pH of the material (pH_o) during pre-titration activities. EPA 1313 was independently performed (in duplicate) using nitric acid (per method) and sulfuric acid, the latter of which is commonly used in industry and where sulfate has the ability to interact with cationic species, potentially leading to complexation, precipitation and/or the fouling of solid surfaces. Alternatively, sulfate can aggravate the leaching of oxyanions (such as common forms of arsenic [As], chromium [Cr], molybdenum [Mo], selenium [Se], and vanadium [V]). As such, it was important to document these effects.

To avoid silica leaching, plastic containers and near zero headspace conditions were used. The extraction times, filtration and analytical suites were identical. Of note was that the combination of the PLS media and acid was exothermic, with reactor temperatures reaching approximately 60°C for the highest acid additions. For this reason, the reactors were quickly vented twice over a 5-minute period immediately following the introduction to the reactor (already containing the PLS media and water) prior to placing them on the tumbler.

3 RESULTS AND DISCUSSION

3.1 Baseline materials

The PLS media was visually classified as moist, dark gray sandy silt, or a sandy silt (ML; non-plastic silt) formally by USCS. The as-received moisture content (MC) was 0.3% by ASTM D2216. One hundred percent of the material passed the No. 4 sieve (4.75 mm) and the sand content was on the order of 34.5 percent based on two replicates per ASTM D6913. The average specific gravity was determined as 3.47, which is consistent with the density of steel slags (Geiseler, 1996).

3.2 Totals

Table 1 summarizes the metals content of the PLS media for the TAL metals suite (element symbols shown in table). The PLS media is rich in common soil minerals (such as Al, Ca, Fe, Mg, manganese [Mn], Si, and sodium [Na]), contains typical alloying, plating, and purifying metals (such as Cr, copper [Cu], Mn, nickel [Ni], V, and zinc) and numerous trace metals. Of note, the average total V content is on the order of 420 mg/kg whereas the mineralogical elemental testing estimated approximately 1,000 mg/kg. Proctor et al. (2000) reported the average metals leaching results from 45 EAF slags from North America (excluding LF slags). Because many of the impurities are already removed in the primary furnace, the PLS media typically contains heavy metals below or near the lower compositional limits for EAF slags.

Table 1 also shows the expected contribution of a 5 wt% dose of PLS to an environmental system as part of an S/S reagent blend or pH buffering amendment, prior to consideration of any cementitious or precipitation reactions that may render said metals insoluble and/or unavailable for environmental leaching. These values are shown in comparison to the median concentrations of conventional Portland Cement (PC) reported by EPA (2014) for the reported sample occurrence frequencies. The 5 wt% PLS dose compares favorably with the PC with respect to many TAL metals except several explicitly used

Table 1. *Comparison of Total Metals Concentrations for New Jersey Urban Soils, PLS Media, and Soils and Soil-Like Materials (mg/kg)*

	NJ Urban Piedmont Soils[a]			NJ Urban Coastal Plain Soils[a]			PLS Media		Soil and Soil-Like Media[b]							
Metal	**n**	**Med.**	**90th Percentile**	**n**	**Med.**	**90th Percentile**	**Average**	**5 wt% Dose**	**Top Soil**	**PS**	**WM**	**B**	**Ka**	**L**	**RCA**	**MV**
Al	67	10,500	14,400	91	6,800	10,800	21,500	1,100	15,100	3,780	1,800	11,600	4,020	2,640	7,610	160
Sb	17	<1.7	3.48	0	<6	<6	5.3	0.27	<0.44	<0.59	0.31	<0.25	<0.24	1.1	1.74	<1
As	67	5.2	24.2	82	5.2	13.6	12	0.6	4.54	3.09	1.3	5.43	<0.24	4.49	4.45	<1.86
Ba	67	80.6	168	60	28.3	65.8	505	25	96.5	40.1	52	468	2.71	6.28	74.2	6.88
Be	65	0.51	0.82	15	<0.5	0.68	0.73	0.037	0.71	0.2	0.14	1.44	0.11	0.18	0.54	<0.044
Cd	21	<0.4	0.67	5	<0.5	<0.5	1.75	0.088	0.75	0.31	0.48	0.34	<0.008	0.096	0.29	0.53
Ca	67	1,425	3,010	59	995	2,000	205,000	10,300								
Cr	67	18.5	29.9	91	11.8	34.7	1,600	100	43.3	11.1	5.6	0.88	5.9	2.25	17	31.1
Co	67	6.3	10.4	7	<5	<5	4.95	0.25								
Cu	67	29.5	75.5	82	9.3	33.3	280	14	80.3	48.3	9.9	3.43	2.68	1.88	17.5	487
Fe	67	14,600	20,000	91	8,830	21,100	150,000	7,500	24,300	5,500	3,200	9,090	292	4,160	7,610	14,400
Pb	67	111	297	82	37.6	144	20	1	12.6	10.5	11	30.6	0.92	<1.05	50.9	<1.02
Mg	67	2,190	4,614	54	673	1,870	60,000	3,000								
Mn	67	311	859	91	62.4	206	31,500	1,600	1,360	237	300	652	0.47	107	220	1,750
Mo							35	1.75								
Ni	67	12.4	24.6	43	<4	12.3	70	3.5	24.6	5.23	3.4	4.05	0.52	3.43	8.2	12.2
K	67	693	1,524	45	<500	1,750	355	18								
Se	61	0.41	0.71	0	<1	<1	19.5	0.98	7.77	3.42	<0.52	2.13	<0.55	<4.37	1.2	55.3
Si							11,500	600								
Ag	28	<0.22	0.86	3	<1	<1	7.45	0.37	<0.062	0.43	<0.21	<0.037	<0.032	1.05	0.45	1.21
Na	60	90.1	141	0	<500	<500	420	21								
Tl	28	<0.20	0.25	2	<1	<1	25	1.25	<0.46	<0.88	<0.05	<0.27	<0.24	2.37	<0.35	<1.82
V	67	29.6	41.7	86	16	35.5	445	22	40.7	8.8	9.9	2.62	10.9	4.02	24	11.7
Zn	67	75.3	162	88	39.9	106	210	11	137	66.8	43	53.4	0.66	10.4	72.8	8,000

