

ABSTRACT

Title of Thesis: ENVIRONMENTAL LEACHING
ASSESSMENT OF EAF AND CASTER
SLAGS FOR BENEFICIAL USE IN
TRANSPORTATION INFRASTRUCTURE

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Steelmaking slags are increasingly considered sustainable alternatives to natural aggregates; however, conventional engineering characterization and single-point leaching tests provide limited insight into their environmental performance under changing conditions. This study develops a structured framework to evaluate the engineering suitability and leaching behavior of Electric Arc Furnace and caster slags for road construction. Engineering characterization examined the physical, gradation, and compaction properties of the slags and shale soil mixtures, showing that slag type affects density, moisture requirements, particle structure, and potential field performance.

Environmental screening combined the Toxicity Characteristic Leaching Procedure with pH-dependent batch extraction testing. Both slags met hazardous waste classification criteria, but batch testing showed pH- and particle-size-dependent constituent release, with several elements exceeding screening benchmarks under specific conditions. Continuous-flow column testing showed that slag-amended soil maintained alkaline buffering unlike unamended soil. Calcium release remained relatively stable, boron showed initial flushing followed by depletion, and vanadium increased during percolation, indicating potential long-term relevance.

Outdoor lysimeter exposure demonstrated that leaching under natural weathering was environmentally sensitive rather than continuous, with precipitation, pH, and seasonal conditions affecting leachate chemistry. Manganese remained the primary regulatory concern, while calcium and magnesium exhibited contrasting behavior. Collectively, the findings show that beneficial reuse requires integrated consideration of engineering properties, pH-dependent leaching, percolation, and natural weathering. The framework supports reliable decisions regarding the environmental management and transportation use of steel slag.

ENVIRONMENTAL LEACHING ASSESSMENT OF EAF AND CASTER SLAGS
FOR BENEFICIAL USE IN TRANSPORTATION INFRASTRUCTURE

by

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Dedication

I dedicate this thesis to my family and friends, for their unwavering support, patience, and the sacrifices they have made along the way.

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Chapter 1-INTRODUCTION

1.1 Introduction

Approximately 16 million tons of steel slag are produced annually at over 120 plants across 33 states in the United States, with electric arc furnace operations alone contributing an estimated 5.9 to 8.9 million tons of this total (USGS Mineral Commodity Summaries, 2025; Committee on Electric Arc Furnace Slag, 2023). Globally, the figures are far larger, with annual steel furnace slag production estimated at 190 to 290 million tons, reflecting a steelmaking industry in which every ton of crude steel generates a substantial volume of slag as its primary co-product (Mineral Commodity Summaries, 2025). The two principal types of steel slag, electric arc furnace and basic oxygen furnace, have long been pursued as alternatives to natural aggregate in asphaltic concrete, road base, and fill applications, with road base construction alone accounting for nearly half of all domestic slag sales (USGS Mineral Commodity Summaries, 2021, 2025). Despite these established uses, the utilization rate remains strikingly low: only 10 to 15 percent of the steel slag produced in the United States finds beneficial application, leaving the vast majority to accumulate in stockpiles and landfills as an underexploited resource and a growing environmental concern (Proctor et al., 2000; USGS Mineral Commodity Summaries, 2025).

Steel slag exhibits physical and mechanical properties that make it a promising replacement for natural aggregate in road structures. The cubical and angular geometry of slag particles is characterized by high internal friction, thereby ensuring high shear strength and low vulnerability to rutting under traffic loads (Engström et al., 2014; National Slag Association, 2025). The rough and porous surface structure of the slag particles provides a high value of the friction coefficient, preventing the polishing effect during its pavement service life; the latter is contrary to the behavior of some natural aggregate materials like limestone or granite (Hao et al., 2026; National Slag Association, 2025). Besides, slag has a sufficiently high resistance to abrasion and fragmentation, with Los Angeles abrasion loss not exceeding 10% and crushing value within the range of 8-15%; these values meet the criteria for high-grade aggregate material for heavy-duty road pavements (Hao et al., 2026). Finally, in unbound base course applications, slag provides higher bearing capacity immediately after compaction than crushed gravel, thereby ensuring sufficient load-bearing capacity for pavement layers subjected to loads from construction vehicles (National Slag Association,

2025). All these characteristics make the use of slag as a construction material possible, despite two mineral-origin limiting factors.

The first limitation is caused by the presence of free oxide phases in slag; the hydration of calcium oxide (CaO) and magnesium oxide (MgO) with water leads to the formation of hydroxides with much lower densities that induce volumetric expansion due to the change of the density (Dayioglu et al., 2014; Yildirim & Prezzi, 2011). Thus, the hydration of calcium oxide occurs quite fast within a several-week period, while magnesium oxide undergoes a slower hydration process that can lead to expansion during a long period up to several months or years; this means that the dimensional stability of slag can be evaluated only at a relatively short time interval (Dayioglu et al., 2014; Long et al., 2023).

The list of environmental issues associated with the use of steel slag does not include only heavy metal leaching. For example, according to Dayioglu et al. (2014), calcium hydroxide forms by reactions between calcium oxide in slag and water. This leads to the dissociation of calcium hydroxide and the release of hydroxide ions, which increases the pH of the equilibrium system to 12.3; thus, the leachate from pure steel slag exceeds the regulatory level of 8.5 set by the Maryland Department of the Environment for waste. In turn, the Committee on Electric Arc Furnace Slag (2023) reports that the most identified environmental stressor for the weathering and leaching of EAF slag is highly alkaline water with a pH over 11, which can degrade surface and groundwater. Over time, water, carbon dioxide, and oxygen influence the slag, altering its mineralogy, complicating mineral phases, and changing the chemical speciation and host phases of major and trace elements. As a result of such weathering, various secondary phases, including carbonates, oxyhydroxides, and mixed hydroxo-carbonate minerals, form (Committee on Electric Arc Furnace Slag, 2023). This study found that the concentrations of total dissolved and suspended solids in slags can vary widely depending on site conditions. The migration of highly alkaline water generated by slag weathering negatively affects surface and groundwater and should be neutralized. Otherwise, rapid carbonate precipitation can smother benthic habitats. Riley and Mayes (2015), using 36 years of monitoring data on slag-affected watercourses in northern England demonstrated the long-term nature of such alkaline drainage conditions. They showed that as the CaO-bearing minerals weather, the calcium concentration and alkalinity are decreasing slowly.

Alongside alkalinity, the issue of heavy metal content in slag is relevant; Mombelli et al. (2016) mentioned that the utilization of EAF slag is limited by the presence of polluting chemical elements, namely chromium, barium, and vanadium. Attention is paid to chromium in this regard because of its toxicity in the hexavalent state. The Committee on Electric Arc Furnace Slag (2023) reported that, upon weathering, trivalent chromium and tetravalent vanadium in the slag minerals can oxidize, converting these elements into more toxic hexavalent and pentavalent forms. However, this process is poorly understood, and little is known about the extent of oxidation under typical weathering conditions. On the other hand, Proctor et al. (2000) stated that metals in slag are firmly bound and do not leach even under extremely acidic conditions (pH 2.8); the partitioning coefficient for metal leaching from slag is higher than that from soil. It means the potential for metal leaching from slag is lower than from natural soil, despite the higher metal concentrations in slag. Dayioglu et al. (2014) also report that numerous contractors have sought permission from the State Highway Administrations to use steel slag. However, there are currently no necessary specifications to regulate this process. At the same time, the Committee on Electric Arc Furnace Slag (2023) found that among 31 states with EAF plants, 13 explicitly exclude slag from waste classification, while other states set different regulations.

Recently, new research has begun to resolve these contradictions through more advanced leaching assessments. So, Teo et al. (2020) analyzed potential methods for recycling EAF slag across multiple industries. Yu et al. (2024) conducted scenario-based release estimates, accounting for the effects of aging and weathering on leaching properties; they found that the pattern of constituent release changes significantly during slag weathering.

Unlike conventional natural aggregates, steel slag is a chemically reactive material whose environmental behavior is governed by complex mineral dissolution and geochemical processes. During weathering, the hydration of free calcium oxide (f-CaO) and magnesium oxide (f-MgO) generates highly alkaline pore solutions that can raise leachate pH to levels exceeding 11 or 12. Under such alkaline conditions, the solubility and mobility of both major and trace elements may change substantially. Although many metals remain incorporated within stable mineral phases, the release of certain constituents depends strongly on environmental factors such as pH, oxidation-reduction conditions, liquid-to-solid ratio, particle size, contact time, and mineral carbonation. Consequently, evaluating only the total elemental composition of steel slag is insufficient for assessing its environmental risk; instead, leaching behavior under representative environmental conditions must be

investigated to determine its long-term suitability for beneficial reuse.

Previous environmental evaluations of steel slag have often relied on single-point leaching tests, such as the Toxicity Characteristic Leaching Procedure (TCLP), which were originally developed for hazardous waste classification rather than for evaluating long-term field performance. While TCLP provides useful regulatory information, it does not adequately represent the wide range of geochemical conditions encountered during transportation applications, including acidic rainfall, fluctuating groundwater chemistry, continuous infiltration, and prolonged weathering. More comprehensive assessment approaches, such as the U.S. Environmental Protection Agency's Leaching Environmental Assessment Framework (LEAF), provide pH-dependent leaching, percolation behavior, and long-term release characteristics that more closely represent field exposure conditions. These methods enable a more mechanistic understanding of constituent release and support scientifically defensible decisions regarding the sustainable reuse of steel slag in transportation infrastructure.

1.2 Research Goal, Problem Statement, and Hypothesis

Although numerous studies have investigated the mechanical performance of steel slag as a construction material, comparatively fewer studies have systematically evaluated its environmental performance using multiple complementary leaching methods. Furthermore, limited information is available regarding the combined effects of pH, particle size, hydraulic percolation, and long-term natural weathering on the release of trace elements from EAF and caster slags produced in the United States. Establishing this knowledge is essential for developing science-based specifications that balance engineering performance with environmental protection and for increasing confidence among transportation agencies considering the beneficial reuse of steel slag.

To address the noted knowledge gaps, this study proposes a structured series of leaching tests, starting with regulatory screening, followed by pH-dependent batch testing, continuous-flow column percolation, and finally a six-month Bench-scale outdoor field lysimeter leaching test. The use of this structured testing scheme allows the study to examine the leaching behavior of EAF and caster slags under increasingly realistic environmental

conditions, from laboratory conditions to field exposure. Alongside leaching tests, SEM/EDS and XRD literature analyses are performed on the slag samples before and after leaching to correlate observed releases with mineralogical changes and to elucidate the geochemical processes underlying these changes.

The major objective of this research is to assess the environmental performance of electric arc furnace (EAF) and caster slag as potential replacement materials for natural aggregate in road base and subbase applications, and to determine whether these materials can be safely reused in highway structures or require proper disposal. This objective is pursued through four specific research questions, each aligned with the corresponding experimental chapter of the dissertation:

1. Do slag materials meet hazardous waste classification criteria, and how do their leachate concentrations compare with toxicity thresholds established by the Resource Conservation and Recovery Act (RCRA), USEPA Maximum Contaminant Levels, and international inert waste acceptance criteria?
2. How does the leaching behavior of heavy metals depend on solution chemistry, particle size, and contact time, and what do these dependencies reveal about the controlling mechanisms of metal solubility in slag?
3. What is the total quantity of metals released when slag is blended with local soil in proportions representative of pavement subbase layers and subjected to percolation conditions, and how does leachate quality change across the full range of liquid-to-solid ratios encountered over the service life of a pavement?
4. What is the short-term leaching behavior of slag under natural precipitation and ambient temperature fluctuations, and what do these dynamics indicate about the environmental risks associated with landfilling as an end-of-life management option for slag?

It is hypothesized that EAF slag and caster slag will exhibit fundamentally different leaching behaviors due to their distinct mineralogical compositions. For instance, caster slag is expected to contain a larger amount of calcium and alkali due to a greater percentage of free lime content, while EAF slag will dissolve and leach out large amounts of constituents due to mineral dissolution. Although the literature indicates that EAF slag contains higher levels of total chromium, vanadium, arsenic, and other heavy metals, the concentrations of these metals are expected to remain low under field-representative leaching conditions, with no single metal posing environmental concerns. However, alkalinity and calcium content are

likely to compromise water quality by slowly degrading its properties.

Moreover, it is hypothesized that the finer slag fraction will release fewer heavy metals due to its larger specific surface area and greater alkali buffering capacity, while coarser particles will provide smaller specific surface area, which will cause faster mineral dissolution of calcium and maintain high pH value, thus facilitating immobilization of metals in the form of insoluble oxides and hydroxides. Thus, during the column experiment, where slag was sieved to 2.36 mm, this effect will hinder the metal mobilization. On the contrary, during the bench-scale outdoor field lysimeter test, where coarser slag was left to weather for six months, slower buffering will more effectively allow for a lower water pH and the release of metals.

Finally, it is expected that single-point tests like TCLP will always underestimate the actual long-term leaching potential of slag due to a lack of pH-dependent solubility controls, depletion-driven changes in the rate of release, dependence of buffering ability on particle size, and seasonal variation in leaching kinetics. Therefore, the combination of all three approaches: batch tests, column tests, and bench-scale outdoor field lysimeter test is expected to help identify the real dynamics and provide a more complete evaluation of the suitability of slag for reuse.

Chapter 2- Materials

2.1 Introduction

With approximately 21 million tons of steel slag generated annually in the United States, the development of reliable beneficial reuse pathways is critical to reducing landfill burden and displacing finite natural aggregates in construction applications. This chapter describes the four materials used throughout this study and their physical, chemical, and mineralogical characterization.

The two primary materials of interest, electric arc furnace (EAF) slag and caster slag, were sourced from the Nucor Steel Norfolk facility in Norfolk, Nebraska, where TMS International manages slag processing and distribution. The Norfolk facility has an annual steel production capacity of approximately 1,134,000 tons, and approximately 90% of the slag generated is sold for beneficial reuse, with the primary end use being unimproved roadway applications. Under Nebraska state law (Nebraska Legislature Section 81-1502(26)), steel slag is classified as a product rather than a waste material, and there are no restrictions on end-uses provided that geotechnical testing adheres to application specifications.

EAF slag and caster slag were selected for comparison because they originate from different stages of the steelmaking process. EAF slag is produced during primary electric arc furnace steelmaking and is typically enriched in iron oxides and residual alloying elements, while caster slag, generated during secondary refining and teeming, is generally characterized by higher free lime content and greater alkalinity. However, at the Norfolk facility, EAF and caster slag are commingled during processing, and there is no routine quality control monitoring of slag composition. The two slag types in this study, therefore, represent material collected from a shared stockpile, and while they are expected to differ in mineralogy and trace-element content, their bulk calcium levels may overlap due to commingling. The

comparison of these two slag types is nonetheless valuable because it reflects the real-world conditions under which slag is produced, stockpiled, and reused in Nebraska, and it allows evaluation of whether compositional variability within a commingled stream produces meaningfully different leaching behaviors.

Nebraska shale soil, classified as AASHTO A-7-2, is a highly plastic clay that is problematic for pavement construction due to its susceptibility to moisture-induced volume change and loss of bearing capacity. Such soils require stabilization before they can serve as reliable subgrades, and steel slag amendment represents a potentially viable stabilization strategy. This soil was therefore selected as a challenging yet realistic case to evaluate whether slag amendment introduces environmental leaching concerns that must be considered alongside its engineering benefits.

Quartz sand (20-30 mesh, US Silica Company) was used as an inert hydraulic medium in the percolation column tests to ensure uniform eluent flow distribution, prevent fine particle migration into drainage ports, and avoid introducing additional chemical reactivity into the system. Test-specific procedures for each experimental method are described in their respective chapters (Chapters 3, 4, and 5).

2.2 Sample Source, Collection, and Storage

2.2.1 Sample Source Location

EAF slag and caster slag were collected from the Nucor Steel Norfolk plant, which is situated at 2911 East Nucor Road, Norfolk, Nebraska (42.0789°N, 97.3609°W). The plant, which began operations in 1979, has an electric arc furnace for manufacturing steel products. Direct operations in the plant are performed by TMS International, which is responsible for slag processing and handling on behalf of Nucor.

2.2.2 Sample Processing and Slag Handling

At the Norfolk plant, EAF and caster slags are initially removed from the production process and placed in separate stockpiles. No preprocessing of the material is performed before the material is fed into the process of sizing and magnetic separation. During processing, larger blocks are separated and crushed by special equipment. Recovered metallics are obtained by magnetic separation, with 1% residual free iron in the slag. The finer material is then ground to aggregate size and size-separated into two fractions: material smaller than 1 inch and material larger than 1 inch.

Stockpiles are placed on a slag-based ground bed and exposed to precipitation and weathering. Material turnover happens only when loading; the average stay in the stockpile is

less than one week. During the current study, EAF and caster slag samples have been taken from separate slag piles rather than from their size-separated fractions.

Figure 2.1 depicts EAF and caster slag stockpiles of the Nucor Steel Norfolk facility during sample collection time.

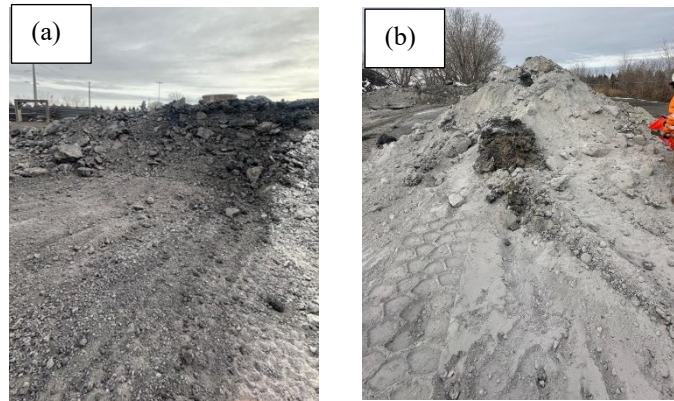


Figure 2.1 (a) EAF and (b) caster slag stockpiles at Nucor Steel Norfolk facility, June

2.2.3 Sample Collection Protocol

The sample collection took place on June 20, 2025, approximately 3-4 days after production, as reported by the contractor. The material was air-dried since its dumping. Preliminary evaluation of the material's physical characteristics from the surface and the heap core revealed their similarity. Due to limitations of the site equipment, samples were collected from several locations on the surface and in the core of each stockpile to improve representativeness.

Five buckets, each containing approximately 30 kg of material, were collected from each slag type (EAF and caster), resulting in 150 kg per slag type in the field. From these samples, about 70 kg of each slag type were shipped to the University of Maryland in sealed buckets for further experiments. Samples were collected in three batches in January, June, and December 2025. The samples from the June 2025 batch were used in the experiments discussed in this dissertation because they were the most recent and had sufficient time to dry.

2.2.4 Transportation and Storage

Shipped samples remained sealed in buckets under ambient laboratory conditions until testing and did not undergo any preprocessing prior to use.

2.3 Physical and Index Properties

Physical and index properties of the four materials were obtained in accordance with the respective ASTM and AASHTO standards. Tests on slag aggregates were done in collaboration with UNL, while shale soil and mineralogical characterization were carried out at UMD. The subsequent subsections highlight results obtained for each group of materials, along with the engineering interpretation of the data.

2.3.1 Specific Gravity, Absorption, and Moisture Content

Specific gravity and water absorption of the fine and coarse fractions of EAF slag and caster slag at UNL were assessed. Fine-fraction specific gravity was measured using a pycnometer in accordance with the ASTM C128 procedure. Bulk and apparent specific gravities of the coarse fractions were determined using the ASTM C127 protocol in three samples for each type of slag.

EAF slag has a notably higher specific gravity. The fine fraction of EAF slag has an average value of 3.72 ± 0.10 , with individual pycnometer readings of 3.69, 3.63, and 3.83. Coarse specimens have a bulk specific gravity between 3.54 and 3.70 (average 3.62 ± 0.08) and an apparent specific gravity between 3.85 and 4.05 (average 3.95 ± 0.10). These numbers are notably higher than the usual aggregate values of 2.6-2.8 and correspond to the high levels of iron oxides in electric arc furnace slag. Absorption in the coarse fraction ranged from 2.26% to 2.35% (average $2.31\% \pm 0.05\%$), indicating that EAF slag has a relatively low porosity. The low absorption suggests limited interconnected pore space, which is expected to reduce the rate of water infiltration and slow the dissolution of Ca-bearing mineral phases during leaching. The received moisture content was 0%, indicating the material was completely dry when tested.

Caster slag has lower specific gravity values compared to EAF slag, with the fine fraction having an average value of 3.34 ± 0.04 (individual pycnometer readings of 3.37, 3.30, and 3.34). The coarse fraction of caster slag has a bulk specific gravity between 3.17 and 3.51 (average 3.31 ± 0.18) and an apparent specific gravity between 3.54 and 4.06 (average 3.75 ± 0.28). Water absorption ranged from 3.32% to 3.84% (average $3.52\% \pm 0.28\%$), significantly higher than that of EAF slag. Increased absorption corresponds to the porosity and vesicular structure of caster slag, which is explained by the process of secondary refining. The greater

interconnected porosity is expected to facilitate contact between water and reactive mineral surfaces, potentially accelerating the release of alkaline phases and dissolved metals during leaching. As the received moisture content of the caster slag was 0.65%, this value is slightly higher, but still allows us to consider the caster slag dry.

Table 2.1 Physical Properties of EAF and Caster Slag (n =3 for all properties)

Property	EAF Slag	Caster Slag	Standard
Specific gravity (fine fraction)	3.72 ± 0.10	3.34 ± 0.04	ASTM C128
Bulk specific gravity (coarse), range	3.54–3.70	3.17–3.51	ASTM C127
Bulk specific gravity (coarse), avg $\pm$ SD	3.62 ± 0.08	3.31 ± 0.18	ASTM C127
Apparent specific gravity (coarse), range	3.85–4.05	3.54–4.06	ASTM C127
Apparent specific gravity (coarse), avg $\pm$ SD	3.95 ± 0.10	3.75 ± 0.28	ASTM C127
Absorption, coarse (%), range	2.26–2.35	3.32–3.84	ASTM C127
Absorption, coarse (%), avg $\pm$ SD	2.31 ± 0.05	3.52 ± 0.28	ASTM C127
As-received moisture (%)	0.00	0.65	ASTM D2216

2.3.2 Particle Size Distribution

Analysis of slag aggregate gradation was done by means of sieves varying from 3/4 inch to No. 200 (0.075 mm), in accordance with the ASTM D6913 standard. The fine fraction below the No. 200 sieve was collected separately and subjected to additional analysis.

The curves of particle size distribution of EAF slag, caster slag, and shale soil are presented in Fig. 2.2. The EAF slag is characterized by gradation, which is dominated by coarse particles, since approximately 85% of the material passes through a 1 mm sieve while just about 25% passes through a No. 200 sieve (0.075 mm). The D₁₀ is approximately 0.01 mm, C_u is close to 20, and C_c is approximately 3.2. Thus, this is the well-graded material with a coarse gradation characteristic. This feature is explained by the natural fracture pattern of air-cooled slag, which produces coarse angular particles.

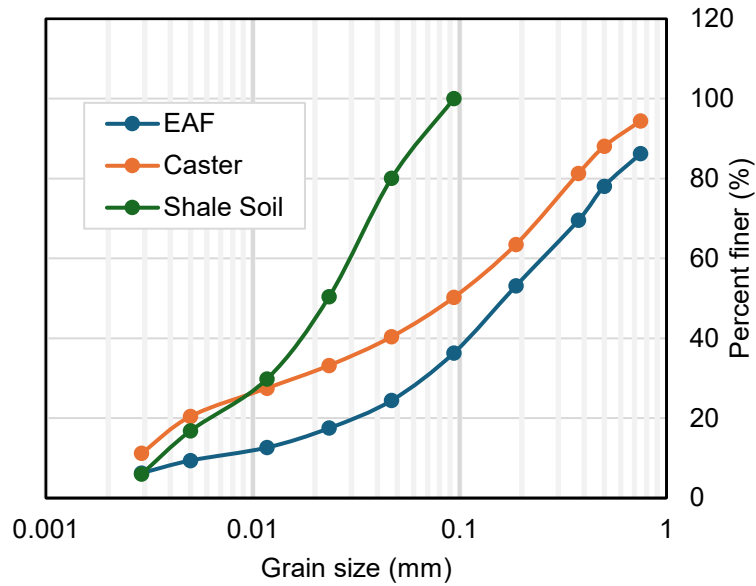


Figure 2.2 Particle size distribution curves for EAF slag, Caster slag and shale soil.

The caster slag has a more uniform gradation, with about 92% passing the 1 mm sieve and approximately 35% passing the No. 200 sieve. D10 is approximately 0.005 mm, Cu is equal to 30, and Cc is approximately 2.1. The presence of a considerable fine fraction of caster slag indicates that this material will have increased porosity and a tendency to breakage, as well as high absorption values.

Shale soil has the finest gradation among the three considered materials; 100% of the material passes approximately a 0.1 mm sieve, while about 45% passes a No. 200 sieve. Its D10 equals approximately 0.004 mm, Cu is close to 15, and Cc is approximately 1.7.

Table 2.2 Grain-Size Parameters for EAF Slag, Caster Slag, and Shale Soil

Parameter	EAF Slag	Caster Slag	Shale Soil
D10 (mm)	~0.01	~0.005	~0.004
D30 (mm)	~0.08	~0.04	~0.02
D60 (mm)	~0.2	~0.15	~0.06
Cu (D60/D10)	~20	~30	~15
Cc ($D_{30}^2 / D_{10} \times D_{60}$)	~3.2	~2.1	~1.7

The particle size distribution determines the leaching properties of such substances. Smaller particles have a larger specific surface area and thus higher dissolution rates, leading to faster release of soluble phases. The coarser gradation of Electric Arc Furnace slag (85% smaller than 1 mm) compared to the caster slag (92% smaller than 1 mm) leads to a reduced surface area-to-mass ratio, which could explain the slower release of calcium in the initial leaching tests conducted in the columns. All materials used in this research meet the criteria of sieve analysis of 9.5 mm (3/8 inch) as set by EPA Method 1311 (TCLP) and EPA Method 1313 (pH-dependent leaching). However, differences in the gradations of EAF slag and caster slag should be considered when comparing their leaching rates, since the normalized flux can differ even when concentrations are the same.

2.3.3 Shale Soil Characteristics

The shale soil used in this study was sourced from O'Neill, Nebraska. The selected highly plastic shale is representative of a subgrade condition commonly found in the Great Plains region, where expansive clays pose challenges for pavement construction. The high plasticity index (36.44%) of the soil indicates the presence of significant amounts of active clay

minerals with high surface areas and cation exchange capacity. This makes the soil an excellent candidate for studying metal adsorption since it possesses adsorption characteristics that make it ideal for evaluating if slag amendment has any effects on the leaching and adsorption of trace elements in soils. In essence, the use of such soil in this study serves two purposes, as it offers both an engineering challenge and a baseline against which slag-induced effects can be determined.

2.3.3.1 Index Properties and Classification

The liquid limit, plastic limit, and plasticity index of the shale soil were determined in accordance with ASTM D4318 at the University of Nebraska-Lincoln (UNL). From the analysis, a liquid limit of 64.76%, a plastic limit of 28.32%, and a plasticity index of 36.44% was recorded. According to these figures, the soil has been classified as A-7-2 under the AASHTO system, indicating that it is highly plastic, fine-grained, and therefore unsuitable for use as a subgrade in its natural condition. Soils in this category are known to exhibit

considerable volume changes due to changes in moisture conditions and a loss of bearing strength when moistened. This prompted a search for slag as a soil stabilizer to improve soil engineering properties.

2.3.3.2 Compaction Characteristics

The Standard Proctor test, according to ASTM D698, was performed at UNL, yielding an Optimum Moisture Content (OMC) of 27.6% and a Maximum Dry Density (MDD) of 1.488 g/cm³. Figure 2.3 displays the compaction curve of the untreated shale soil.

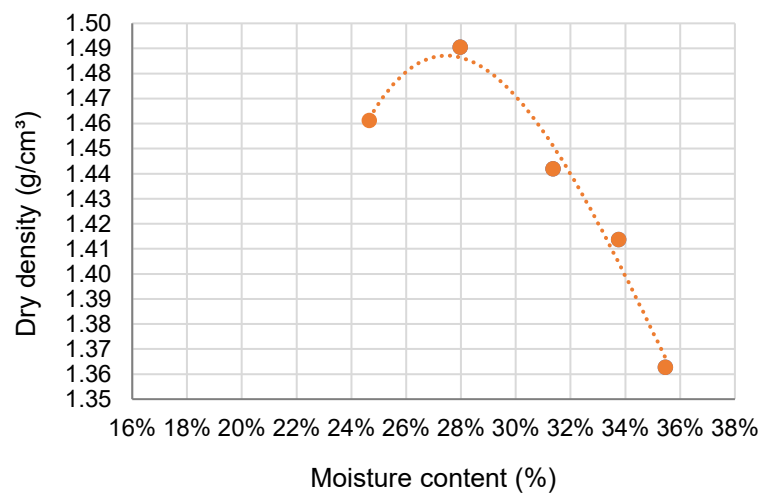


Figure 2.3 Standard Proctor compaction curve for untreated shale soil showing optimum moisture content (27.6%) and maximum dry density (1.488 g/cm³).

In combination with 10% slag by weight, the compaction properties varied with the slag type. The inclusion of 10% EAF slag led to a reduction of the OMC to 21.2% and an increase of MDD to 1.557 g/cm³, while the use of 10% caster slag resulted in a decrease of OMC to

28.3% and MDD to 1.471 g/cm³.

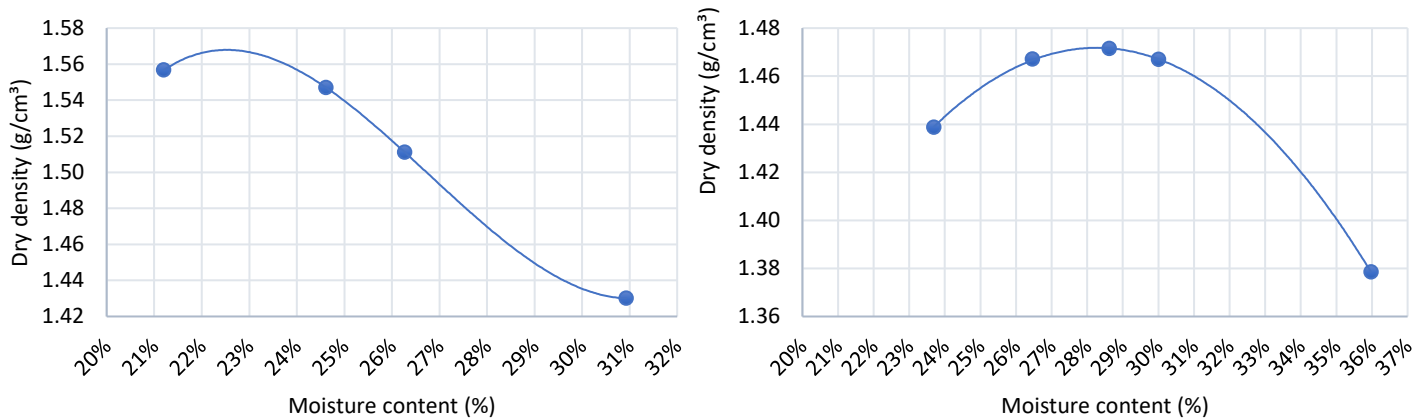


Figure 2.4 Standard Proctor compaction curves for (a) shale soil with 10% EAF slag (OMC 21.2%, MDD 1.557 g/cm³) and (b) shale soil with 10% caster slag (OMC 28.3%, MDD 1.471 g/cm³).

The increase in density with the inclusion of electric arc furnace (EAF) slag is attributed to the high specific gravity of the slag relative to soil, thereby increasing the unit weight of the mixture. However, the decrease in MDD due to the inclusion of caster slag, even though the specific gravity of caster slag is higher compared with that of soil, could be due to the increased porosity of the particles of the caster slag, thus forming voids in the compacted mass. The decrease in OMC with the use of EAF slag could be due to the higher density and lower porosity of EAF slag particles, which have displaced soil particles, thereby requiring more water to achieve MDD. The initial moisture content of the shale soil at the time of arrival in the laboratory was 3.34%, far lower than the OMC of the soil.

2.3.3.3 Natural pH

The natural pH of the soil was determined by preparing a suspension of the dried soil sample in deionized water at a 1:2 (mass ratio of soil: water = 10 g:20 mL). This solution was stirred for 30 minutes, then allowed to settle for 10 minutes. The pH was then found using a calibrated Symphony B40PCID pH meter.

Table 2.3 Index and Compaction Properties of Shale Soil

Property	Value	Standard
Source location	O'Neill, Nebraska	-
Liquid limit (%)	64.76	ASTM D4318
Plastic limit (%)	28.32	ASTM D4318
Plasticity index (%)	36.44	ASTM D4318
AASHTO classification	A-7-2	AASHTO M 145
Natural pH	7.11	-
OMC, untreated (%)	27.6	ASTM D698
MDD, untreated (g/cm ³)	1.488	ASTM D698
OMC, 10% EAF (%)	21.2	ASTM D698
MDD, 10% EAF (g/cm ³)	1.557	ASTM D698
OMC, 10% Caster (%)	28.3	ASTM D698
MDD, 10% Caster (g/cm ³)	1.471	ASTM D698

2.3.4 Quartz Sand

Pre-washed 20-30 mesh quartz sand from US Silica Company was used as the packing material of the percolation columns. The choice of quartz sand was driven by the following reasons: (1) its chemical inertness due to lack of chemical reactions between SiO₂ and alkaline leachate of the slag and absence of dissolved ions which can affect the process of leaching; (2) hydraulic homogeneity because the fine fraction of 20-30 mesh provides the highly permeable layer; (3) minimizing the preferential flow due to placement of sand layer at both input and output sides of each column ensuring the even distribution of the leaching fluid; (4) prevention of fines migration since the sand provides the filtration layer which would prevent the clogging of the tubing and collection system with fines of the slag or soil sample. The 1 cm layer of sand was placed on both sides of each column. The density of quartz is equal to 2.65 g/ml, which is the standard value for this mineral.

2.3.5 Geo Textile

The geotextile fabric membrane (MIRAFI RS380i, Solmax/TenCate Geosynthetics) was installed at four places inside each column underneath the end-cap of the outlet, between the

quartz sand on the outlet side and the slag-soil composite sample, between the sample and the quartz sand pre-filter layer on the inlet side, and under the end-cap of the inlet to provide separation and filtering of the individual material layers during up-flow percolation testing using EPA Method 1314. In this scenario, the geotextile played two main functions: (1) keeping separate the quartz sand layers from the slag-soil sample to maintain the layered structure intact for the whole period of the test, and (2) retaining sample particles within the slag-soil layer while allowing free passage of leachate through the column, thus avoiding fines clogging the effluent without creating a hydraulic choke-point, for this reason it was also used in the inlet of the outdoor lysimeter test.

Table 2. 4 Properties of Geotextile

Property	Test method	Value
Pore size distribution, O95	ASTM D6767	392 microns
Pore size distribution, O50	ASTM D6767	195 microns
Apparent opening size (AOS)	ASTM D4751	U.S. Sieve No. 40, 0.425 mm or 425 microns
Hydraulic flow rate	ASTM D4491	75 gal/min/ft ² , equivalent to 3,056 L/min/m ² ; minimum average roll value
Permittivity	ASTM D4491	0.9 sec ⁻¹ ; minimum average roll value
Yarn composition	Product specification	Black fibrillated polypropylene for tensile strength; orange yarn for anti-clogging; blue yarn for wicking

2.3.6 Mineralogical Analysis

The combination of Scanning Electron Microscopy (SEM) and Energy-Dispersive Spectroscopy (EDS) was used to determine the surface morphology and elemental composition of the slag particles and to identify the phases responsible for the leaching of Ca, Fe, Mn, and other metals from the particles. SEM provides images of physical textures (such as smooth/vesicular and crystalline/amorphous) and determines the surface area. In addition, the EDS technique allows the acquisition of semi-quantitative elemental maps that provide

information for distinguishing among calcium silicate, calcium aluminate, and iron oxide phases. This information is needed for Chapter 4 to understand which mineral surfaces interact with the leaching fluid and how the surfaces change during the process.

The SEM of raw and after-column slag samples was done using a Hitachi SU-70 Schottky Field-Emission-Gun microscope. Imaging was carried out at an accelerating voltage of 15 kV. EDS data were used to determine the elemental composition of the sample surface.

CHAPTER 3– BATCH TEST

3.1 Introduction

Slags are by-products of the pyrometallurgical processing of various ores in the steel industry (Piatak et al., 2015). Callaghan (2026) describes slags in (Mineral Commodity Summaries 2026) as material formed by reacting slagging agents with impurities produced during the production of crude and raw steel. Slags are typically classified as Blast Furnace slag (BFS), Basic Oxygen Furnace slag (BOFS), electric arc furnace slag (EAF), and Caster slag, also called refining slag (Setién et al., 2009). Until the 1990s, slags were considered waste materials; this attitude changed, and these raw materials are now processed and used in the cement and construction industries (Piatak et al., 2015; Džupin & Zubek, 2026). Due to their similar or superior physical properties to those of natural aggregates such as gravel, steel slags are widely used in road construction and paving (Mombelli et al., 2016).

Global steel slag production in 2024 was estimated at approximately 190 to 290 million tons, while in the United States, EAF slag accounts for approximately 7 to 9 million tons annually, generated at a rate of 65 to 85 kilograms per metric ton of crude steel produced (Yu et al., 2025; Callaghan, 2026). In an EAF steelmaking operation, steel scrap is melted in an electric arc furnace along with fluxing agents to produce products like those of a Basic Oxygen Furnace: steel and steel slag (Džupin & Zubek, 2026). Since the EAF process has a lower carbon footprint and the United States is gradually shutting down blast furnaces as part of its decarbonization efforts, demand for EAFs is expected to increase (Callaghan, 2026). Due to their availability and physical and chemical properties, EAF slags are utilized in various applications (Yu et al., 2025), most prevalently as construction aggregates, in road base, riprap, landscaping, and as the cover for unpaved roads (Steel furnace slag: The premier construction material (National Slag Association, 1982).

The slags produced by the secondary metallurgical processes of the BOF and EAF are collectively referred to as Caster slag (Manso et al., 2011; Setién et al., 2009). Production data for Caster slag are not explicitly mentioned in any federal or state documents. Caster slag has a very high CaO content (30-40%), exhibits spontaneous reactivity at room temperature, and carbonation and hydration reactions can provide strength over time, making

the product more durable (Setién et al., 2009; Yu et al., 2025). Thus, it can be used as a partial replacement of lime in the primary metallurgical process. Findings from Manso et al. (2011) and Václavík et al. (2024) reveal that using caster slags in cement and masonry mortar does not compromise performance; in turn, it improves workability and mortar durability, even though caster slag reduces the use of sand. It meets standard requirements by producing high-quality masonry mortars; the only limitation is its retarding effect on setting time when used as an admixture in cement paste.

A detailed study of the leaching behavior of the slags is needed before their use in large-scale construction applications (Singh et al., 2021). There is no standardized leaching characterization test approach for EAF, and data on caster slag are very scarce (Yu et al., 2025; Lončar et al., 2016). The role of the chemical composition of steel slag in leaching has not been investigated extensively (Heidarinejad et al., 2026). The lack of a standardized test can produce variable, conflicting results and may not align with laboratory-measured concentrations, raising questions about the ability to model slag leaching over the long term (Piatak et al., 2015; Yu et al., 2025).

The objectives of this chapter include four points: (1) determining if EAFS and Caster slags from Nucor Steel, Norfolk, Nebraska, satisfy the toxicity characteristic criterion according to the EPA Toxicity Characteristic Leaching Procedure (TCLP, Method 1311); (2) measuring the pH-dependent leaching profile of major and minor elements under environmentally realistic pH levels through the use of the EPA Leaching Environmental Assessment Framework (LEAF) parallel batch extraction procedure (Method 1313); (3) determining the impact of particle size on the release of constituents, taking into consideration the resulting pH of the eluate; and (4) identifying which of the constituents are the major sources of concern for the environment based on their pH-dependent leaching behavior under acidic, natural, and alkaline conditions. The TCLP test is a one-time screening test conducted under strongly acidic conditions to assess RCRA hazardous waste criteria. Method 1313 provides more information by presenting a full pH-dependent leaching profile, which explains how the mobility of constituents varies with geochemical conditions that may be encountered during the material's lifetime.

3.2 Methods

3.2.1. Modified Toxicity Characteristic Leaching Procedure (TCLP)

The Toxicity Characteristic Leaching Procedure (TCLP), also known as EPA SW-846 Method 1311, is an investigation used to determine whether a given material meets the toxicity limit specified by the Resource Conservation and Recovery Act (RCRA), 40 CFR Part 261.24. The procedure mimics the leaching conditions of a municipal solid waste material disposed of in a sanitary landfill. The extract is collected after mixing and shaking it with the dilute acidic solution at a L/S ratio of 20:1 for 18 hours. The leachate obtained is then compared with the RCRA limit for this test to determine whether the sample is hazardous.

This is a preliminary test of both Caster and EAF slag samples to assess their potential classification as hazardous waste under RCRA limits, based on their heavy-metal leaching potential, especially under acidic conditions, which are most common at disposal sites.

3.2.1.1 Sample Preparation

The method requires particles passing through the 9.5 mm (3/8-inch) sieve, obtained by dry sieving of EAF and Caster slags.

The slags were oven-dried at 105 ± 2 °C for 24 hours and then kept in a desiccator until the mass stabilized, as shown in Figure 3.1. Then, the moisture content was determined by weighing the as received and dried samples.

$$SC (\%) = (\text{Dry mass} / \text{Wet mass}) \times 100$$

All sample masses mentioned here are expressed as dry-mass equivalents. The wet mass in each extraction vessel was determined by dividing the target dry mass by the measured solids content.



Figure 3.2.1.1 Oven Dried Samples :(A) Caster Slag and (B) EAF Slag

3.2.1.2 Extraction Fluid Selection and Preparation

Prior to extraction, the pH of each slag sample was determined. Five grams of each sample was mixed with 96.5 mL of ASTM Type II deionized water (conductivity < 10 $\mu\text{mho}/\text{cm}$) and stirred for 5 minutes before measuring the pH using a Symphony B40PCID combination pH electrode meter. The determined pH of the EAF slag sample and lignite fly ash slag sample were 11.18 and 11.83, respectively. Since both measurements were above pH 5, extraction fluid #2 was chosen after the first screening step. The extraction fluid verification step mentioned in EPA Method 1311 Section 12.2, i.e., heating of the sample with 3.5 mL of 1N HCl at 50 ± 2 °C for 10 minutes, is omitted since the initial pH measurement of both slag samples is greater than pH 5 by more than six units, thus resulting in deterministic output from the extraction fluid verification step. Therefore, the test is considered the modified EPA Method 1311 (TCLP). This modification does not affect the validity of the extraction fluid or the corresponding leachate concentrations, since the purpose of the verification step is to address the borderline case near pH 5.

Extraction Fluid No. 2 was freshly prepared on the day of use following EPA Method 1311. For each 1 L of fluid, 5.7 mL of glacial acetic acid (ACS reagent grade) was added to approximately 500 mL of reagent-grade deionized water, and the mixture was brought to 1 L.

with deionized water. The pH was verified to be 2.88 ± 0.05 using a calibrated pH meter before use. The solution was prepared in a 1 L Class A volumetric flask and labeled with the fluid type and date of preparation.

3.2.1.3 Extraction Procedure

Extraction was performed using 1-liter HDPE bottles with screw caps, as shown in Figure 3.2.1.2 All bottles were rinsed three times with reagent-grade deionized water and acid-washed with 5% nitric acid (HNO_3) before use. For each slag sample, 20 g of dry mass was weighed to the nearest 0.01 g on a top-loading analytical balance and placed into the cleaned extraction bottle. The wet mass corresponding to the slag was then added to account for its moisture content. Extraction fluid #2 was used in 400 mL quantities, yielding a liquid-to-solid (L/S) ratio of 20 mL/g, according to the EPA Method 1311 procedure. Slag samples were confirmed to be less than 9.5 mm in size before being placed in the bottles.

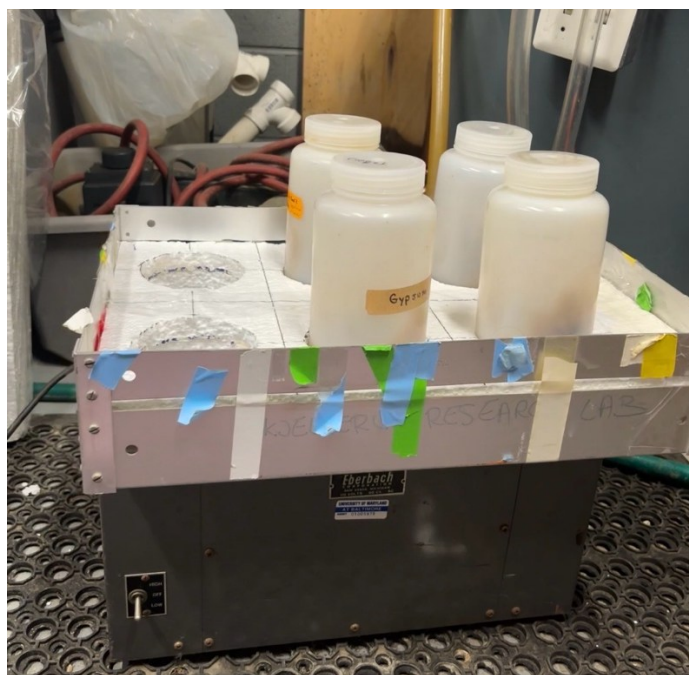


Figure 3.2.1.2 HDPE bottles containing EAF and Caster slag with Extraction Fluid No. 2 on an orbital shaker.

Seven extraction bottles were prepared in total: three replicates for EAF slag and three for Caster and one method blank. Each replicate was prepared individually, with the appropriate amounts of sample and extraction fluid. A single method blank was prepared

with extraction fluid #2 without any solid. The bottles were shaken using an orbital shaker operating at 30 ± 2 RPM for 18 ± 2 hours.

3.2.1.4 Filtration

After 18 hours of extraction, the samples were removed from the agitator, and their pH was measured with a Symphony B40PCID pH meter using three buffer solutions as calibration standards. The post-extraction pH readings for the three replicate samples of EAF slag were 4.96, 4.86, and 4.90 (average 4.91 ± 0.05), whereas for the three replicate samples of CASTER SLAG, they were 5.26, 5.31, and 5.36 (average 5.31 ± 0.05). To minimize atmospheric CO₂ absorption, all samples were filtered within 15 minutes of being removed from the agitator.

To perform vacuum filtration, 45-mm borosilicate glass fiber filters with 0.6–0.8 μm pore size were used. The vacuum was applied slowly until the leachate became clear, and filter papers were changed after filtering each sample. The obtained filtered leachate was collected in a clean 250 mL sampling bottle.

3.2.2 EPA Method 1313: Liquid-Solid Partitioning as a Function of Extract pH

One of the four tests in the Leaching Environmental Assessment Framework (LEAF) is Liquid-Solid Partitioning as a Function of Extract pH, using a Parallel Batch Extraction Procedure (also known as EPA 1313). Unlike EPA 1311, a single fixed-acidic-pH test, EPA 1313 is a multi-point pH test ranging from pH 2 to 13, which assesses the liquid-solid partitioning (LSP) curve for all components across different pH levels. This method determines how the materials behave with varying pH and geochemical conditions.

Both samples collected from Nucor Steel in Nebraska were subjected to this test. Three particle sizes were considered to determine the impact of particle size on leachate chemistry across a wide range of pH levels. The results will then be compared with the EPA limits to examine the suitability of the slag materials for unencapsulated road construction.

3.2.2.1 Pre-Test Titration

A pre-titration was done to examine the acid/base neutralization capacity of both the slags and to determine the acid and base required for the actual test to reach the target pH levels. The slags were found to be highly basic, with pH values of 11.18 and 11.83 for EAF and Caster slags, respectively, in the absence of any acid/base addition, and were classified as

highly alkaline. This is mainly due to the high levels of CaO and Calcium Silicate phases, which make it more alkaline when in contact.

The pre-test titration was conducted using five parallel extractions per slag following the High Alkalinity pre-test schedule specified in Method 1313 Table 3.2.1.3. For each slag, approximately 20 g dry-equivalent of the less-than-0.3-mm fraction was placed in each of five 1000 mL HDPE bottles. 0, 5, 10, 15, and 25 milliequivalents per gram dry mass (meq/g-dry) of 2N HNO₃ were added to the five bottles, along with base additions of -1 and -2 meq/g-dry of 1N KOH for the alkaline side. Deionized water was added to each bottle to achieve an L/S of 10 mL/g-dry. The bottles were sealed and tumbled end-over-end for 15–20 min at 20 ± 2°C. After agitation, the pH of the eluate from each bottle was measured and plotted against the acid equivalents added to generate the titration curve, as shown in Figure 3.2.1.3.

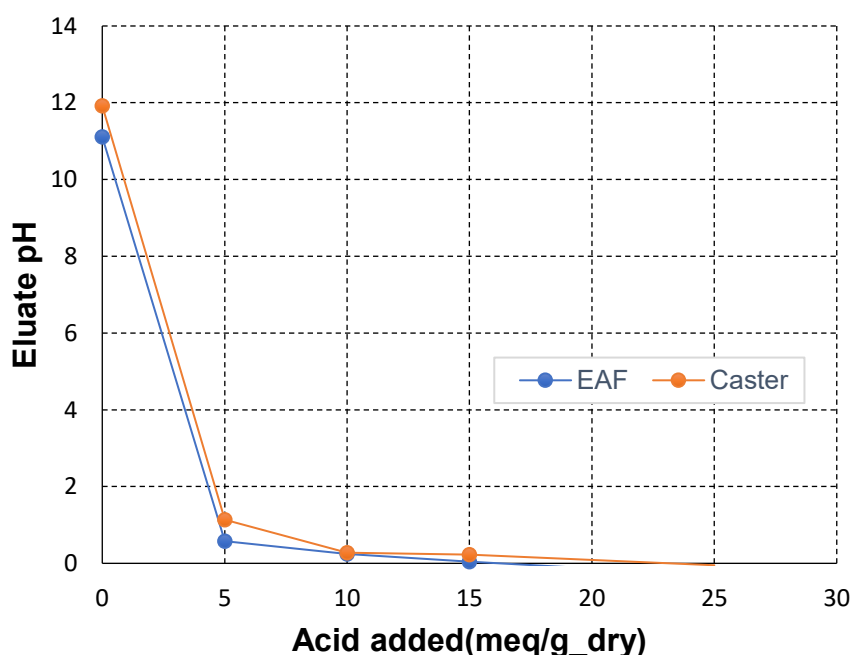


Figure 3.2.1.3 Pre-test titration curve for EAF slag Caster slag, showing the equilibrated eluate pH as a function of acid and base additions (meq/g-dry) at a liquid-to-solid ratio of 10 mL/g-dry.

Titration curves for both EAF and Caster slag confirm their status as high-alkalinity slags, as there was a sharp decrease in pH from approximately pH 11 to below pH 1 as acid addition

increased from 0 to 5 meq/g-dry, with minimal further changes in pH at higher acid additions. The high concentration of alkali in these slags creates a narrow pH range for neutralization and, thus, all acidic target pH values (pH 8, 5.5, 4, and 2) are concentrated in a narrow range of acid additions between 0 and 5 meq/g-dry. Therefore, to obtain the acid additions needed to reach each acidic target pH value, linear interpolation was used between pre-test data points at 0 and 5 meq/g-dry.

It reveals an issue with the pre-test titration procedure, which, according to EPA Method 1313, Section 11.3.4, recommends adding more points if the existing points do not provide sufficient resolution. In this case, the additional points between 0 and 5 meq/g-dry, for instance, at 1, 2, and 3 meq/g-dry, would have allowed more precise acid additions to reach the target pH values. Those points were not included in the pre-test titration process. As a result, the estimated acid additions for the extraction were based on a linear approximation of the non-linear region of the titration curve, which inevitably led to a systematic underestimation of the acid additions required to reach acidic targets, especially for the 0.3 mm fraction. This issue is discussed further in Section 3.3.2.1.

Different target pH values were chosen to cover a wide spectrum of environmental conditions, including strongly acidic (pH 2) to strongly alkaline (pH 13). Natural pH value corresponded to the absence of acid or base additions. The target pH values are specified in the table above.

Table 3.2.1 Acid and base additions (meq/g-dry) required to achieve each target extraction pH for EAF slag and CASTER SLAG, determined from the pre-test titration on the less-than-0.3-mm fraction.

Test position	Target extraction condition	EAF (meq/g-dry)	CASTER SLAG (meq/g-dry)
T01	pH 13	-0.87	-0.79
T02	pH 12	-0.41	-0.06
T03	pH 10.5	0.29	0.66
T04	pH 9	1	1.35
T05	pH 8	1.48	1.82

T06	Natural (no acid/base addition)	0	0
T07	pH 5.5	2.66	2.98
T08	pH 4	3.38	3.67
T09	pH 2	4.33	4.6

3.2.2.2 Sample Preparation

As per EPA Method 1313, reducing particle size is necessary to better approach the liquid-solid equilibrium during extraction. Three different standard particle sizes are defined in the method: 0.3 mm, 2.0 mm, and 5.0 mm. For the current study, three different particle sizes have been prepared and studied: <0.3 mm, ~5mm, and ~19mm. The first two sizes, i.e., <0.3 mm and 4.75-9.5 mm (5 mm), comply with the particle size requirement per Method 1313. The last one, ~19mm, is not covered in Method 1313 and is a modification in the existing process. This has been done since the slag is to be used as coarse construction aggregate, and the leaching behavior of such a fraction could not be inferred from the first two. The standard 2.0 mm fraction has been replaced with a 19mm fraction to cover the particle size range from fine to coarse aggregate for practical application. Thus, two fine fractions, which would provide the same information, have been avoided.

It cannot be determined from the available data whether a true equilibrium is reached for each fraction, as no kinetic monitoring (e.g., pH or conductivity measurements during the extraction process) was performed. This means that the results obtained for the 19mm fraction cannot be treated as evidence of equilibrium and are valid only as concentrations after 144 hours. All fractions are subject to the same limitation, though the two smaller ones might reach equilibrium in their contact time due to the larger specific surface area.

All fractions were sieved using standard ASTM sieves on a mechanical shaker. Different fractions and their contact times are listed in Table 3.2.2

After sieving, all fractions were stored in airtight zip-lock bags in a closed box at room temperature to prevent exposure to air and moisture before testing. The fractions were not dried after sieving and were tested in the as-sieved state. The portion under 0.3 mm to be

used in Method 1313 was separated from the portion set aside for SEM. The SEM samples were sieved using a No. 8 sieve.

For each particle-size test, there were 12 extraction bottles. Nine bottles were used to test at different pH levels, while the remaining three were method blanks. Each bottle was assigned a unique combination of slag types, particle sizes, and desired pH values, with no experimental replicates. Since the three method blanks did not contain any solid sample, their purpose was only to serve as contamination controls, not as replicates of the extraction process. Consequently, the current work is unable to assess the heterogeneity of the materials, extraction variability, analytical reproducibility, or uncertainties associated with individual concentration measurements.

Table 3.2.2 Particle size fractions, extraction contact times, and Method 1313 compliance status for EAF slag and Caster slag batch leaching tests.

Particle size fraction	Contact duration	
	(hours)	Method 1313 status
Less than 0.3 mm	24 +/- 2	Standard
4.75 to 9.5 mm (5 mm)	72 +/- 2	Standard
Retained on 19.05 mm sieve (19 mm)	144 +/- 2	Modified (not specified in Method 1313)

All extractions were conducted in 1000 mL wide-mouth high-density polyethylene (HDPE) bottles with leak-proof screw caps. HDPE is the recommended vessel material for inorganic constituent analysis under Method 1313 Section 6.1.1. The same vessel size (1000 mL) was used for all three particle-size fractions, including the less-than-0.3-mm fraction, which required only 200 mL of extractant. While Method 1313 recommends 250 mL vessels for the 0.3 mm fraction, the use of larger 1000 mL bottles did not affect the test conditions, since only inorganic metals were analyzed, and headspace minimization is primarily relevant for semi-volatile organic analyses. All the extraction vessels were washed with dish soap, rinsed three times in deionized water, soaked in 5% HNO₃ for 24 hours, and air-dried for a day before use in the test procedure. This procedure was performed to ensure the containers were

free of contaminants that could affect the test procedure. 12 bottles were prepared for each extraction with different particle sizes: 9 for testing at varying pH, and 3 as method blanks. These bottles were labeled with slag type, fraction size, test position number, and date of extraction before placing them in the refrigerator.

3.2.2.3 Extraction Procedure

Each particle size was tested separately for each slag type, using an orbital shaker. A total of six extraction runs were conducted across the two slag types. While the amounts of acid/base and slag added varied slightly between samples, the procedure remained consistent. The extractions were carried out using particle sizes ranging from the smallest to the coarsest. The solids content of both slags was accounted for, as moisture could significantly affect the liquid-to-solid (L/S) ratio. EAF slag had an SC of 1.00 g-dry/g, and Caster had an SC of 0.994 g-dry/g. The 0.01-gram precision was maintained when weighing each slag sample using a calibrated analytical balance. The method blank contained no solids.

2N nitric acid (HNO_3), an acidic reagent, and 1N potassium hydroxide (KOH), an alkaline reagent, were used to adjust the pH to the target value. These stock solutions were used consistently throughout the testing process for all slag samples. Potassium was not among the 13 target analytes in this study; therefore, the use of KOH as the base reagent did not introduce any analytical interference, as specified.

For each test position bottle, reagent water was first added to the bottle using a graduated cylinder to within 5% of the target volume, followed by the appropriate volume of acid or base using an adjustable pipette to within 1% of the target volume. The pre-test titration curve determined the amount of acid/base to be added in each extraction vessel, and adjustments were made based on the moisture content of the Caster slag when calculating reagent water to achieve an exact L/S ratio of 10 mL/g-dry (Table 3.2). No adjustments were made to the reagent water for EAF slag because we did not detect any moisture in it. Acid and base additions were completed approximately 10 minutes before the bottles were sealed and placed on the tumbler. For the three method blank bottles, the same volumes of reagent water, maximum acid, and maximum base were added as used in the corresponding test positions, but without any solid slag material.

After sealing all 12 bottles with leak-proof caps, the extraction vessels were placed on two Eberbach orbital shakers where the end-over-end tumblers ran simultaneously, with six

bottles per tumbler. The tumblers' speed of 30 ± 2 RPM was kept constant throughout the extraction. A slight deviation from the 28 ± 2 RPM specified in modified Method 1313 Section 11.5.6 occurred due to equipment unavailability; the orbital shaker was approved for the test. The lab maintained a temperature of around 22°C, with a $\pm 2^\circ\text{C}$ margin. Each fraction's contact time was as follows: less than 0.3mm for 24 $\pm$ 2 hours, 4.75 to 9.5mm for 72 $\pm$ 2 hours, and greater than 19mm for 144 $\pm$ 2 hours. Throughout the process, all fractions remained comfortably below the lab's steady temperature. To avoid any problems, bottles were kept out of direct light during extraction, as shown in Figure 3.2.

After the designated contact time ended, the 12 bottles were carefully removed and placed upright for about 15 minutes to allow the solids to settle. Once the liquids appeared clearer, approximately 25 mL was withdrawn from each bottle and transferred to clean containers. The pH of the leachate was measured before filtration, after calibrating the pH meter with 3 buffer solutions. To ensure accuracy, we completed all steps within 30 minutes to prevent CO₂ in the air from affecting the results, since the extracts were already alkaline.

3.2.2.4 Filtration

After analyzing the pH values of the samples, the samples were filtered with minimal disturbance to reduce the risk of mobilizing solid particles that had precipitated at the bottom. Filtration was performed using a vacuum filtration system with a membrane filter (0.45 μm pore size). A new piece of filter paper was used for each extract. About 100 mL of the filtered solution from each sample bottle was placed in an HDPE storage bottle labeled with the date, particle size, slag type, and target pH. This amount of liquid was sufficient to perform all 15 target-analyte analyses on the Shimadzu ICPE-9820 ICP-OES instrument when diluting high-metal-concentration samples.

For extract analysis, 15 target analytes (Al, As, B, Ba, Be, Ca, Cd, Cr, Fe, Mg, Mn, Ni, Pb, V, and Zn) were determined. The analytical procedure used 10 calibration standards. The instrumental method detection limit (MDL) was 0.01 mg/L. Each analytical batch began with an initial calibration verification (ICV) standard and continued with a continuing calibration verification (CCV) standard after analyzing 15 samples. All analyzed method blanks run in parallel with the samples showed concentrations below the detection limit, indicating low contamination from reagents and laboratory processing. In this study, no duplicate precision or

matrix spike recovery was determined, which is one limitation in evaluating the precision of the results.

For analytes present in fewer than 3 replicates, the mean concentration and standard deviation were calculated using only detected values, and the non-detected values were considered as MDL/2. The number of detected analytes across three replicates is reported for each analyte. The coefficient of variation (CV%) was calculated only in the case of the detection of three or more replicates.

Samples with dissolved metal concentrations exceeding the maximum concentration of the calibration standard were diluted with 3% HNO₃ solution and re-analyzed. The dilution factor varied from 1:2 to 1:500 depending on the analyte concentration. No internal standard was used during analysis.

3.2.3 Preservation and Storage

Once filtration was complete, concentrated nitric acid (HNO₃) was added to each leachate sample to bring the pH below 2. The amount of acid added varied with sample volume, ranging from 0.05 to 0.15 mL per sample. This was done to ensure the samples' pH was lowered to 1.5-2.0. The preserved samples were kept at 4°C and analyzed within 3 months of collection, which is standard, as samples should be analyzed within 6 months.

3.3 Results and Conclusion

3.3.1 TCLP test

The TCLP test was performed with 3 replicates of EAF and Caster slag to assess the potential for environmental leaching of heavy metals under simulated co-disposal conditions. The initial pH of the EAFS and Caster was 11.18+/-0.2 and 11.83+/-0.2, respectively, indicating high alkalinity in the natural environment, which is why we used Extraction Fluid #2.

According to the protocol, eight analytes (Ag, As, Ba, Cd, Cr, Pb, Hg, and Se) were tested against the RCRA TC limits to assess heavy-metal exceedances under aggressive landfill conditions. Only three out of eight target metals were detected, as shown in Table 3.3.1. Even though small amounts of leaching were observed for Barium, selenium, and Chromium, none exceeded the RCRA regulatory thresholds specified in 40 CFR Part 261.24.

Table 3.3.1 TCLP leachate concentrations (mg/L), coefficient of variation (CV%), and RCRA Toxicity Characteristic (TC) compliance assessment for EAF slag and Caster slag under EPA Method 1311

Sample/Parameters	As (mg/L)	Ba (mg/L)	Cd (mg/L)	Cr (mg/L)	Pb (mg/L)	Ag(mg/L)	Se(mg/L)	Hg(mg/L)
EAFS 1	<0.025	1.22	<0.025	0.05	<0.05	<0.01	0.52	<0.05
EAFS 2	<0.025	1.92	<0.025	1.06	<0.05	<0.01	0.80	<0.05
EAFS 3	<0.025	0.61	<0.025	<0.01	<0.05	<0.01	<0.1	<0.05
mean	-	1.25	-	0.55	-	-	0.66	-
CV%	-	52.49	-	128.85	-	-	30.04	-
CASTER SLAG 1	<0.025	0.51	<0.025	-	<0.05	<0.01	<0.1	<0.05
CASTER SLAG 2	<0.025	2.29	<0.025	1.64	<0.05	<0.01	<0.1	<0.05
CASTER SLAG 3	<0.025	0.98	<0.025	0.09	<0.05	<0.01	<0.1	<0.05
mean	-	1.26	-	0.87	-	-	-	-
CV%	-	73.40	-	126.70	-	-	-	-
RCRA TC (mg/L)	5	100	1	5	5	5	1	0.2
Result	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass

Moreover, barium showed the most consistent leaching behavior, as its concentrations were detected in all three replicates of both slag samples. The mean of Ba concentrations in EAF slag amounted to 1.250 ± 0.656 mg/L (CV = 52.5%) with a maximum value of 1.92 mg/L, which provided a ratio between the mean value and the RCRA limit of 1.25% and between the maximum value and the RCRA limit of 1.92% out of 100 mg/L. In Caster slag, Ba concentrations were 1.259 ± 0.924 mg/L (CV = 73.4%), with a maximum of 2.29 mg/L. Therefore, the mean-to-limit ratio was equal to 1.26%, while the maximum-to-limit ratio was 2.29%. Barium had the highest concentration, exceeding 1 mg/L and being the highest among all metals analyzed (Proctor et al., 2000; Singh et al., 2021). Leaching of barium is associated with relatively higher content of larnite in slags (Mombelli et al., 2016).

Piatak et al. (2015) noted that chromium behaves abnormally in high concentrations in ferrous slag compared to other slag types. For EAF slag, chromium was detected in 2 out of 3 replicates (concentrations of 0.0493 and 1.06 mg/L; mean of detected values = 0.555 ± 0.715 mg/L; CV = 128.9%). The maximum amount of chromium detected was 1.06 mg/L, which is

equivalent to 21.2% of the RCRA limit of 5 mg/L. Furthermore, the Caster slag contained chromium in 2 out of 3 replicates (1.64 and 0.09 mg/L; mean detection value = 0.865 ± 1.096 mg/L; coefficient of variation = 126.7%), with a maximum detection value of 1.64 mg/L, which is 32.8% of the RCRA limit. The oxidation state of chromium in the slag needs to be determined to understand its leaching characteristics, as chromium leaching is not strongly correlated with phase data (Engström et al., 2014; Mombelli et al., 2016).

Selenium was detected only in EAF slag, in two of three replicates (0.521 and 0.802 mg/L; mean of detected values = 0.662 ± 0.199 mg/L; CV = 30.0%), while remaining below MDL in all Caster slag replicates. The maximum EAF selenium concentration (0.802 mg/L) represents 80.2% of the RCRA regulatory limit of 1.0 mg/L. Yu et al. (2024) found that these concentrations can be reduced by a factor of 10 when aged slag is used for the intended purpose.

All metal concentrations tested were below the RCRA hazardous waste regulatory levels. None of the EAF slag and Caster slag showed toxicity characteristics based on EPA Method 1311 (40 CFR Part 261.24) for eight metals listed in regulations. These slags may therefore be classified as non-hazardous under RCRA regulations. However, TCLP is a single-point, aggressive extraction technique used for screening purposes. This procedure does not account for pH-dependent leaching behaviors, long-term release kinetics, or dissolution processes for different compounds. Modifications to the EPA Method 1313 batch test and the field exposure test presented in the following chapters will help fill these knowledge gaps.

3.3.2 Liquid-Solid Partitioning as a Function of Extract pH Using a Parallel Batch Extraction

3.3.2.1 Eluate pH and Buffering Behavior

Figures 3.3.1a and 1b show the actual eluate pH for EAFS and Caster slag across 3 different particle sizes. The pre-test titration curve (Figure 3.3.1) was used to determine the amounts of acid and base added as a function of the pH of the natural samples. EAFS and Caster slag showed high alkalinity of 11.18 and 11.83 during the initial investigation. This can be attributed to the presence of rapidly dissolving calcium silicates, which result in high pH values. Both slags showed significant deviation from the target pH, achieving the alkaline targets and falling short of the acid targets.

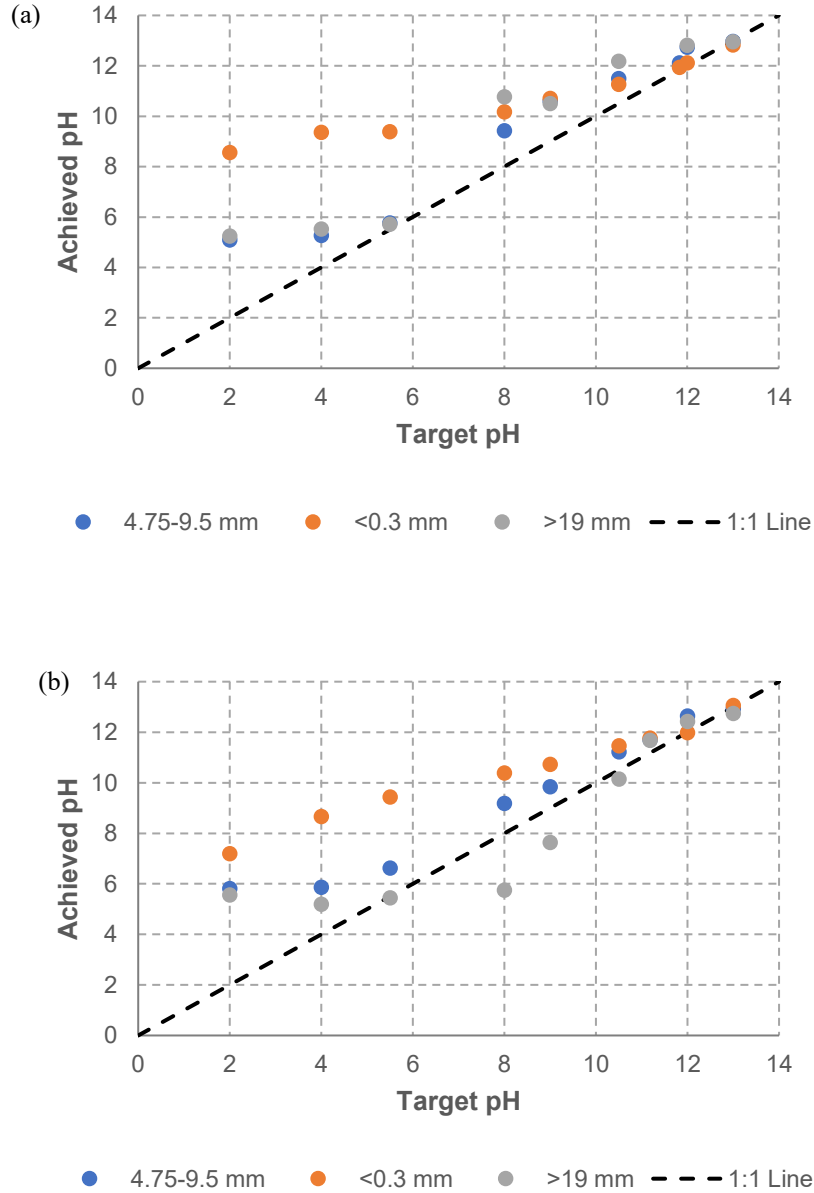


Figure 3.3.1 Actual measured eluate pH versus target pH for (a) Caster slag and (b) EAF slag across three particle sizes (< 0.3 mm, 4.75 to 9.5 mm, and > 19 mm) under modified EPA Method 1313 parallel batch extraction. The dashed diagonal line represents perfect agreement between the target and achieved pH; points above the line indicate alkaline buffering, while points below indicate the achieved pH fell short of the target. The natural-pH extraction (no acid or base addition) is labeled on each plot.

The less-than-0.3 mm fraction of EAF slag did not reach any of the three specified acidic pH targets and showed pronounced buffering, resulting in achieved pH values of 9.44, 8.66, and 7.20 instead of targeted pH values of 5.5, 4.0, and 2.0, respectively. All three acidic targets yielded alkaline eluates upon acid addition, consistent with the titration curves obtained

before the test (Section 3.2.2.1). Linear interpolation applied during preliminary titration resulted in acid additions on the steep 0 to 5 meq/g-dry interval, where any inaccuracy in acid volume leads to significant deviations of the achieved pH. During 24 hours of extraction, less-than-0.3 mm fraction of EAF slag continued dissolving and releasing alkaline minerals (mainly calcium silicates), resulting in buffering of eluate pH up to an alkaline value despite additional acid additions. At the same time, 4.75-9.5 mm and greater-than-19 mm fractions, with lower reactive surface area per unit mass, were less capable of buffering; therefore, the same acid additions led to a lower pH. Similarly, Caster slag did not achieve the target pH of 2.0 in the less-than-0.3 mm fraction, reaching only pH 8.56 with maximum acid addition, whereas coarser fractions approached the acidic target more closely. It can be concluded that increasing particle size reduces the buffering effect during the extraction process; however, as prescribed by fine-fraction titration, acid additions might be insufficient for coarse fractions due to different dissolution kinetics. The acid addition schedule determined from the pre-test titration prescribed 4.33 and 4.60 meq/g-dry of 2N HNO₃ to target pH 2 for EAF and Caster slag, respectively. However, these acid additions were insufficient to achieve the target, with the 0.3 mm fraction reaching only pH 7.20 and 8.56 for EAF and Caster slag, respectively. This is consistent with the findings of Yu et al. (2025), who reported that ~5 mol or ~20 mol of acid per kg of slag are required to reduce the actual pH from 7 to 2, and that the titration curve indicated that the acid neutralization capacity of the EAFS was very high.

For all three particle sizes and for both slags, the target pH of 12 and 13 alkalines was reached with an accuracy of ± 0.5 pH units. Grubb et al. (2023) replaced the pH 13 target with an additional pH 4 extract because the natural pH of their powdered Caster slag was 12.5, making it impossible to reach the target pH of 13 with base additions alone. In this research, the natural pH of EAF slag (11.18) and Caster slag (11.83) was sufficiently below 13, which made it possible to reach the target value by base additions. As Grubb et al. (2025) stated, when the natural pH value of the material is above 11.5, it becomes impossible to reach pH values of 12 and 13 by means of base additions. As both types of slag in this research were below that value, base additions were required to reach the solution's alkaline pH. According to Mahedi (2019), conducting a multi-day ANC test and plotting its titration curve would provide more precise volumes of acid and base required to reach the target pH values.

However, the dependency of pH attainment on particle size deserves special consideration. In particular, the sub-0.3 mm fraction with estimated specific surface areas of 0.00538 m²/g

(EAF) and $0.00599 \text{ m}^2/\text{g}$ (Caster) had about 16.6 and 16.7 times more surface area available for reactions than the 4.75–9.5 mm fraction and about 63 times more than the >19 mm fraction. This estimate was made using the specific gravities of 3.72 (EAF slag) and 3.34 (Caster slag), with geometric calculations assuming spherical particles. According to Mombelli et al. (2016), contrary to expectations, the leachate pH was almost the same for powder and bulk slag, with only some samples showing a slight increase of pH (5–10%) in case of powder. They came to the conclusion that "the high S/V ratio of the fine particles favors a greater release of Ba and V and a concomitant reduction of Cr if compared with the marginal effect of the reduction of size on the final leachate pH". Current results contradict to their findings as the sub-0.3 mm fraction showed a poorer achievement of pH relative to 4.75–9.5 mm and >19 mm fractions, which implies the effect of particle size on buffering capacity is much stronger for the slags studied in this research than for the ones studied by Mombelli et al. (2016), since in their research leachate pH of fine particles (7–8 μm) and coarser bulk slag (<50 μm) were almost the same. Yu et al. (2025) considered three different slags and found no considerable changes in leaching patterns and concentrations with particle-size differences, which additionally suggests that carbonation of aged slag can reduce its natural pH up to 9 with a little influence on coarser particles, while the same leaching effect of fresh slag can be shown if the aged coarser particles are crushed for experiments. However, in the current study, the sub-0.3 mm fraction was obtained via sieving of as-received stockpiled slag, not via crushing of the coarser fraction, as in the research by Yu et al. (2025). Unlike the crushed fractions, which show fresh alkaline surfaces after crushing, the sieved fine fraction retains its original surface characteristics. Slag samples were collected in June 2025 and were tested within six months. The particle-size effect on pH attainment is not caused by carbonation of the fine fraction but by a larger reactive surface area that is capable of neutralizing added acid during the extraction.

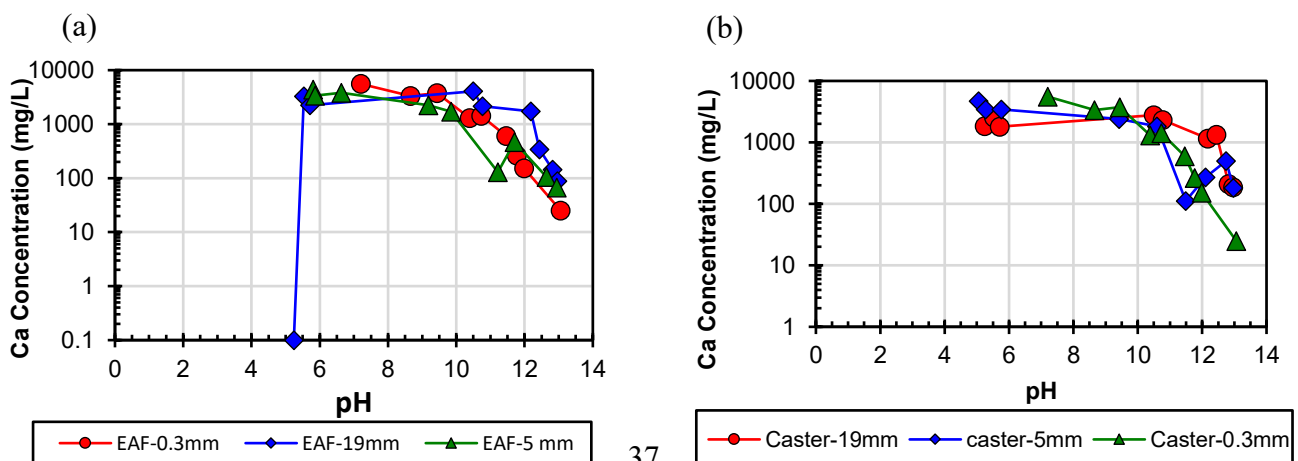
Particle size, achieved pH, and extraction contact time are confounded in this study. In particular, acid and base additions for all three particle-size fractions were calculated according to a single pre-test titration of the sub-0.3 mm fraction. Since the buffering capacity and dissolution kinetics differ between the coarse fractions, the same acid/base volumes provided different pH attainments in each fraction. Besides that, the extraction contact times were deliberately varied to obtain 24 hours for the sub-0.3 mm fraction, 72 hours for the 4.75–9.5 mm fraction, and 144 hours for the >19 mm fraction. Thus, the observed differences in concentrations among particle-size fractions cannot be explained

solely by particle size; they might also result from differences in the achieved pH or extraction contact time. Therefore, the results obtained should be understood as indicating that coarse fractions reach different pH values under the same acid/base schedule and, accordingly, yield different leachate concentrations. To isolate the particle-size effect, a particle-size-specific titration schedule is necessary to ensure consistent pH values across all fractions under comparable extraction contact conditions.

3.3.2.2 Leaching Behavior of Major Elements

The leaching behavior observed in this study is divided into 3 major classifications based on their patterns: cationic behavior (Ca, Mg, Ba, and Fe), amphoteric behavior (Al, Zn), and oxyanionic behavior (B). These patterns are broadly consistent with pH-dependent solubility controls reported for analogous slag systems (Mahedi, 2019; Mombelli et al., 2016; Piatak et al., 2015), and each group is discussed together in the section below.

Steel slag is an example of an alkaline type of waste in which the dissolution process leads to the predominance of cation release, as expected from reports on the dissolution of oxide and silicate phases (Grubb et al., 2023; Loncnar et al., 2022). Even though no mineralogical investigation (such as XRD and sequential extraction) was conducted during the research, the observed cationic composition can be explained by the expected dissolution of minerals in the slag's surface layer under alkaline conditions. Several factors seem to influence the leaching process: the pH value of the eluate, the solubility of the constituent phases, and the liquid-to-solid ratio. As the pH increases, cations become less concentrated due to their lower solubility under alkaline conditions. At low pH (whether experimental or natural), there will be no buffering effect from slag, and therefore the cation concentration in the solution will be high. This means the actual leaching behavior may vary with seasonal changes, but the current study was conducted under laboratory conditions.