[a] From Table 1 of Sanders (2003).
[b] From Grubb et al. (2014).
"<" represents analytical results not detected at detection limit. Equivalent to "U" in lab report.
n = Detections; Med. = Median; PS = Potting Soil; WM = Wood Mulch; B = Bentonite; Ka = Kaolinite; L = Limestone; RCA = Recycled Concrete Aggregate; MV = Multivitamin

for alloying/purifying steel (for example, Cr, Mn) and the trace quantities of antimony (Sb), cadmium and thallium, all of which were insoluble at the natural pH of both media (refer to the following section). Interestingly, the median V concentration for PC is nearly three times higher than the expected 5 wt% PLS media dose.

Lastly, Table 1 shows how the total concentrations of the PLS media compare to typical soils from the urbanized regions of New Jersey (Sanders, 2003) and several soil and soil-like media used on/at residential and commercial sites, including commercially available bagged topsoil (TS), two potting soils (PS#), two wood mulches (WM#), bentonite (B), kaolinite (Ka), Department of Transportation (DOT)-approved limestone aggregate (L) and recycled concrete aggregate (RCA) (Grubb et al., 2014). Table 1 also includes the compositional analysis for a multivitamin (MV), which implies direct ingestion.

The total metal contents of the 5 wt% PLS dose are less than New Jersey Urban Piedmont Soils (90th percentile), except for total Cr, Mn, Se, and thallium (Tl), all of which are insoluble at the natural pH of the PLS media. For perspective, a MV contains somewhat more Mn, 55 times more Se, and potentially more Tl than a 5 wt% PLS dose. The Se content of the 5 wt% PLS media dose was less than bagged TS and PS obtainable at garden centers and RCA used for conventional roadway/site construction. The Tl content of the 5 wt% PLS dose represents less than contained in some natural, DOT-approved limestone materials. The 5 wt% PLS media dose has a total V content less than the New Jersey urban soils (90th percentile), bagged TS and RCA.

3.3 Mineralogy

The as-received MC was less than 1 percent with a free metal (metallic Fe and steel) content on the order of 2.5 weight percent (wt%). The free lime index was on the order of 2.8 based on ASTM C25 (2018) using chemical reactivity and/or colorimetry techniques.

Mineralogically, the major cations were distributed across an array of silicates and oxides, the three most dominant being merwinite (~15%), gehlenite (~6.6%) and iron magnesium oxide (6.2%) as summarized in Table 2. Mayenite ($Ca_{12}Al_{14}O_{33}$) was not detected, contrary to it being the dominant mineral reported by Tossavainen et al. (2007) and Loncnar et al. (2016) for LF slags, and by Loncnar et al. (2022) for EAF/LF slag mixtures. Crystalline lime was also not detected and the portlandite content was on the order of 0.6%., which suggests that the free lime index was comprised primarily of reactive Ca originating from the amorphous (non-crystalline) phase, which was on the order of 33 to 37%. Carbon (0.8%) and sulfur (0.5%) were primarily associated with the amorphous phase.

Neuhold et al. (2019) studied Austrian EAF slags to ascertain the conditions that mitigated chromium (Cr) and V leaching. The organizing principle for their work was to understand the role of various mineral groups on the actual and modeled leaching behavior of V because of the extensive cationic substitutions that can occur in slag systems. The four key solid phases included:

Wuestite:	(Fe,Mg,Mn)O	
Spinel:	AB_2O_4	where A=Ca, Fe, Mg, Mn, and B=Al, Cr, Fe, Mn
Olivine:	A_2SiO_4	where A=Ca, Fe, Mg, Mn
Melilite:	$Ca_2M(XSiO_7)$	where M=Al, Fe, Mg and X=Al, Si

In this framework, the PLS media is dominated by olivines (~27.9%; merwinite included due to similar ratios) followed by almost equal amounts of wuestites (~14%) and melilites (12.7%; includes cuspidine) and trailed by spinels (~3.7%).