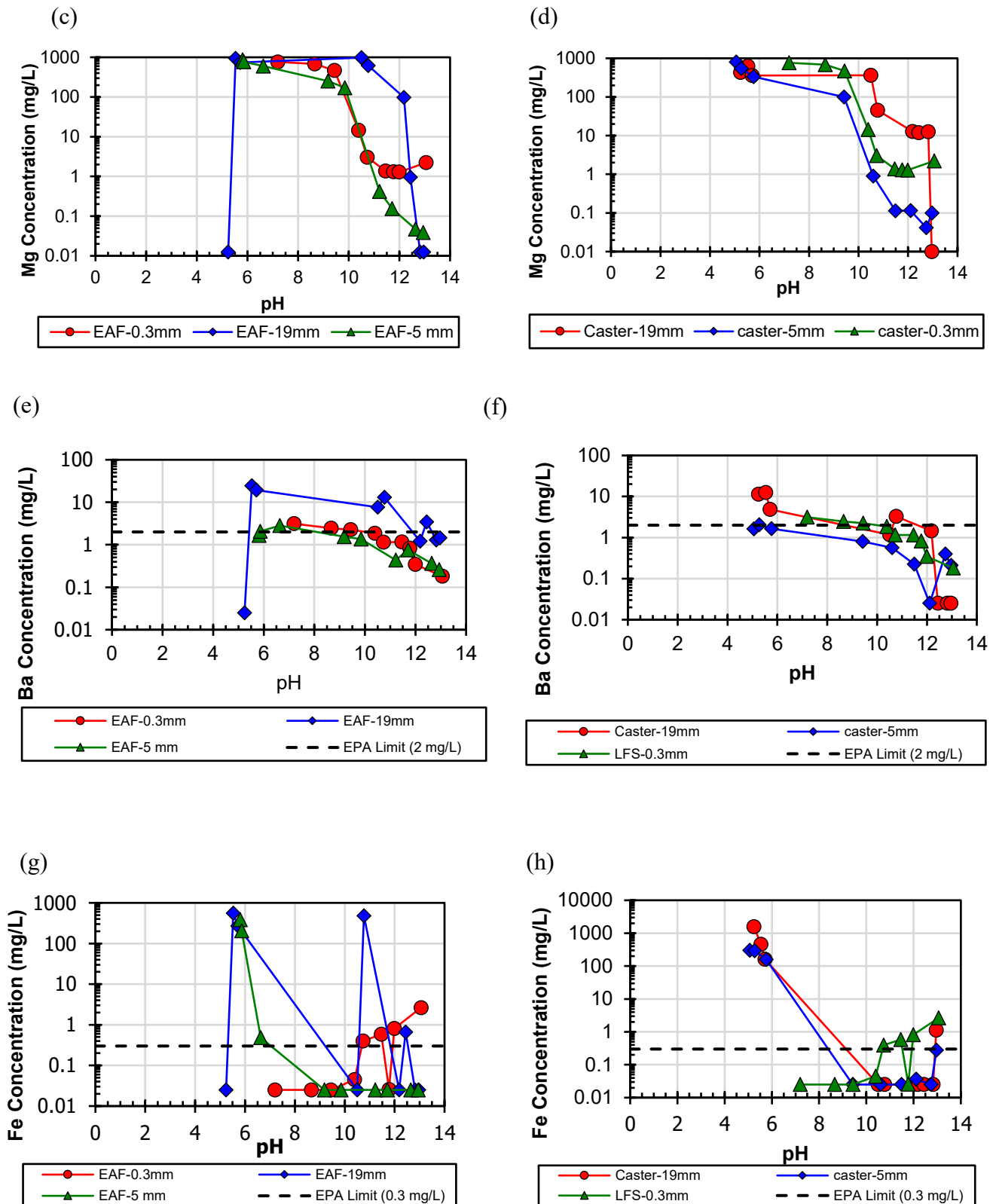


Figure 3.3.2 pH-dependent leachate concentrations (mg/L) of cationic elements — Calcium (Ca), Magnesium (Mg), Barium (Ba), and Iron (Fe) — as a function of actual measured eluate pH for EAF slag and Caster slag across three particle sizes (< 0.3 mm, 4.75–19 mm,

and > 19 mm), EPA Method 1313: (a) Ca — EAF slag, (b) Ca — Caster slag, (c) Mg — EAF slag, (d) Mg — Caster slag, (e) Ba — EAF slag, (f) Ba — Caster slag, (g) Fe — EAF slag, (h) Fe — Caster slag. Horizontal dashed lines indicate applicable regulatory thresholds: Ba — EPA Primary MCL = 2.0 mg/L; Fe — EPA Secondary SDWL = 0.3 mg/L. There is no federal limit for Ca or Mg. X-axis values represent the actual measured eluate pH after agitation. Concentrations below the method detection limit are not plotted.

Calcium had the highest concentration across all pH values, particle sizes, and both slags, as shown in Figure 3.3.2(a and b). Energy dispersive X-ray spectroscopy revealed that the cations in these slags were dominated by calcium at the level of 11.8% to 31.5%, while the proportion of silicon was at 3.2% to 7.3%, and that of magnesium and aluminum were 1.2% to 5.6% and 2.0% to 3.3%, respectively. These compositional results coincide with those reported in the literature, showing Ca^{2+} as the main cationic species and Al and Mg as the second-leaking ions at considerably lower concentrations (Piatak et al., 2015; Engström et al., 2014; Loncnar et al., 2022).

The electric arc furnace slag and Caster furnace slag both exhibited a cationic-species leaching trend, with concentrations increasing in acidic environments and decreasing in alkaline ones. Fine-grained samples (< 0.3 mm) showed the most pronounced decrease in concentration: the maximum concentration in the most acidic medium investigated was 5,570 mg/L for EAFS and 5,110 mg/L for CASTER SLAG, while these samples had 264 mg/L and 242 mg/L, respectively. This cationic leaching trend had statistical significance in the form of significant Pearson correlation coefficients across most of the particle size fractions and two types of slags (EAF 0.3 mm: $r = -0.891$, $p = 0.001$; 5 mm: $r = -0.893$, $p = 0.001$; 19 mm: $r = -0.727$, $p = 0.027$; Caster 0.3 mm: $r = -0.891$, $p = 0.001$; 5 mm: $r = -0.873$, $p = 0.002$). Only the fraction Caster 19 mm ($r = -0.656$, $p = 0.055$) was insignificant, probably due to the small range of pH variation observed for it.

This observed pattern of calcium leaching can be explained through the theory of sequential dissolution, proposed by Grubb et al. (2023) and Loncnar et al. (2022), where lime and portlandite, reported to make up 10–15 wt.% of steel slag, control the first step of calcium solubility, while the next step is a slower dissolution of calcium silicates like larnite (Ca_2SiO_4). Silicon was present in the EDS analysis at 3.2% to 7.3% by weight, confirming the possibility of calcium silicates. Mombelli et al. (2016) stated that the co-release of Al, Ca,

and Mg may be related to larnite content. These phase assignment conclusions should be considered speculative, as XRD and sequential extraction were not performed on the samples used in this experiment.

Magnesium showed a trend like that of calcium across all particle sizes and both slag types, as shown in Figure 3.3.2(c and d). A high concentration of magnesium was observed in acidic pH, and it drastically decreased in response to pH changes toward an alkaline state. This cationic leaching follows the trends reported by Mahedi (2019) for Ca, Mg, Fe, Mn, and SO₄, with concentrations decreasing as effluent pH increases.

The cationic leaching trends of Mg were supported by negative Pearson correlations across all particle sizes and both slag types, although the magnitude and statistical significance varied. For the EAF slag, there were significant correlations found in the 0.3 mm size of particles ($r = -0.893$, $p = 0.001$) and in the 5 mm size of particles ($r = -0.875$, $p = 0.002$); however, the 19 mm size did not have significant correlations ($r = -0.731$, $p = 0.062$). For the Caster slag, there was only a significant correlation found in the 5 mm size of particles ($r = -0.894$, $p = 0.001$); the 0.3 mm size has only 4 detected values ($r = -0.739$, $p = 0.261$) and 19 mm size did not show a significant correlation ($r = -0.731$, $p = 0.062$), probably because of having few detected values. Overall, magnesium was one of the most consistently detected elements for all fractions.

One of the remarkable results is that 19 mm-sized particles leached a higher amount of magnesium than the fine-sized particles. This result has been confirmed by the following two complementary mechanisms, which are explained in the literature. Engström et al. (2014) showed that pH reduction from 12 to 11 is enough to make the Mg (OH)₂ into a soluble form of Mg²⁺, which directly increases Mg leaching; coarser size of particles, which showed lower values of eluate pH, crossed this threshold. Mombelli et al. (2016) also reported that the high concentrations of Ca and Ba in the leachate inhibit Mg dissolution; hence, the high Ca leaching from finer particles at alkaline pH can contribute to Mg inhibition. The solubility of brucite (Mg (OH)₂) is consistent with the decreasing Mg leaching above pH 9; it is the mechanism acting as a limiting factor in alkaline conditions (Loncnar et al., 2022). Grubb et al. (2023) indicated that the nitric acid extraction liquid used in this study does not appear to alter the Mg leaching trends, as Mg release may depend on carbonate mineral solubility rather than the extraction fluid's anion type.

Using energy-dispersive X-ray spectroscopy (EDS), magnesium was detected at 1.2% to 5.6% by weight across multiple sample points, indicating that magnesium is a minor, variable element in both slags. Engström et al. (2014) showed that magnesium leaching cannot be predicted solely by the total magnesium content but also by the mineralogical phase in which magnesium is present. Mombelli et al. (2016) also showed that slags with a lower Mg-Cr spinel phase, which helps immobilize MgO, exhibit higher magnesium leaching. Hence, the mineralogical analysis was not performed in this study. It is noteworthy that the slags in use were freshly collected (less than 8 months old), whereas aged slags typically exhibit a lower natural pH and increased Mg leaching.

Barium (Ba) exhibited a steady cationic leaching pattern regardless of particle size and slag type (Figures 3.3.2(e) and 3.3.2(f)). The Ba concentration was highest at acidic pH and then gradually decreased as pH increased. According to Mombelli et al. (2016), Barium primarily occurs as BaO, which is an alkaline oxide. This compound readily dissolves in water in the presence of other alkaline elements; therefore, Ba migration in the leachate would be consistent with increased inhibition as the environment becomes more alkaline. The effect of particle size on Ba mobility is clear. EAFS produced the highest Ba amount (27.7 mg/L at pH 5.56), approximately 14 times the EPA Primary Maximum Contaminant Level (MCL) standard of 2.0 mg/L, which was used as a conservative screening standard in this study. Additionally, the 0.3 mm and 5 mm fractions exceeded the MCL benchmark at acidic pH (3.13 mg/L at pH 7.2 and 2.82 mg/L at pH 6.63, respectively).

The cationic leaching pattern of Ba in Caster slag was like the above and showed the highest concentration under the most acidic condition (12.6 mg/L in the >19 mm fraction), followed by a reduction in concentration as the pH approached the naturally alkaline values of the slag. The statistical support of Ba cationic leaching pattern was also high with significant negative Pearson correlations in all the particles size and both slag types (EAF 0.3 mm: $r = -0.928$, $p < 0.001$; 5 mm: $r = -0.765$, $p = 0.016$; 19 mm: $r = -0.915$, $p < 0.001$; Caster 0.3 mm: $r = -0.897$, $p = 0.001$; 5 mm: $r = -0.922$, $p = 0.001$; 19 mm: $r = -0.917$, $p = 0.010$), and this was the most significant correlation out of all cationic elements evaluated in this study. The coarser fractions, which had the lowest eluates pH due to low neutralization capacities, correlated with higher Ba concentrations in the leachate since BaO is expected to dissolve more in those environments (Mombelli et al., 2016). While at natural pH, the 0.3 mm and 5 mm fractions

were below the MCL for both slag types, the EAF>19 mm fraction had a level of 3.42 mg/L at the natural pH of 11.68, which surpassed the 2.0 mg/L screening standard, while the Caster >19 mm fraction at natural pH 12.44 was below the detection limit.

The dependence of pH and cationic composition on Fe release was studied for the 5 mm and 19 mm fractions of both slag types, as shown in Figures 3.3.2(g) and 3.3.2(h). A significant increase in Fe concentration was observed upon shifting conditions from alkaline to acidic. The 19 mm particles showed an Fe concentration of 1,585 mg/L at pH 5.24 in caster slag and 704 mg/L at pH 5.56 in EAFS, which is similar to ~1,000 mg/L reported by Yu et al. (2025) at low pH. The increased Fe concentration in Caster Slag corresponds to a higher content of acid-soluble Fe-containing minerals. It means that even a slight change in pH will promote Fe leaching.

The sharp decrease in Fe concentration from acidic to alkaline conditions seen for the 5 mm and 19 mm fractions supports the explanation provided by Grubb et al. (2025), who associated this phenomenon with the solubility of ferrous hydroxide. According to this interpretation, Fe leaching is mainly driven by Fe(II) minerals such as wüstite and spinel, which are abundant in EAF and Caster Slag. At acidic pH, Fe concentrations exceeded the SDWL of 0.3 mg/L by many orders of magnitude. At natural pH, the EAF >19 mm fraction showed 0.955 mg/L (achieved pH 11.68), which exceeds the screening benchmark. Similarly, the Caster >19 mm fraction at target pH 13 (achieved pH 12.96) showed 1.11 mg/L, meaning that Fe release at very alkaline conditions also exceeds the benchmark for coarser fractions.

In contrast to the coarser fractions, the 0.3 mm fraction did not show this trend. Increased Fe concentrations at most alkaline pH (up to 2.64 mg/L at pH 13.06 in EAF and 3.40 mg/L at pH 12.83 in Caster) do not mean a novel inversion of Fe leaching because of the experimental procedure – 0.3 mm fraction has significant acid-neutralizing capacity and therefore does not allow the system to reach the targeted acidic pH. The minimum achieved pH was 7.2 for EAF and 8.66 for Caster. In this case, Fe release at high pH corresponds to dissolution of Fe-containing minerals under very alkaline conditions, while the absence of increased Fe release at the acidic target pH indicates that the latter was not achieved. To attribute the difference in Fe leaching among fractions to their size, it is necessary to compare the fractions at the same actual pH.

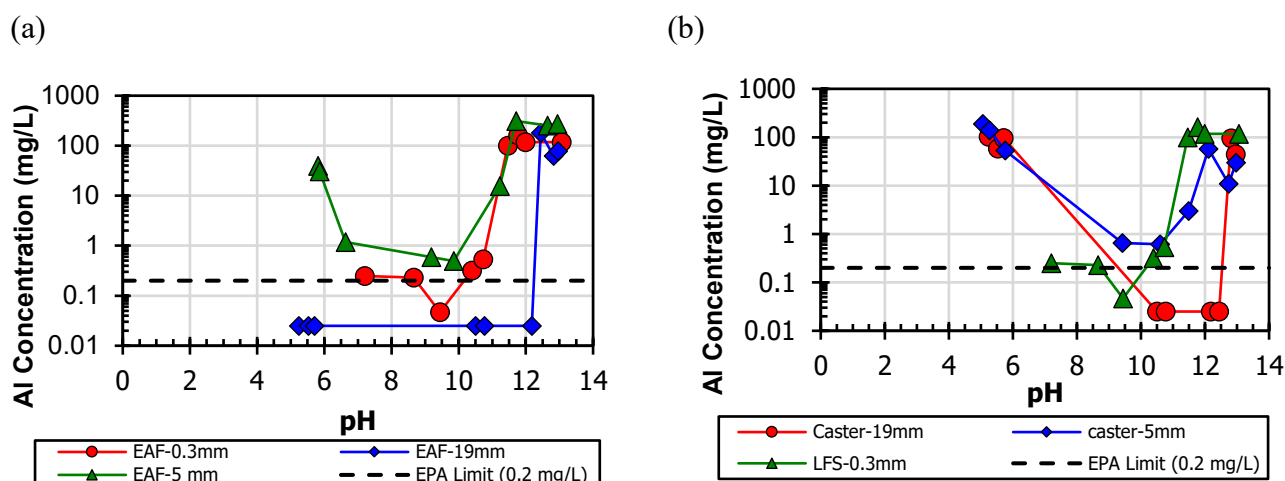


Figure 3.3.3 pH-dependent leachate concentrations (mg/L) of amphoteric elements, Aluminum (Al), as a function of actual measured eluate pH for EAF slag (a) and Caster slag (b) across three particle sizes (< 0.3 mm, 4.75–9.5 mm, and > 19 mm), EPA Method 1313. Horizontal dashed lines represent applicable regulatory thresholds where established. X-axis values represent the actual measured eluate pH after agitation. Concentrations below the method detection limit (MDL) are considered as MDL/2.

The detected aluminum concentrations generally exhibited an amphoteric or U-shaped pattern across the tested pH conditions. However, non-detect values were represented using one-half of the applicable MDL for graphical presentation, and the 19 mm fraction had insufficient detections to establish a complete trend, as seen in Figure 3.3.3(a) and 3.3.3(b). High levels of aluminum were recorded in strongly alkaline and acidic pH environments, while the lowest levels were found in intermediate pH environments. Mahedi (2019) noted a U-shaped pattern for Al and pointed out that the precipitation of $\text{Al}(\text{OH})_3$ decreases Al concentration in a mildly alkaline environment. As shown in the current research, the low Al concentration was observed at pH 9 to 10 (for example, 0.047 mg/L at pH 9.44 for EAF 0.3 mm), which is consistent with the precipitation of $\text{Al}(\text{OH})_3$ under such pH conditions. The speciation changes from AlO_2^- at strongly alkaline pH through $\text{Al}(\text{OH})_3(\text{s})$ to Al_3^+ as pH decreases are well known (Engström et al., 2014). The relatively slow dissolution rates of gehlenite and tricalcium aluminate may explain the current leaching results.

The U-shaped pattern is similar across all fractions; however, its shape and intensity vary with particle size. The highest Al concentration of 162 mg/L was recorded at the natural pH of EAF 0.3 mm, with an achieved pH of 11.77, and decreased to a low value under slightly alkaline conditions. For the Caster 0.3 mm fraction, an Al concentration of 61.0 Mg/L was recorded at an achieved pH of 12.83 (target pH 13); however, the full data set across all pH values was not available to confirm the exact position of the maximum. For the 5 mm fraction, the similar U-shaped trend was recorded; however, Al concentrations in Caster slag were the highest in the acidic environment (188 mg/L at pH 5.09), as it corresponds to the lower pH achieved by coarse particles; meanwhile, for the EAF 5 mm fraction, the maximum Al concentration was recorded at natural pH 11.71 (312 mg/L) and not in the acidic environment. Data for the 19 mm fraction were insufficient to establish a complete trend, and most acidic and intermediate pH values were below the detection limit. According to Mombelli et al. (2016), a direct co-release relationship between Ca and Al is associated with the dissolution of the hydraulic phase in EAF slags; in this research, the inverse relation was observed, as the highest Al concentrations correspond to intermediate to high Ca concentrations and not to the lowest Ca concentrations, as is observed in a strongly acidic environment.

Al concentrations exceeded the EPA SMCL of 0.2 mg/L under almost all test conditions for both slag types. High Al concentrations at strongly alkaline pH correspond to the dissolution of aluminous phases like brownmillerite and mayenite. Insolubility windows of Al, Fe, and Mn in this research represent the conditions closer to the real-field situation, as nitric acid-based extraction fluid used in the EPA Method 1313 does not cause the shift of the window by 1 to 1.5 pH units in comparison to sulfate-based extraction systems according to Grubb et al. (2023).

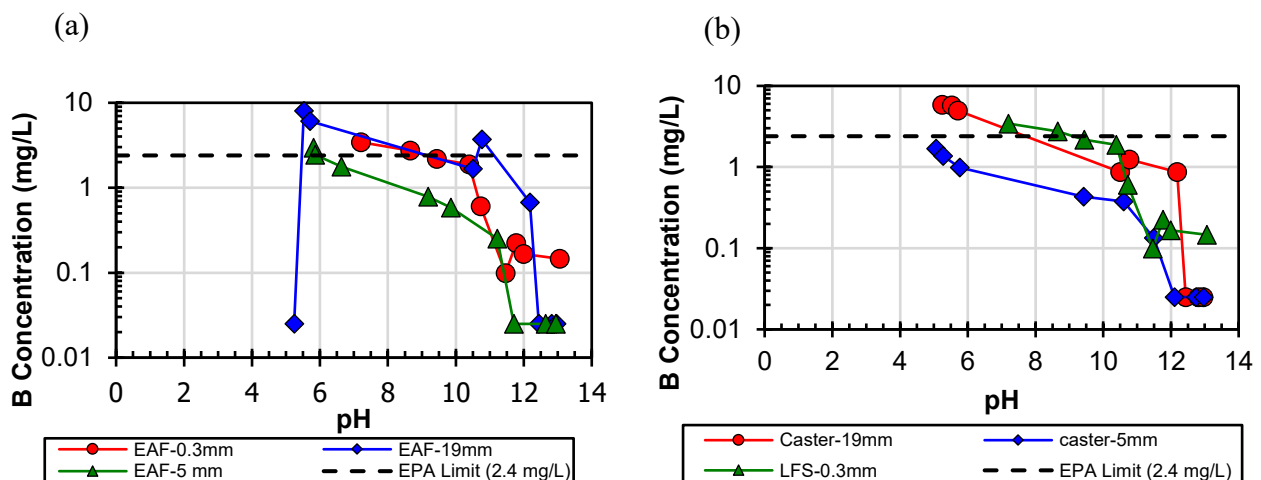


Figure 3.3.4 pH-dependent leachate concentrations (mg/L) of Boron (Ba) are a function of actual measured eluate pH for EAF slag (a) and Caster slag (b) at three particle sizes (< 0.3 mm, 4.75–9.5 mm, and > 19 mm), EPA Method 1313. Horizontal dashed lines represent applicable regulatory thresholds where established. X-axis values represent the actual measured eluate pH after agitation. Concentrations below the method detection limit (MDL) are considered as MDL/2.

A different trend was observed for boron, contrary to that for cations, as it exhibited oxyanion-type leaching behavior irrespective of particle size and slag type. The trend shows a high release concentration at low pH and a decrease as pH increases toward alkaline conditions (Yu et al., 2025). Boron emerged as the element of concern at low pH, where COPCs exceeded 8. Boron exceeds in our coarser fractions (5mm and 19mm) below pH 8, since exceedances of the EPA health reference level (HRL) of 1.4 mg/L were observed below pH 8. However, in our 0.3 mm fraction, there was a deviation from the trend, with boron exceeding the trend at pH levels as high as 10.39 (1.88 mg/L). This was probably due to the high buffering capacity of the finer particles, which prevented the system from reaching acidic pH, at which the maximum release of boron occurs. In all fractions with exceedances, boron concentrations increased as pH decreased. For example, in EAF 0.3 mm, the boron concentration was 3.44 mg/L at pH of 7.2, EAF 5 mm, it was 2.96 mg/L at pH 5.81, and EAF 19 mm, it was 8.05 mg/L at pH 5.19. The oxyanion leaching trend of boron was statistically proven with significant negative Pearson correlations in most of the fractions and both slag types, with the 5mm fraction showing the highest correlations in this study (EAF 5 mm: $r = -0.994$, $p < 0.001$; Caster 5 mm: $r = -0.945$, $p = 0.004$). The 19 mm fraction did not show significance ($r = -0.802$, $p = 0.055$), probably because there were few exceedances of boron above pH 8 in this fraction. A particle-dependent trend was observed in boron, with larger particles showing higher concentrations at low pH, suggesting that coarser fractions reach more acidic pH values, which favours boron leaching.

		EAF Slag — < 0.3 mm									Ladle / Caster Slag — < 0.3 mm								
Metal (Limit)	Target pH	13	12	10.5	9	8	Natural (11.18)	5.5	4	2	13	12	10.5	9	8	Natural (11.83)	5.5	4	
	Achieved pH	13.06	11.99	11.46	10.73	10.39	11.77	9.44	8.66	7.2	12.83	12.12	11.26	10.71	10.17	11.94	9.39	9.36	
Al	SDWL=0.2	117	117	100	0.538	0.320	162	0.047	0.229	0.250	61.0	51.0	n.d	1.16	0.262	52.5	0.150	0.113	
As	MCL=0.01	0.141	0.189	0.115	0.584	0.185	0.277	n.d	n.d	0.310	0.087	0.084	0.149	0.518	n.d	0.106	n.d	n.d	
B	HRL=1.4	0.146	0.167	0.099	0.606	1.88	0.224	2.18	2.74	3.44	0.083	0.090	n.d	0.511	0.599	0.093	1.41	1.45	
Ba	MCL=2.0	0.181	0.346	1.16	1.15	1.85	0.825	2.25	2.46	3.13	0.039	0.218	0.491	0.657	1.01	0.202	1.45	1.53	
Be	MCL=0.004	0.187	0.342	1.16	1.26	1.98	0.800	2.36	2.62	3.30	n.d	0.258	0.482	0.676	1.02	0.200	1.51	1.58	
Ca	—	25.0	153	601	1420	1304	264	3756	3350	5570	52.0	198	882	1394	1886	242	4270	4385	
Cd	MCL=0.005	n.d	n.d	n.d	n.d	n.d	n.d	1.72	2.65	3.57	n.d	n.d	n.d	n.d	n.d	n.d	1.65	1.74	
Cr	MCL=0.1	0.355	0.077	0.028	n.d	n.d	0.059	n.d	n.d	n.d	0.395	n.d	0.016	n.d	n.d	n.d	n.d	n.d	
Fe	SDWL=0.3	2.64	0.809	0.583	0.398	0.045	0.025	n.d	n.d	n.d	3.40	1.18	0.117	0.488	0.101	0.066	0.041	n.d	
Mg	—	2.22	1.28	1.38	3.03	14.4	1.31	469	680	764	2.33	n.d	n.d	n.d	n.d	449	460	504	
Mn	SDWL=0.05	0.077	0.078	0.117	4.26	16.2	0.093	0.054	16.6	207	0.175	0.096	0.346	3.20	0.057	1.12	n.d	n.d	
Ni	—	0.318	0.077	n.d	n.d	n.d	n.d	n.d	14.8	209	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	
Pb	AL=0.015	0.382	n.d	n.d	n.d	n.d	n.d	0.222	0.050	n.d	0.138	n.d	n.d	0.231	0.349	n.d	0.210	0.045	
V	—	0.136	n.d	n.d	0.230	0.352	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	
Zn	SDWL=5.0	0.133	0.064	n.d	0.238	0.364	0.043	0.212	n.d	0.063	0.088	0.056	n.d	n.d	0.028	0.045	0.011	n.d	

Table 3.3.2: Leachate concentrations (mg/L) of all target metals for EAF slag and Caster slag at nine target pH levels, < 0.3mm particle size fraction, EPA Method 1313. Values represent individual extraction results; Leachate concentrations with one-half-MDL substitution for nondetect values¹

Metal		EAF Slag - < 0.3 mm									Ladle / Caster Slag - < 0.3 mm								
(Limit)	Target pH	13	12	10.5	9	8	Natural -11.18	5.5	4	2	13	12	10.5	9	8	Natural -11.83	5.5	4	

¹ For concentrations below the analyte-specific MDL, values were substituted as one-half of the corresponding MDL for graphical and tabular presentation. Substituted values are estimates and do not represent exact measured concentrations. Detected concentrations are reported as measured.

Table	Achieved pH		13.06	11.99	11.46	10.73	10.39	11.77	9.44	8.66	7.20	12.83	12.12	11.26	10.71	10.17	11.94	9.39	9.36	3.3.3
	Al	SDWL=0.2	117	117	100	0.54	0.32	162	0.05	0.23	0.25	61	51	0.01	1.16	0.26	52.5	0.15	0.11	
	As	MCL=0.01	0.14	0.19	0.12	0.58	0.19	0.28	0.01	0.01	0.31	0.09	0.08	0.15	0.52	0.01	0.11	0.01	0.01	
	B	HRL=1.4	0.15	0.17	0.10	0.61	1.88	0.22	2.18	2.74	3.44	0.08	0.09	0.01	0.51	0.60	0.09	1.41	1.45	
	Ba	MCL=2.0	0.18	0.35	1.16	1.15	1.85	0.83	2.25	2.46	3.13	0.04	0.22	0.49	0.66	1.01	0.20	1.45	1.53	
	Be	MCL=0.004	0.19	0.34	1.16	1.26	1.98	0.80	2.36	2.62	3.30	0.01	0.26	0.48	0.68	1.02	0.20	1.51	1.58	
	Ca	—	25	153	601	1420	1304	264	3756	3350	5570	52	198	882	1394	1886	242	4270	4385	
	Cd	MCL=0.005	0.01	0.01	0.01	0.01	0.01	0.01	1.72	2.65	3.57	0.01	0.01	0.01	0.01	0.01	0.01	1.65	1.74	
	Cr	MCL=0.1	0.36	0.08	0.03	0.01	0.01	0.06	0.01	0.01	0.01	0.40	0.01	0.02	0.01	0.01	0.01	0.01	0.01	
	Fe	SDWL=0.3	2.64	0.81	0.58	0.40	0.05	0.03	0.01	0.01	0.01	3.40	1.18	0.12	0.49	0.10	0.07	0.04	0.01	
	Mg	—	2.22	1.28	1.38	3.03	14.40	1.31	469	680	764	2.33	0.01	0.01	0.01	0.01	449	460	504	
	Mn	SDWL=0.05	0.08	0.08	0.12	4.26	16.20	0.09	0.05	16.60	207.00	0.18	0.10	0.35	3.20	0.06	1.12	0.01	0.01	
	Ni	—	0.32	0.08	0.01	0.01	0.01	0.01	0.01	0.01	14.80	209.00	0.01	0.01	0.01	0.01	0.01	0.01	0.01	
	Pb	AL=0.015	0.38	0.03	0.03	0.03	0.03	0.03	0.22	0.05	0.03	0.14	0.03	0.03	0.23	0.35	0.03	0.21	0.05	
	V	—	0.14	0.05	0.05	0.23	0.35	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	
	Zn	SDWL=5.0	0.13	0.06	0.01	0.24	0.36	0.04	0.21	0.01	0.06	0.09	0.06	0.01	0.01	0.03	0.05	0.01	0.01	

Leachate concentrations (mg/L) of all target metals for EAF slag and Caster slag at nine target pH levels, 4.75-9.5 mm (5 mm) particle size fraction, EPA Method 1313. Leachate concentrations with one-half-MDL substitution for nondetect values.²

Metal (Limit)	Target pH	EAF Slag - 4.75 – 19 mm (5 mm)									Ladle / Caster Slag - 4.75 – 19 mm (5 mm)								
		13	12	10.5	9	8	Natural -11.18	5.5	4	2	13	12	10.5	9	8	Natural -11.18	5.5	4	2
	Achieved pH	12.94	12.64	11.22	9.85	9.18	11.71	6.63	5.86	5.81	12.97	12.74	11.49	10.6	9.42	12.11	5.76	5.27	5.09
Al	SDWL=0.2	274	252	15.6	0.493	0.593	312	1.19	30.9	39.2	29.9	10.9	2.98	0.614	0.648	57	53.5	140	188
As	MCL=0.01	0.143	0.157	0.012	0.012	0.012	0.224	0.012	0.012	0.012	0.012	0.012	0.012	0.012	0.012	0.012	0.012	0.012	0.012

² For concentrations below the analyte-specific MDL, values were substituted as one-half of the corresponding MDL for graphical and tabular presentation. Substituted values are estimates and do not represent exact measured concentrations. Detected concentrations are reported as measured.

B	HRL=1.4	0.012	0.012	0.252	0.585	0.783	0.012	1.78	2.44	2.96	0.012	0.012	0.134	0.376	0.432	0.012	0.989	1.37	1.69
Ba	MCL=2.0	0.259	0.362	0.434	1.35	1.55	0.756	2.82	2.06	1.65	0.209	0.397	0.224	0.566	0.799	0.012	1.64	2.04	1.62
Ca	—	67	106	129	1695	2247	465	3815	3365	4395	182	498	112	1818	2403	271	3445	3445	4705
Cd	MCL=0.005	0.012	0.012	0.012	0.665	2.27	0.012	5.15	6.3	7.9	0.012	0.012	0.012	0.012	0.95	0.012	3.02	4.17	6.5
Fe	SDWL=0.3	0.012	0.012	0.012	0.012	0.012	0.012	0.481	206	387	0.278	0.012	0.012	0.012	0.012	0.037	158	291	301
Mg	—	0.038	0.047	0.416	170	254	0.155	600	774	864	0.1	0.042	0.114	0.902	99.6	0.115	336	546	798
Mn	SDWL=0.05	0.012	0.012	0.012	0.012	0.012	0.012	132	255	292	0.012	0.012	0.012	0.012	0.012	n.d	29.8	61.8	111
Ni	—	0.012	0.012	0.012	0.012	0.012	0.012	330	0.116	0.19	0.012	0.012	0.012	0.012	0.012	0.012	82	134	271
V	—	0.086	0.032	0.283	0.473	0.557	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.095	0.078	0.05	0.114	0.164	0.093
Zn	SDWL=5.0	0.072	0.012	0.012	0.012	0.012	0.012	1.1	4.77	5.96	0.259	0.091	0.012	0.012	0.012	0.018	1.13	4.61	6.55

Table 3.3.4 Leachate concentrations (mg/L) of all target metals for EAF slag and Caster slag at nine target pH levels,> 19 mm particle size fraction, EPA Method 1313. Values represent individual extraction results; Leachate concentrations with one-half-MDL substitution for nondetect values.³

		EAF Slag — > 19 mm									Caster Slag — > 19 mm								
Metal (Limit)	Target pH	13	12	10.5	9	8	Natural (11.18)	5.5	4	2	13	12	10.5	9	8	Natural (11.18)	5.5	4	2
	Achieved pH	12.75	12.43	10.15	7.64	5.75	11.68	5.45	5.19	5.56	12.96	12.82	12.18	10.5	10.77	12.44	5.71	5.53	5.24
Al	SDWL=0.2	78.0	62.5	0.012	0.012	0.012	181	0.012	0.012	0.012	44.5	95.0	0.012	0.012	0.012	0.012	96.5	58.0	103
B	HRL=1.4	0.012	0.012	0.670	1.67	3.70	0.012	6.10	8.05	4.85	0.012	0.012	0.865	0.865	1.24	0.012	4.97	5.75	5.85
Ba	MCL=2.0	1.45	1.29	1.20	7.60	12.9	3.42	19.2	24.3	27.7	0.012	0.012	1.45	1.17	3.25	0.012	4.83	12.6	11.3
Ca	—	88.0	145	1730	4060	2140	342	2225	3300	4950	188	210	1155	2780	2330	1335	1800	2560	1855
Cd	MCL=0.005	0.012	0.012	0.012	2.83	4.51	0.012	6.95	7.15	8.65	0.012	0.012	0.012	2.16	0.012	0.012	6.45	7.45	7.40
Cr	MCL=0.1	0.012	0.012	0.012	0.012	0.012	0.660	0.012	0.012	0.012	0.012	0.012	0.012	0.012	0.012	0.012	0.012	0.012	0.012

³ For concentrations below the analyte-specific MDL, values were substituted as one-half of the corresponding MDL for graphical and tabular presentation. Substituted values are estimates and do not represent exact measured concentrations. Detected concentrations are reported as measured.

Fe	SDWL=0.3	0.012	0.012	0.012	0.012	478	0.955	269	555	704	1.11	0.012	0.012	0.012	0.012	0.012	162	460	1585
Mg	—	0.005	0.005	98.0	980	615	0.005	740	935	1855	0.005	12.6	12.8	364	45.5	11.9	359	625	433
Mn	SDWL=0.05	0.012	0.012	0.012	398	300	0.012	386	565	1075	0.012	0.012	0.012	0.012	0.012	0.012	104	265	180
Ni	—	0.012	0.012	0.012	0.012	0.012	0.012	0.012	0.012	8.45	0.012	0.012	0.012	0.012	0.012	0.012	0.012	1.31	8.65
Pb	AL=0.015	0.025	0.025	0.025	21.0	0.025	0.025	0.025	0.025	0.025	0.025	0.025	0.025	0.025	14.2	0.025	0.025	75.5	0.855
V	—	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.855
Zn	SDWL=5.0	0.012	0.012	0.012	0.012	0.770	0.012	1.29	5.15	0.012	0.012	0.012	0.012	0.012	0.012	0.012	65.0	20.9	17.9

Complete sets of leachate concentrations for all target metals across all particle-size fractions and pH levels can be found in Tables 3.3.2- 3.3.4. Some elements showed significantly increased leachate concentrations at acidic pH values due to the dissolution of metal-containing minerals at low pH, which is consistent with previously published data on EAF and Caster slag leaching. Namely, iron leachate concentration was up to 1,585 mg/L in the Caster 19 mm fraction at pH 5.24; manganese – 1,075 mg/L in the EAF 19 mm fraction at pH 5.56; nickel – 330 mg/L in the EAF 5 mm fraction at pH 5.81; lead – 75.5 mg/L in the Caster 19 mm fraction at pH 5.53; and zinc – 65.0 mg/L in the Caster 19 mm fraction at pH 5.71. This magnitude of concentration agrees with previous LEAF Method 1313 testing results, when more than 1,000 mg/L concentration of manganese was obtained at a low pH level (Yu et al., 2024) and high total iron content (26.8% Fe₂O₃) in EAF slags (Proctor et al., 2000; Piatak et al., 2015). The significant increase in cationic metals releases at low pH values is caused by the progressive dissolution of oxide and silicate minerals (wustite, spinel, litharge) at decreasing pH values below their solubility limits, which was previously described in steel-slag leaching research (Mombelli et al., 2016; Engström et al., 2014).

Several isolated measurements of Ni, Pb, Cr, and Fe at alkaline pH values in the 0.3 mm fraction (Fe – 3.40 mg/L at pH 12.83; Ni – 209 mg/L at pH 7.2; Pb – 0.382 mg/L at pH 13.06) require careful consideration. These values were measured in case the 0.3 mm fraction did not reach the target acidic pH due to considerable buffering capacity. It is rare to obtain a non-zero concentration of cationic metals at alkaline pH values. Possible reasons can include: (a) high specific surface area of the 0.3 mm fraction and the release of trace amounts of metals from adsorption phases during prolonged equilibration time; (b) spectral interferences in ICP-OES analysis (e.g., Fe interference on adjacent wavelengths of analytes at high concentrations of dissolved solids); or (c) true but very low-level release of metals from small amount of minor mineral phases not controlled by bulk solubility. These isolated measurements cannot be considered in the context of established pH-dependent leaching behavior due to insufficient data and a lack of Method 1313 replication. However, these values are provided in Tables 3.3.2- 3.3.4 for independent validation.

Certain elements (e.g., Cd, Cr, Pb, Se, V) were measured at only one to three pH levels in a certain particle-size fraction. Frequently, these measurements had very close values to the method detection limit. Due to lack of observations and replication, the pH-dependent leaching pattern cannot be reliably identified, but these observations are still ecologically

relevant as even single exceedance of drinking-water screening benchmarks (e.g., Cd – 7.90 mg/L compared to MCL 0.005 mg/L in the EAF 5 mm fraction at pH 5.81; Pb – 75.5 mg/L compared to AL 0.015 mg/L in the Caster 19 mm fraction at pH 5.53) demonstrates that constituent release is possible under similar conditions. Interpretation of these measurements is further complicated by the lack of replicate measurements at each pH level, the combination of particle size and achieved pH values, and the use of drinking-water screening benchmarks rather than site-specific release thresholds. These aspects are discussed in the Limitations section.

3.4 Conclusion

Results of batch tests performed by the EPA using the two methods for slag materials collected from Nucor Steel in Norfolk are as follows. All three replicates of EAF and CASTER SLAG met the RCRA Toxicity Characteristic screening limits when evaluated by the TCLP method under 40 CFR Part 261.24. In turn, results from parallel batch extraction according to Method 1313 (LEAF) indicate significant pH-dependent leaching, with several constituent concentrations exceeding drinking water screening benchmarks across a wider pH range than expected. Natural pH of the EAF 0.3 mm fraction resulted in the following constituent concentrations in the leachate: Al – 162 mg/L (SDWL 0.2 mg/L), As – 0.277 mg/L (MCL 0.01 mg/L), and Mn – 0.093 mg/L (SDWL 0.05 mg/L). At the most alkaline pH achieved (13), exceedances were recorded for Cr (0.355 mg/L, MCL 0.1 mg/L), Fe (2.64 mg/L, SDWL 0.3 mg/L), and Pb (0.382 mg/L, AL 0.015 mg/L) in the EAF 0.3 mm fraction. At acidic pH achieved in coarser fractions, Ba, Fe, Mn, and Zn exceeded screening limits. EAF 19 mm Ba was measured at 27.7 mg/L (MCL 2.0 mg/L) at pH 5.56, and Mn – 1,075 mg/L (SDWL 0.05 mg/L) at pH 5.56. The TCLP alone is not sufficient to define leaching risks, as it evaluates slag under a single acidic condition and does not capture the pH-dependent behavior of slag leaching determined using Method 1313.