3.4 EPA LEAF leaching

Figures 1 through 4 summarize the combined EPA 1313 leaching results for the nitric and sulfuric acid titrations of the PLS media. The average of the duplicate samples was plotted as one curve for each acid type for clarity purposes. Beginning with **Figure 2**, the EPA 1316 data are cross-plotted as a function of L/S to show the influence of the water dilution on the measured concentrations of the PLS media (quality of alkaline leachates generated for potential pH neutralization applications). The self pH (pH_o) conditions are denoted by the large open circles in the respective figures, and the plotted RL and MDLs correspond to that initial testing condition. Given that these are very concentrated systems, many instances occurred where a COC was not detected above its MDL, but the MDL of that analysis point

was elevated due to the necessary dilutions required for chemical analysis. Such data are plotted with open symbols on the metal concentrations curves below pH_0.

Table 2. *Qualitative X-ray Powder Diffraction Results for PLS Media (wt%)*

		Replicate 1	Replicate 2	Average
Merwinite	$Ca_3Mg(SiO_4)_2$	15.1	14.6	14.8
Gehlenite	$Ca_2Al_2SiO_7$	6.94	6.22	6.58
Iron Magnesium Oxide	$Fe_{0.76}Mg_{0.24}O$	6.35	5.89	6.12
Cuspidine	$Ca_4Si_2O_7F_2$	6.26	5.95	6.11
Wuestite	FeO	5.55	5.14	5.35
Bredigite	$Ca_7Mg(SiO_4)_4$	5.10	4.80	4.95
Kirschsteinite	$Ca(Fe_{0.77}Mg_{0.23})SiO_4$	4.09	3.95	4.02
Larnite	Ca_2SiO_4	2.83	2.12	2.48
Periclase	MgO	2.43	2.53	2.48
Hercynite	$FeAl_2O_4$	1.97	1.96	1.97
Calcio-Olivine C2S beta	Ca_2SiO_4	1.91	1.41	1.66
Quartz	SiO_2	1.71	2.36	2.04
Magnesioferrite	$MgFe_2O_4$	1.64	1.82	1.73
Nordstrandite	$Al(OH)_3$	1.48	0.80	1.14
Calcite	$CaCO_3$	0.97	0.81	0.89
Hematite	Fe_2O_3	0.85	1.00	0.93
Portlandite	$Ca(OH)_2$	0.63	0.55	0.59
Iron	Fe	0.42	0.59	0.51
Brucite	$Mg(OH)_2$	0.32	0.43	0.38
Amorphous Material		33.5	37.0	35.3
	Total	100.0	100.0	100.0

Figure 1 shows that the PLS media is a strongly alkaline buffered solid, consistent with other iron- and steel-making slags (Ziemkiewicz and Skousen, 1998; Huijgen et al., 2005; Grubb et al., 2011; Grubb and Berggren, 2018; Loncnar et al. 2022), cement, lime, and solid systems containing these solids as shown by EPA 1313 itself (EPA, 2017a). Typically, BOF and EAF slags can have up to 10 to 15% residual lime (Shi, 2004; Grubb et al., 2011), which is usually taken to be the main source of the alkalinity. However, the PLS media had only 2.9% free lime, suggesting that the majority of its alkalinity is associated with portlandite, reactive silicates, and the amorphous phase.

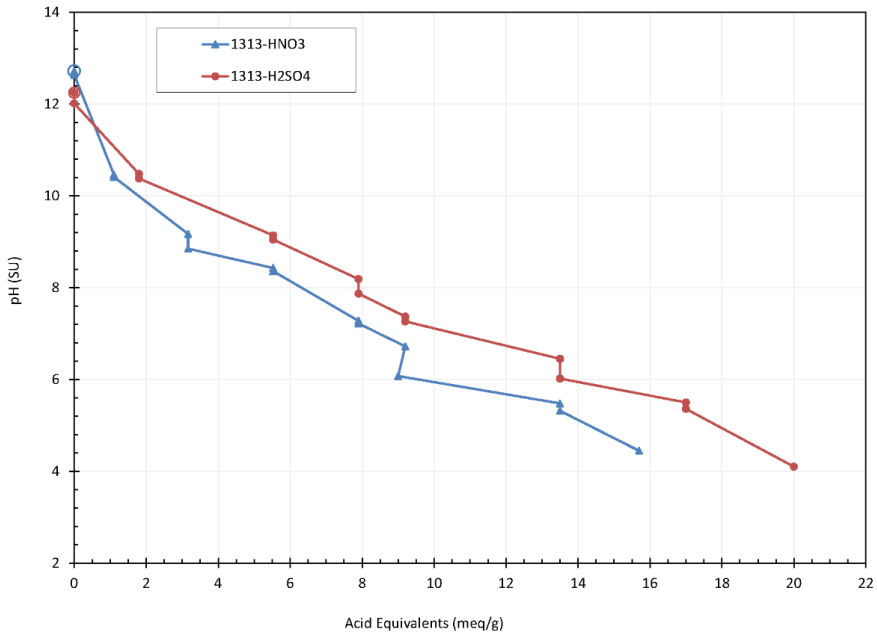


Figure 1. *USEPA 1313 titration results for the PLS media using nitric and sulfuric acids. Large open circles indicate pH_0 of PLS media.*

The two acid titration curves plotted on Figure 1 are very similar; the sulfuric acid curve sits somewhat higher, which suggests it is less effective than nitric acid in terms of acid buffering. Nitric acid is a strong dissociative acid, whereas sulfate may interact with dissolved cations as a complexing or precipitating ligand, thus reducing metals acidity, which indirectly impacts the measured pH. That the two curves diverge with increasing acid addition is strongly suggestive of this phenomenon, especially considering that Ca and Ba are two of the more soluble cations leached from slags and that significant complexation and/or precipitation occurs with sulfate over a broad range of pH, including gypsum/anhydrite ($CaSO_4$•$2H_2O$/$CaSO_4$) and barite ($BaSO_4$).

The EPA 1316 test covers a broad range of L/S ratios as tested here, so while all occur in DIW, the corresponding pH can drift. For the most part, the TAL metals were frequently at or below their RLs at the high pH of the LF slag. Ba (**Figure 3b**) is relatively soluble over a wide range of pH, its concentrations dropping off quickly with increasing L/S (dilution). Concentrations of select trace metals (**Figure 4**) such as cobalt (Co), Mo, and V were above the MDLs, the latter two of which occur as oxyanions. All three are amphoteric, and Co and Mo express available content-controlled leaching behavior as the L/S increases (dilution) regardless of the pH shift. V was thought to be associated with calcium vanadate [$Ca_3(VO_4)_2$] (Huijgen and Comans 2006) and strong evidence shows that larnite (Ca_2SiO_4), hatrurite (Ca_3SiO_5), kirschsteinite [$Ca(Fe_{0.77}Mg_{0.23})SiO_4$] and srebrodolskite ($Ca_2Fe_2O_5$) can be V-substituted (with VO_4^{3-}) (van Zomeren et al., 2011; Spanka et al., 2018). As pH drops below pH_o and into the 11.5 range, these minerals increasingly dissolve releasing V into solution. There is a log dissociation constant (pK_a) for vanadate at 11.5 (Pourbaix, 1974) which may also promote disassociation. Beyond mineral phases, Loncnar et al. (2016, 2022) and Neuhold et al. (2022) stressed the role of hydrous ferric oxides (HFOs) regulating V concentrations through sorption.

Thus, whether used as solid to treat water directly, or to provide an alkaline water as a reagent substitute (for lime water, for example) via PLS leaching similar to Grubb (2017) and Caicedo-Ramirez et al (2018), the environmental quality of the PLS contact water is of fairly good depending on the L/S chosen for equilibration or leaching and thus enables an array of pH neutralization applications.

The EPA 1313 test covers a broad range of pH; therefore, it is important to view the results in a situational context because not all outcomes are relevant to an envisioned exposure condition (for example, the placement of PLS media in environmental systems or the built environment). Because the PLS media is unlikely to be exposed to stronger alkaline agents in nature, the pH_o of the PLS media essentially denotes the upper limit of the “range of environmental interest.” The lower limit of this range is generally recognized as the carbonation endpoint of iron/steel making slags weathered to a limestone/dolomite coordinate due to the uptake of atmospheric CO_2, or approximately pH 8. The main reason for this is that the dissolution of atmospheric CO_2 typically constitutes the only potential acid addition to strong alkaline solids in natural environmental systems unless there is a supplemental anthropogenic source of acidity (such as acid mine drainage, neat acids, acidic wastes, or similar).

Accordingly, Figures 2 to 4 show the range of environmental interest for the PLS media in natural systems being $8 \leq pH \leq 12.5$ (shaded region) generally consistent with S/S applications (ITRC, 2011); the resulting solids are typically very strongly buffered, even when treating acidic media. More specifically, reagent overdosing is intentionally practiced in S/S applications of acidic wastes to maintain the long-term pH in the alkaline range and to ensure the stability of the solids.

Figure 2 shows the EPA 1313 leaching concentrations for common soil minerals from the PLS media versus their respective total metal contents reported in Table 3, converted to an equivalent maximum dissolved concentration using L/S 10. It is important to recognize that the measured EPA 1313 concentrations shown on Figures 2 to 4 are associated with a pure, powdered material with more than 60% of the solids passing the No. 200 sieve. As such, applications using the PLS media will not likely involve its pure dry form (either in the short- or long-term), especially S/S applications, and the dosing strategy may have a significant influence on the observed leaching.

The leaching of common soil minerals appears to be generally similar for the nitric and sulfuric acid titrations with the exception of Ca. In the nitric system, the initial Ca concentrations are likely governed by free lime, portlandite, and a series of CSH compounds down to about pH 10, and the Ca leaching trends are consistent with BOF slags (Huijgen et al., 2005; Huijgen and Comans, 2006, van Zomeren et al., 2011; Grubb et al., 2011, 2014) and EAF and LF slags (Loncnar et al., 2016, 2022; Neuhold et al., 2019). In the sulfuric system, Ca solubility is likely regulated by gypsum/anhydrite. The measured

Table 3. *Comparison of Total Metals Concentrations for PLS Media and Portland Cement (mg/kg)*