Acid neutralization capacity (ANC) is a fundamental physical factor that influences all leaching observations, as it governs the material's ability to reach the target pH during extraction. A particle size of 0.3 mm has a surface area 16.6 times higher than that of a 5 mm particle and 63 times higher than that of a 19 mm particle, thereby increasing acid consumption and demonstrating its buffering properties in achieving alkaline pH within the

target pH range. With increasing particle size, the difference between the achieved and target pH decreased by 1 to 2 pH units. As a result, metals became more concentrated in the leachate, especially in Ba, Fe, Mg, and B. This dependency was consistent and prevalent across both slag types, indicating that coarser particles are more prone to leaching under acidic field conditions.

Distinct patterns of element leaching are governed by the geochemical behavior of these elements. Calcium is dominant in the entire range of pH values for both slag types due to the sequential dissolution of portlandite, larnite, and other calcium silicate phases. Magnesium, Barium, and Iron show cationic leaching with increasing concentration under acidic conditions and decreasing under natural and alkaline conditions, due to the solubility of brucite, the inhibition of BaO dissolution, and the precipitation of iron hydroxide. Aluminum is amphoteric, with minimum solubility at pH 9-10 due to the self-limiting release of the element under moderately alkaline field conditions. Boron shows oxyanionic pattern with concentration increase as pH decreases; B exceeded the EPA health reference level (HRL) of 1.4 mg/L at pH from 6 to 11 in all particle size fractions, with the maximum exceeding 8.05 mg/L in EAF 19 mm fraction at pH 5.19. The novel observation is the inversion of the Fe leaching pattern at the 0.3 mm fraction, where Fe concentration is higher at alkaline pH rather than at acidic pH. This was due to the high buffering capacity of fine particles, which prevented the system from reaching the acidic pH required to drive Fe release.

According to the TCLP, both EAFS and CS are non-hazardous. However, Method 1313 results showed exceedances of the screening benchmark under both acidic and alkaline conditions, thus demonstrating the pH- and particle-size dependence of leaching risk. The 19 mm fraction exceeded the MCL of Ba under acidic conditions, and the 5 mm fraction exceeded the SDWL of Fe and Mn under acidic conditions. These results indicate that coarser aggregates can release higher concentrations of some elements in contact with acidic soil. As particle size, pH, and contact time were confounded in this study, and Method 1313 conditions were not replicated, further testing and scenario-based transport assessment are necessary to determine suitability for unencapsulated reuse.

3.5 Limitations

Some limitations of this study need to be considered. The nature of the TCLP extraction fluid was not independently confirmed prior to the test. Method 1313 testing used modified particle-size fractions (0.3 mm, 5 mm, and 19 mm) rather than a complete field-relevant gradation. The 0.3 mm fraction failed to achieve three of the five acidic target pH values due to buffering. The time of contact was not constant for different particle sizes, as finer fractions equilibrated faster than coarser fractions. Method 1313 conditions were not replicated; each pH–particle-size combination was extracted once. Drinking water-based benchmarks (MCLs, SMCLs, and HRLs) were used only as screening criteria and not as regulatory limits for landfill leachate, and they do not account for dilution, attenuation, or transport of the chemicals. Field transport, dilution, and attenuation modeling were not done. The control of mineral phases on leaching patterns was assumed based on the literature but not confirmed by XRD analysis of slag samples. Non-detected values were treated as values below the detection level rather than as missing. Pearson correlation results for elements with few detections. Finally, ICP-OES analytical quality values were below the detection limit and are therefore not included in the audit table.

Appendix

Table A.1 Pearson correlation coefficients, coefficients of determination, number of detected values, p-values, and statistical significance for all target metals across three particle-size fractions (< 0.3 mm, 4.75– mm, and > 19 mm) – EAF slag, EPA Method 1313.

Particle Size	Metals	Pearson r	R ²	n (detected)	p-value	Significant?	Direction
0.3mm	Al	0.6074	0.3689	9	0.083	Not significant	Increases with pH
	As	-0.3459	0.1197	7	0.447	Not significant	Decreases with pH
	B	-0.8877	0.7880	9	0.001	Significant	Decreases with pH
	Ba	-0.9281	0.8613	9	0.000	Significant	Decreases with pH
	Be	-0.9230	0.8519	9	0.000	Significant	Decreases with pH
	Ca	-0.8911	0.7941	9	0.001	Significant	Decreases with pH
	Cd	-0.9964	0.9927	3	0.054	Insufficient data	--
	Cr(total)	0.6146	0.3777	4	0.385	Insufficient data	--
	Fe	0.8480	0.7192	6	0.033	Significant	Increases with pH
	Mg	-0.8627	0.7442	9	0.003	Significant	Decreases with pH
	Mn	-0.6422	0.4124	9	0.062	Not significant	Decreases with pH
	Ni	-0.7363	0.5421	4	0.264	Insufficient data	--
	Pb	ND	ND	1	ND	Insufficient data	--
5mm	V	0.1613	0.0260	5	0.796	Not significant	Increases with pH
	Zn	0.0466	0.0022	7	0.921	Not significant	Increases with pH
	Al	0.4714	0.2222	9	0.200	Not significant	Increases with pH
	As	-1.0000	1.0000	3	0.004	Insufficient data	--
	B	-0.9942	0.9885	6	0.000	Significant	Decreases with pH
	Ba	-0.7650	0.5853	9	0.016	Significant	Decreases with pH
	Ca	-0.8931	0.7976	9	0.001	Significant	Decreases with pH

	Cd	-0.9919	0.9838	5	0.001	Significant	Decreases with pH
	Cr(total)	ND	ND	0	ND	Insufficient data	--
	Fe	-0.9929	0.9859	3	0.076	Insufficient data	--
	Mg	-0.8937	0.7986	9	0.001	Significant	Decreases with pH
	Mn	-0.9286	0.8623	3	0.242	Insufficient data	--
	Ni	0.8219	0.6755	3	0.386	Insufficient data	--
	V	-0.9665	0.9342	5	0.007	Significant	Decreases with pH
	Zn	-0.8554	0.7318	4	0.145	Insufficient data	--
19mm	Al	-0.9619	0.9253	3	0.176	Insufficient data	--
	As	ND	ND	0	ND	Insufficient data	--
	B	-0.8023	0.6437	6	0.055	Not significant	Decreases with pH
	Ba	-0.9148	0.8368	9	0.001	Significant	Decreases with pH
	Be	ND	ND	0	ND	Insufficient data	--
	Ca	-0.7267	0.5281	9	0.027	Significant	Decreases with pH
	Cd	-0.9725	0.9458	5	0.005	Significant	Decreases with pH
	Cr(total)	ND	ND	0	ND	Insufficient data	--
	Fe	-0.6512	0.4241	5	0.234	Not significant	Decreases with pH
	Mg	-0.7310	0.5344	7	0.062	Not significant	Decreases with pH
	Mn	-0.8444	0.7130	5	0.072	Not significant	Decreases with pH
	Ni	ND	ND	1	ND	Insufficient data	--
	Pb	ND	ND	0	ND	Insufficient data	--
	V	ND	ND	0	ND	Insufficient data	--
	Zn	-0.8483	0.7196	3	0.355	Insufficient data	--

Particle Size	Metals	Pearson r	R ²	n (detected)	p-value	Significant?	Direction
0.3mm	Al	0.607	0.369	9	0.083	Not significant	Increases with pH
	As	-0.346	0.120	7	0.447	Not significant	Decreases with pH
	B	-0.888	0.788	9	0.001	Significant	Decreases with pH
	Ba	-0.928	0.861	9	0.000	Significant	Decreases with pH
	Be	-0.923	0.852	9	0.000	Significant	Decreases with pH
	Ca	-0.891	0.794	9	0.001	Significant	Decreases with pH
	Cd	-0.996	0.993	3	0.054	Insufficient data	--
	Cr(total)	0.615	0.378	4	0.385	Insufficient data	--
	Fe	0.848	0.719	6	0.033	Significant	Increases with pH
	Mg	-0.863	0.744	9	0.003	Significant	Decreases with pH
	Mn	-0.642	0.412	9	0.062	Not significant	Decreases with pH
	Ni	-0.736	0.542	4	0.264	Insufficient data	--
	Pb	ND	ND	1	ND	Insufficient data	--
	V	0.161	0.026	5	0.796	Not significant	Increases with pH
	Zn	0.047	0.002	7	0.921	Not significant	Increases with pH
5mm	Al	0.471	0.222	9	0.200	Not significant	Increases with pH
	As	-1.000	1.000	3	0.004	Insufficient data	--
	B	-0.994	0.989	6	0.000	Significant	Decreases with pH
	Ba	-0.765	0.585	9	0.016	Significant	Decreases with pH
	Ca	-0.893	0.798	9	0.001	Significant	Decreases with pH
	Cd	-0.992	0.984	5	0.001	Significant	Decreases with pH
	Fe	-0.993	0.986	3	0.076	Insufficient data	--
	Mg	-0.894	0.799	9	0.001	Significant	Decreases with pH
	Mn	-0.929	0.862	3	0.242	Insufficient data	--
	Ni	0.822	0.676	3	0.386	Insufficient data	--

	V	-0.967	0.934	5	0.007	Significant	Decreases with pH
	Zn	-0.855	0.732	4	0.145	Insufficient data	--
19mm	Al	-0.962	0.925	3	0.176	Insufficient data	--
	B	-0.802	0.644	6	0.055	Not significant	Decreases with pH
	Ba	-0.915	0.837	9	0.001	Significant	Decreases with pH
	Be	ND	ND	0	ND	Insufficient data	--
	Ca	-0.727	0.528	9	0.027	Significant	Decreases with pH
	Cd	-0.973	0.946	5	0.005	Significant	Decreases with pH
	Fe	-0.651	0.424	5	0.234	Not significant	Decreases with pH
	Mg	-0.731	0.534	7	0.062	Not significant	Decreases with pH
	Mn	-0.844	0.713	5	0.072	Not significant	Decreases with pH
	Zn	-0.848	0.720	3	0.355	Insufficient data	--

Table A.2 Pearson correlation coefficients (r), coefficients of determination (R^2), number of detected values (n), p-values, statistical significance, and direction of pH-dependent leaching trends for all target metals across three particle size fractions (< 0.3 mm, 4.75–9.5 mm, and > 19 mm) — Caster slag, EPA Method 1313 batch leaching test.

Particle Size	Metals	Pearson r	R^2	n (detected)	p-value	Significant?	Direction
0.3mm	Al	0.600	0.369	8	0.110	Not significant	Increases with pH
	As	0.041	0.002	6	0.938	Not significant	Increases with pH
	B	-0.886	0.784	8	0.003	Significant	Decreases with pH
	Ba	-0.897	0.804	9	0.001	Significant	Decreases with pH
	Be	-0.875	0.765	8	0.004	Significant	Decreases with pH
	Ca	-0.891	0.793	9	0.001	Significant	Decreases with pH

	Cd	-0.926	0.857	3	0.247	Insufficient data	--
	Cr (mg/L)	1.000	1.000	2	ND	Insufficient data	--
	Fe	0.772	0.596	7	0.042	Significant	Increases with pH
	Mg	-0.893	0.798	9	0.001	Significant	Decreases with pH
	Mn	-0.838	0.702	7	0.019	Significant	Decreases with pH
	V	0.199	0.040	5	0.748	Not significant	Increases with pH
	Zn	0.896	0.804	5	0.039	Significant	Increases with pH
5mm	Al	-0.825	0.680	9	0.006	Significant	Decreases with pH
	B	-0.994	0.988	6	0.000	Significant	Decreases with pH
	Ba	-0.922	0.851	8	0.001	Significant	Decreases with pH
	Ca	-0.873	0.762	9	0.002	Significant	Decreases with pH
	Cd	-0.995	0.990	4	0.005	Insufficient data	--
	Fe	-0.844	0.713	5	0.072	Not significant	Decreases with pH
	Mg	-0.875	0.765	9	0.002	Significant	Decreases with pH
	Mn	-0.999	0.999	3	0.024	Insufficient data	--
	Ni	-0.986	0.972	3	0.108	Insufficient data	--
	V	-0.400	0.160	5	0.504	Not significant	Decreases with pH
	Zn	-0.806	0.650	6	0.053	Not significant	Decreases with pH
19mm	Al	-0.407	0.166	5	0.496	Not significant	Decreases with pH
	B	-0.945	0.893	6	0.004	Significant	Decreases with pH
	Ba	-0.917	0.841	6	0.010	Significant	Decreases with pH
	Ca	-0.656	0.431	9	0.055	Not significant	Decreases with pH
	Cd	-0.930	0.865	4	0.070	Insufficient data	--
	Mg	-0.739	0.546	4	0.261	Insufficient data	--
	Mn	-0.738	0.545	8	0.037	Significant	Decreases with pH
	Ni	-0.393	0.154	3	0.743	Insufficient data	--

Pb	-1.000	1.000	2	ND	Insufficient data	--
V	-1.000	1.000	2	ND	Insufficient data	--

CHAPTER 4 - COLUMN TEST

4.1 Introduction

Steel slag is the residue produced during iron and steel manufacturing in the metallurgical industry (Aydilek, 2015). In the US, approximately 21 million tons are generated annually, of which 10-15% originates from the electric arc furnace (EAF) process (Aydilek, 2015; National Academies, 2023). In Sweden, annual slag production amounts to 1.4 million tonnes, with over 200,000 tonnes from EAF steel refining (Engström et al., 2013). Despite its favorable physical and mechanical properties, including abrasion resistance, hardness, and mechanical stability comparable to natural aggregates (Sas et al., 2015; Medina, Teixeira, & Bueno, 2026), most steel slag is deposited in landfills, resulting in economic losses and inefficient land use (Aydilek, 2015). In Sweden, underutilization is attributed to leaching risks, environmental regulations, and competition from readily available virgin materials (Engström et al., 2013).

The principal environmental concern associated with the use of steel slag in construction is the leaching of potentially hazardous elements under alkaline conditions. The most common environmental stressor is highly alkaline leachate ($\text{pH} > 11$), caused by the presence of CaO and Ca-Mg oxides and silicates (Riley & Mayes, 2015; National Academies, 2023). Several elements of concern have been identified, including manganese, chromium, vanadium, and arsenic, with hexavalent chromium and pentavalent vanadium oxyanions being of regulatory significance due to their enhanced mobility at elevated pH (National Academies, 2023). The leaching behavior varies significantly with slag composition, which depends on the type of steel produced and the manufacturing process (Medina, Teixeira, & Bueno, 2026). Particle size also influences leaching, with finer fractions exhibiting higher specific surface area and increased contact with solution, although coarser particles may leach comparable or greater amounts due to their lower buffering capacity and faster transition to acidic conditions where metal release is enhanced (Mombelli et al., 2016; Gan et al., 2022; Chapter 3).

A variety of leaching test methods have been used to evaluate slag environmental performance, including TCLP (46%), EN 12457 (35%), EPA Methods 1312 and 1313 (3% each), and column leaching tests (Medina, Teixeira, & Bueno, 2026). While batch tests such as TCLP and EN 12457-2 provide single-point extraction data under fixed conditions, EPA Method 1313 allows assessment across the full pH range (2-13), enabling estimation of solid-liquid partitioning (Medina, Teixeira, & Bueno, 2026). However, neither batch nor pH-static tests replicate the percolation conditions encountered in pavement subbase applications, where infiltrating water interacts with slag under steady-flow, field-like conditions over extended periods. The lack of methodological standardization is well recognized in the literature (Medina, Teixeira, & Bueno, 2026).

The objective of this chapter is to evaluate the long-term leaching behavior of two slag types from Nucor Steel under column percolation conditions simulating pavement subbase applications. Specifically, this study: (1) characterizes the leaching kinetics of pH, electrical conductivity, and selected major and trace elements (Ca, Fe, Mg, B, V) as a function of cumulative liquid-to-solid ratio (L/S) using EPA Method 1314; (2) compares the leaching behavior of electric arc furnace (EAF) slag with caster slag in 10:90 slag-soil mixtures; and (3) examines the microstructural characteristics of the pre- and post-column materials by SEM-EDS to provide morphological context for the leaching results. The experimental variables are slag type (EAF vs. Caster), cumulative liquid-to-solid ratio ($L/S = 0$ to approximately 11), and the presence or absence of slag amendment (10:90 slag-soil mixture vs. unamended soil control).

It was hypothesized that: (1) both slag-amended columns would maintain persistent alkaline buffering throughout the test period, in contrast to the unamended soil column, which would show declining pH due to depletion of readily soluble salts; (2) calcium release would exhibit a first-flush effect followed by steady-state behavior governed by slow dissolution of calcium-bearing mineral phases; (3) magnesium would show a transient first-flush pattern, as initially high concentrations decline once soluble phases are depleted; (4) iron would remain relatively stable throughout the test, controlled by solubility under the consistently alkaline conditions; and (5) boron and vanadium would exhibit more complex behavior, with boron showing a depletion-

driven peak-and-drop pattern and vanadium showing a rising trend governed by the dissolution kinetics of vanadium-bearing phases.

The unamended soil-only column serves as a control to distinguish slag-attributable leaching behavior from the background behavior of the shale soil matrix. Any differences in pH, electrical conductivity, or element concentrations between the slag-amended and unamended columns can therefore be attributed to the presence of the slag.

This study is novel in directly comparing the leaching behavior of EAF slag and caster slag under identical modified column conditions, using EPA Method 1314 with a 10:90 slag-soil mixture. While previous studies have examined the leaching of individual slag types using batch tests or pH-static methods, the comparative column approach used here provides insight into the time-dependent leaching kinetics of two distinct slag types from the same steel production facility, combined with pre- and post-column SEM-EDS microstructural analysis.

4.2 Methodology

In this research, a modified up-flow column procedure in accordance with the EPA Method 1314 was used; a synthetic precipitation solution at pH 5.0, as described in EPA Method 1312, was used to prepare the leachant. The up-flow percolation column method is part of the LEAF test procedure. The purpose of the procedure is to saturate the test column completely and minimize air bubbles; the eluate flows upward through the column of granular material to allow leaching of heavy metals and other inorganic constituents. Contrary to the batch tests like EPA 1311 (TCLP) or EPA 1313 (pH-dependent leaching), the results obtained by means of the column procedure give information about constituent leaching over several liquid-to-solid (L/S) ratios and can be used for the determination of leaching behavior as a function of the total eluent contact time. Thus, the method is well-suited to predicting the long-term leaching of granular slag materials used for paving.

There have been deviations from the regular EPA Method 1314 procedure in this research, and they are stated and explained below: (1) pH 5.0 synthetic precipitation solution (Method 1312

type) was used as eluant instead of reagent water or 1 mM CaCl_2 as it is prescribed in Method 1314, to simulate the acidic rainfall; (2) the size of the column differs from the recommendations of the Method 1314 (it was 30 cm long and 5 cm in diameter); (3) no filtration of the eluates through 0.45- μm membranes has been performed; and (4) one fraction of eluate has been missed during the test due to the non-standard L/S ratios.

This research was conducted using an exploratory comparative column experiment. Just one column for each condition (EAF slag–soil, Caster slag–soil, soil only control) has been used, so it is impossible to make any statistical comparisons. The differences between the slag types reported in this paper are purely observational and not statistically significant. The mean values and standard deviations given for the sequential L/S fractions reflect variability with leaching stage, not experimental reproducibility. If any error bars are shown, they represent analytical variability among fractions and should not be interpreted as replicate uncertainty. Moreover, the soil-only control column was operated sequentially after the slag columns had finished, not simultaneously, which might create differences due to eluent batch composition, pump performance, laboratory temperature, sample aging, analytical sequence, and so on. This sequential operation can be seen as a limitation when comparing the soil-only column to slag-amended columns.

Three individual columns have been prepared according to the procedure of the modified EPA Method 1314 described below: the first one contained EAF slag-soil mixture, the second one contained Caster slag-soil mixture, and the third one contained only the shale soil to serve as a background control.

The columns were made of acrylic cylinders. Slag-soil mixture columns (Columns 1 and 2) have been made with an inner diameter of 64 mm and a height of 150 mm, while the soil-only column (Column 3) has been made with an inner diameter of 66 mm and a height of 150 mm. The diameter-to-maximum-particle-size ratio was greater than 10:1 to minimize the wall effect; the materials were sieved to No. 8 (2.36 mm). End caps have been made of acrylic slabs and drilled for the inlet and outlet ports with pipe connections. The joints were glued with acrylic adhesive to prevent leakage. Each column has been partially assembled, allowed to cure for 12 hours, then

fully assembled and allowed to cure for an additional 12 hours, allowing the glue to dry before filling with the sample.

The two slag-soil mixture columns have been made with an inner diameter of 64 mm, while the soil-only control column has been made with a slightly larger inner diameter of 66 mm. This accounts for the small difference in cross-sectional area (3,217 mm² vs. 3,421 mm², ~6.3%) and thus the slightly different superficial flow velocities at the same volumetric flow rate. All columns were operated at the same target flow rate of 225 mL/day, resulting in a slightly lower linear flow velocity in the soil-only column. This difference is considered small, but all three columns still meet the diameter-to-particle-size ratio recommendation of at least 10:1 specified in EPA Method 1314.

The column dimensions used in this study (15 cm in height, 6.4 cm in diameter) are shorter than the EPA Method 1314 recommendations (30 cm in height and 5 cm in diameter). The shortened columns have been chosen because a 10:90 slag-soil mixture serves as a fine-grained, low-permeability material (AASHTO A-7-2 clay), and preliminary experiments have shown that the longer columns require unreasonably long saturation and equilibration periods. The diameter-to-maximum-particle-size ratio exceeded 10:1, thereby minimizing wall effects. Although the shortened columns have resulted in reduced residence time of the eluent in the sample layer, the up-flow saturation procedure and 24-hour soaking period have been chosen to saturate the pores completely before eluate collection.

Slags have been provided by the Nucor Steel plant in Nebraska through TMS International. The shale soil has been taken from O'Neill, Nebraska, and belonged to the AASHTO A-7-2 category according to the liquid limit (64.76%), plasticity index (36.44%), optimum moisture content (27.6%), and maximum dry density (1.488 g/cm³). No treatment was applied to the received samples. The EAF slag has been dried to the complete solids content (1.0000 g-dry/g), while the Caster slag contained 0.65% moisture (solids content = 0.9935 g-dry/g). The soil had the solids content of 0.9666 g-dry/g and moisture content of 3.34%. All materials were sieved to No. 8 to comply with the maximum particle size for the given column dimensions. The available masses were 1,106 g for EAF slag, 1,014 g for Caster slag, and 1,656 g for soil.

The target dry mass for each column was 300 g. The slag-soil mixture columns have been prepared at a 10:90 ratio, yielding 30 g of slag and 270 g of soil per column – this is a typical road-construction blend for pavement subbase. The soil-only column contained 300 g of dry soil. The full material specification and properties are presented in Table 4.2.1.

Table 4.2.1 Composition and material properties of column test specimens: EAF slag + soil, Caster slag + soil, and soil-only control.

Parameter	EAF + Soil	Caster + Soil	Soil Only
Mix composition			
Slag type	EAF	Caster	—
Slag dry mass (g)	30	30	—
Soil dry mass (g)	270	270	300
Total dry mass (g)	300	300	300
Mix ratio — slag: soil (dry mass)	0.111	0.111	0
Material properties			
Slag, SC (g-dry/g)	1	0.9935	—
Slag moisture content (%)	0	0.65	—
Soil, SC (g-dry/g)	0.966	0.966	0.966
Soil moisture content (%)	3.34	3.34	3.34
Mix particle density (g/cm ³)	2.757	2.719	2.65
As-weighed (wet) masses			
Slag wet mass weighed (g)	30	30.2	—

Soil wet mass weighed (g)	279.33	279.33	310.35
Total wet mass weighed (g)	309.33	309.53	310.35
As-tested sample mass (g)	309.78	309.93	310.35
Dry mass equivalent (g)	300	300	300

The sample was packed using a multilayered packing scheme to create a uniform flow distribution across the column cross-section. Packing of the column started from top to bottom as follows: geotextile membrane; 1 cm thick quartz sand (20-30 mesh, specific gravity = 2.65) layer; second geotextile membrane to avoid mixing of sand and sample; slag-soil mixture sample; third geotextile membrane; 5 cm thick quartz sand pre-filter layer; fourth geotextile membrane; acrylic end cap. After packing the column, it was turned upside down so that the 5 cm sand layer acts as the inlet layer and the 1 cm sand layer as the outlet layer, holding the sample.

Slag-soil mixture was made manually in a clean jar by sieving slag and mixing it with soil to achieve a homogeneous distribution before adding it to the column. The slag-soil mixture specimen was added to the column in 5 equal portions of approximately 60 g weight each (total dry mass = 300 g). Each portion was added to the column, then the column was gently tapped on the laboratory table to achieve a uniform packing density. The number of taps for each portion was kept the same in all three columns.

The height of the resulting specimen was approximately 9 cm in all three columns. [Note: Enter dry density, void ratio, and porosity data here. The theoretical values are EAF slag-soil dry density $\approx 1.70 \text{ g/cm}^3$, void ratio ≈ 0.60 ; caster slag-soil dry density $\approx 1.70 \text{ g/cm}^3$, void ratio ≈ 0.60 ; soil-only dry density $\approx 1.72 \text{ g/cm}^3$, void ratio ≈ 0.56 .]

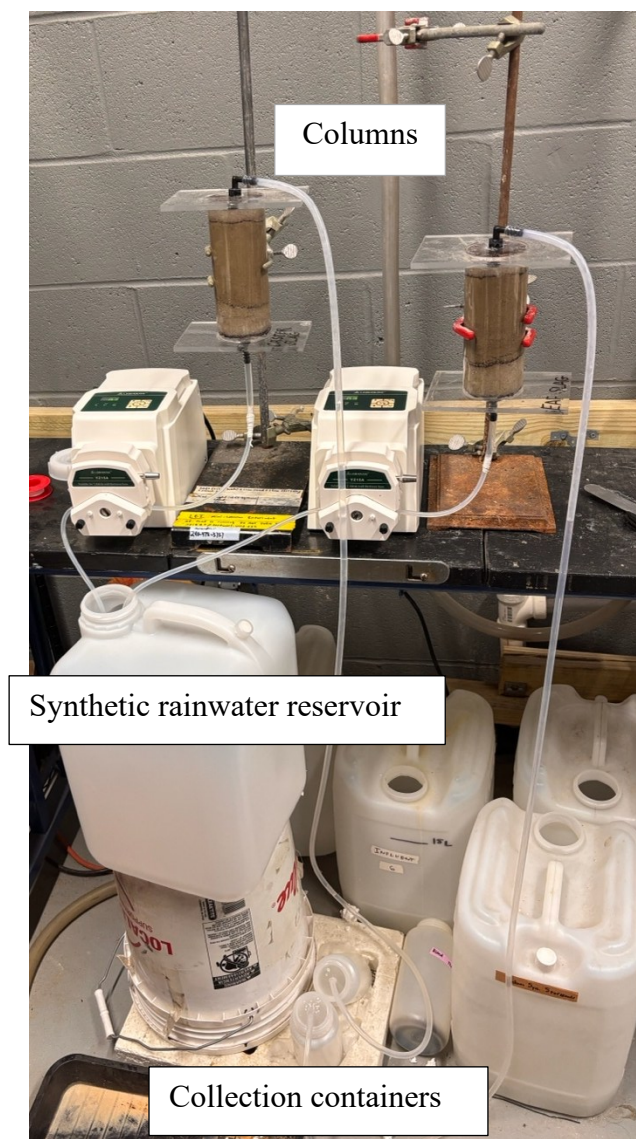


Figure 4.2.1 Laboratory setup for EPA Method 1314 up-flow column leaching tests, showing the acrylic test columns, synthetic rainwater reservoir, peristaltic pumps, and eluate collection containers.

The eluent was a pH 5.0 synthetic precipitation solution consisting of a 60:40 (w/w) mixture of trace-metal-grade H_2SO_4 and trace-metal-grade HNO_3 , prepared in deionized water in a 15-liter carboy with constant stirring until $\text{pH } 5.0 \pm 0.05$ was reached. Such eluent composition is chosen according to EPA Method 1312 (synthetic precipitation leaching procedure) instead of the recommended reagent water in the standard EPA Method 1314. This choice simulates the

influence of acidic rainwater on slag-soil mixtures under field conditions. The prepared eluent had a pH value of 5.01.

An 8-liter volume was prepared in advance and used simultaneously in Columns 1 and 2. The eluent tank was left open to prevent pressure buildup and reduce evaporation. Blanks were collected from the eluent before and after the experiment to estimate the metal concentration in the blank solution.

Columns were operated under up-flow conditions. Eluent was supplied from the bottom of the column and flowed up through the sand pre-filtration layer, the sample, and was discharged from the top of the column. Such a scheme provides thorough saturation of the sample and eliminates the creation of preferential flow paths.

At first, each column was saturated with the artificial precipitation eluent to fill the pores and release air from the sample. Eluent was pumped at a rate of 0.312 mL/min, twice the target collection rate, to ensure effective wetting of the highly plastic shale soil sample. After the eluent reaches the top outlet, the pump is turned off, and the column remains undisturbed for 24 hours. The height of the specimen in each column was approximately 9 cm (the total height of the column, 15 cm, minus 5 cm of the inlet sand layer and 1 cm of the outlet sand layer). Based on the reported porosities and inner diameters, the pore volumes of the specimen parts in the columns are approximately 176 mL for the EAF slag column (64 mm diameter, 61.8% porosity) and 175 mL for the Caster slag column (64 mm diameter, 61.3% porosity).

After the soaking time, the eluate collection process started. Eluent was supplied to the column inlet from the carboy with two Labhouse YZ15A peristaltic pumps. Two pumps worked simultaneously; each fed one of the first two columns, and the third column was activated after the first two were done. The target flow rate of 225 mL/day (approximately 0.156 mL/min) was obtained for all three columns, which corresponds to the flow rate range suggested by EPA Method 1314. The flow rate was measured after each collection stage using a stopwatch and a calibrated graduated cylinder and adjusted by varying the pump speed as necessary.

Eluates were collected in nine fractions (T01 through T09) according to the cumulative L/S ratios listed in EPA Method 1314. The sampling was carried out for 2.5 weeks. The target L/S endpoints and the achieved values are presented in Table 4.2.1.

Table 4.2.1 Eluate collection schedule for EPA Method 1314 column leaching tests, showing fraction number, actual collected volume, cumulative volume, and corresponding cumulative liquid-to-solid (L/S) ratio.

Fraction	Actual Volume (mL)	Actual Cumulative Volume (mL)	Actual Cumulative L/S (mL/g-dry)
T01	60	60	0.2
T02	90	150	0.5
T03	150	300	1
T04	150	450	1.5
T05	150	600	2
T06	750	1350	4.5
T07	1350	2700	9
T08	400	3100	10.33
T09	150	3250	10.83

Due to an error in scheduling, the fraction corresponding to L/S = 5.0 target was accidentally omitted from all three columns. As a result, the range between T06 (L/S = 4.5) and T07 (L/S = 9.0) exceeds the protocol requirement, due to a jump in cumulative volume from 1,350 mL to 2,700 mL. It means that any phenomenon or behavior in the L/S 4.5-9.0 range will be averaged into one fraction and will not be distinguished. The total mass release in this extended range was calculated as the difference between cumulative values at T06 and T07. The last fraction (T09) was collected after the protocol endpoint of L/S = 10 to obtain additional data points for the cumulative release curves.

According to the protocol, the endpoint is $L/S = 10$. Fractions past $L/S = 10$ (T08 and T09) were collected to obtain additional data points for the cumulative release curves.

Different collection bottle volumes, ranging from 100 mL to 2.5 L, were used depending on the expected volume of the fraction to be collected. Each collection vessel was marked with the required volume level and checked regularly to ensure it reached the required liquid volume. All collection vessels were subjected to an acid wash, followed by rinsing with deionized water, before use. Collection vessels were sealed tightly after eluate collection to prevent exposure to CO_2 .

There were two protocol deviations during the test procedure. The first one is skipping one fraction with an L/S target of 5.0 due to the collection schedule across all three columns. This protocol deviation was found post hoc, and collection was continued. The second protocol deviation is collecting the T09 fraction beyond the protocol endpoint to ensure the cumulative L/S ratio reaches 10.9. It was done to collect additional fractions for the cumulative release data.

pH and electrical conductivity (EC) were measured right after collecting each fraction at a constant laboratory temperature of 23 ± 2 °C. No additional measurements were made during the eluate collection process. According to the EPA Method 1314, eluates should be filtered through a 0.45- μ m membrane prior to preservation. However, filtration was not performed in this study. The geotextile layers placed on the inflow and outflow sides of the column capture large solid-phase particles, and the collected eluates appeared visually clean; nevertheless, geotextile fabric is not a substitute for a filtration membrane and does not filter colloidal and fine particulate matter. Acidification of unfiltered eluates might dissolve colloidal or fine particulate matter, thereby increasing concentrations of particle-associated elements such as Fe, Al, and Cr. In this way, concentrations reported in this study should be considered as “acid-preserved concentrations in unfiltered eluates”, but not as “dissolved” concentrations. This protocol deviation is known to be a possible source of uncertainty in the results.

After measuring pH and EC, samples were acidified in collection vessels with 0.1–0.2 mL of trace-metal-grade nitric acid to achieve a $\text{pH} < 2$ and preserve acid-soluble metal fractions for further analysis. The samples were tightly closed and stored at 4 °C until analysis.

The preserved samples were then analyzed for Al, As, Ba, Be, B, Cd, Ca, Co, Cr, Fe, Pb, Mg, Mn, V, and Zn utilizing a Shimadzu ICPE-9820 inductively coupled plasma optical emission spectrometer (ICP-OES). Multi-element standards covering the expected concentration range for each individual element were used in calibration. Instrument settings and analytical wavelengths for each element were determined as per the manufacturer's instructions. The Method Detection Limits (MDLs) were calculated from repeated analyses of low-concentration standards and varied from one element to another. Considering that each sample was analyzed at several dilution factors (undiluted, 1:10, 1:50, 1:100, and 1:400) to place major element concentrations into the calibrated range, the reporting limit of each sample equals the dilution factor used. Each sample dilution factor was chosen based on the expected concentration range, with major elements (Ca, Mg) requiring high dilution and trace elements (As, Cd, Pb) analyzed at low dilution or undiluted. Each analytical run included method blanks, and all blank concentrations were below the MDL for all target elements. Continuing Calibration Verification (CCV) standards were repeatedly included in each analytical run, and measured values were within the acceptable recovery limits for all elements. All concentrations below the MDL were reported as half of MDL. All instrument method parameters, element-specific analytical wavelengths, MDL, calibration procedure, and QC summary statistics are presented in the supplementary analytical report.

4.3 Results and Discussion

The electrical conductivity reduced in all three columns during the test: Soil+Caster went down from 4.36 to 1.24 mS cm⁻¹ (72% decrease); Soil+EAF went down from 3.20 to 2.30 mS cm⁻¹ (28% decrease, with an unexpected increase to 2.29 mS cm⁻¹ in the soil-only column at the last point, see below); and Soil-only went down from 3.045 to its minimal value of 1.545 mS cm⁻¹ at L/S = 10.4. This indicates a first-flush process, in which the most soluble ions were released

initially and further depleted as the L/S ratio increased, regardless of slag amendment application.

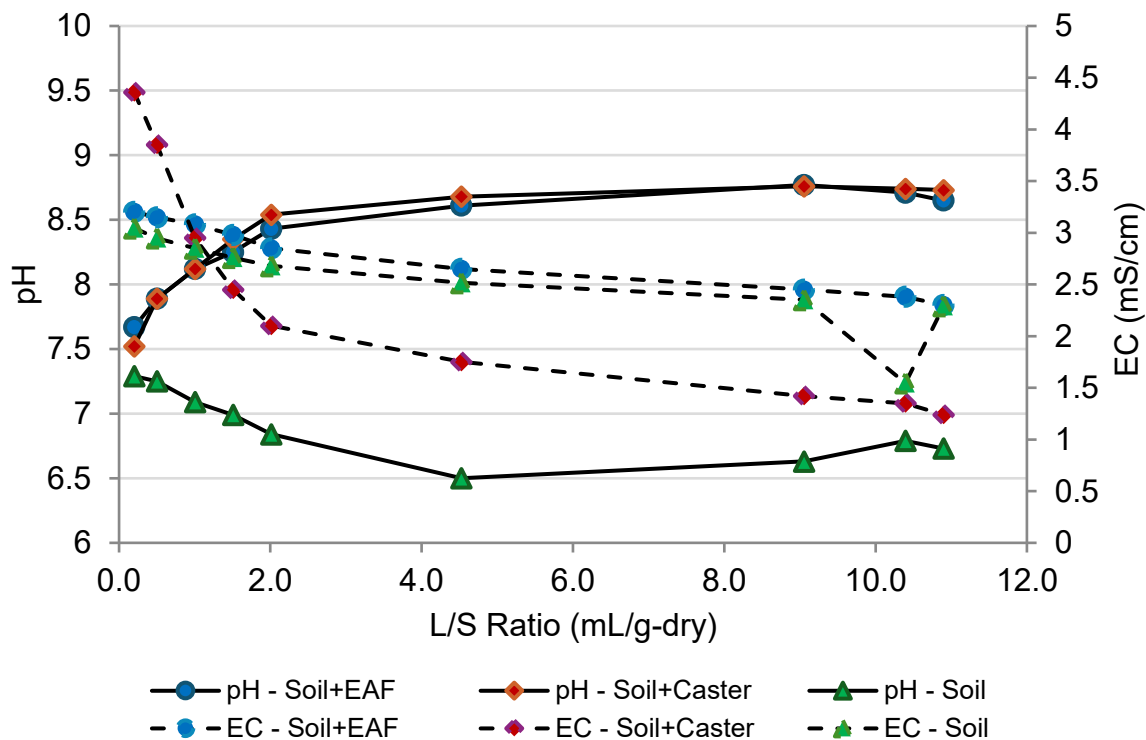


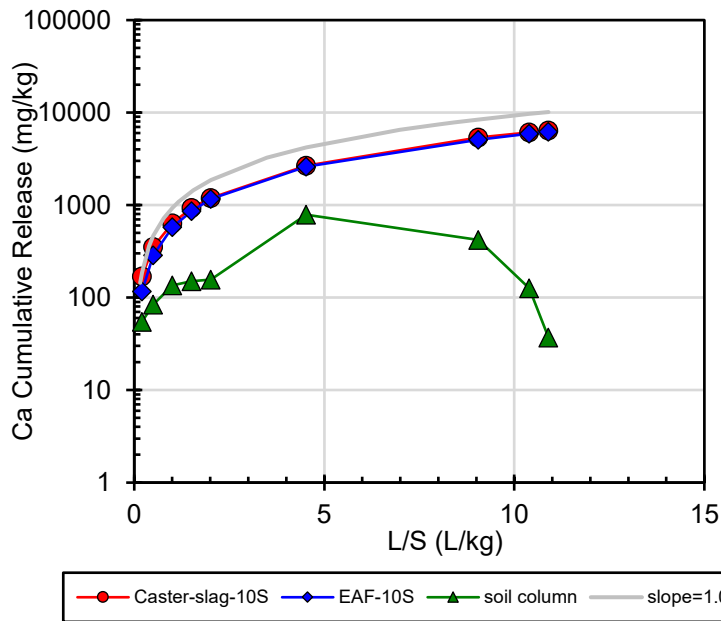
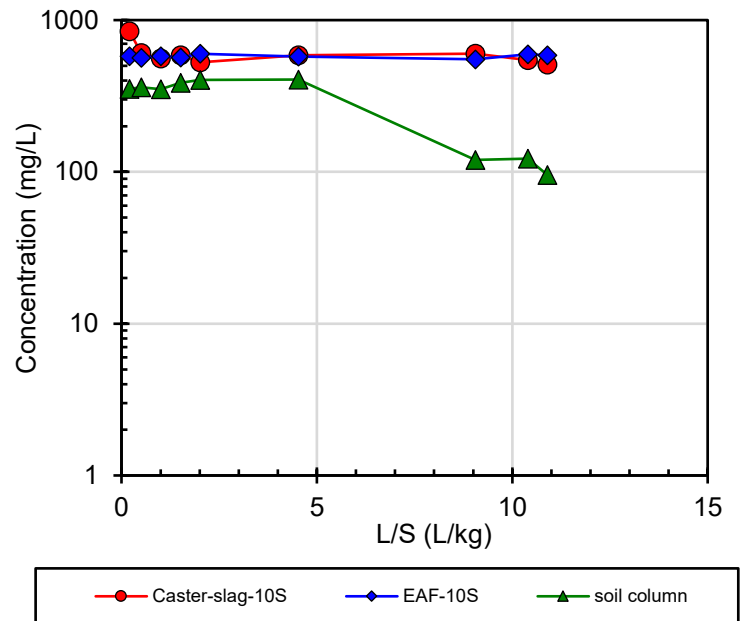
Figure 4.3.1 pH and electrical conductivity (EC) as a function of liquid-to-solid (L/S) ratio for Soil+EAF, Soil+Caster, and Soil-only column leaching tests. Solid lines on the primary (left) y-axis represent pH; dashed lines on the secondary (right) y-axis represent EC (mS/cm).