Metal	PLS Media			EAF Slag[a]			Portland Cement		PLS Media 5 wt% Dose
	Rep 1	Rep 2	Ave.	Ave.	St. Dev	Det. Freq.[b]	Med.[b]	Ave.[c]	
Al	21,000	22,000	21,500	35,009	11,693	11/11	26,250	20,350	1,100
Sb	5.5	5.1	5.3	4	3.4	2/94	0.10	3.80	0.27
As	12	12	12	1.9	1.1	64/109	12.4	3.9	0.60
Ba	500	510	505	557	285	98/98	205	96	25
Be	0.73	0.73	0.73	1.1	1	93/94	0.98	0.53	0.037
Cd	1.8	1.7	1.75	7.6	5.9	42/98	0.03	0.72	0.088
Ca	200,000	210,000	205,000					332,000	10,300
Cr	1,600	1,600	1,600	3,046	1373	109/109	58.6	27.6	100
Co	5.1	4.8	4.95	4.8	2.2	12/15	10.0	6.7	0.25
Cu	340	220	280	178	84	15/15	36.0	14.2	14
Fe	150,000	150,000	150,000					10,830	7,500
Pb	19	21	20	28	43	88/109	6.3	3.9	1.0
Mg	59,000	61,000	60,000					13,000	3,000
Mn	31,000	32,000	31,500	39,400	7712	15/15	465	395	1,600
Mo	30	40	35	30	22	1/4	5.0	2.1	1.75
Ni	67	73	70	30	47	97/108	25.0	12.5	3.5
K	340	370	355					6,150	18
Se	19	20	19.5	18	5.2	6/98	2.0	3.1	0.98
Si	13,000	10,000	11,500					141	600
Ag	6.5[d]	8.4[d]	7.45	8.4	18	93/98	8.6	<0.52	0.37
Na	410	430	420					1,970	21
Tl	25	25	25	11	7.5	32/94	0.30	<10.5	1.25
V	430	460	445	513	248	15/15	64.0	19.4	22
Zn	210	210	210	165	148	14/15	64.0	284	11

[a] Values from Table 2 of Proctor et al. (2000).
[b] Values from Table 2-1 of EPA (2014).
[c] Values from Type IL Portland Cement measured by EPA 6010.
[d] Linear range check (LRC) is outside acceptance limits, low biased
Rep = Replicate; Ave. = Average; St. Dev = Standard deviation; Det. Freq = Detection Frequency; Med. = Median

K, Na, Mg, and Si concentrations appear to be essentially indifferent to acid type. For K and Na, this is because they are highly soluble and generally express available content-controlled behavior. Mg appears to be solubility-controlled by carbonate minerals and not impacted by the presence of sulfate. The leaching of Fe, Al, and Mn was somewhat enhanced by sulfate; it appears that their insolubility regions (in pure water) were shifted 1 to 1.5 pH units higher.

For most of the pH domain, Si leaching was likely regulated by amorphous silica because the log of the first acid dissociation constant (pK_{a1}) of silicic acid is approximately 9.5 (Snoeyink and Jenkins, 1980). The measured Si concentrations shown on Figure 2c are readily converted to silicon dioxide (SiO_2) by multiplying the measured Si values by 2.14. Therefore, the corresponding SiO_2 concentrations are consistent with the solubility of silicon (as SiO_2) in water systems from amorphous sources, or up to 130 mg/L, as reported by McKeague and Cline (1963a, 1963b) and Iler (1979). Quartz (crystalline SiO_2), however, tends to regulate SiO_2 concentrations on the order of 10 mg/L (that is, approximately 5 mg/L Si). Though other amorphous silicates are also likely to form in this chemical environment, amorphous silica is viewed as the most common, and is used here as a simple representative of this group of solids.

Figure 3 shows the EPA 1313 leaching for the RCRA metals (Hg excluded). In the environmental range of interest, most of the RCRA metals are near, at or below their RL values for both acids. The exception to this is Ba, which exhibits classic cationic behavior with pH in the nitric acid system. However, barite ($BaSO_4$) is relatively insoluble (log K_{sp} = -10), and the Ba concentrations in the sulfuric acid system are suppressed by 2 orders of magnitude below pH approximately 8. Most of the other RCRA metals gradually increase in concentration and approach their total contents, with the sulfuric acid-leached concentrations typically plotting somewhat higher despite the scatter in the curves. The scatter in the data is likely due to fluctuating MDLs of the actual replicates tested, the challenges with creating adjacent titrations, and the role of mineralogical variability (and or nugget effects) even on the scale of silts and clays.