In contrast to electrical conductivity, the pH varied with slag amendments. The soil-only column showed a decreasing, unstable pH that fell from 7.29 to a minimum of 6.50 at L/S = 4.53 and only partially recovered to 6.63-6.79 at the end of the experiment, consistent with the absence of an alkaline buffering component in the unamended soil sample. In turn, both slag-amended columns showed a steady increase in pH, rising from approximately 7.5-7.7 at L/S = 0.2 to 8.4-8.5 at L/S = 2.01, then plateauing at 8.6-8.8 at L/S $\approx$ 4.5. That trend can be attributed to the gradual dissolution of portlandite and dicalcium silicate (C_2S), which continuously supplies OH^- ions to the solution. At the beginning of the process, the soil sample acts as a buffer toward neutrality; however, as alkalinity increases due to slag dissolution, the system gradually shifts to a new pH buffering range as the test proceeds.

The opposite trends of pH increase, and EC decrease in slag-amended columns indicate two different processes. As stated earlier, EC is affected by the total ionic strength of the solution, with readily soluble substances dominating and being released first, followed by further depletion (see the first-flush process above). However, pH is controlled by the concentration of hydroxyl ions in solution, as supported by the continued dissolution of alkaline calcium-bearing phases that provide OH^- ions even after the bulk ionic first flush. That is consistent with the finding of Engström et al. that conductivity and pH decrease over time for all samples in pure slag leaching (Engström et al., 2013); the EC behavior in the present study is similar, whereas the pH differs. In the 10% slag-to-soil system analyzed here, pH increases rather than decreases, which can be attributed to soil buffering, reducing the impact of increased alkalinity from slag and resulting in a gradual increase rather than the sharp increase followed by a decrease expected for pure slag.

The pH plateau observed in slag-impacted columns (8.6-8.8 for $\text{L/S} \approx 4.5$) lies in the upper range of the carbonate buffer region. In a simple water-carbonate system, the calcite buffer region operates near $\text{pH} \sim 8.2$ at atmospheric CO_2 concentration (Yu et al., 2025). However, the slightly elevated pH plateau observed here (8.6-8.8) may be due to the dynamic nature of the system, in which Ca is continuously leached from the slag, thereby shifting the calcite buffer region upward relative to that in a static system. The interactions between the hydroxides and the silicates in the slag with CO_2 result in carbonates (Piatak et al., 2015), and the maintenance of the plateau at 8.6-8.8, instead of increasing to the region of portlandite ($\text{pH} > 10$), is consistent with the possibility that carbonate formation has begun to neutralize the excess OH^- . Therefore, starting from $\text{L/S} \approx 4.5$, both slag-amended columns appear to have entered a pH buffering regime consistent with carbonate buffering, where interaction of the alkaline leachate with atmospheric or dissolved CO_2 may result in calcium carbonate precipitation, establishing a pH buffering point, rather than allowing unlimited pH increase from continuous dissolution of alkaline calcium phases. This interpretation is based on the observed pH range and an analogy to published carbonate-buffering studies; no independent confirmation of carbonate mineral formation (e.g., XRD) was obtained from the column residues.

There is no explanation for the final point increase in the soil-only column (from 1.545 to 2.29 mS cm⁻¹ at L/S = 10.9 and converging with the Soil+EAF column at 2.30 mS cm⁻¹) in terms of the mechanisms discussed above, and it is a puzzling feature of the data obtained. It should be recognized as a possible late-stage dissolution phenomenon rather than incorporated in the general first-flush or buffering picture.



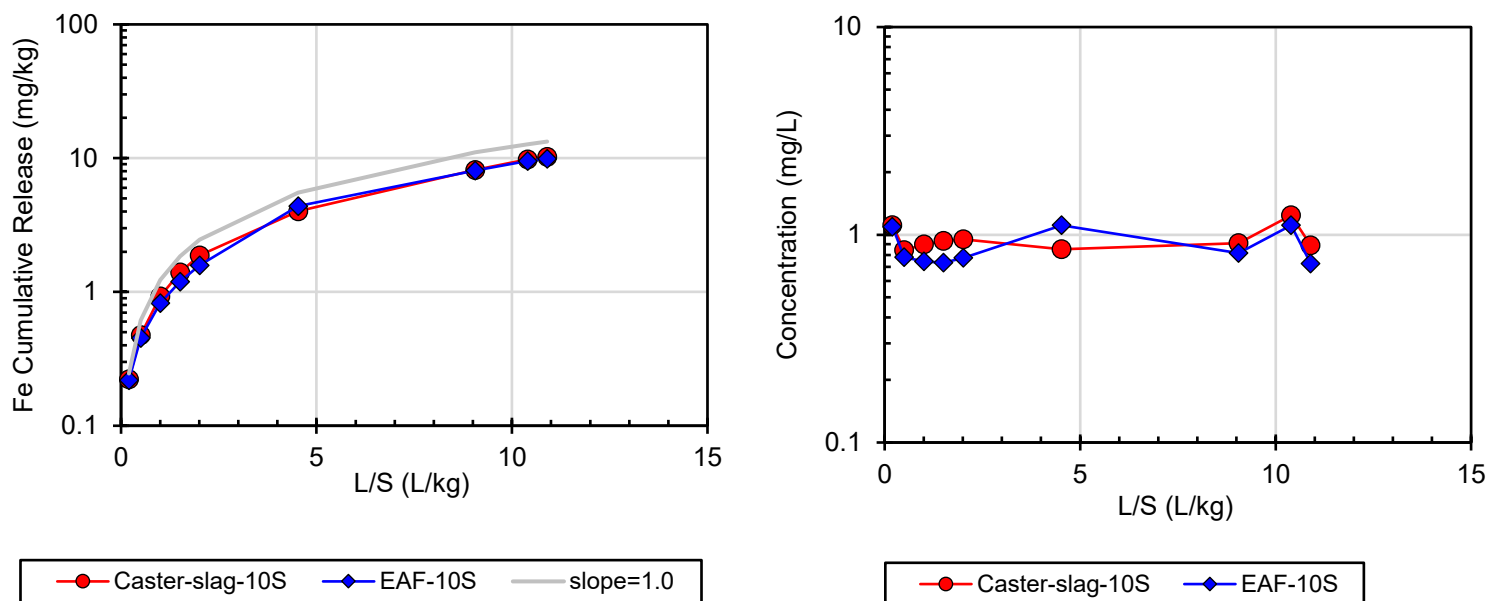


Figure 4.3.2 Caster-slag, EAF slag, and soil column leaching tests. (Top left) Cumulative Ca release (mg/kg) vs. L/S (L/kg); (top right) L/S-dependent Ca concentration (mg/L) vs. L/S; (bottom left) cumulative Fe release (mg/kg) vs. L/S; (bottom right) L/S-dependent Fe concentration (mg/L) vs. L/S. The grey reference line represents a slope of 1.0, indicating a dissolution-controlled release in which cumulative release increases proportionally with L/S. Soil column data are not included in the Fe plots, as Fe concentrations in the soil column leachate remained below the analytical detection limit throughout the test.

The concentration of calcium in both slag columns remained relatively constant across the whole L/S ratio tested and persisted between 510–846 mg/L in the Caster slag column (mean 596.7 ± 99.4 mg/L) and 552–600 mg/L in the EAF slag column (mean 577.3 ± 15.1 mg/L). The cumulative Ca release reached 6,390 mg/kg (Caster) and 6,200 mg/kg (EAF) at L/S = 10.9, and both closely followed the slope = 1.0 reference line (Figure 4.3.2).

The similar calcium concentration and cumulative release from the two slag columns are unexpected, given the distinctive bulk oxide compositions of Caster and EAF slags. Mei et al. (2023) mentioned that although the total Ca content in all three SS samples was about the same, the major Ca-bearing minerals were significantly different, hence the difference in potential Ca

extraction (Mei et al., 2023). Specifically, BOFS is dominated by tricalcium silicate, EAFS by merwinite, and Caster Slag by calcium aluminate. Nonetheless, both slag columns achieved similar Ca equilibrium concentrations (about 500–600 mg/L) at pH 7.5–8.8, indicating a degree of convergence in solubility-controlling behavior at moderate pH values. Loncnar et al. (2016) described a similar convergence, stating that the leaching curves derived from the pH dependence test showed very consistent leaching behaviour of all three slag samples for the three major elements (i.e., Ca, Si, and Mg), suggesting that solubility was controlled, in the case of all three slag samples, by the same mineral phases (Loncnar et al., 2016). Though Loncnar compared the effects of cooling treatments within a single slag type, the idea is applicable here as well: within the study pH range, the thermodynamically stable calcium phase in the literature is calcite (Loncnar et al., 2016, 2022), which may explain the similar equilibrium concentrations observed for both slag types regardless of different initial mineral assemblages. This interpretation is an inference based on the pH range and an analogy to published studies; no independent solid-phase speciation (e.g., XRD, geochemical modeling) was performed on the column residues in this study.

This non-decreasing profile is consistent with the claim that the pH and concentration of solubility-controlled COPCs will remain constant over the assessment period until the available content of a COPC is depleted (Yu et al., 2024). The lack of any decreasing trend in the calcium concentration across the whole L/S range indicates that Ca-bearing solid phases in both slags remain undepleted during the experiment, in contrast to the soil-only column, whose calcium concentration declines after $L/S \approx 5$ due to lower availability.

The initially high concentration of calcium in the Caster column (846 mg/L at L/S 0.2) is higher than the subsequent steady-state values. This is in line with the first-flush phenomenon, in which the most readily available Ca-bearing minerals dissolve first. Hobson (2017) describes the same process during laboratory leaching tests. After 1 hr the pH value and the Ca and Si concentrations were very similar to those observed in the aerated experiments, indicating similar processes were occurring (i.e., rapid dissolution of free lime and fine-grained dicalcium silicate particles) (Hobson, 2017). Moreover, Hobson states that the magnitude of the initial rise in pH was mass-limited (i.e., controlled by the amounts of CaO and reactive dicalcium silicate that are

readily available for dissolution) rather than $\text{Ca}(\text{OH})_2$ solubility-limited (Hobson, 2017). Hence, the higher CaO content in the Caster slag may indicate a larger reservoir of readily soluble surface calcium minerals, resulting in a more pronounced initial pulse. As Hobson (2017) notes, between the first sampling point and day 5, there was a slow increase in pH, Ca, and Si, probably the result of continued dicalcium silicate dissolution (Hobson, 2017), describing the transition from the initial elevated fraction to the steady-state plateau. These mechanistic interpretations are drawn from Hobson's (2017) study of pure BOF slag and have not been independently verified for the EAF and Caster slags tested here.

This interpretation is additionally supported by the pH and Electrical Conductivity (EC) measurements (Figure 4.3.1). Both slag-amended columns (Soil+EAF, Soil+Caster) show the rise in pH from an initial 7.5–7.7 to the plateau at 8.6–8.8 by $L/S \approx 9$ –11, despite the continuous addition of pH 5 synthetic rainwater to the system, while the soil-only column shows a decline from 7.3 to approximately 6.5 with a slight late recovery. The EC in both slag columns peaks at the initial fraction (3.2 mS/cm for Soil+EAF, 4.36 mS/cm for Soil+Caster at $L/S \approx 0.2$) and then gradually decreases, while the soil-only column's EC decreases more gradually from a lower starting value. Yu et al. (2025) noted that the acid neutralization capacity of EAF slag is quite high (i.e., ~5 mol or ~20 mol of acid per kg of slag are required to decrease eluate pH to pH 7 or 2). These titration curves suggest that EAF slags can buffer the alkaline conditions of leachates for extended periods (Yu et al., 2025). The sustained increase in pH in both slag columns despite the acidic influence directly reflects this acid-neutralization capacity, while the initial EC peak followed by decrease demonstrates the fast release of soluble ionic compounds followed by the gradual moderation of the process, whereas the soil-only column's declining pH and generally lower steady decline in EC show that the rise in pH and sustained ionic strength are the results of slag addition, not the soil matrix itself.

The higher rate of EC decreases in the Caster column (from 4.36 to 1.24 mS/cm, a 72% reduction) compared to the EAF column (from 3.2 to 2.3 mS/cm, a 28% reduction) indicates that the Caster slag releases a larger initial pulse of soluble compounds that is faster to deplete. Mei et al. (2023) have shown that different slag types contain different assemblages of Ca-bearing phases with different dissolution kinetics: BOFS was identified to be rich in tricalcium silicate,

while merwinite phase and calcium aluminate were the major Ca-bearing phases for EAFS and Caster slag, respectively (Mei et al., 2023). The faster initial dissolution of Ca-bearing phases in the Caster slag and the lower sustained Ca release may indicate that different Ca-bearing mineral assemblages with different dissolution kinetics operate in the two slags, though this interpretation is based on literature reports for other slag types and was not independently confirmed in this study. Both columns reach similar Ca concentrations at steady state, suggesting a similar solubility-controlling mechanism operates in both columns, though with different initial pulse and depletion rates.

Hobson (2017) describes the mechanism of alkalinity generation in slag as follows: weathering of these phases in contact with water leads to rapid generation of a high-pH (10 to 12.5) leachate due to the dissolution of CaO and calcium silicates, and the subsequent release of hydroxyl ions (OH^-). In the earliest stages, this mechanism is characterized by rapid initial release of alkalinity, Ca, and Si due to the hydration and dissolution of both free lime and dicalcium silicate phases (Hobson, 2017). The pH range in the present study (7.5–8.8) is noticeably lower than Hobson's reported 10–12.5, which can be expected because Hobson's data are obtained from the pure slag, while the columns in the present study are made of 10:90 slag-soil ratio; the soil matrix dilutes and buffers the CaO-derived alkalinity, and the pH-5 synthetic rainwater serves as a push towards lowering pH. The general mechanism described by Hobson (2017) of hydration and dissolution of alkaline calcium phases to produce OH^- is consistent with the trends observed here, though the specific phases responsible were not independently identified in this study; only the magnitude of the effects depends on the dilution.

Loncnar et al. (2016) describe the specific solubility-controlling phases for Ca release from Caster slag as pH-dependent: The leaching of Ca at $\text{pH} > 12$ was adequately described by CaF_2 , portlandite, and to a much lesser extent by calcite, while portlandite and ettringite are the solubility-controlling phases for Ca leaching from fresh BOF slags in the pH range (Loncnar et al., 2016). Given the maximum measured pH of 8.8, portlandite is unlikely to be the major Ca-controlling phase here. Loncnar et al. (2022), describing the more weathered lower-pH slag conditions, report that the leaching of Ca seems to be adequately described by calcite (CaCO_3), and to a lesser extent by hydrates of the calcium ferrites, ettringite, and the solid solution of

CEM18_CNASH (Loncnar et al., 2022). Within the 7.5–8.8 pH window in the current study, the observed constant Ca concentrations are consistent with solubility control potentially by carbonate-bearing phases, though it should be stated that this conclusion is an inference from the pH range and analogy to weathered-slag studies, while no independent solid-phase speciation (e.g., XRD, geochemical modeling) was done on the column residues.

The absence of Ca depletion by L/S 11 has several practical implications for field conditions. Riley and Mayes (2015) monitored steel slag leachates for 36 years and concluded that there was a consistent decrease in Ca concentration, estimating that it would take between 52 and 80 years for such Ca values to be apparent in the Dene Burn assuming the monotonic trend continued (Riley & Mayes, 2015), while for the Howden Burn it would take, in excess of 150 years, before Ca concentrations fall below 50 mg/L (Riley & Mayes, 2015). This long-term field experience demonstrates that Ca release from the slag persists for many decades. On the other hand, Hobson (2017) states that long-term monitoring of steel slag leachate shows a general decline in both pH and Ca concentrations over time as available CaO and Ca-silicate phases are depleted and weathering rinds comprising Ca-Si-H and carbonate minerals are formed (Hobson, 2017). Loncnar et al. (2022) note that in the literature, calcite formation is reported to occur on the grains' reaction rims via two steps: calcium is leached from the Ca-minerals, and then subsequently it reacts with the dissolved carbonate to form calcite, which precipitates on the surface of the steel slag particles (Loncnar et al., 2022). The current column test thus describes an early-phase leaching scenario; over longer time scales, the literature suggests that carbonate precipitation on slag grain surfaces may gradually slow the rate of Ca release beyond the current test (Loncnar et al., 2022; Hobson, 2017).

Concentration behavior. Iron concentration was low and flat across the whole L/S range for both slag columns, being 0.843–1.24 mg/L (mean 0.959 ± 0.131 mg/L) in Caster and 0.727–1.11 mg/L (mean 0.876 ± 0.173 mg/L) in EAF columns. Both started at 1.1 mg/L at L/S 0.2, demonstrated a slight mid-range dip, and showed a minor rise at L/S 10.4 before returning to baseline at the last fraction. There was no first-flush phenomenon: unlike Ca, which starts at 846 mg/L and declines, the Fe concentration in the initial fraction is not notable relative to the series and shows no trend. The iron concentration for both slags remained within the narrow range of

0.7–1.2 mg/L and showed no systematic increase or decrease. Proctor et al. (2000) explain this non-decreasing behavior as follows: although concentrations of metals in slag are elevated relative to concentrations in soil, the metals in slag are tightly bound to the slag matrix and not readily leached (Proctor et al., 2000). Mahedi (2019), citing Komonweeraket et al., reports that Fe exhibits cationic leaching with sharp decreases in concentration under mildly acidic to neutral conditions (pH ~5–7), while Fe concentrations are lower in other pH ranges (Mahedi, 2019). Since neither slag column had its pH drop into the 5–7 range, the low and steady iron concentration is consistent with the reported pH dependence.

Cumulative release. Both slag columns follow the slope = 1.0 reference line closely and almost overlap throughout the test, achieving 10.3 mg/kg (Caster) and 9.92 mg/kg (EAF) at L/S = 10.9, differing by $\approx$ only 4%. The cumulative curve is smooth and continuously rising, with no plateau, indicating that Fe release remains a steady, unsaturated flux within the tested L/S range. For context, the totals are roughly 600 times lower than the Ca cumulative release from the same columns ($\approx$ 6,200–6,390 mg/kg). This steady low-magnitude release is consistent with Fe being hosted in slowly dissolving phases within the slag matrix rather than in a readily accessible surface pool, though the specific host phases were not identified in this study. Yildirim and Prezzi (2011) mention the RO phase (solid solution of CaO-FeO-MnO-MgO) as a relevant host phase in steel slags (Yildirim & Prezzi, 2011), and Ragipani et al. (2019) describe the structural background of this slow release: Steel slag, which is non-porous and contains RO phase globules embedded in calcium silicate and dicalcium ferrite matrix, was found to release the RO phase globules with the dissolution of the matrix (Ragipani et al., 2019). If the RO-phase model applies to the slags in this study, the embedding of the Fe-bearing RO phase within the surrounding silicate matrix could explain the steady, low-level Fe release in both columns, though this interpretation has not been independently verified.

Connection to pH and EC data. The flat, low Fe concentration is in line with the pH behavior as both slag columns maintain the elevated pH (7.5–8.8) throughout the L/S range, despite the continual influx of pH-5 synthetic rainwater, while the soil-only column pH drops to approximately 6.5. Under such sustained alkaline conditions, Fe solubility is expected to be suppressed, maintaining a low and stable dissolved Fe concentration. Since neither slag column

had a pH that dropped into the range of enhanced Fe mobilization, no Fe release pulse was expected, which is in line with the observed flat profile. Komonweeraket et al. (Mahedi, 2019) describe literature reports on the solid phases proposed as responsible for the suppression of the Fe concentration: precipitation/dissolution reactions of oxide/hydroxide minerals are reported to control the solubility of Al^{3+} and Fe^{3+} at all pH values, and Fe^{3+} leaching is reportedly mainly controlled by Fe-hydroxides such as ferrihydrite ($\text{Fe}(\text{OH})_3$) and goethite ($\alpha\text{-FeO}(\text{OH})$) (Mahedi, 2019). Leiviskä et al. (2012) confirmed this threshold, showing that at higher pH values (>4), Fe solubility is reported to be controlled by $\text{Fe}(\text{OH})_3$. With pH maintained above 4, suppression of Fe solubility by hydroxide phases is expected based on the literature, matching the observed lack of Fe concentration excursions. These phase attributions are drawn from the published literature and have not been independently verified for the column residues in this study.

The near-identical Fe behavior between the two slag columns is especially interesting given the differences in slag type. For Ca, the similar bulk content implies the similar leachate outcome; for Fe, however, the leachate concentrations are almost identical (within 0.1–0.2 mg/L) despite the differences in slag composition. This means that bulk Fe content is not the controlling factor for Fe release; instead, the solubility of Fe-bearing phases likely controls the dissolved concentration, with similar solubility at the maintained pH values. This decoupling of the bulk content and leachate concentration is also well-known in the literature on slag leaching: Piatak et al. (2019) show that the bulk chemical concentrations do not correlate with the amount leached, implying multiple mineralogical phases with different solubilities, and that simulated weathering tests imply that elements are present in generally insoluble phases suitable for water-treatment applications. This explains the treatment of Fe as an element controlled by mineral phase solubility rather than by bulk composition.

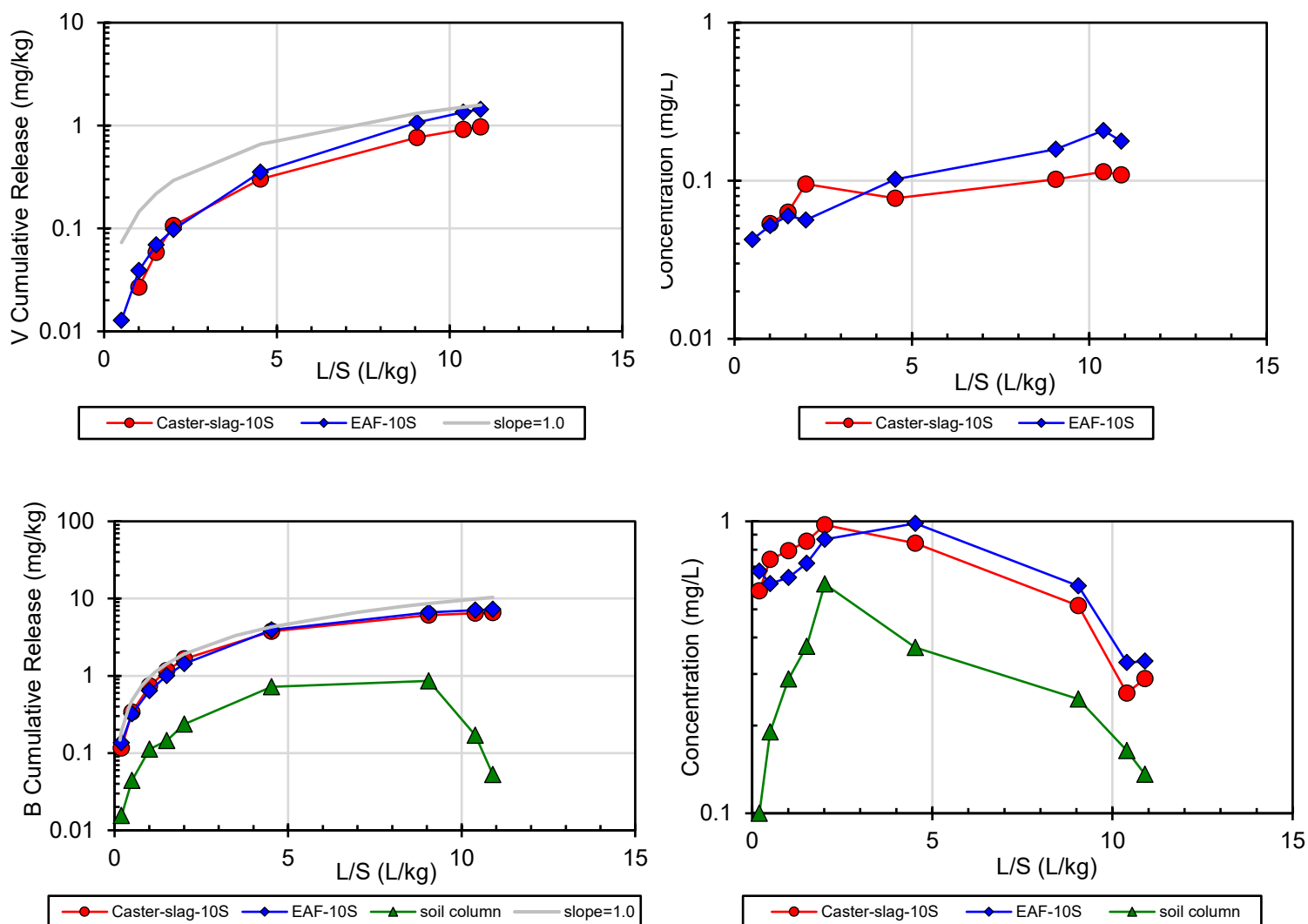


Figure 4.3.3 L/S-dependent concentration and cumulative release of boron and Vanadium from Caster slag, EAF slag, and soil column leaching tests. (Top Left) Cumulative B release (mg/kg) vs. L/S (L/kg), with slope=1.0 reference line; (Top right) L/S-dependent B concentration (mg/L) vs. L/S. (Bottom Left) Cumulative V release (mg/kg) vs. L/S (L/kg), with slope=1.0 reference line; (Bottom right) L/S-dependent V concentration (mg/L) vs. L/S. Note the linear (non-log) concentration axis on the right panel, in contrast to the log-scale concentration axes used for Ca and Fe.

The concentration of boron had a profile distinctly different from those of calcium and iron, with a clear peak before dropping, rather than remaining constant throughout the test. For the caster slag, the boron concentration started at 0.577 mg/L ($L/S = 0.201$), peaked at 0.972 mg/L at $L/S = 2.01$, and then declined to 0.258–0.289 mg/L at $L/S \approx 10.4$ – 10.9 . EAF slag also had a characteristic rise followed by a drop in boron; however, the peak came later and at a higher level, from 0.675 mg/L to 0.984 mg/L at $L/S = 9.05$, then to 0.328–0.332 mg/L in the last two fractions. Total cumulative boron release of both slag types followed the slope = 1.0 reference line up to approximately $L/S \approx 2$, but then flattened out, reaching 6.59 mg/kg (Caster) and 7.24 mg/kg (EAF) at $L/S = 10.9$.

Such a profile indicates that the boron release process is governed by a finite, diminishing source, rather than by equilibrium-controlled dissolution at a constant solubility, as appears to be the case for calcium. Durinck et al. (2008) stated that boron in stainless-steel slag is not a single mineral but a component of two different hosts: only a limited fraction of the added borates forms a solid solution with the C_2S phase, while the main fraction is found in a calcium borosilicate phase (Durinck et al., 2008). The C_2S -hosted fraction of boron is relatively low, with only 7% of the added borates forming a solid solution with S and contributing -hosted fraction of boron is relatively low, with only 7% of the added borates forming a solid solution with S and contributing to chemical stabilization (Durinck et al., 2008), while the matrix holds the main fraction of the borates (Durinck et al., 2008). If applicable to the slags in this study, such a two-host boron system, one being a smaller fraction, contained in C_2S and being more easily released in a percolation process, another one being larger but matrix-contained, could be consistent with the observed peak-and-drop boron concentration profile, with the former part potentially standing for the boron release from C_2S and the latter standing for depletion of the easily-accessible part of the source and consequent inability to maintain such concentration. However, because no XRD or microchemical analysis was performed on the leached residues in this study, this two-host interpretation remains a hypothesis drawn from the literature rather than a directly confirmed mechanism.

Durinck et al. (2008) further noted that slag stabilization with borates not only depends on the chemical stabilization but also on the cooling rate and the matrix constraint (Durinck et al.,

2008). Different cooling rates or matrix structures between the caster and EAF slags could be one factor contributing to the distinctly different observed times of the boron concentration peak in the two cases, early one for Caster slag at $L/S \approx 2$ and much later one for EAF at $L/S \approx 9$, without changing the total amount of the boron released, which is converging to nearly the same cumulative value of 6.59 mg/kg for Caster and 7.24 mg/kg for EAF by $L/S = 10.9$. This interpretation is speculative, however, as the cooling histories of the specific slags used here were not characterized, and the difference in peak timing could arise from other mineralogical or textural factors.

Strandkvist et al. (2015) gave direct evidence that boron-stabilized dicalcium silicate has an extremely fast dissolution speed compared to other mineral phases, stating that the boron-stabilized beta-dicalcium silicate has the highest dissolution rate of the studied minerals; almost all of the acid addition is within the first hour (Strandkvist, Björkman, & Engström, 2015). Such fast dissolution of the B-stabilized C_2S fraction could correspond to the early part of the concentration profile, which would then represent the quick boron release from the reactive fraction. According to Strandkvist et al. (2015), the dissolution rate is the same in pH 4 and 7 for this phase (Strandkvist, Björkman, & Engström, 2015). Moreover, the authors warned that although boron is expected to release protons at alkaline pH, its reaction rate may be too slow (Strandkvist, Björkman, & Engström, 2015). The pH-independent dissolution behavior reported by Strandkvist et al. (2015) is consistent with the consistently alkaline pH of both slag types throughout the test (Figure 4.3.2, pH 7.5–8.8), although this consistency does not confirm that boron-stabilized C_2S is the phase responsible, as other fast-dissolving boron-bearing phases could produce a similar profile. In this interpretation, the timing of the concentration peak would be governed by the kinetics of boron mineral dissolution and the accessible surface area, rather than by the bulk pH.

Vanadium concentration had a generally flat but rising trend through the entire L/S ratio range, unlike a flat plateau for Ca/Fe, and a peak-and-drop one for boron. Caster slag concentration increased from 0.0536 mg/L ($L/S = 1.01$) to 0.109 mg/L ($L/S = 10.9$), having a slight non-monotonous dip at $L/S = 4.53$ (0.0776 mg/L). EAF concentration rose to a greater extent, from 0.0425 mg/L ($L/S = 0.503$) to a peak of 0.208 mg/L at $L/S = 10.4$, then dropped slightly to 0.178

mg/L at the final fraction. Concentration of the caster slag exceeded that of the EAF for the first fractions (at L/S = 2.01, 0.0953 mg/L versus 0.0564 mg/L for the EAF), with the crossover point between L/S = 2.01 and L/S = 4.53. Thereafter, EAF concentrations surpassed Caster concentrations in all subsequent fractions; the divergence between the slags increased over the course of the test, from approximately 0.024 mg/L at L/S = 4.53, 0.056 mg/L at L/S = 9.05, to 0.094 mg/L at L/S = 10.4. While Caster's last three concentrations (0.102, 0.114, 0.109 mg/L) were flat, the last three EAF's ones (0.158, 0.208, 0.178 mg/L) were still rising, then dropped at the very end. Mean concentration was higher for EAF (0.107 ± 0.061 mg/L) than for Caster (0.0878 ± 0.0216 mg/L), and the cumulative release of both slags stayed under the slope = 1.0 reference line, with EAF's total (1.44 mg/kg) being approximately 48% higher than that of Caster (0.971 mg/kg) by L/S = 10.9. Notably, after L/S $\approx$ 2, both slags maintained a stable pH range of 8.6–8.8 (Figure 4.3.1), but their vanadium concentrations continued to rise beyond this pH stabilization point.

A rising trend over time, divergent late-stage behavior, and increasing after pH stabilization indicate that vanadium release is unlikely to be either depletion-limited or solely pH-driven. The observations are consistent with the dissolution of vanadium-containing mineral phase(s) that are distinct from the easily accessible surface Ca/Si phase, which was responsible for the first flushes of calcium and electrical conductivity. Hobson et al. (2017) identified specific vanadium-hosting phases by microfocus XAS analysis, namely, V was hosted at 1.14 ± 0.14 wt% in dicalcium aluminoferrite and 0.44 ± 0.23 wt% in dicalcium silicate (Hobson et al., 2017). They found that V was released as V⁵⁺ during the dissolution of dicalcium silicate (Hobson et al., 2017). If the same host phases are present in the slags studied here, the Hobson et al. (2017) observation that pH decrease is associated with depletion of reactive V-containing calcium silicate phases (Hobson et al., 2017), and that the release of V to solution was primarily controlled by considerably slower Ca-Si-H dissolution rates, which decreased the rate of V release by an order of magnitude (Hobson, 2017) on a long timescale, provides one possible framework for interpreting the data. Since pH did not decrease in this study but stabilized at 8.3–8.7 in both slag columns (Figure 4.3.1), the rising tendency of vanadium concentration (particularly in EAF) is consistent with the continuing dissolution of V-hosting mineral phases through the whole test duration, while the leveling-off tendency in the case of Caster could

reflect depletion of its V-hosting mineral phase pool. However, because no XRD or microchemical analyses were performed on the leached residues, the identity and abundance of the vanadium-hosting phases in these specific slags remain unconfirmed.

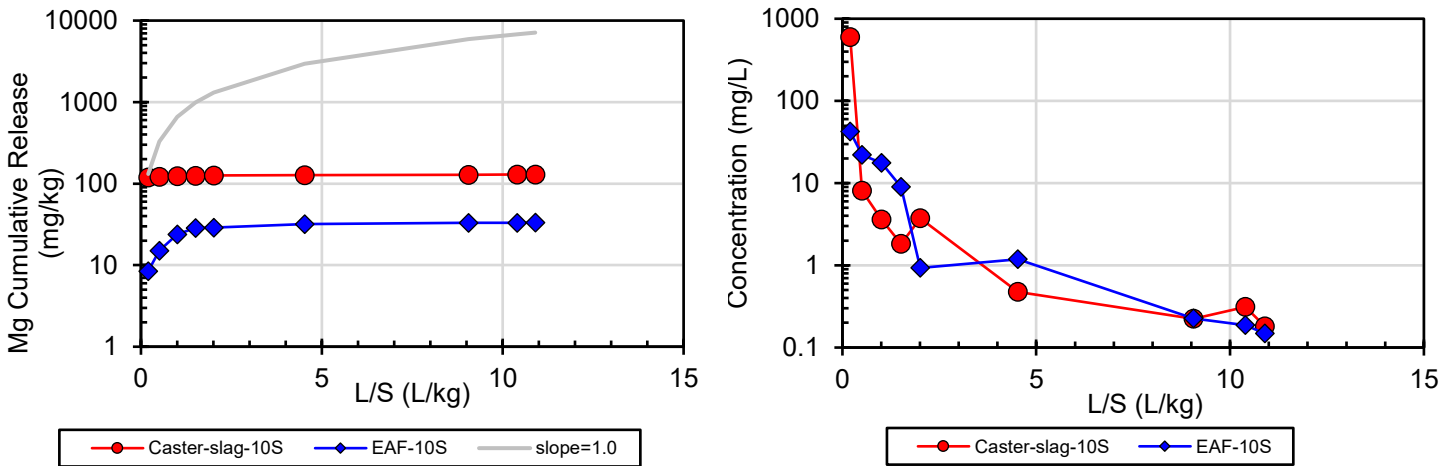
One additional aspect to consider is the influence of calcium concentration on vanadium. Indeed, vanadium concentration in the solution can depend on $\text{Ca}_3(\text{VO}_4)_2$ solubility limit, meaning that low calcium concentration leaves enough space for vanadium to stay in the solution (Hobson, 2017). However, this mechanism does not drive the vanadium release but can be considered as a permissive condition: as can be seen from calcium concentration profile in Figure 4.3.2, there is a first-flush decrease in calcium concentration from 846 mg/L to approximately 510–600 mg/L by $L/S \approx 2$ and this moderate level was kept until the end of the test; since calcium concentration does not return to the initial value, the solution stays relatively unsaturated with respect to $\text{Ca}_3(\text{VO}_4)_2$ and therefore is permissive for vanadium release but does not cause it directly. The rise in vanadium concentration up to $L/S = 10.4$ is consistent with two mechanisms acting simultaneously: the calcium concentration remaining at the permissive level and the continued dissolution of vanadium-bearing dicalcium silicate/aluminoferrite phases. The involvement of these specific phases is inferred by analogy to Hobson et al. (2017); it is not directly confirmed by the present study.

Lončnar et al. (2016) offered an additional mineral phase that can play a role in controlling oxyanions' release, noting that they have noted the importance of ettringite as a controlling mechanism for the leaching of oxyanions, including vanadate (Lončnar et al., 2016).

Ettringite was also detected by SEM-EDS in this study in the Caster slag. Transient re-incorporation of vanadate into ettringite is one possible explanation for the slight non-monotonous dip in vanadium concentration in Caster slag at $L/S = 4.53$. However, without longitudinal XRD monitoring of the residues, this explanation remains speculative, and the dip could also reflect analytical variability or a transient change in flow path within the column.

The consistent and growing difference in vanadium concentration is well explained by the significantly higher content of vanadium in EAF slag compared to caster-type slag. Neuhold et

al. (2019) noted total vanadium contents in EAF slag as 730, 885, 955, 880, and 1085 mg/kg (Neuhold et al., 2019). In contrast, Grubb et al. (2023), reporting on Caster furnace slag, found that it contained vanadium on the order of 30–40 mg/kg (Grubb et al., 2023). The reason for such a significant difference in vanadium composition between the two slag types can be found in Piatak, Ettler, and Hoppe (2021), who noted that BOF and EAF slags are similar in composition, yet the concentrations of elements in EAF slag can vary widely depending on the types of recycled steel scrap added to the furnace (Piatak, Ettler, & Hoppe, 2021), while the composition of Caster slag depends on refining process: the chemical composition of Caster slag is highly dependent on the grade of steel produced. As a result, compared to BOF and EAF slags, the chemical composition of Caster slag is highly variable (Yildirim & Prezzi, 2011).



slag, EAF slag leaching tests. (Left) Cumulative Mg release (mg/kg) vs. L/S (L/kg), with slope=1.0 reference line; (right) L/S-dependent Mg concentration (mg/L) vs. L/S. Note the linear (non-log) concentration axis on the right panel, in contrast to the log-scale concentration axes used for Ca and Fe.

In particular, the striking nature of the first-flush/depletion trend demonstrated for Mg, the most prominent of all elements investigated in this study, along with a considerable difference in cumulative quantity for Caster (129 mg/kg) and EAF (33.3 mg/kg), corresponds to well-known differences in periclase (free MgO) distribution and crystallization behavior in Caster-type vs EAF slag.

Indeed, Hobson clearly described the dissolution mechanism, stating that Periclase hydrates in water to form brucite, which readily dissolves at pH values < 10.4 (Hobson, 2017). It is crucial to understand why release occurs only after some lag period and quickly thereafter: No significant Mg release to solution was observed during the first 24 hours of leaching because brucite is relatively insoluble at the then prevailing high pH value that was imposed by CaO and calcium silicate weathering (Hobson, 2017), and that Dissolution of brucite leads to a switch in solution chemistry from a Ca to an Mg dominated system (Hobson, 2017). Thus, the two-stage process of periclase hydrating to brucite with its subsequent dissolution being the limited-rate rapid process can be used to explain the occurrence of a fast, brief burst of Mg in both columns observed in this study; moreover, it provides the rationale behind the correlation between early EC peak (which is driven by the same process of intense mineral dissolution) and Mg spike while latter fails to establish a prolonged plateau as Ca: once all brucite has been dissolved, there is no additional buffering mineral phase left to support elevated levels of Mg.

The significant difference in magnitude between Caster and EAF can be explained through differences in periclase abundance and crystallization behavior in these two slags. In particular, according to the systematic review carried out by Medina et al. (2026), periclase was reported as one of the main mineral phases in studies of Caster slag (9 papers) but is much less prevalent in EAF slag studies (7 papers), where wüstite (16 papers) and larnite (13 papers) prevail (Medina, Teixeira, & Bueno, 2026). In a direct comparison of mineral phases in these two slags, Andreas et al. (2014) list for Caster slag: Periclase MgO, Calcium Silicate c and a-Ca₂SiO₄, Iron Fe, Spinel MgAl₂O₄, Mayenite, while for EAF slag: Iron Fe, Merwinite, Monticellite CaMgSiO₄, Clinoenstatite, Calcium silicate, Magn. alum. oxide. Therefore, periclase is the major mineral phase in Caster slag but not in EAF slag, where Mg is distributed among multiple silicate phases (merwinite, monticellite, clinoenstatite) rather than occurring as free periclase. (Andreas et al., 2014)

Yildirim and Prezzi (2011) explained why this difference is important for reactivity: Caster slag cooled rapidly with water granulation is nearly fully amorphous with crystallized periclase, while rapidly cooled BOF and EAF slag samples have a complicated crystalline structure similar to slowly cooled samples (Yildirim & Prezzi, 2011). Therefore, in the case of Caster slag, periclase

crystallizes as a separate and isolated phase in spite of the vitrification of the surrounding matrix and thus becomes easily accessible to water, while in EAF slag, Mg is usually incorporated into complicated silicate crystal structures, dissolving more slowly and releasing Mg less abruptly, as reflected in the observed gradual decline of Caster and first-fraction spike of EAF.

Moreover, the origin of periclase differs in these two types of slags. Specifically, Jacob (2024) reported that, in case of Caster furnace slag, addition of dolomite as a flux to help impurities removal increases MgO content in slag, while in case of EAF slag MgO comes from two sources: flux (dolomite) and refractory material, meaning that Mg burden of EAF slag consists not only of flux component but also of refractory material in more resistant mineral form than Caster slag periclase. (Jacob, 2024)

Loncnar et al. (2017) described periclase morphology in EAF stainless steel slag, finding it to be evenly distributed in air-cooled EAF S slags. Periclase crystallites were cubic in shape, and their dimensions ranged from 30 μm to 250 μm in length and 20 μm to 100 μm in width, while grains included metallic particles (Loncnar et al., 2017). Hao et al. (2026) estimated EAF-specific free MgO content, stating that Electric arc furnace (EAF) slag has a high periclase content (MgO 8%). The free MgO content in EAF slag ranges from 5% to 12% and undergoes hydration-induced expansion, with a volume expansion rate of approximately 117% upon exposure to water (Hao et al., 2026). Therefore, although this confirms the presence of a significant fraction of free periclase in EAF slag, the coarser morphology of crystals (cubic grains of 30-250 μm with metallic inclusions) provides less surface area per unit mass than the fine-grained periclase crystals in rapidly cooled Caster slag and explains the gradual and low magnitude release of Mg from EAF compared to Caster.

Literature-Based Mineralogical Interpretation

The elemental analysis of electric-arc furnace (EAF) slag and caster slag via energy-dispersive X-ray spectroscopy (EDS) is consistent with the mineral assemblages reported for analogous slag types in the scientific literature that used X-ray diffraction (XRD) for mineral identification. The EAF slag consists of elemental values O (28.44–35.40%), Ca (14.11–25.87%), Fe (8.39–

10.67%), Si (3.73–5.97%), Al (3.43–4.26%), Mg (2.21–4.29%), Mn (2.86–3.57%), and Cr (0.22–0.90%). The Caster slag has elevated Ca (15.37–31.54%) but lower Fe (1.60–14.42%).

While EDS elemental data alone cannot distinguish among specific mineral phases, these elemental compositions are compatible with the mineral assemblages reported in published XRD studies of analogous slag types, and these reported assemblages are used below to frame a working mineralogical interpretation of the leaching concentrations of each element in the ICP-OES eluates from the EPA 1314 column tests.

According to published XRD studies of analogous EAF slags, larnite (Ca_2SiO_4) is reported as the main mineral in EAF slag in combination with wüstite (FeO), magnetite (Fe_3O_4), gehlenite, and (Mg, Al, Fe, Cr) spinel (Mombelli et al., 2016; Singh et al., 2021).

These reported minerals would be consistent with all elements detected in the EAF slag EDS spectrum measured in this study (Mombelli et al., 2016). Similarly, published XRD studies of analogous Caster slags report that the minerals in the caster slag include mayenite, periclase (MgO), portlandite, and fluorite (in addition to calcium silicates) due to the higher content of CaO in such slag (Setién, Hernández, & González, 2009; Lončnar et al., 2016). These mineral identifications are drawn from the referenced literature and not from direct XRD analysis of the materials used in this study.

Based on the published XRD mineral assemblages described above, the following interpretation of the leaching data is proposed. Calcium from both slag types would occur in larnite if present, and consequently, its dissolution would provide Ca^{2+} ions and increase the pH of the eluate. In the long term, carbonation of calcium-containing minerals may form calcite (CaCO_3) on the surfaces of mineral grains, potentially preventing the leaching of calcium ions (Engström et al., 2013; Lončnar et al., 2022). Iron would be partitioned between wüstite and magnetite if these phases are present; wüstite dissolves faster, which could explain the elevated iron concentration in early fractions of the columns (Singh et al., 2021). Manganese is known to substitute for iron in wüstite and spinel in analogous slags, and therefore could co-release with iron (Neuhold et al., 2019).

In the case of trace elements, the spinel mineral $(\text{Mg,Fe,Mn})(\text{Cr,Al})_2\text{O}_4$ has been identified in analogous slag types and is important since chromium is incorporated into the crystal lattice of the spinel mineral and not in the form of a dissolved phase, which could explain the presence of significant amounts of total chromium with a very small amount of leached chromium (Neuhold et al., 2019). According to published studies on analogous slag weathering, the secondary mineral phases formed by weathering include portlandite, calcite, brucite, and ettringite (Lončnar et al., 2022; Piatak, Parsons, & Seal, 2015). If formed in this study's columns, brucite $(\text{Mg}(\text{OH})_2)$ could form at increased pH and prevent magnesium release at alkaline conditions, which would be consistent with the magnesium trends observed in the columns (Lončnar et al., 2022). However, it must be emphasized that none of these mineral phases were directly identified in the column materials by XRD in the present study; the mineralogical interpretation presented here is based on EDS elemental data from the tested materials and mineral phases reported for analogous slag types in the published literature.

SEM-EDS Analysis

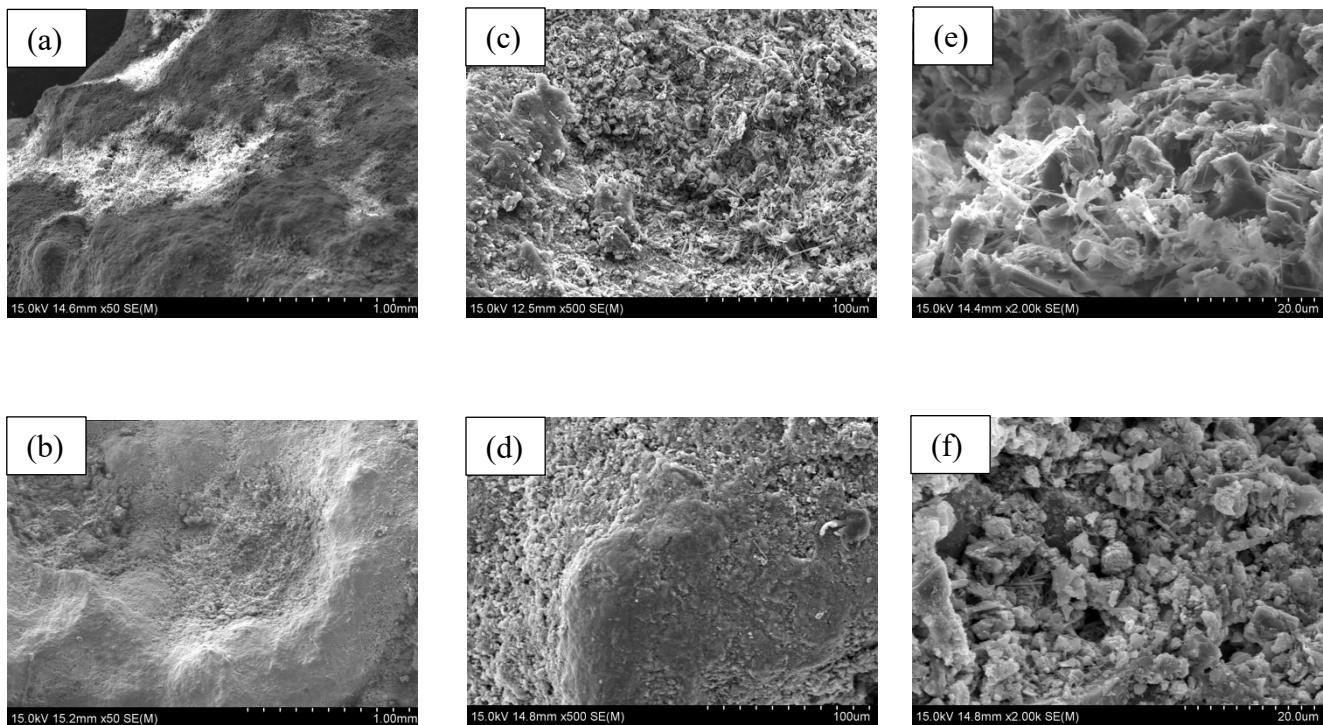


Figure 4.3.5 SEM micrographs of Caster slag surface morphology at increasing magnification (50x, 500x, 2,000x; left to right), comparing pre-column (top row) and post-column (bottom row) conditions following EPA Method 1314 leaching.

In all magnifications investigated, the images of pre-column Caster slag and post-column Caster slag revealed two broad feature types, which included needle-shaped or fiber-type features and spherical or globular-type features. Both feature types were present in both pre-column and post-column Caster slag, without either being unique to one. Because the images were taken using secondary electron imaging, brightness variations within the images were not used to identify any elements or mineral phases present. Spot EDS analysis on specific features was not performed; hence, the following interpretations are speculative comparisons based on morphology alone.

At 50× magnification, both samples showed broadly granular and particulate surface textures. No consistent difference was apparent in the selected fields at this magnification.

At 500× magnification, needle-like and globular features were observed in both the pre-column and post-column samples. Differences between individual fields were observed, but these comparisons are limited by differences in sampling location, surface heterogeneity, and working distance. Therefore, the images do not establish a leaching-induced change in morphology.

At 2000× magnification, the selected pre-column field contained more visible needle-like features than the paired post-column field. This difference is reported as an observation at the field level only. Because the images represent different surface regions and identical-particle tracking was not performed, the apparent difference in needle density cannot be attributed confidently to column leaching.

Needle lengths were estimated from calibrated SEM images. The pre-column measurements ranged from 4.95 to 13.96 μm, while the post-column measurements ranged from 4.77 to 7.70 μm. Because only three features were measured for each condition, these values should be regarded as descriptive measurements rather than representative population statistics. The measured dimensions do not, by themselves, establish the growth environment or identify the features as ettringite. Confirmation would require spot EDS, BSE imaging, XRD, or another phase-specific technique.

Rounded to sub-rounded globular features were also observed in isolated fields. Their morphology can be compared with descriptions of RO-type inclusions reported in the steel-slag literature. However, because the present observations were made using secondary-electron imaging and were not confirmed by spot EDS or BSE imaging, the features are described here as globular particles rather than definitively identified as RO phase.

Overall, the SEM images support the presence of needle-like and globular features in both the pre-column and post-column Caster slag. They do not provide sufficient evidence to establish a systematic change in morphology, confirm mineral phase identity, or demonstrate that any apparent difference resulted from leaching.

Table 4.3.1 Reliable elemental composition (relative error <10%) of Caster pre-column and post-column EDS maps. Elements with relative error >10% in all maps of a given session (O, Cr, and multiple trace elements) were excluded from quantification. Mass-normalized percentages are affected by variable Au-Pd sputter-coating contributions between sessions (see text) and should not be compared quantitatively across pre- and post-column conditions.

Element	Map 1-Pre-column (mass% norm.)	Map 2-Post-column (mass% norm.)
Ca	15.37–31.54	11.77–29.46
Fe	1.60–14.42	4.07–22.58
Si	3.59–7.29	3.24–6.98
Mg	1.17–2.02	3.09–5.56
Al	2.04–2.53	2.06–3.32
Mn	0.56 (only one map reliable)	1.16–7.00
S	1.08 (only one map reliable)	excluded
O	excluded (10.9–10.93% error, both maps)	33.64–34.39 (only one map reliable)
Cr	excluded (both maps)	excluded (both maps)
C, Ni, Zn, Nb, N, B, Co, V, Ti, Ba, As, F, Pd*, Au*	excluded (>10% error)	excluded (>10% error)

The Supplementary Figure S.2 shows SEM micrographs suggesting the selected areas for the EDS mapping of the Caster slag both before and after column leaching. The analyzed regions are labeled directly on the respective SEM micrographs. Two general area EDS maps were generated for the Caster slag before the column leaching process, while two more EDS maps were generated after the column leaching process.

The elemental compositions were derived based on the characteristic X-ray spectral lines during EDS mapping scans. The Mass Norm. (%) refers to software-normalized elemental mass percentages, where the detected elemental mass percentages were scaled such that, their total was made to be 100%. An elemental composition result was accepted to be reliable when its relative error was less than 10%. In the event of an element being reliable in one of the EDS maps, then that element was considered separately rather than using it to determine the whole composition of the sample.

EDS mapping of Caster slag performed before column leaching demonstrated compositional heterogeneity within the pre-column material, as revealed by two general-area maps. In Map 1, the composition is primarily characterized by high levels of Ca (31.54%) and Si (7.29% normalized), with small amounts of Fe (1.60%) and Mg (2.02%). Additionally, Mn could not be reliably detected in this map, as its relative error was 53.66%. In Map 2, the local composition is significantly different: the share of Ca drops down to 15.37%, Si down to 3.59%, while the share of Fe is very high, at 14.42%, almost ten times larger than in Map 1; additionally, Mn (0.56%) and S (1.08%) are detected reliably for the first time. Thus, the heterogeneity of composition in the pre-column data set includes 15.37-31.54% Ca, 1.60-14.42% Fe, 3.59-7.29% Si, 1.17-2.02% Mg, and 2.04-2.53% Al (Table 4.3.1). These values reflect the range of compositions detected across two general-area maps on a heterogeneous surface and should not be interpreted as bulk composition. It can be tentatively concluded that, prior to column leaching, the surface of the Caster slag included two compositionally distinct domains: one Fe-enriched and one Ca-Si dominated.

Similar compositional heterogeneity is observed in EDS maps after column leaching. The general-area Map 1 remains broadly dominated by Ca-Si matrix composition (Ca 27.88-29.46%,

Si 6.40-6.98%, Fe 4.07-4.47%, Mn 1.16-1.22%). In contrast, Map 2 is characterized by a marked shift towards an Fe-Mn-Mg-rich composition (Fe 22.58%, Mn 7.00%, Mg 5.56%, Ca 11.77%, Si 3.24%, Al 2.06%). This shift is consistent with, but does not quantitatively prove, the selective dissolution of the calcium-rich matrix and exposure of the resistant RO phase (Ragipani, Bhattacharya, & Suresh, 2019), because the two maps represent different locations on a heterogeneous surface, not the same field tracked over time. Since both post-column maps represent general-area scans, this heterogeneity should be considered as localized. Moreover, the substantially higher Au-Pd sputter-coating contribution post-column (approximately 20-22% sum vs. approximately 0.7-9.0% sum pre-column) means that mass-normalized elemental percentages are not directly comparable between sessions.

Comparison of pre- and post-column EDS maps. The pre- and post-column data sets independently show the same two-domain structure of the surface comprising a Ca-Si-dominated region and a discrete Fe-Mn (Mg)-enriched region present under both conditions, which suggests that this heterogeneity is inherent to the material rather than a product of leaching. Maximum Fe content in the pre-column sample (14.42%) is within the same order of magnitude as the Fe content in the enriched post-column region (22.58%). Mn is reliably detectable in one map in both samples (0.56% in the pre-column vs. 7.00% in the post-column enriched region). Ca in the matrix-dominated region does not differ greatly between the conditions (31.54% vs. 27.88-29.46%), but in the enriched region, the Ca content is lower in the post-column sample (11.77%) compared to the lowest pre-column value (15.37%). While this pattern is consistent with the hypothesis that column leaching preferentially removes the Ca-rich matrix and exposes the Fe-Mn-rich domain, this interpretation cannot be confirmed quantitatively because the pre- and post-column maps represent different fields of view on a heterogeneous surface, the sputter-coating contributions differ substantially, and no identical-particle tracking was performed. The EDS mapping results are therefore best interpreted as qualitative compositional evidence that both Ca-Si and Fe-Mn(Mg)-rich domains exist in the Caster slag, rather than as quantitative proof of selective dissolution.

Li et al. (2022) stated that under four cooling methods, steel slags consist mainly of C_2S , C_2SP , C_3S , RO, C_2F , and f-CaO phases, with the RO content decreasing in samples as the cooling rate

increases. The RO phase is a solid solution of Fe, Mn, and Mg oxides and appears as dendrites or skeletons typical for fast cooling (Jonczy, 2019). In the process of leaching, the mechanism described in the literature is that the RO phase appears as globules within a calcium silicate matrix containing dicalcium ferrites, and these globules become exposed as the calcium silicate matrix dissolves (Ragipani, Bhattacharya, & Suresh, 2019). This mechanism provides a plausible framework for interpreting the EDS patterns observed here, but it was not directly confirmed by sequential mineralogical analysis of the column residues.

This mapping evidence is consistent with the interpretation of the leachate results presented in the section on ICP results: both pre- and post-column Caster slag include a Ca-Si-dominated domain and a discrete Fe-Mn (Mg)-rich domain. The apparent post-column enrichment of the Fe-Mn (Mg)-rich domain is consistent with the leaching-related exposure of RO-phase globules embedded in the matrix, but this interpretation is qualitative and limited by the methodological constraints described above.

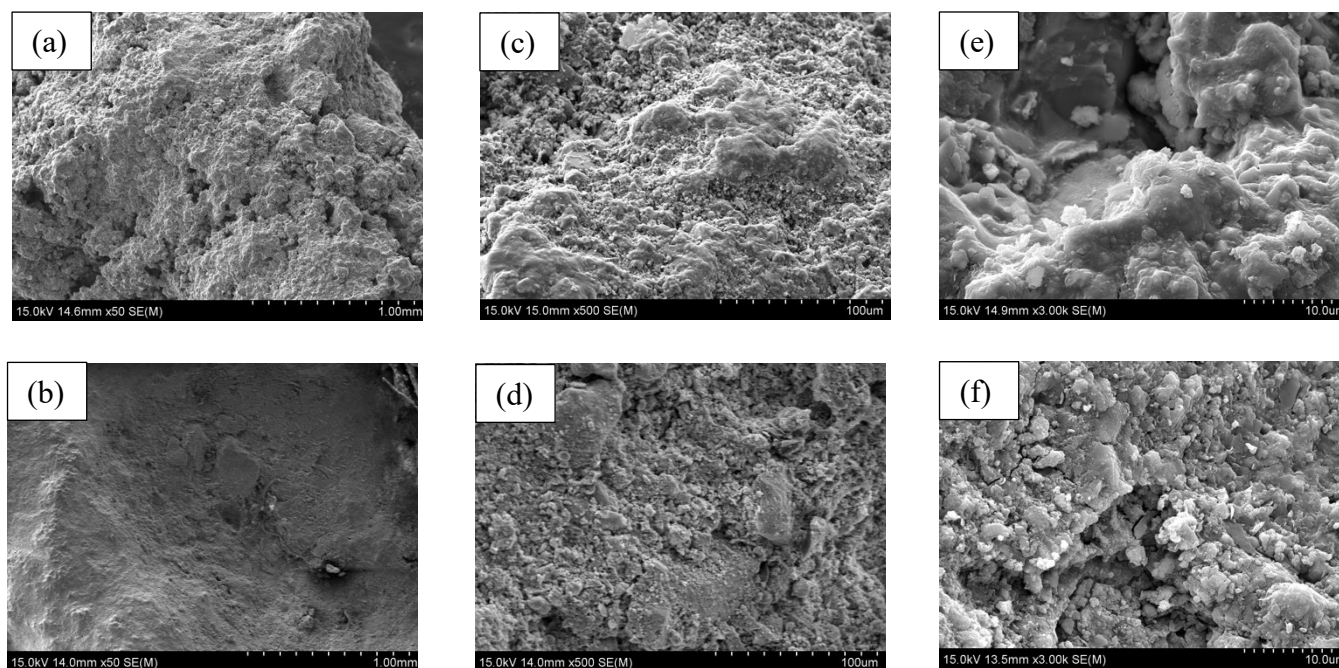


Figure 4.3.6 SEM micrographs of EAF slag at three magnifications (50x, 500x, 3000x). Top row: pre-column (a, c, e), showing rounded, globular particle morphology. Bottom row: post-

column (b, d, f), showing surface textural changes following EPA Method 1314 column leaching. Note: differences in working distance between paired images (see text) may contribute to apparent morphological differences; these should not be interpreted as confirmed leaching effects. All images acquired at 15.0 kV in SE(M) mode with Au-Pd sputter coating. Scale bars: 1.00 mm (50x), 100 μ m (500x), 10.0 μ m (3000x).

In the examined magnifications, pre-column and post-column EAF slag displayed predominantly spherical or globular particle morphologies. The needle-like morphologies were seen occasionally in isolated fields for both types of EAF slag samples. As the SEM images were generated using secondary-electron imaging and spot EDS was not done individually on the features, the images contain only qualitative information about the morphologies.

In 500 $\times$ magnification, there were clusters of needle- or blade-like structures present in one field of post-column sample, and in addition to that, needle-like structures were observed in one or more pre-column fields under varying imaging conditions. Thus, the features were not confined to a particular treatment condition among the analyzed fields. Nonetheless, the images do not provide enough data to conclude if the frequency of occurrence of such features changes with the leaching process.

In 3000 $\times$ magnification, the overall grain morphologies and the presence of cracks were different between pre-column and post-column fields. However, the fields were not identical, and the working distances were not identical between images. These variations may be attributed to spatial heterogeneities and imaging conditions; hence, the variations cannot be concluded as being the result of surface transformation caused by the leaching process. The bright particulate flecks and the cracks seen in some selected fields have been described as unidentified morphological features as no phase specific analysis has been done on those features.

The sizes of the globular particles showed significant overlapping between the pre-column and post-column samples. Since only three particles were measured for each type of EAF slag, no definitive conclusion on the size difference of globular particles can be drawn. The globular

morphology may be compared to RO-type inclusion morphology reported in the literature, yet such a comparison would not be conclusive without spot EDS, BSE imaging, or XRD analysis.

Thus, no distinct and reproducible morphological difference between the analyzed pre-column and post-column EAF fields has been found.

Table 4.3.2 Reliable elemental composition (relative error <10%) of EAF pre-column and post-column EDS maps.⁴

Element	Map 1 (Pre-column, mass% norm.)	Map 2 (Post-column, mass% norm.)
Ca	20.23–25.87	12.40–25.84
Fe	10.16–10.67	5.68–21.18
Si	4.80–5.97	3.62–6.85
Mg	2.21–4.29	2.27–5.06
Mn	3.14–3.57	1.32–7.27
Al	3.61–4.26	1.63–2.71
Cr	0.81–0.90	1.35 (only one map reliable)
S	excluded	1.28–1.29 (only one map reliable)
C, O, Ni, Zn, Nb, N, B, Co, V, Ti, Ba, Pd*, Au*	excluded (>10% error)	excluded (>10% error)

SEM micrographs showing the areas chosen for energy dispersive X-ray spectroscopy (EDS) mapping are provided in Supplementary Figure S.1. Mapped regions are indicated on the

⁴ The pre-column ranges indicated in the table are those only corresponding to the three maps taken at 15 kV. The pre-column ranges that are wider (Ca 14.11-25.87%, Fe 8.39-10.67%, Si 3.73-5.97%, Al 3.43-4.26%, Mn 2.86-3.57%) include the 30 kV map.

relevant SEM micrographs. In the case of the electric arc furnace (EAF) slag, Three EDS maps of general areas were produced before the column leaching process, and two maps were acquired after the column leaching treatment. Three EDS maps of general areas before column leaching were performed under an accelerating voltage of 15 kV, and these maps were used to calculate the primary ranges shown in Supplementary Table S.1. Elemental data are based on the characteristic X-ray spectra measured during EDS mapping analysis. Mass Norm. (%) values reported in the tables are normalized mass percentages of elements calculated by the software, in which the detected mass percentages are re-normalized so that their sum is equal to 100%. Only values having relative error below 10% have been considered reliable. Since the EDS maps are based on different surface regions and Au-Pd coating contribution to the EDS signal differs for the pre- and post-column leaching samples, the mass-normalized values can only be treated as local semi-quantitative compositional markers.

General area mapping before the column (EAF slag) suggested a calcium-iron-silicon-dominated composition that is compatible with the typical mineralogy of steel slag reported in the published XRD literature (see Table 4.3.2). Calcium content in the four general area maps ranged from 14.11% to 25.87% norm., iron content from 8.39% to 10.67%, and silicon from 3.73% to 5.97% norm. Aluminum content was between 3.43% and 4.26% norm., while magnesium was between 2.21% and 4.29% norm. One of the four maps was done at 30 kV, while the rest were made at 15 kV; the Ca content in the former map (14.11%) was far below that of the latter (20.23, 21.92, and 25.87%), and the reason may be the higher acceleration voltage, which enlarges the electron penetration depth and can impact quantification, especially for light elements. The latter map, therefore, was treated separately from the 15 kV maps, and the unqualified range of Ca contents in the four maps is 14.1-25.9 mass% norm.

Chromium content was reliably measured (less than 10% relative error) in three of the four pre-column maps: 0.81% (7.93% relative error), 0.83% (8.75% relative error), and 0.90% (7.38% relative error) mass% norm.; the fourth was excluded due to an unreliable 23.15% relative error. Manganese was reliably measured in all four maps (3.99-4.13% relative error) within the 2.86-3.57 mass% norm. range. Reliable below-threshold elements across the pre-column maps include Ni, Zn, Nb, As, B, Ba, V, Ti, and Co; these elements were excluded from quantification.

Post-column analysis yielded two EDS maps. Map 1 had a matrix-like composition, very similar to the pre-column one, with Ca at 25.84% norm., Fe at 5.68%, and Si at 6.85%, with these three elements being reliable (relative error less than 10%). Map 2 shifted significantly to Fe-Mn-Mg-rich composition: Fe at 21.06-21.18% norm., Mn at 7.08-7.27%, Mg at 5.02-5.06%, Ca at 12.40-12.57%, Si at 3.62-3.66%, and Al at 1.63-1.65 (the range reflects two reprocessed variants of the table, page 7 without Cr and page 8 with Cr). This shift is consistent with, but does not quantitatively demonstrate, the selective dissolution of the calcium-rich matrix and the exposure of the more durable RO phase (Ragipani et al., 2019); however, since the two maps represent different locations on a heterogeneous surface, the apparent enrichment cannot be attributed solely to leaching. Chromium was reliably measured in Map 2 during reprocessing (1.35% norm., 6.27% relative error). Sulfur was reliably measured in Map 2 (1.28-1.29% norm., approximately 6.7% relative error), even though it was unreliable pre-column and in Map 1 (45.65% relative error); this localized sulfur detection is consistent with sulfur being localized in the exposed micro-region rather than being uniformly distributed, but this interpretation is limited by the small number of maps and the absence of identical-particle tracking.

Methodological note: The sum of Au+Pd sputter-coating signal was much higher post-column (approximately 20-22% sum) than pre-column (0.7-9.0% sum), thus mass normalization exaggerates the other element contents post-column. Consequently, direct comparison of mass-normalized elemental percentages between pre- and post-column EAF maps should be avoided; the EDS mapping results are best interpreted as qualitative compositional indicators rather than quantitative evidence of dissolution-driven changes.

The pre- and post-column data sets independently show the same two-domain structure of the surface, comprising a Ca-Si-dominated region and a discrete Fe-Mn (Mg)-enriched region present under both conditions, which suggests that this heterogeneity is inherent to the material rather than a product of leaching. Maximum Fe content in the pre-column sample (10.67%) is within the same order of magnitude as the Fe content in the enriched post-column region (21.18%). Mn is reliably detectable in both samples, with the pre-column range (3.14-3.57%) being lower than the post-column enriched region (7.08-7.27%). Ca in the matrix-

dominated region does not differ greatly between the conditions (20.23-25.87% vs. 25.84%), but in the enriched region, the Ca content is lower in the post-column sample (12.40-12.57%) compared to the pre-column minimum (20.23%). While this pattern is consistent with the hypothesis that column leaching preferentially removes the Ca-rich matrix and exposes the Fe-Mn-rich domain, this interpretation cannot be confirmed quantitatively because the pre- and post-column maps represent different fields of view on a heterogeneous surface, the sputter-coating contributions differ substantially, and no identical-particle tracking was performed. The EDS mapping results are therefore best interpreted as qualitative compositional evidence that both Ca-Si and Fe-Mn (Mg)-rich domains exist in the EAF slag, rather than as quantitative proof of selective dissolution.

4.4 Conclusions

As mentioned before, the 10:90 slag-amended columns exhibited continuous alkaline buffering throughout the test period, maintaining leachate pH well above neutral regardless of the liquid-to-solid ratio. Such behavior was markedly different from that observed in the unamended soil column, where no buffering action was present, and leachate pH tended towards acidic values due to depletion of easily soluble salts. In contrast, slag-mixture columns-maintained leachate pH within the carbonate buffer zone, slightly above the theoretical calcite pH. Such behavior is associated with ongoing system development, driven by the dissolution of the remaining free lime and the carbonate buffer action. This conclusion was based on the leaching test data collected over the 2.5-week period and is not supported by any post-test mineralogical analysis.

Calcium release was shown to be the dominating leaching process in slag-amended columns. After the initial first-flush effect, related to the fast dissolution of the easily accessible free lime, a stable concentration of calcium was formed, changing insignificantly depending on the liquid-to-solid ratio. Such behavior is consistent with calcite being the controlling phase in the long-term dissolution process, owing to its low dissolution rate and ability to release the remaining free lime without increasing its concentration. However, as there is no XRD analysis of the column residue, this attribution is based on the pH value and information found in the literature.

Magnesium behavior showed the classic first-flush depletion effect, involving a peak followed by a decline, consistent with the formation of brucite, an insoluble secondary phase that can appear in the high pH zone in the presence of slag. In the case of brucite formation, the decreasing magnesium concentration at higher liquid-to-solid ratios can be explained. However, as no post-test mineralogical analysis, including XRD, was conducted on the column residues, the presence of brucite is just an assumption based on the leaching data and published works.

Iron concentrations were much lower and did not change much throughout the test period. Iron did not exhibit a first-flush effect, and its concentration changed only slightly within a certain range. Such behavior can be explained by iron release being controlled by the solubility of secondary iron oxyhydroxides, consistent with the always-present alkaline pH and information from the literature; the exact minerals that control iron release in the studied system cannot be determined in the course of this work without further mineralogical analysis.

Boron and vanadium behavior differs from that of the other elements studied. Boron showed a peak-and-drop concentration profile: in the Caster column, boron reached a maximum of 0.972 mg/L at L/S = 2.01 and then dropped; in the EAF column, the peak was 0.984 mg/L at L/S = 9.05. Such behavior shows that there is a limited source of boron, consisting of easily dissolvable borates, which are eventually exhausted. The difference between the peaks of the two columns may be related to differences in the host mineralogy or matrix of the slags; however, this could not be confirmed without mineralogical analysis of the residue. Vanadium concentrations, on the other hand, kept rising throughout the test process: from 0.0536 mg/L at L/S = 1.01 to 0.109 mg/L at L/S = 10.9 in the Caster column, and from 0.0425 mg/L at L/S = 0.503 to 0.208 mg/L at L/S = 10.4 in the EAF column. This behavior correlates with vanadium release mechanisms reported in the literature and is explained by the persistent dissolution of vanadium-bearing mineral phases under alkaline conditions during the test. These mechanisms include destabilization of vanadium-bearing iron-containing phases at high pH, leading to vanadium dissolution (Hobson et al., 2017). However, vanadium concentrations (maximum 0.208 mg/L) were obtained in a 2.5-week laboratory column test in a single replicate per slag type, and the results cannot be extrapolated to field performance of slags in pavement subbase application.

Qualitative microstructural and compositional information for the leaching results was obtained using SEM-EDS analysis. The analysis of the Caster slag before and after leaching, using secondary electron imaging and elemental mapping, showed that it consists of two compositionally different domains: A Ca-Si-dominated matrix and a separate Fe-Mn(Mg)-rich domain. The post-leaching maps showed an apparent enrichment of the Fe-Mn(Mg)-rich domain relative to the Ca-Si matrix, which is consistent with, but does not prove, the dissolution of the calcium-rich matrix and the exposure of more resistant phases, such as RO phase globules. It should be noted that the results of such analysis are limited by the use of secondary electron imaging, different fields of view and working distances, and the lack of identical particle tracking, which make it impossible to interpret the results quantitatively. Mass-normalized elemental percentages cannot be considered as proof of selective dissolution, as there were differences in Au-Pd sputter coating percentage between sessions (approximately 20-22% post-column vs 0.7-9.0% pre-column). The needle-like crystals in the Caster slag, having sizes from 4.77 to 13.96 μm , have morphologically different sizes compared to the 20-50 μm long secondary ettringite needles found in literature in air-cooled EAF slags (Loncar et al., 2017). The shorter size and presence in both pre- and post-column samples are consistent with, but do not confirm, the presence of a pre-existing phase in the slag pore space. At this moment, the identification of the crystals as ettringite is based on morphology and needs to be confirmed by spot EDS or XRD analysis.

The EAF slag showed mostly globular grains before and after the test in the same amount, with no noticeable differences in any magnification. The globular grains (with an average diameter of 23.58 μm before the test and 18.50 μm after) are morphologically similar to RO phase $[(\text{Fe},\text{Mg},\text{Mn})\text{O}]$ described in literature for steel slag (Loncar et al., 2017; Li et al., 2022); however, the identification was not confirmed by spot EDS or XRD analysis in this study.

In conclusion, the 10:90 slag-amended columns exhibited persistent alkaline buffering throughout the test period. Calcium release in the columns was dominated by the initial first-flush and subsequent steady-state behavior, typical for calcite-buffered dissolution. Magnesium showed the first-flush depletion pattern typical for brucite formation. Boron showed a peak-and-drop profile indicating a finite, diminishing source, and vanadium concentration rose over the

test period, consistent with the dissolution of vanadium-bearing mineral phases. The information on the microstructure and elemental composition of the columns, obtained via SEM-EDS analysis, supports the interpretation of the leaching results. However, all mineralogical attributions are based on leaching data and information from the literature and require further confirmation by XRD or other mineralogical analyses of the column residue. Major limitations of this research include single-replicate columns per slag type, a 2.5-week testing period, and the lack of post-test mineralogical analysis; thus, the mechanisms underlying the processes should be considered a working hypothesis.

Supplementary information

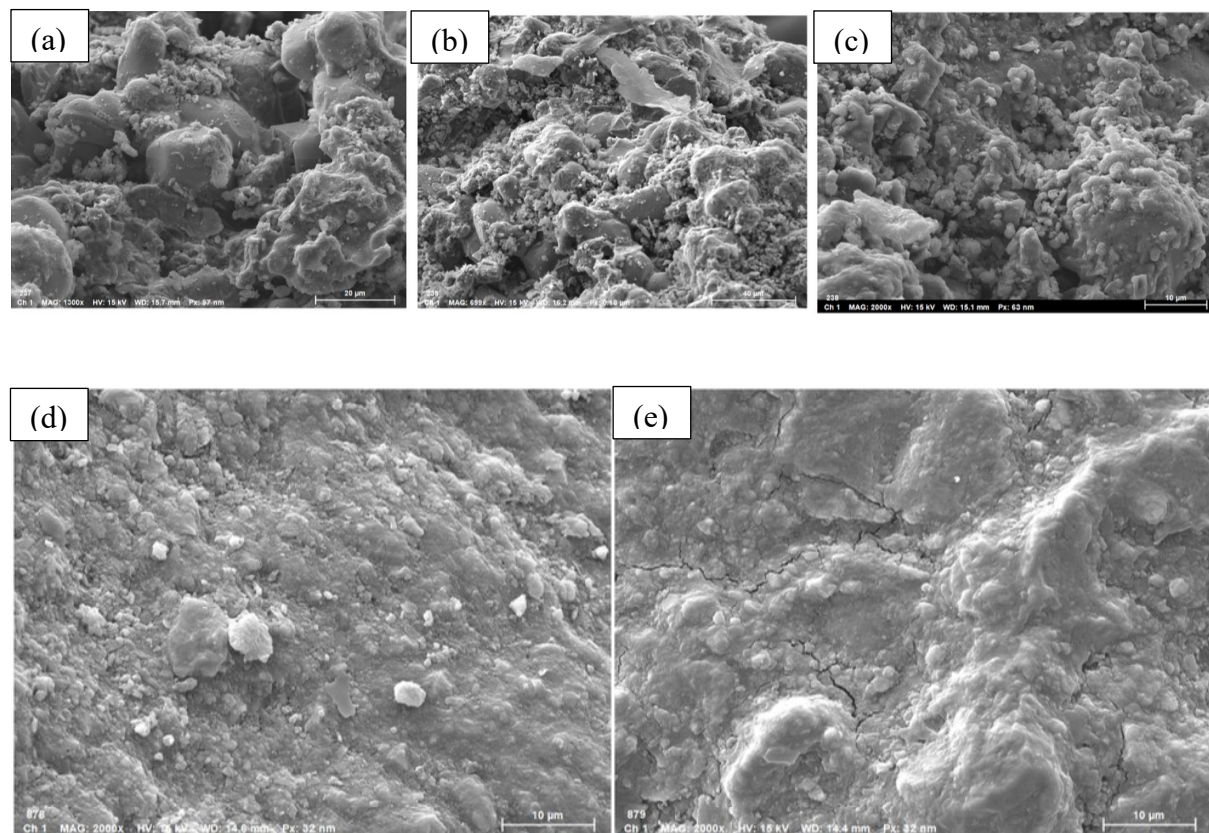
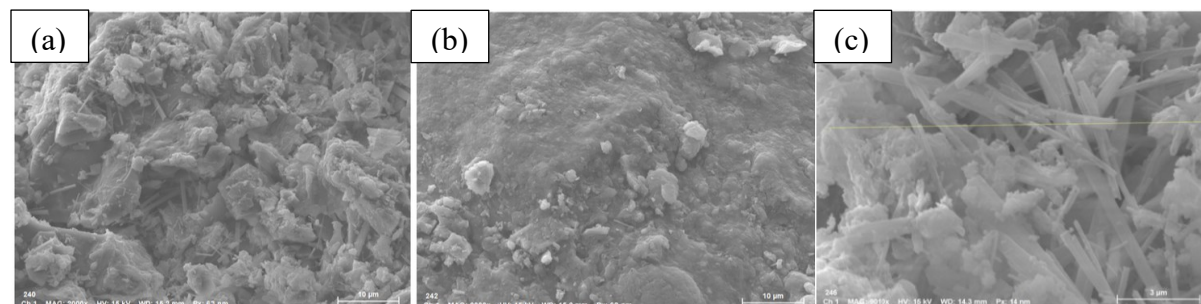


Figure S.1 SEM images showing the locations selected for EDS mapping of EAF slag before and after column leaching. The outlined regions indicate the general areas analyzed by EDS. Three maps were collected before column leaching, and two maps were collected after column leaching. The corresponding elemental composition results are reported in Table 4.3.2 in the main text.



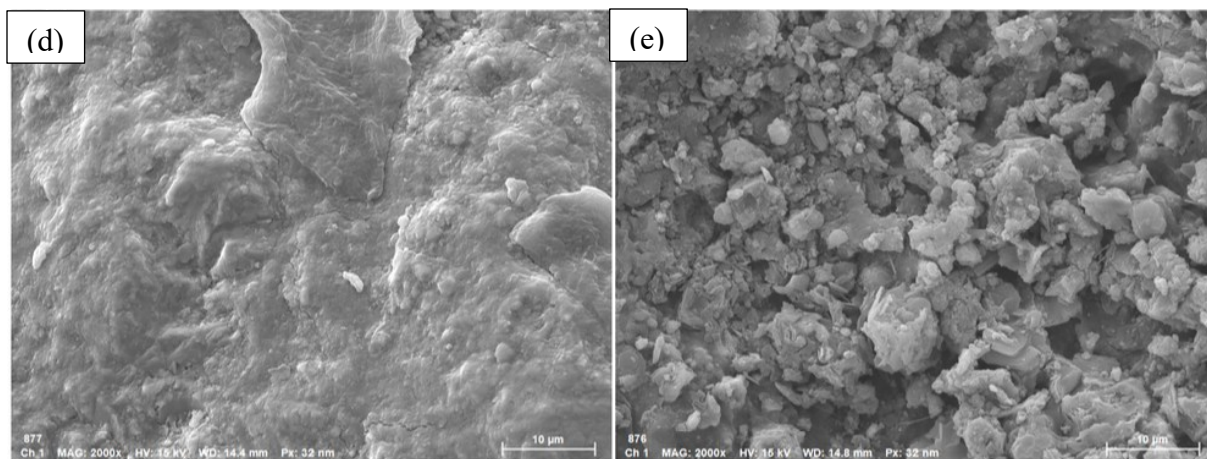


Figure S.2 SEM images showing the locations selected for EDS mapping of Caster slag before and after column leaching. The outlined regions indicate the general areas analyzed by EDS. Three maps were collected before column leaching and two maps were collected after column leaching. The corresponding elemental composition results are reported in Table 4.3.1 in the main text.