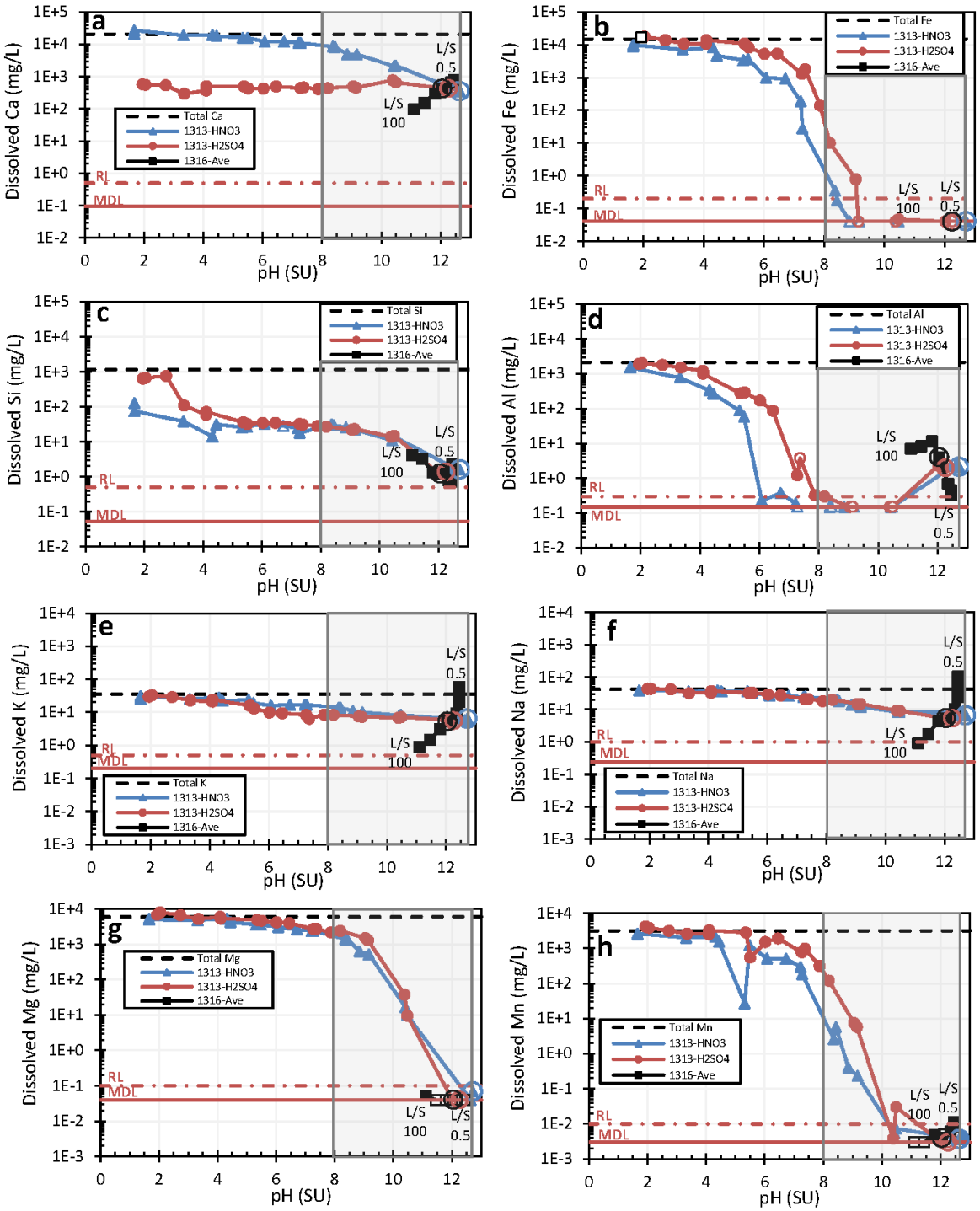


Figure 2. *USEPA 1313 leaching results of common soil minerals from PLS media. Large open circles indicate pH_0 of PLS media. The shaded region represents the range between the natural pH of the PLS and its lower estimated carbonation endpoint (pH~8.0). Both RL and MDL shown represent the limits for natural pH conditions. The equivalent total metal contents by ICP also shown for L/S 10. Open symbols indicate that the element concentration was not detected above the MDL for the analysis of that eluate due to dilution. USEPA 1316 data for L/S 100, 50, 20, 10, 5, 2, 1, 0.5 coplotted for reference.*

For example, there were many non-detects for As, lead (Pb), and silver (Ag) in the acidic range owing to specific replicate MDL issues; therefore, the general trend should be taken as representative. Also, it is not known why the measured EPA 1313-Cd concentrations exceeded the totals content (theoretically impossible). It might be related to an inverted nugget effect, which is to say that the smaller totals sample

(1 to 2 g; singlet tested) was somewhat deficient in Cd relative to the larger EPA 1313 sample size (here, approx. 46 g).

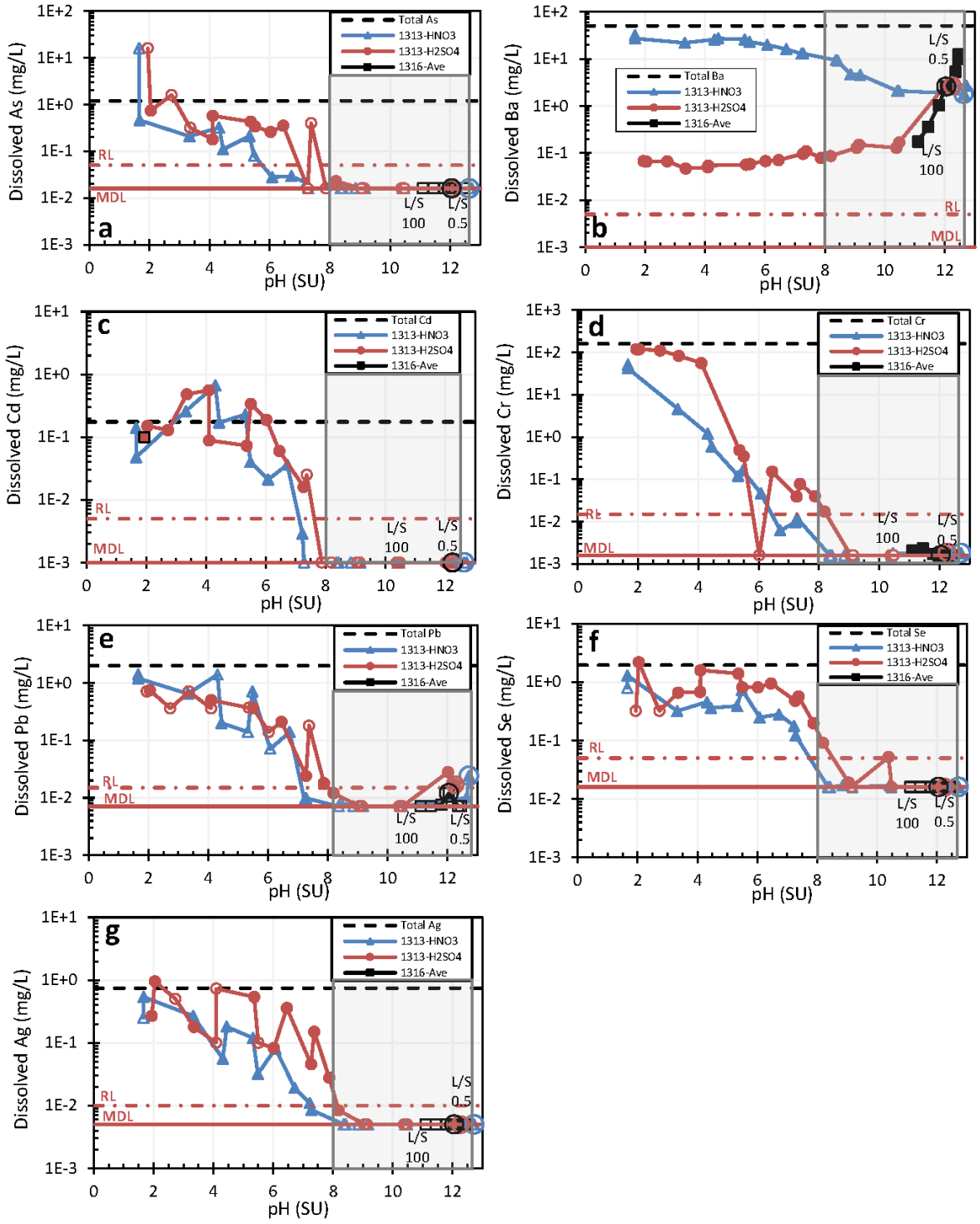


Figure 3. *USEPA 1313 leaching results of RCRA Metals (Hg excluded) from PLS media. Large open circles indicate pH_0 of PLS media.The shaded region represents the range between the natural pH of the PLS and it's lower estimated carbonation endpoint (pH~8.0). Both RL and MDL shown represent the limits for natural pH conditions. The equivalent total metal contents by ICP also shown for L/S 10. Open symbols indicate that the element concentration was not detected above the MDL for the analysis of that eluate due to dilution. USEPA 1316 data for L/S 100, 50, 20, 10, 5, 2, 1, 0.5 coplotted for reference*