Chapter 5 - Field Exposure Experiment

5.1 Introduction

Riley and Mayes gathered a 36-year dataset from long-term ambient monitoring of physicochemical parameters and elemental concentration in samples from two steel slag leachate-affected watercourses in northern England. The waters had high pH levels (over 10), high alkalinity, and were loaded with dissolved metals such as calcium (Ca), aluminum (Al), and Zinc (Zn) (Riley & Mayes, 2015). Over the monitoring period, calcium and alkalinity have decreased only slightly, while water pH has remained about the same. If the current steady decline of alkalinity and calcium continues in the largest stream, calcite precipitation should approach baseline levels in about 50-80 years (Riley & Mayes, 2015). Hobson et al. (2017) reported that leachates from BOF slag at Consett, U.K., showed only small reductions in alkalinity and calcium concentrations over the 36 years since closure, resulting in slightly higher vanadium concentrations than at younger sites. Vanadium in site leachates often exceeds chronic toxicity thresholds (19 ug/L), and Hobson et al. (2017) reported that vanadium may also decline over longer timescales as calcite precipitation sequesters calcium vanadate. Bayless et al. (1998) found that, compared to background wells in the Calumet aquifer, wells screened in slag across northwestern Indiana and northeastern Illinois usually had higher pH and specific conductance, and contained higher levels of alkalinity, dissolved solids, calcium, potassium, sodium, chloride, aluminum, barium, and possibly magnesium. Mal et al. (2022) examined the impact of slag dumping over the past 60 years on the hydrogeological environment in Durgapur, an industrial city in eastern India. The groundwater survey showed the unconfined nature of the shallow aquifer and elevated concentrations of Ca and Mn in the area. The saturation index for groundwater samples indicated supersaturated conditions with respect to aragonite, calcite, dolomite, and rhodochrosite near the slag dump. Testing leachate from slag samples showed high Mn concentrations in the slag dump leachate.

Loncnar et al. (2022) examined EAF and Caster slag heaps in Slovenia and found that across the landfill, the same minerals and sorptive phases govern how problematic elements leach, even though the chemical makeup varies from spot to spot. Carbonation occurred in the steel slags they examined, with a $\text{CO}_3/(\text{Ca}+\text{Mg})$ molar ratio of 0.53 compared to fresh slag; however, this process did not substantially alter element leaching behavior. EAF slag

maintains high acid-neutralization capacity (Yu et al., 2025). To drop the eluate's pH to 7, approximately 5 mol/kg is required. These titration results indicate that EAF slags can maintain alkaline leachates for extended periods (Yu et al., 2025). Diener et al. (2010) found that aging slags in high CO₂ reduced the pH by about 2 points and halved the acid neutralization capacity. After 10 months of aging, trace-element release from steel slags was essentially undetectable for elements such as As, Cd, Co, Cu, Hg, Mn, Ni, Pb, and Zn (Diener et al., 2010). Engström et al. (2013) reported that calcium and aluminum leaching exhibit behavior analogous to that of chromium and molybdenum. Their leachability decreases by factors of 3.0 to 9.0, 3.0 to 64.0, and 2.3 to 2.9 for three different EAF slags over 24 months. Magnesium, though, becomes more leachable with age (Engström et al., 2013).

Mal et al. (2022) used HYDRUS-1D to model manganese movement through the vadose zone beneath a slag dump. The findings suggest that manganese may be detected in groundwater about 4 years after dumping begins, and that maximum pollution will occur in 40 years. The study by Baumgartner et al. (2026) focused on Cr(VI) emissions from ferrochrome slag heaps, using a dynamic model that goes beyond what is captured by the life-cycle assessment tool. Rather than predicting a uniform emission of 1 kg over the slag's lifetime, the model "predicts reactively driven" pulses. Specifically, 80% of the total Cr (VI), which means that 80% mass will be emitted over just five years in the form of high-concentration pulses. These pulses could exceed acute toxicity thresholds, a risk that would be obscured in a 100-year average assessment (Baumgartner et al., 2026). Yu et al. additionally demonstrated that chromium is not exhausted for 30 years when EAF slags are used as ground cover material and are left unprotected (Yu et al., 2024). Seignez et al. (2006) conducted an outdoor weathering experiment on Pb-Zn slags and found that the reaction rate was somewhat slower than in the laboratory column experiment, although the qualitative nature of the alteration was similar.

Gomes et al. (2019) found that constructed reedbeds effectively removed calcium (98%), aluminum (81%), barium (98%), chromium (90%), gallium (80%), nickel (98%), and zinc (98%), while lowering the pH and alkalinity. There was no statistical difference in arsenic and vanadium levels between leachate influent and wetland samples, indicating that arsenic and vanadium were not effectively removed.

Existing research indicates that steel slag leachates exhibit sustained alkaline pH, a pH decline due to carbonation, and elemental release rates that depend on mineral solubility and the redox environment. However, three important knowledge gaps remain. First, most datasets on steel slag leaching are based on laboratory batch/column experiments that involve controlled liquid-to-solid ratios and temperatures and cannot account for natural variability in leachate chemistry driven by infiltration, evapotranspiration, snowmelt, and temperature cycles. Second, while long-term monitoring programs have provided information on the evolution of leachate quality over multiple decades for a few legacy slag sites, the temporal resolution of these datasets is too coarse to capture the seasonal or event-based changes in elemental release. Third, no studies have compared the leaching characteristics of EAF slag and furnace slag deposits under similar open-air environmental conditions over the same monitoring period. Without this comparison, it is impossible to ascertain whether the differences in leachate quality stem from slag characteristics or environmental conditions.

To address the identified gaps, the current study conducted a six-month field exposure test (December 2025 to May 2026) comparing the leaching properties of EAF and caster slags under outdoor ambient conditions at the University of Maryland. Specifically, the main objectives were: (1) to determine the leaching kinetics of four principal leachate constituents (Ca, Mg, Mn, S) across five sampling events spanning winter and spring; (2) to investigate the role of seasonal changes in precipitation, temperature, and humidity on leaching chemistry; and (3) to identify the prevailing mechanisms of element release using Pourbaix diagrams and log-log regression analysis of cumulative release versus cumulative liquid-to-solid ratio.

5.2 Methodology

The potential for leaching from EAF and caster slag under landfill exposure conditions was studied in a weathering experiment, with the slags exposed to natural conditions in the open air. The test material was subjected to open-air conditions for more than six months (from December 2025 to May 2026), receiving precipitation, snowfall, and variable temperatures, mimicking the exposure conditions at a landfill site. This experimental setup represents weathering under stockpile conditions, not an engineered landfill with a leachate collection system. Due to material and logistics limitations, only one basin was used per slag type.

Therefore, it is advisable to consider results only for the demonstrated temporal trends, not for statistical generalization across multiple installation replicas.

Approximately 55 kg of each pure slag type was placed in a medium-sized polypropylene basin measuring approximately 43 x 33 cm (Figure 5.2.1) and exposed to the natural environment at the University of Maryland. The slag samples were purchased as individual streams from TMS International, Norfolk, Nebraska. The basins were open on three sides and received natural precipitation; no extra liquid was added, and there was no controlled liquid/solid ratio. The slags were not mixed with any other materials, as the aim was to study the leaching potential under the most pessimistic case scenario for the unprocessed materials. There was a drainage pipe at the bottom of each basin, capped with a stopper, to reduce evaporation and reactions that change metal phases. The drainage pipe had a capacity to hold up to 600 mL of leachate. After each sampling event, the pipe was emptied and closed again until the next sampling period. A geotextile membrane at the drainage pipe entrance was used as a coarse filter to prevent suspended solids from entering the leachate. Leachate volumes were not quantified for each sampling event; thus, only trends in concentration changes can be demonstrated in this study.

The initial solid phase pH was determined according to the procedure described in EPA Method 1311 (Toxicity Characteristic Leaching Procedure), Section 7.1. An aliquot of approximately 5 g of each slag was added to reagent-grade water at a 20:1 ratio (5 g of the slag sample in 96.5 mL of deionized water). The mixture was stirred for 5 minutes, and the pH was measured. The slag particles were sufficiently fine to be analyzed directly without grinding. As a result, the initial solid pH values were 11.18 for EAF slag and 11.83 for caster slag; those values demonstrate high alkalinity and match the presence of CaO and Ca(OH)₂. The mineral phase identification is based on information from the literature on EAF and caster slag compositions; there was no pretest mineralogical characterization of the slags used in the testing (XRD).

The leachate was collected at five sampling points over six months of the experiment (approximately once a month). During each sampling event, the leachate pH and electrical conductivity (EC) were measured approximately 15 minutes after the collection. Samples were acidified to pH ≤ 2 with 67% HNO₃ and stored at 4°C before analysis. The elemental

concentrations in the samples were determined by inductively coupled plasma optical emission spectrometry (ICP-OES) using a Shimadzu ICPE-9820 spectrometer in accordance with EPA Method 6010B. The multi-element calibration standards were prepared with a matrix like the leachate matrix. The periodic calibration verifications were conducted during each analytical run. The instrument blanks, CCV (calibration check verifications), and matrix spike recoveries using an ICP multi-element stock solution were analyzed as part of the QA/QC procedures; all the QA/QC results meet the laboratory acceptance criteria. All the samples were analyzed within 6 months of collection, within the specified holding time per EPA Method 6010B. The nominal detection limit for Shimadzu ICPE-9820 is 0.01 mg/L; results below this level are reported as half of the MDL.

Environmental variables such as daily precipitation, snowfall, temperature, and relative humidity were obtained from the NOAA Cooperative Observer Program station in College Park, Maryland. Total precipitation was 365.6 mm, and snowfall was 357.8 mm during the study period. Snow depth was converted to water equivalent using a 10:1 ratio (a commonly used default value for hydrological studies; Baxter et al., 2005). Given that the average daily high temperature during the winter part of the study period is 7.1°C (above freezing), the above ratio may be underestimated, as the actual ratio may range from 5:1 to 8:1 for warm, wet snow. The total water input from snowfall is, thus, approximately 36 mm. Thus, the total water input to the basins is approximately 401 mm (366 mm precipitation + 36 mm snow water equivalent). It should be noted that the exact water balance cannot be obtained for the current experimental setup due to the lack of confinement, open drainage, and uncontrolled evaporation from the surfaces, as well as absorption by the surrounding soil. The precipitation and snowfall data are considered climatic exposure factors, not exact infiltration values.

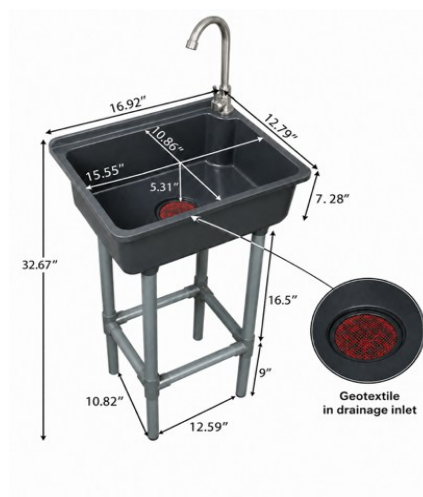


Figure 5.2.1 Field lysimeters containing Caster slag (left) and EAF slag (right), installed outdoors at the University of Maryland for the field exposure experiment, December 2025 - May 2026. Leachate was collected through the drainage outlet at five sampling intervals over the monitoring period.

5.3 Results and Discussion

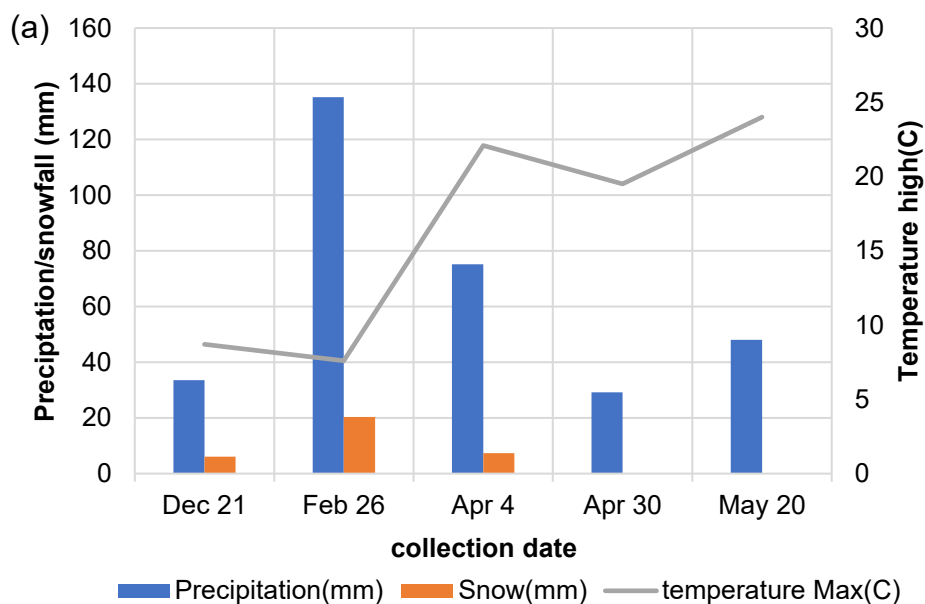
The field exposure test was observed over a six-month span, December 2025 to May 2026, with five sampling times taken for both EAF and Caster slag. The initial pH values of the EAF and Caster slags were 11.18 and 11.83, respectively. This indicated the highly alkaline nature of the air-cooled slag samples due to their high CaO and Ca(OH)_2 contents.

Environmental variables, such as precipitation, snowfall, temperature, and relative humidity, were taken at thirteen biweekly intervals throughout the experiment to evaluate climatic impacts on leachate chemistry (Figure 5.3.1). The leachate pH and electrical conductivity (EC) were measured at the five sampling points to observe the electrochemical response of slag to different environmental stimuli (Figure 5.3.2).

The precipitation data were collected from the Climate Data Online station of College Park, Maryland. NOAA provides total precipitation (rainfall + snowfall) as a single parameter. The snowfall data were treated independently of total precipitation as snow-water equivalent (SWE), using the standard 10:1 ratio of snow depth to SWE to avoid double-counting in the total NOAA precipitation data. Total rainfall was 321.1 mm across five sampling periods. Precipitation values at each period were: 33.5 mm (T1, Dec 21), 135.1 mm (T2, Feb 26), 75.2 mm (T3, Apr 4), 29.2 mm (T4, Apr 30), and 48.0 mm (T5, May 20). Maximum precipitation

was seen during T2 (135.1 mm), while minimum precipitation was seen during T4 (29.2 mm). There was a total SWE of 33.7 mm over the observation period, broken down into 6.1 mm (T1), 20.3 mm (T2), and 7.3 mm (T3).

According to the results obtained from seasonal observations, winter sampling events (from December 2025 to February 2026, denoted as T1 and T2) had a higher mean rainfall (84.3 mm per event) and higher mean snowfall (13.2 mm snow-water equivalent per event) compared with spring sampling events (April to May 2026, T3, T4, and T5) that had a lower mean rainfall (50.8 mm per event) and almost no snowfall with one exceptional case of snowfall (7.3 mm SWE) at T3 (late April). It is crucial to acknowledge that precipitation amount itself is not the primary factor determining leachate composition; infiltrated leachate can be reduced due to evapotranspiration losses (Andreas, Diener, & Lagerkvist, 2014; Engström et al., 2014). The spring period (April–May) had higher temperatures; therefore, evapotranspiration was higher, and net precipitation was lower. It should be noted that seasonal precipitation, leachate volume, overflow and runoff, snowmelt contribution, and the amount of water in the slag or drainage system were not measured in this experiment. Thus, changes in concentration cannot distinguish between increased elemental release and decreased dilution. The transition from winter to spring needs to be considered when interpreting the data.



(b)

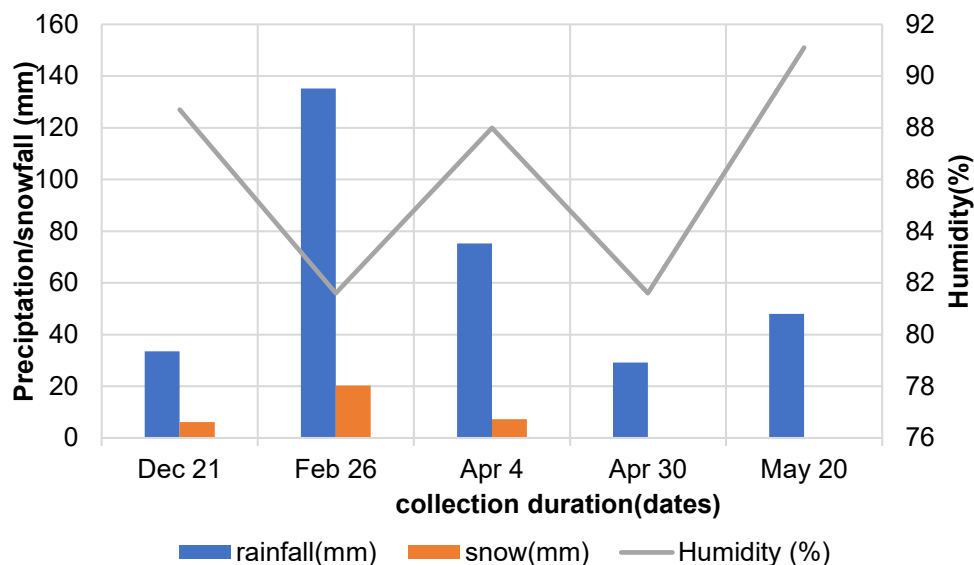
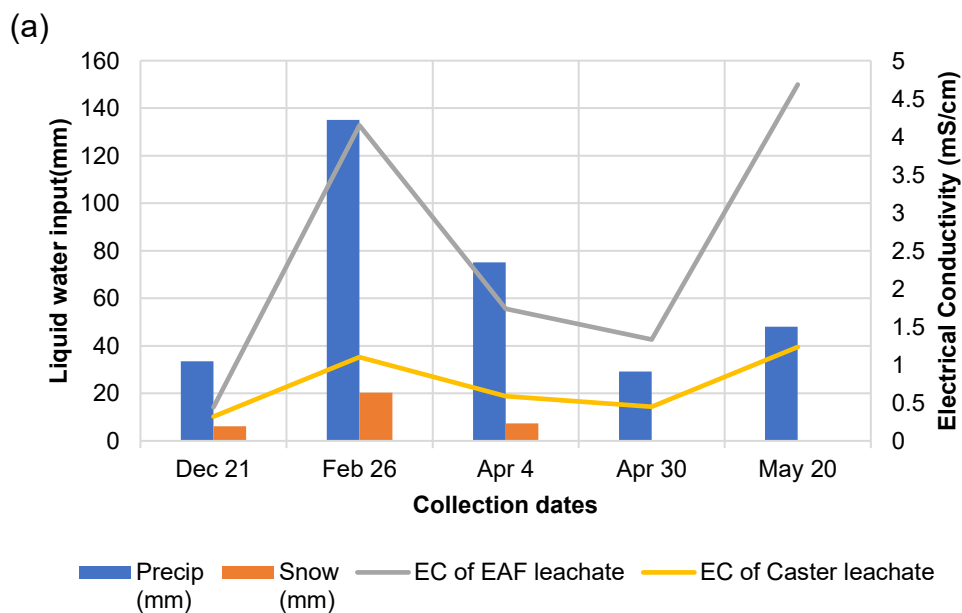


Figure 5.3.1 Environmental conditions during the monitoring period (December 2025 to May 2026): (a) precipitation and daily high temperature, (b) precipitation and relative humidity. Temperature. Maximum daily temperatures for six months range from -1.27°C to 24.97°C (29.71°F to 77.04°F). The period from December 2025 to March 2026 was characterized by lower temperatures, with an average maximum daily temperature of 7.13°C (44.83°F).

Temperatures increased in spring up to 21.83°C (71.30°F) for the period of April to May 2026 (Figure 5.3.1a). Diener et al. (2020) analyzed the effect of temperature on the reaction across three regimes – 5°C , 30°C , and 60°C . They found that higher temperatures led to a faster transformation of the Ca-bearing phase into the much more stable form of CaCO_3 . Similarly, Engström et al. (2014) analyzed whether temperature affects the morphology of the slag and found that morphology remained unchanged, which means that the reactions took place on the surface. As a result of temperature change, CaCO_3 formation was observed on the surface after 24 months. Hobson et al. (2017) noted that when rainwater passes through slag deposits, dissolved CO_2 is rapidly consumed by reaction with the highly alkaline material. This reaction shifts the $\text{Ca}(\text{OH})_2$ equilibrium towards the formation of a calcium-rich, highly alkaline leachate. Accordingly, the progression from winter to spring in the current study is equivalent to a transition from a period of high precipitation and dilute leachate to one of low precipitation and more alkaline conditions.

Relative humidity was measured for each of the 13 biweekly monitoring sessions over the course of six months (refer to Figure 5.3.1b). The relative humidity ranged from 81.6% to 91.1%, with an average of about 86.2%. At the time of collecting the samples during the five sessions, the humidity was measured to be 88.7% (T1, December 21), 81.6% (T2, February 26), 88.0% (T3, April 4), 81.6% (T4, April 30), and 91.1% (T5, May 20). Maintaining a high humidity level during the two seasons implies that a constant moisture level was created in the experimental area throughout the study. In this case, evaporation from the slag surface would not occur because humid air has a low capacity to hold water vapor. This ensures continuous interaction between precipitation infiltrating the slag and the slag material, promoting its dissolution and leaching. According to Diener et al. (2010), relative humidity does not affect leaching behavior, as indicated by their PLS model, and it has no influence on leachate composition. The experiment conducted by Andreas, Diener, and Lagerkvist (2014) had a vegetative layer on top of the slag, stimulating evapotranspiration and preventing infiltration through the slag liner.



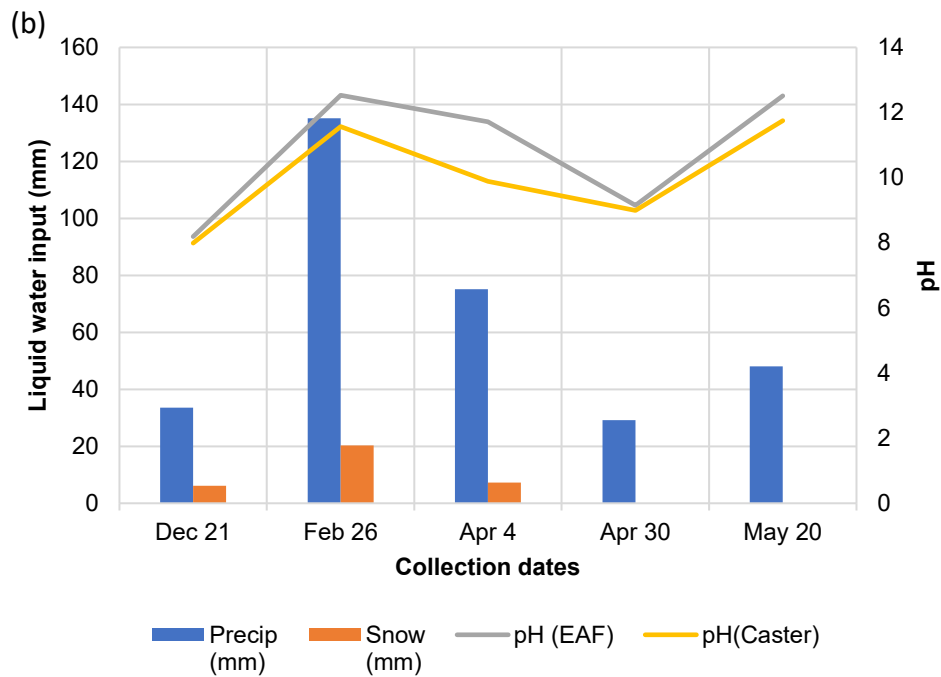


Figure 5.3.2 Seasonal variation in leachate chemistry of EAF and Caster slag throughout the six-month monitoring period (December 2025 to May 2026). (a) Electrical conductivity (EC) of EAF and Caster leachate in relation to cumulative precipitation and snowfall across five collection periods. (b) Leachate pH of EAF and Caster in relation to cumulative precipitation and snowfall across five collection periods.

Electrical conductivity and pH of the leachate. Electrochemical measurements and pH analysis showed no monotonic change in leachate composition throughout the research period; instead, the results demonstrated a variable trend with two overlapping peaks (Figure 5.3.2). In the case of the EAF slag, the pH was strongly alkaline, ranging from 8.19 (T1) to 12.53 (T2), then decreased to 9.15 (T4) and rose to 12.51 (T5). The seasonal mean pH values for the EAF slag were 10.36 in winter and 11.13 in spring. The EC in the EAF leachate varied from 0.44 mS/cm (T1) to 4.69 mS/cm (T2).

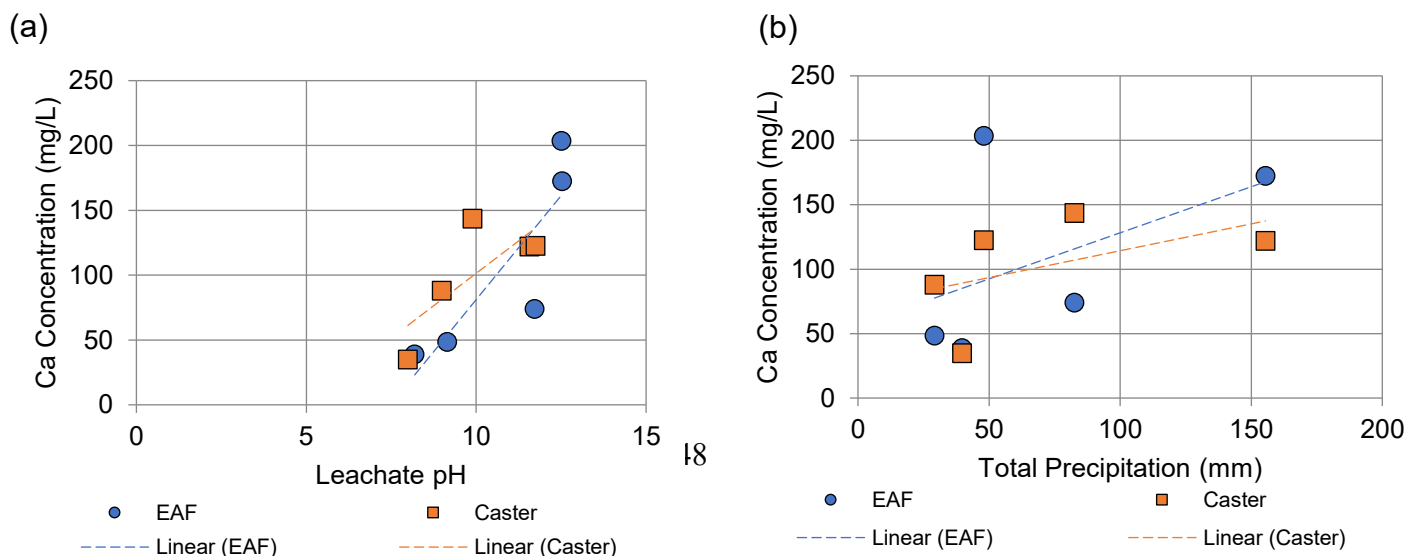
The Caster slag had a comparable but less pronounced trend. The pH in the Caster leachate ranged from 7.99 (T1) to 11.75 (T5); intermediate values included 11.57 (T2), 9.89 (T3), and 8.99 (T4). The EC in the Caster leachate was consistently lower, at 0.32 mS/cm (T1) and 1.24 mS/cm (T2). According to Riley and Mayes (2015), variations in the chemical composition of the leachate can be caused by seasonal effects through hydrological events, where pH does not change even after a reduction in slag alkalinity and calcium content. As seen in the

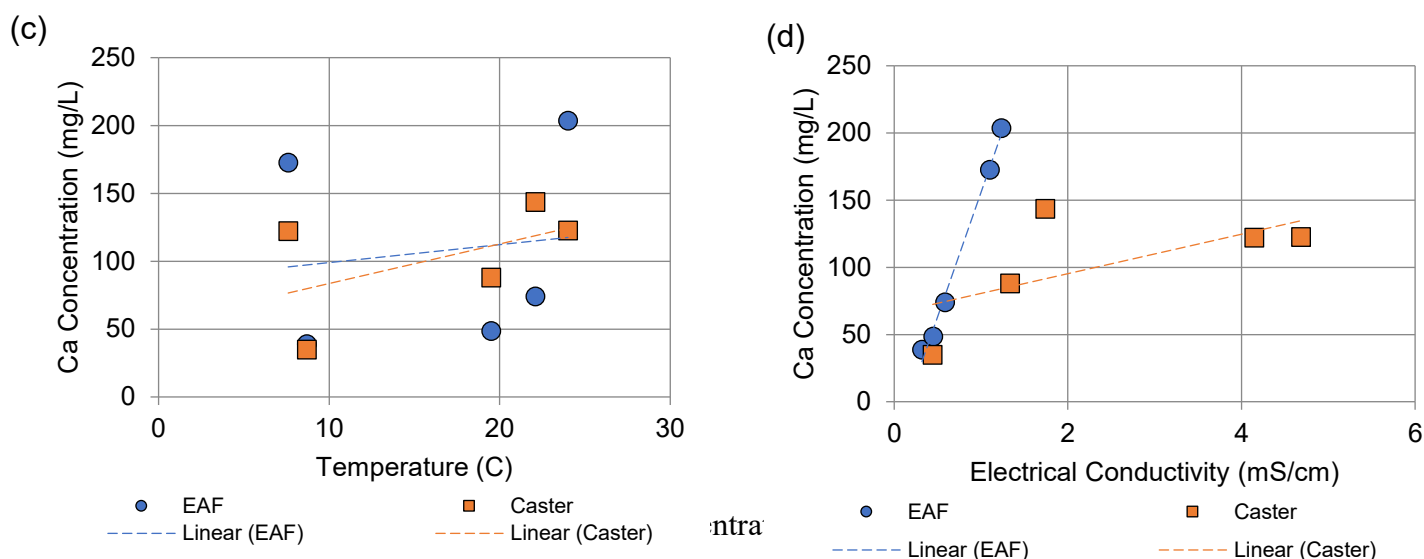
current study, both slags had the highest pH and EC values in the winter season with high precipitation (T2); a decrease was noted in the spring events with low precipitation (T3, T4), and a rise at T5. Thus, the hypothesis that initial heavy rains mobilized the easily soluble fraction, increased pH and EC values, and that the following drier spring season allowed depletion of this fraction could be assumed.

Table 5.3.1 Descriptive statistics of major leachate constituents (Ca, Mg, Mn, and S) in EAF and Caster slag leachate across five sampling events during the six-month field exposure study (December 2025 to May 2026). Values represent mean, standard deviation (SD), and range of measured concentrations (mg/L) for each slag type

Parameter	EAF Mean	EAF SD	EAF Range	Caster Mean	Caster SD	Caster Range
Ca (mg/L)	107.43	68.73	38.75 – 203.50	102.18	42.56	34.90 – 143.50
Mg (mg/L)	6.99	3.62	3.26 – 11.75	8.13	2.77	4.76 – 11.00
Mn (mg/L)	1.04	0.55	0.12 – 1.47	1.76	1	0.94 – 3.38
S (mg/L)	44.7	52.98	0.53 – 136.50	35.71	15.94	15.70 – 57.50

The table presents the Descriptive analysis of the 4 most abundant elements detected in the landfill leachate. Calcium and sulfur are released at higher concentrations, and magnesium is released at a slightly lower concentration than the others. Dissolved calcium characterizes the alkalinity and concentration of the steel slag leachate (Riley and Mayes, 2015). The differences in concentration across these five intervals suggest that leaching is not a static process; it tends to respond to changing environmental conditions, such as precipitation and temperature.





EAF and Caster slag across five sampling events: (a) Ca concentration versus leachate pH, (b) Ca concentration versus total precipitation (rain + snow, mm), (c) Ca concentration versus average temperature (°C), and (d) Ca concentration versus electrical conductivity (mS/cm). Dashed lines represent linear regression trends for each slag type. With only five sampling events per slag type, these correlations are exploratory.

The scatter plots (Figure 5.3.3) were created to investigate the relationships between environmental variables and calcium concentrations in the leachates. Each data point represents values for EAF slag (blue circles) and Caster slag (orange squares) with corresponding linear regression trends illustrated by dashed lines. Given the low number of observations ($n = 5$) per slag type, the correlations should be treated as exploratory.

A weak positive correlation between pH and calcium in leachate was identified for both slags. Calcium concentration correlated positively with leachate pH. So, at pH 8.19, the Ca concentration was 38.75 mg/L, while at pH 12.53 it was 203.5 mg/L for the EAF slag. It has been confirmed with Pearson's correlation coefficient, where $r = 0.86$ and $p = 0.063$ (Figure 5.3.3a). For Caster slag, the correlation was slightly weaker ($r = 0.76$, $p = 0.132$); Ca varied from 34.9 to 143.5 mg/L, and pH varied from 7.99 to 11.75. Although neither correlation reaches the 0.05 significance level, both are positive, consistent with the hydrolysis of CaO , as mentioned below. The correlation between Ca and total precipitation was weak and insignificant for both slag types (Figure 5.3.3b; EAF: $r = 0.49$, $p = 0.407$; Caster: $r = 0.50$, $p = 0.388$), which means that precipitation-induced dilution does not dominate the variation of Ca

in leachate. There was no correlation between Ca concentration and temperature (Figure 5.3.3c; EAF: $r = 0.13$, $p = 0.829$; Caster: $r = 0.53$, $p = 0.362$).

There is a strong correlation between calcium and electrical conductivity in the EAF slag plot (Figure 5.3.3d; $r = 1.00$, $p < 0.001$). The strong correlation confirms that Ca plays a significant role in the leachate conductivity. The EC range for the Caster slag was lower (0.32 to 1.24 mS/cm compared with 0.44 to 4.69 mS/cm for the EAF slag), and the correlation between Ca and EC was lower ($r = 0.64$, $p = 0.247$), which is consistent with the lower total ion content in Caster slag.

Despite the positive correlation between pH and Ca in the leachate, it should be interpreted with caution in batch tests, as the addition of acid causes both pH reduction and calcium dissolution, resulting in a negative correlation between pH and dissolved Ca; under natural conditions, the causality is reversed, while pH increases as Ca^{2+} forms portlandite or calcite (Lončnar et al., 2016). Under natural conditions, the causality is reversed: hydrolysis of CaO and subsequent dissociation of $\text{Ca}(\text{OH})_2$ lead to the formation of Ca^{2+} and OH^- in stoichiometric amounts, making Ca dissolution the source of the increased pH rather than its result (Riley and Mayes, 2015). Differences in mechanisms lead to differences in the signs of the correlations: while in the batch test it is negative, under natural conditions it is positive (Lončnar et al., 2016). The positive correlation between pH and Ca in field leachate has been shown by Riley and Mayes (2015), who studied steel slag-affected watercourses in northern England and attributed it to the effect of CaO weathering on leachate alkalinity.

All changes from the original version are bolded above. They include changing from bar-and-line to scatter plots, rearranging panels (new (b) = precipitation, new (c) = temperature, new (d) = EC), adding the explicit r and p -values for each panel, describing the precipitation relationship as "weak and non-significant" instead of "moderate inverse", including the exploratory caveat, and fixing some grammatical issues in the old text.

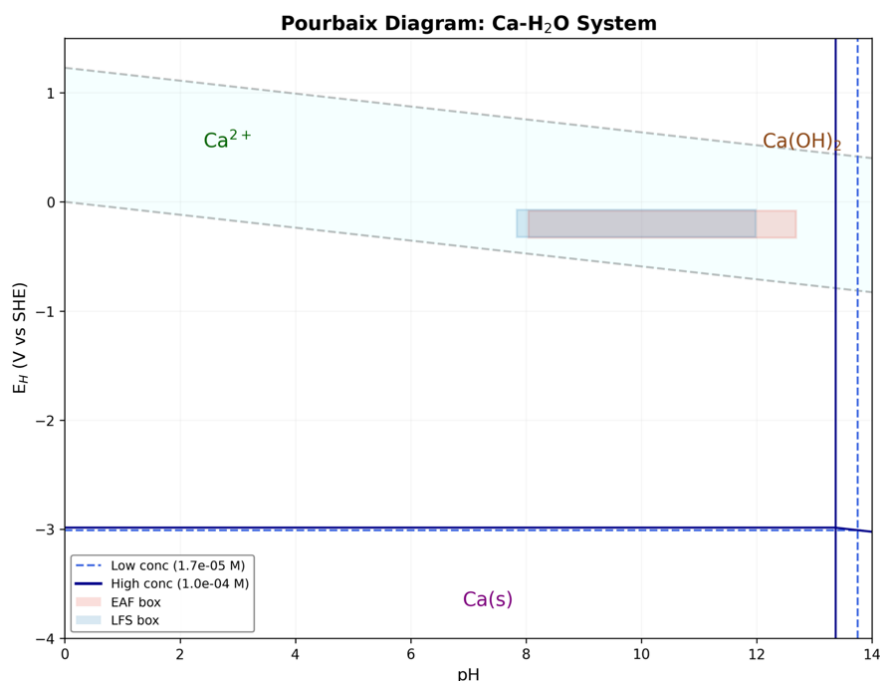


Figure 5.3.4 Pourbaix diagram (Eh-pH) for calcium showing Stability fields of Ca^{2+} and $\text{Ca}(\text{OH})_2$ in the $\text{Ca-H}_2\text{O}$ system.

A $\text{Ca-H}_2\text{O}$ Pourbaix diagram was constructed at 25°C and 1 atm to determine the thermodynamically stable calcium phases as a function of pH and Eh for the conditions of interest in the EAF and Caster slag leachates. Eh was measured during each sample collection using the same pH electrode as the pH measurement and was used to plot the sample data on the Eh-pH diagram. The rectangular region representing EAF and Caster conditions on the diagram covers the observed range of Eh and pH values across the five collection events. The $\text{Ca-H}_2\text{O}$ Pourbaix diagram shows that Ca^{2+} is the only stable species in terms of dissolved calcium over the field pH range observed (EAF: pH 8.19–12.53; Caster: pH 7.99–11.83), whereas portlandite ($\text{Ca}(\text{OH})_2$) occurs only when $\text{pH} > 13$ for the Eh values corresponding to near-surface oxidation conditions.

The stability field of portlandite was not obtained in either the EAF or Caster leachates, since the highest pH measured in both samples was less than one or two pH units needed to ensure portlandite stability, thus keeping the leachate in the Ca^{2+} field. This thermodynamic approach implies that it is possible to dissolve calcium minerals and solubilize Ca^{2+} ions in solution without the leachate being buffered to portlandite saturation. However, as mentioned earlier, the Pourbaix diagrams provide information on thermodynamically stable species

rather than rate-controlling processes; therefore, the observed behavior requires confirmation via other approaches as well.