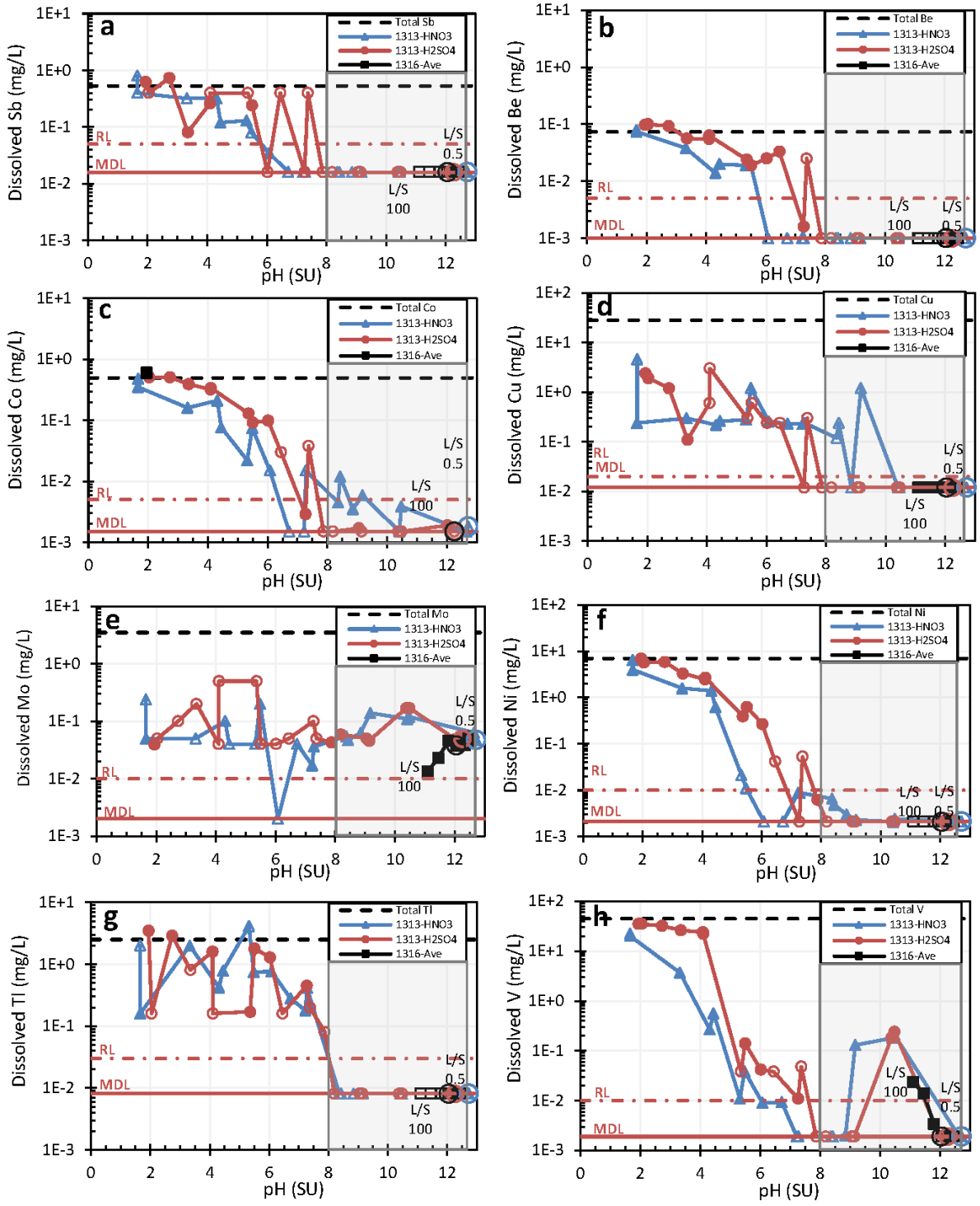


Figure 4. *USEPA 1313 leaching results for trace metals from PLS media. Large open circles indicate* pH_0 of PLS media*. The shaded region represents the range between the natural pH of the PLS and it's lower estimated carbonation endpoint (pH~8.0). Both RL and MDL shown represent the limits for natural pH conditions. Open symbols indicate that the element concentration was not detected above the MDL for the analysis of that eluate due to dilution. The equivalent total metal contents by ICP also shown for L/S 10. USEPA 1316 data for L/S 100, 50, 20, 10, 5, 2, 1, 0.5 coplotted for reference.*

The remaining TAL metals have their EPA 1313 leaching concentrations plotted on **Figure 4**. In the acid range, the MDLs again vary widely making the data trends very erratic for several trace metals (such as Sb, Cu, Mo, Tl, and V). Cu generally begins solubilizing around pH 9 consistent with its aqueous solubility (in nitric) but remains suppressed by S until pH approximately 7. Mo appears relatively indifferent to nitrate and sulfate, and Cu and Mo appear to be expressing available content-controlled behavior

beginning at pH approximately 6 and pH_o, respectively. Because both plot well below their respective total content curves by almost 2 orders of magnitude, the large discrepancies could be the result of a fixation in insoluble oxide/silicate phases, sorption, and/or an inverted nugget effects. Spanka et al. (2018) report that Mo is primarily bound in Fe-containing minerals, such as srebrodolskite, magnetite, hematite, and wuestite. The remaining Mo is likely controlled by sorption to iron oxyhydroxides (Huijgen and Comans, 2006) until lower pH when MoO_3(s) or other Mo oxides may precipitate (e.g. Pourbaix, 1974). In contrast, V expresses solubility-controlled behavior.

Above pH~8, many of the trace metals concentrations plot near, at, or below their respective RLs, regardless of the fluctuating MDLs. The exceptions to this are Cu, Mo, and V, the latter two of which are oxyanions. Mo and V are essentially the only trace metals that leach above their RLs for a significant portion of the range of environmental interest. The observed Mo concentrations are somewhat less than observed for BOF slag (Huijgen and Comans, 2006) and express the same sorption-controlled behavior, as indicated herein.

4 CONCLUSIONS

The key findings of this testing indicated:

- The PLS media tested here was found to be a similar composition to conventional EAF/LF slags and characterized with an alkaline buffer capacity consistent with lime- or cement-rich materials despite the low free lime content. The total metal contents suggested that at 5 wt% dose of PLS media added to soil and soil-like media can be consistent with regional soil quality and those materials frequently used in landscaping and/or earthwork construction. In this regard, it was also similar to PC except for the greater Mn content.
- The EPA 1316 results showed that all RCRA metals were at or below their RLs for L/S up to 100 except Ba. For trace metals, only Mo was above the RL for all L/S up to 100, whereas V exceeded its RL at approximately L/S=40. The associated water quality thus enables strong consideration of PLS media directly or the associated alkaline waters for pH neutralization applications.
- EPA 1313 results showed that leaching with sulfuric acid almost always increased the concentration of the TAL metals, except for Ca and Ba. In mid-range pH, the difference was up to 4 orders of magnitude for common soil mineral elements (e.g. Al), but for most other metals, the enhancement was about a factor of 10.
- In the pH range of environmental interest for S/S systems (8 to 12.5), Ba, Mo, and V were the only non-soil mineral metals routinely detected above their respective RLs. Literature surveys and geochemical modeling suggested that the early (high-pH) leaching of V from larnite and other silicates and hydrous ferric oxides (HFOs) attributed as the solubility-controlling phases at lower pH values.

Overall, the results were considered satisfactory and site specific S/S trials using the PLS media are currently under way with an industrial client.

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