Limitations of the binary Ca–H₂O system. The binary Ca–H₂O system ignores the presence of carbonate ligand (CO₃²⁻) and therefore does not consider calcite (CaCO₃) as a stable solid phase. Moreover, the diagram does not account for the effects of activities, ionic strength, alkalinity, and carbonate concentration, as the model assumes unit activity for all aqueous phases. Under natural conditions, the continuous dissolution of atmospheric CO₂ in percolating rainwater produces carbonic acid, which dissociates to supply carbonate ions in the system. The inclusion of CO₂ in the system results in the ternary Ca–CO₂–H₂O system, in which calcite is the thermodynamically stable calcium solid phase over the entire pH range studied (approximately pH 7 to 14), except when Ca²⁺ ion concentration decreases. This observation is in agreement with Engström et al. (2014), who showed the precipitation of calcite on EAF slag through a process involving three steps: dissolution of atmospheric CO₂ in rainwater to form carbonate ions, weathering of calcium-rich silicates from slag, and finally the rapid precipitation of calcite from the products of the first two reactions (Engström et al., 2013). Through XRD analysis, it was shown that calcium carbonate forms on slag surfaces within a 6- to 12-month time frame, and that calcite would be the most prominent mineral in aqueous solutions at pH 7-14, depending on Ca content (Engström et al., 2013). The field data obtained by this study support the carbonation-driven mechanism. During the second collection schedule, the pH reached 11.94, thereby increasing the calcium concentration. This indicates rapid dissolution of Ca-bearing slag minerals at high pH. As the leachate pH decreases (for example, during periods of higher precipitation and dilution), the calcium concentration also decreases. This covariation is consistent with two possible processes: (1) dilution of leachate by infiltrating precipitation, reducing the concentration of all dissolved species, and (2) carbonation, where dissolved CO₂ provides carbonate ions that bind Ca²⁺ into insoluble CaCO₃, removing calcium from solution and contributing to pH reduction. This mechanism was confirmed by Hobson et al. (2017), who observed that CaCO₃ controls the extent of Ca leaching in water. Since calcite is less soluble than the Ca-bearing phases in the slag, carbonation progressively reduces the amount of Ca released to the leachate. Our short-term leaching behavior study seems to yield results like those of the 36-year study by Riley and Mayes (2015) on the correlation between pH and Ca, which found that each year, Ca concentration decreased, as did pH.

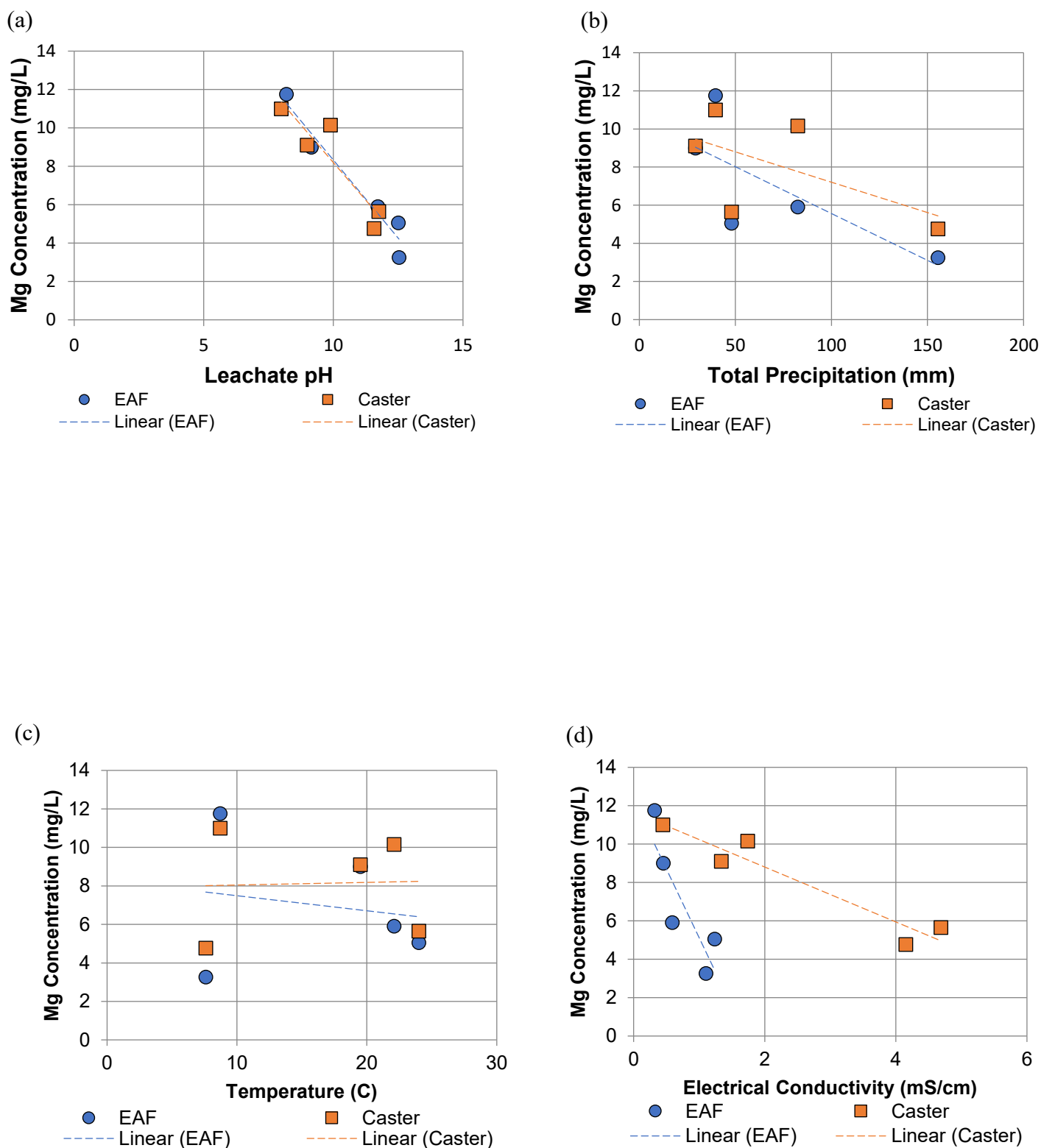


Figure 5.3.5 Scatter plots of leachate Mg concentration versus environmental variables in EAF and Caster slag across five sampling events: (a) Mg concentration versus leachate

pH, (b) Mg concentration versus total precipitation (rain + snow, mm), (c) Mg concentration versus average temperature (°C), and (d) Mg concentration versus electrical conductivity (mS/cm). Dashed lines represent linear regression trends for each slag type.

Unlike calcium, the magnesium concentration in the leaching solution behaved differently as pH increased. While the increase in pH resulted in a rise in calcium concentration, magnesium concentration decreased rapidly with increasing pH. A maximum concentration of 11.75 mg/L was measured in the EAF slag at pH 8.19 (T1), and a minimum value of 3.26 mg/L at pH 12.53 (T2). Similarly, for the caster slag, the maximum concentration of 11.0 mg/L was measured at pH 7.99 (T1), while the minimum magnesium concentration of 4.76 mg/L was detected at pH 11.57 (T2). Magnesium concentration did not exceed 6 mg/L at pH values higher than 11 (T2 and T5). Magnesium concentrations were consistently higher than 5 mg/L at pH lower than 10 (T1, T3, and T4).

As shown by the scatter plots (Figure 5.3.5), magnesium has a clear pH-dependent behavior. Negative correlations between the concentration of magnesium and leachate pH for both slag types (EAF: $r = -0.97$, $p = 0.005$; caster: $r = -0.92$, $p = 0.027$) indicate that the pH is the only environmental parameter with a statistically significant relationship to magnesium at the 0.05 level of significance. Moderately negative correlation with total precipitation (EAF: $r = -0.75$, $p = 0.148$; caster: $r = -0.75$, $p = 0.146$) is demonstrated in panel (b) of Figure 5.3.5. There is no significant relationship between magnesium and temperature (EAF: $r = -0.17$, $p = 0.784$; caster: $r = -0.13$, $p = 0.840$), shown in panel (c). The negative correlation between magnesium and electrical conductivity shown in panel (d) follows the fact that high-pH events decrease magnesium solubility (high-pH events have higher EC due to the dominant contribution of calcium conductivity). Therefore, there is a negative correlation between magnesium and electrical conductivity (EAF: $r = -0.87$, $p = 0.056$; caster: $r = -0.85$, $p = 0.069$). Since our study includes only five samples for each slag type, these correlations are merely exploratory. However, the magnesium-pH correlation is clearly the strongest one. This explanation is in line with the experimental results of Hobson et al. (2018), which showed that there is no significant release of Mg to solution for the first 24 h of leaching due to the relatively low solubility of brucite because of its high pH value as a result of the CaO and calcium silicate weathering (Hobson et al., 2018, p. 8). With the decline in pH level, it is noted that insoluble $\text{Mg}(\text{OH})_2$ will turn into soluble Mg^{2+} as the solution pH declines, thus

increasing the leaching rate of magnesium (Engström et al., 2013, p. 613). In the same line, the same authors obtained the same result through Pourbaix analysis, in which it is stated that the main magnesium phase at pH 12 (10^{-6} M) is $\text{Mg}(\text{OH})_2(\text{s})$, while if the pH level is decreased to 11, the main magnesium phase becomes Mg^{2+} (Engström et al., 2013, p. 612). Notably, magnesium is the only element that becomes more leachable with aging because of natural carbonation on pH.

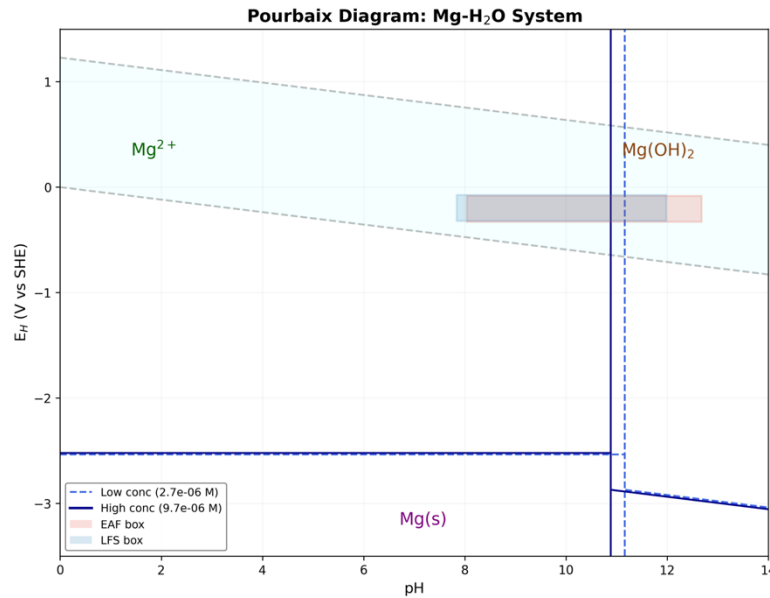
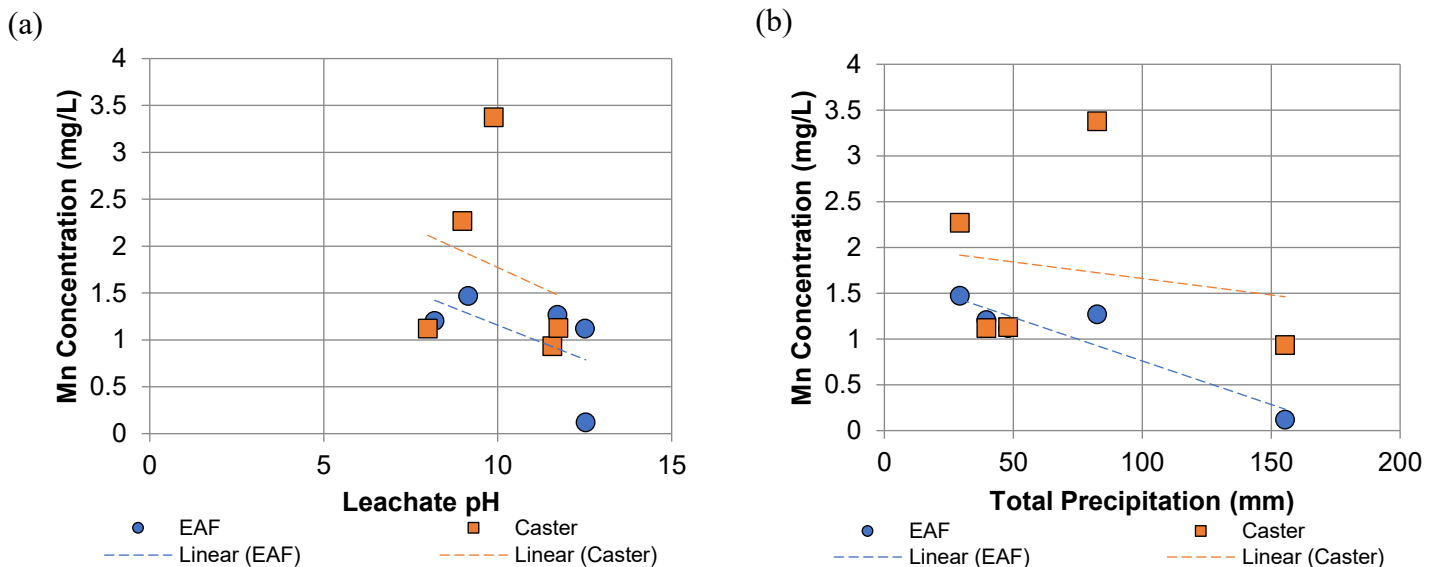


Figure 5.3.6 Pourbaix diagram (Eh-pH) for magnesium showing stability fields of Mg^{2+} , MgCO_3 , and $\text{Mg}(\text{OH})_2$ with overlaid leachate data points from EAF and Caster slag simulations

The Mg-H₂O Pourbaix diagram (Fig. 5.3.6) demonstrates the thermodynamic principles behind this phenomenon. For pH greater than 10.5 to 11.2, thermodynamically stable magnesium phase is $\text{Mg}(\text{OH})_2$ (brucite) – an insoluble substance which precipitates, thus removing Mg^{2+} ions from the solution. At lower pH values, Mg^{2+} ions predominate, and magnesium remains dissolved in the leachate. The EAF and Caster data boxes shown on the diagram belong to this zone, which explains why even small variations in pH could lead to considerable fluctuations in Mg^{2+} content. T2 and T5, where pH was greater than 11, belonged to the brucite stability field, which explains the low levels of magnesium. On the contrary, T1, T3, and T4, where pH was less than 10, contained dissolved magnesium in the form of Mg^{2+} .

Limitations of the binary system. The Mg-H₂O binary system lacks the carbonate ligand (CO_3^{2-}) and thus cannot illustrate magnesite ($\text{Mg}(\text{CO})_3$) as a stable phase. Although the original caption referenced MgCO_3 stability fields, this phase doesn't appear in the Mg-H₂O binary diagram and has been removed. In field conditions, the presence of CO_2 in the atmosphere would allow the formation of $\text{Mg}(\text{CO})_3$ at intermediate pH, where both Mg^{2+} and CO_3^{2-} ions are present. Moreover, this diagram doesn't consider factors such as activities, ionic strength, alkalinity, and carbonate concentration; the system presupposes unit activity for all aqueous species. This should be kept in mind while interpreting the stability fields shown here.

The above interpretation agrees well with the results of Hobson et al. (2018), who found no notable magnesium dissolution during the first 24 hours of leaching due to the low solubility of brucite at high pH values, driven by CaO^- and calcium silicate weathering processes (Hobson et al., 2018, p. 8). When pH decreases, insoluble $\text{Mg}(\text{OH})_2$ is converted into soluble Mg^{2+} , thereby increasing the dissolution rate of magnesium (Engström et al., 2013, p. 613). Also, the same authors have obtained similar results using the Pourbaix approach, showing that the main magnesium phase at pH 12 (10^{-6} M) is $\text{Mg}(\text{OH})_2$ (s), but at pH 11 the predominant magnesium phase becomes Mg^{2+} (Engström et al., 2013, p. 612). Magnesium is the only element that becomes more leachable after aging due to pH changes caused by natural carbonation.



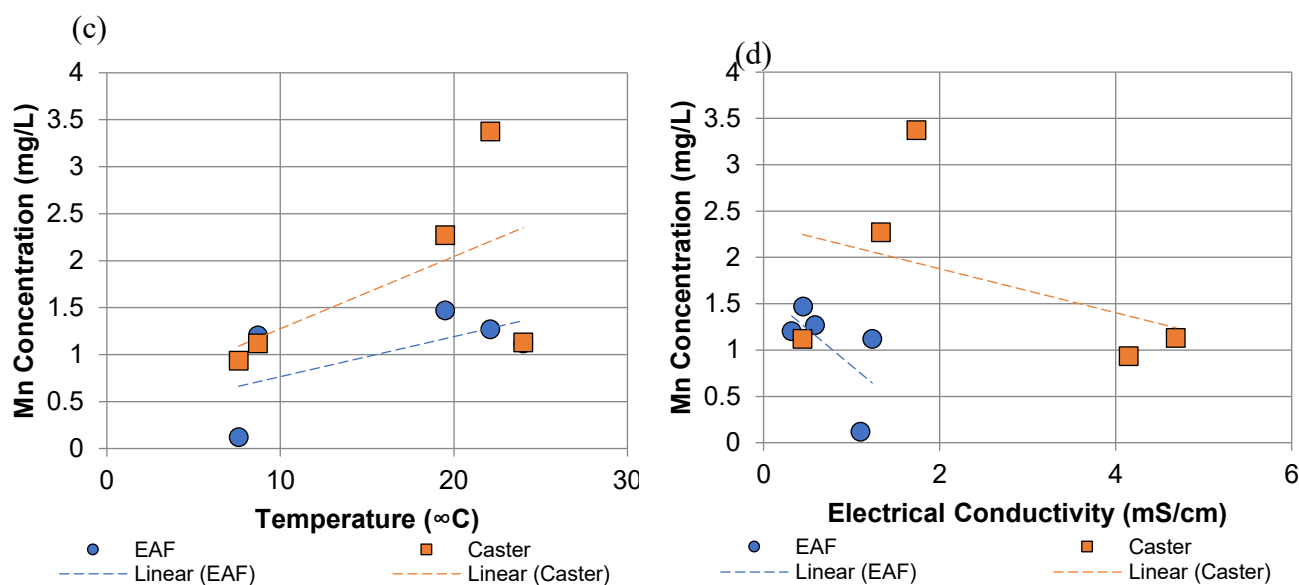


Figure 5.3.7 Scatter plots of leachate Mn concentration versus environmental variables in EAF and Caster slag across five sampling events: (a) Mn concentration versus leachate pH, (b) Mn concentration versus total precipitation (rain + snow, mm), (c) Mn concentration versus average temperature (°C), and (d) Mn concentration versus electrical conductivity (mS/cm). Dashed lines represent linear regression trends for each slag type.

Contrary to the observed trends for calcium and magnesium, manganese behaved differently. Unlike the increase in calcium concentration with increasing pH, manganese did not show any apparent relationship with any environmental parameter. This can be confirmed from the scatter plots (Figure 5.3.7). Panel (a) shows that there is no statistically significant relationship between Mn and leachate pH (EAF: $r = -0.13$, $p = 0.843$; Caster: $r = -0.53$, $p = 0.356$). Panel (b) indicates no apparent correlation with the total precipitation (EAF: $r = -0.24$, $p = 0.694$; Caster: $r = 0.48$, $p = 0.415$). Panel (c) demonstrates no relationship with temperature (EAF: $r = -0.17$, $p = 0.784$; Caster: $r = 0.31$, $p = 0.612$). Similarly, there seems to be no apparent relationship between Mn and the electrical conductivity of slag samples (panel d). The variation in Mn concentration is shown in Figure 5.3.7, where EAF Mn ranges from 0.12 to 1.47 mg/L across the intervals, and Caster Mn ranges from 0.94 to 3.38 mg/L, indicating a nonlinear trend for both slags. For both slags, the common feature is that the Mn concentration is lowest as pH increases at T2.

It has been reported by Gan et al. (2022) that pH does not control Mn leaching and the leaching process depends on the asphalt content, gradation, and asphalt type; hence, Mn leaches out regardless of the pH level within the investigated pH range under either oxidizing or reducing conditions (Gan et al., 2022). In addition, Mn is present as Mn^{2+} in the spinel structure (Piatak et al., 2015), which undergoes reductive dissolution under mild reducing conditions and across a wide pH range (Gan et al., 2022).

It is noteworthy that Mn concentrations exceed the USEPA SMCL of 0.05 mg/L on all sampling occasions for both slag types. The range of Mn concentrations for EAF (0.12–1.47 mg/L) is 2.4–29.4 times the SMCL, while for Caster (0.94–3.38 mg/L) it is 18.5–67.6 times the SMCL. Therefore, Mn is the most critical element for regulatory-based waste management purposes.

The Mn release mechanism was assessed using power-law regression analysis of the log-log plot of cumulative release (mg/kg) versus cumulative liquid-to-solid ratio (L/S, L/kg) according to EPA Method 1314. Mn showed the slope value of 0.63 ($R^2 = 0.730$) for EAF and 1.18 ($R^2 = 0.961$) for Caster (Table 5.3.2). The EAF slope of 0.63 falls within the diffusion-controlled range (0.35–0.65); however, the relatively low R^2 indicates large scatter in the data, attributable to irregular Mn concentration behavior driven by redox conditions rather than pH. The slope of 1.18 for Caster implies the dissolution-controlled release of Mn. Different Mn slopes for the two slags indicate that Mn is more sensitive to redox conditions, which are independent of pH across sampling occasions. With the insufficient data (five points for each slag), these slope classifications should be considered as indicative only.

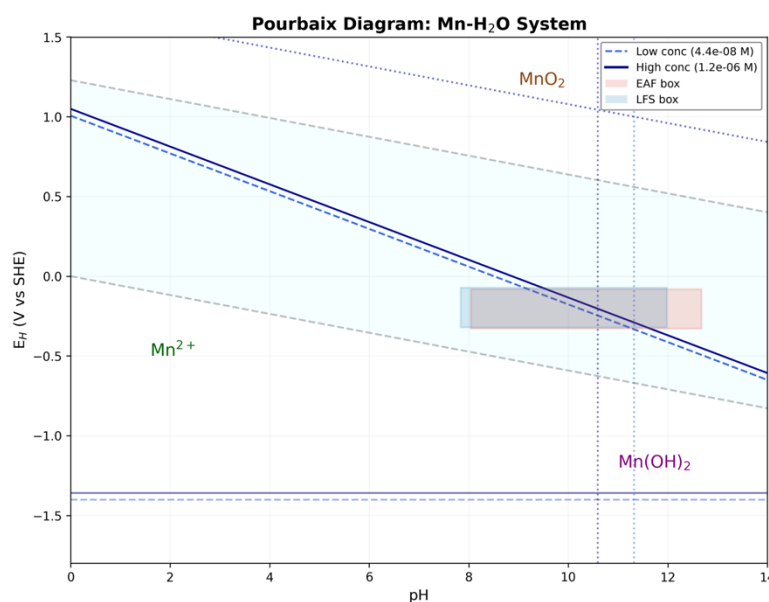


Figure 5.3.8 Pourbaix diagram (Eh-pH) for the Mn-H₂O system showing stability fields of Mn^{2+} , MnO_2 , and $Mn(OH)_2$, with overlaid leachate data points from EAF and Caster slag simulations.

Based on the Mn-H₂O Pourbaix diagram (Figure 5.3.8), there are three Mn compounds that are stable under different conditions: Mn^{2+} (soluble) for low pH and moderate Eh, MnO_2 (insoluble) for high Eh, and $Mn(OH)_2$ (insoluble) for high pH and low Eh. According to the diagram, the data boxes for EAF and Caster fall within the region that borders the Mn^{2+} and $Mn(OH)_2$ stability fields; thus, as with magnesium, the system is close to the thermodynamic turning point.

The Eh values were measured at each sampling event using the same pH meter along with the pH values; these two sets of values were used to plot the leachate points on the Eh-pH diagram. As soon as the pH reached 11 at T2 and T5, the system entered the $Mn(OH)_2$ stability field, as indicated by the low Mn concentrations. Conversely, when pH was below 10 for T1, T3, and T4, the system shifted toward the Mn^{2+} stability field, where manganese remains soluble. Unlike magnesium, Mn concentrations exhibit much greater scatter relative to the Pourbaix diagram, especially in Caster, where Mn concentration is highest at T3 (pH 9.89) rather than at T1 (pH 7.99).

Limitations of the Mn-H₂O binary system. The Mn-H₂O binary system does not consider the presence of carbonate ligand (CO_3^{2-}), hence it does not take into consideration rhodochrosite ($MnCO_3$). Moreover, the diagram does not consider activity, ionic strength, alkalinity, or

carbonate concentration. The unit activity is assumed for all aqueous species. The Eh values are measured in the field; hence, they are approximate.

This is in line with the results reported by Sun et al. (2019), where it has been observed that during pH-dependent leaching of EAF slag, the concentrations of iron (Fe) and manganese (Mn) are very low in an alkaline environment but increase significantly in an acidic environment owing to the formation of dissolved (oxy)hydroxides of the two elements. This can be explained by using the thermodynamic values shown in the Pourbaix diagram of iron at 25°C (Beverkog & Puigdomenech, 1996). The findings suggest that (oxy)hydroxide phases of iron and manganese are stable in alkaline environments, whereas they dissolve in acidic environments. In relation to manganese, Lefkowitz et al. (2013) showed that the reduction of birnessite by aqueous Mn(II) is pH-dependent and shows maximum activity in a circumneutral to slightly acidic pH range. Similarly, Hinkle et al. (2016) have shown that phyllomanganates change structure in aqueous Mn(II) solutions, resulting in increased Mn oxidation states and altered mineral properties. These findings make it clear why there is no direct relationship between Mn concentrations in field data and any environmental parameters. That is because the processes of Mn dissolution, precipitation, and sorption depend on the combined effects of pH, redox potential, and Mn(II) concentrations.

Sulfur content in the EAF slag leachate ranged from 0.53 to 136.50 mg/L, with an average of 44.7 ± 22.8 mg/L. On the other hand, the range for the Caster leachates was more restricted, at 15.70 – 57.50 mg/L, with an average sulfur content of 35.71 ± 17.7 mg/L. No significant differences were observed between the two slag types ($p=0.447$). However, upon conversion to sulfate equivalence, the EAF slag at T2 and T5 exceeded the U.S. EPA SMCL of 250 mg/L SO₄, reaching 409.5mg/L, respectively, while the Caster remained below the limit (maximum 205.2 mg/L) (Mahedi 2019).

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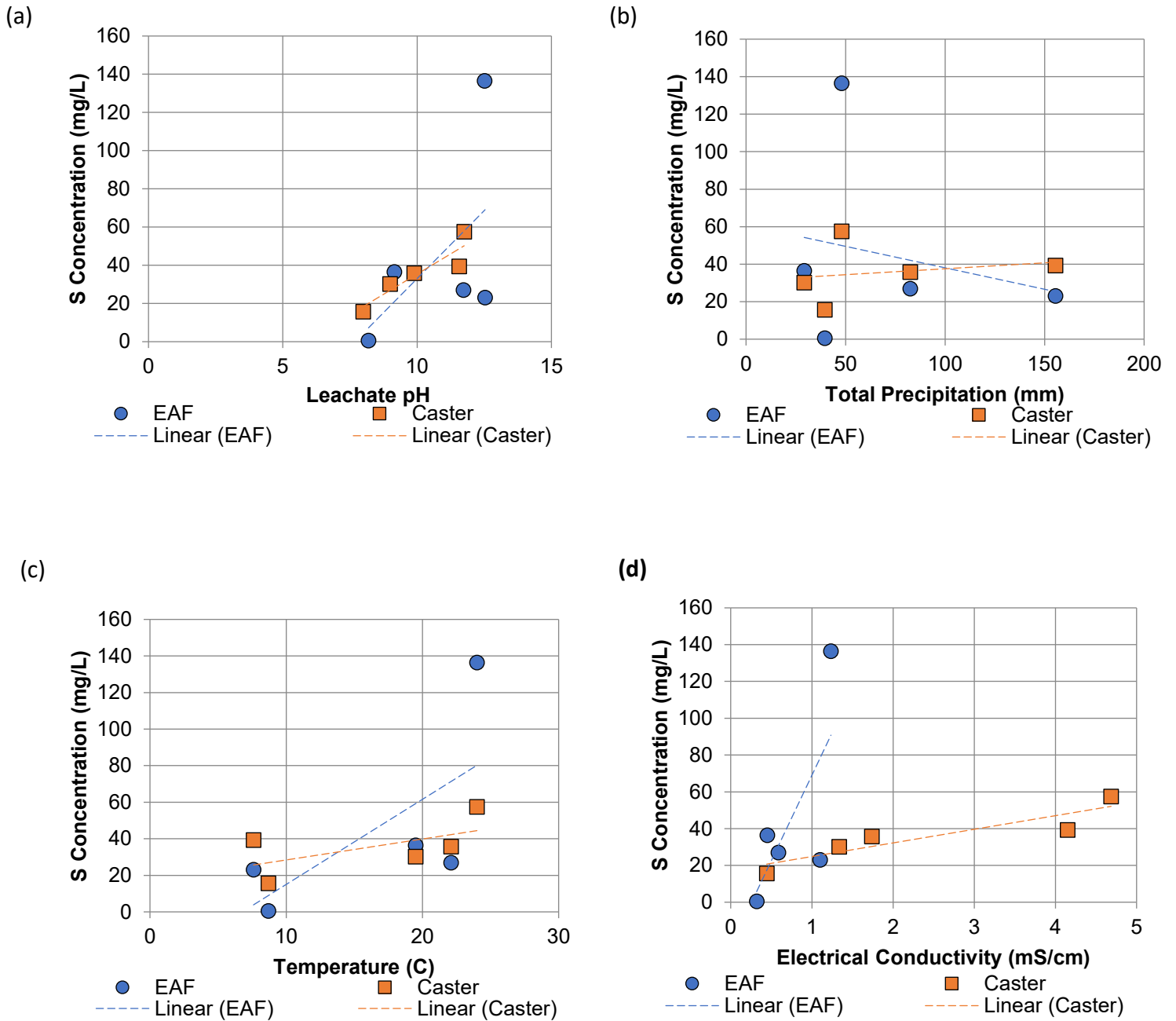


Figure 5.3.9 Scatter plots of leachate S concentration versus environmental variables in EAF and Caster slag across five sampling events: (a) S concentration versus leachate pH, (b) S concentration versus total precipitation (rain + snow, mm), (c) S concentration versus average temperature (°C), and (d) S concentration versus electrical conductivity (mS/cm). Dashed lines represent linear regression trends for each slag type. With only five sampling events per slag type, these correlations are exploratory and should be interpreted with caution.

Figure 5.3.9 shows the graphs of the interrelations between sulfur (S) concentrations and environmental parameters. Contrary to the other elements, sulfur showed statistically significant positive interrelation with pH in the case of Caster slag ($r = 0.91$, $p = 0.033$; Figure 5.3.9a), while there was no statistically significant correlation in EAF slag ($r = 0.54$, $p = 0.345$). The range of S concentrations in EAF slag was much wider – from 0.53 to 136.50 mg/L, while the mean value was 44.7 ± 54.4 mg/L. Sulfur concentrations in Caster slag were from 15.70 to 57.50 mg/L, while the mean value was 35.71 ± 17.7 mg/L. There were no statistically significant interrelations between S concentration and precipitation for either slag (Figure 5.3.9b; EAF: $r = -0.22$, $p = 0.720$; Caster: $r = 0.21$, $p = 0.730$). Sulfur showed a statistically significant positive correlation with temperature for Caster slag ($r = 0.90$, $p = 0.036$; Figure 5.3.9c), while the correlation in EAF slag was weaker and non-significant ($r = 0.71$, $p = 0.177$). No significant correlation was found between S and electrical conductivity for either slag type (Figure 5.3.9d; EAF: $r = 0.68$, $p = 0.211$; Caster: $r = 0.58$, $p = 0.304$). It should be emphasized that sulfur was transformed into sulfate (SO_4^{2-}) using a stoichiometric coefficient of 3.0 according to molar masses, and the EAF slag at T5 resulted in the sulfate concentration of 409.5 mg/L. This exceeds the U.S. EPA SMCL for sulfate concentration (250 mg/L). For Caster slag, the maximum sulfate concentration was 172.5 mg/L (T5), which is below the limit. The previous version of the chapter contained errors in calculating the sulfate equivalent of sulfur; those errors have been corrected above.

The current study aligns with previous studies showing that sulfate concentration changes slightly over the pH range 2 to 10.5; however, it decreases at higher pH due to ettringite formation. The field pH is usually between 8.0 and 11.75, which falls within the plateau of the sulfate leaching profile when solubility is determined by gypsum and anhydrite rather than pH (Mahedi, 2019).

The mechanism of sulfur release was further investigated using log-log plots of cumulative release vs. cumulative L/S ratios (Table 5.3.2). The slope values were highest for sulfur in this dataset: 3.10 ($R^2=0.992$) for the EAF and 1.44 ($R^2=0.997$) for the Caster. In both cases, the slope values are well above the dissolution-controlled process threshold of 1.0. Yet, the slope of 3.10 for EAF requires further analysis. Considering only five data points, the extremely high slope value could be an artifact of the large concentration range (0.53 to 136.50 mg/L) and the leverage of the T5 sampling point, rather than evidence of a physical

mechanism leading to a faster release rate.

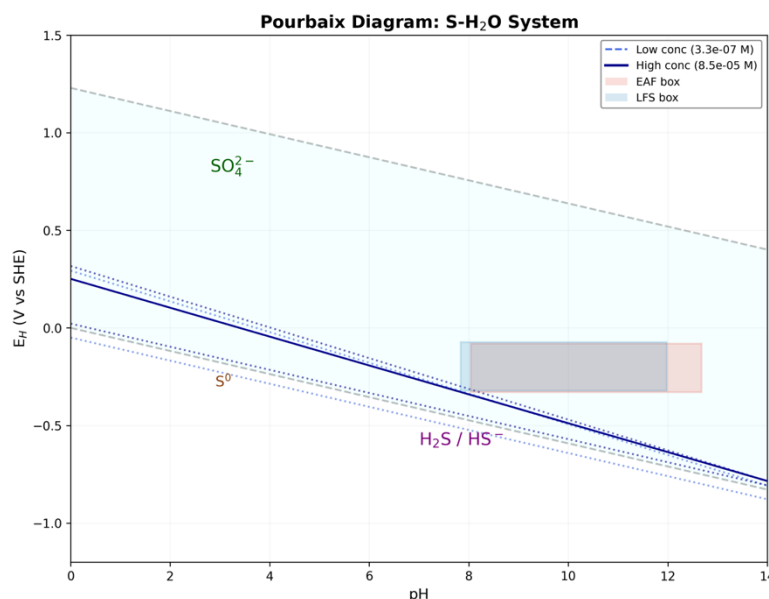


Figure 5.3.10 Pourbaix diagram (Eh-pH) for sulfur showing stability fields of SO_4^{2-} , H_2S , and S^0 with overlaid leachate data points from EAF and Caster slag simulations

The Pourbaix diagram for S-H₂O reveals that the compositions of slag leachates fall in the stability range of SO_4^{2-} , reflecting the oxidative nature of the field. Under such conditions, sulfur exists mainly as sulfate ions rather than as sulfides or elemental sulfur. The major sulfur-containing compounds in the slag may be gypsum and anhydrite, both of which are highly soluble in slightly to moderately basic environments. At the high pH levels observed in some EAF samples, limited precipitation of ettringite may occur, explaining the slight decrease in sulfur concentrations at high pH (Mahedi, 2019). The shortcomings of the binary system. The binary S-H₂O system is inadequate for assessing the solubility of gypsum, anhydrite, or ettringite because these minerals require the presence of calcium and aluminum in a ternary or quaternary system. Moreover, the system ignores activity, ionic strength, and alkalinity. The system also assumes that all aqueous species have unit activity.

Table 5.3.2 Power-law regression parameters (slope and coefficient of determination) from log-log plots of cumulative release versus cumulative L/S ratio for Ca, Mg, Mn, and S in EAF and Caster slag leachate

Metal	Caster slope	
	EAF slope (R^2)	(R^2)
Ca	1.65 (0.985)	1.64 (0.997)
Mg	0.58 (0.960)	0.76 (0.971)
Mn	0.63 (0.730)	1.18 (0.961)
S	3.10 (0.992)	1.44 (0.997)

For all four main components of the leachate solution, log-log plots of cumulative release vs. cumulative L/S ratio were generated to identify the dominant release mechanisms. The slope values obtained for calcium ions were 1.65 ($R^2 = 0.985$) for EAF and 1.64 ($R^2 = 0.997$) for Caster. Both slopes were above unity, implying a dissolution-controlled mechanism with increasing reaction kinetics as Ca-containing minerals dissolve. On the other hand, magnesium had a slope of 0.58 ($R^2 = 0.960$) for EAF and 0.76 ($R^2 = 0.971$) for Caster, meaning that magnesium ions have a diffusion-controlled mechanism for EAF, but it approaches a dissolution-controlled mechanism for Caster because brucite precipitation occurs with high pH, restricting magnesium ions from leaching out. Furthermore, manganese ions showed a slope of 0.63 ($R^2 = 0.730$) for EAF, indicating diffusion-controlled leaching, with the relatively low R^2 value attributed to the variability of the oxidation state. On the other hand, Caster had a slope of 1.18 ($R^2 = 0.961$), indicating a dissolution-controlled mechanism. In addition, sulfur showed the highest slopes, with values of 3.10 ($R^2 = 0.992$) and 1.44 ($R^2 = 0.997$) for EAF and Caster, respectively, implying a dissolution-controlled leaching mechanism, as sulfate minerals dissolve to form SO_4 ions.

In addition to the four key components (Ca, Mg, Mn, and S), the ICP-OES analysis has also identified Al, B, Ba, Cr, Fe, K, and V in the leachates. Complete data for the above-mentioned components, including all samples and both slag types, are available in the supplementary material (Table S1). Values below the equipment's detection limit (0.01 mg/L) are marked as not detected (n.d.).

5.4 Conclusions

Based on the six-month simulation of the field landfill, leaching of EAF and Caster slags occurs in an environmentally sensitive manner rather than continuously. This is based on a

single basin per slag type, five sampling events, a single climatic location, and a six-month duration.

From the observations, Ca release tends to be pH-dependent, with concentrations ranging from 38.75 to 203.50 mg/L in EAF slags and from 34.90 to 143.50 mg/L in Caster slags. Such patterns are consistent with the dissolution of CaO and calcium silicates. A log-log slope greater than 1 for both EAF and Caster slags confirms the hypothesis that dissolution is dominant in both cases. According to Pourbaix analysis, all the samples are in the Ca^{2+} stability field, which supports dissolution. In the Ca-H₂O binary diagram, carbonate minerals are ignored, and the activities of all aqueous species are set to 1.

On the other hand, Mg is released at decreasing concentrations as pH increases. The log-log slope for EAF of 0.58 agrees with a diffusion-controlled mechanism, whereas the one for Caster, 0.76, is close to the dissolution boundary. These patterns are consistent with the prediction of brucite precipitation at high pH according to the Mg-H₂O Pourbaix diagram. However, because of the small sample size (n=5) and lack of mineralogical analysis before and after the test to check if brucite was formed, there is difficulty in making such a claim.

Mn shows the highest variability among the four elements, as it has no statistically significant relationship with any environmental parameter tested in this experiment. Such behavior is expected for Mn, which is highly sensitive to redox conditions. A low R² value (0.730) in the log-log regression for EAF is consistent with the interpretation that Mn release is controlled by parameters not represented in the current dataset. Mn concentrations exceeded the USEPA SMCL of 0.05 mg/L in all events for both slags. Caster reached 67.6 times the SMCL, making Mn the most significant element in regulatory terms.

Finally, sulfur is released without correlation to pH. It is controlled by the high solubility of gypsum and anhydrite. The log-log slopes of 3.10 (EAF) and 1.44 (Caster) exceed the limit, indicating that dissolution is controlled by the mechanism. However, the EAF slope is subject to interpretation due to the small sample size and the contribution of the T5 sampling event.

The spring season adds complexity to the leaching process due to increased temperatures (which accelerate the carbonation reaction on the slag surface) and changes in precipitation,

which alter leachate dilution. However, the six-month period and one-location design do not allow for separating the aging effects from seasonal ones.

Limitations. The study relies on one basin per slag type, five sampling events in six months at one location in Norfolk, Nebraska; measurement of Eh values with the same pH meter at each event and redox conditions not continuously measured; lack of hydrologic mass balance and normalization of cumulative mass release; binary Pourbaix diagrams based on simple binary systems without carbonate and ionic strength and activity corrections; log-log regressions based on five data points per slag type. Therefore, these mechanisms should be viewed as plausible explanations in agreement with the data, not demonstrated facts.

Practical implications. The conclusions of the experiment highlight several considerations regarding the management of stockpiles and the beneficial use of steel slag. Firstly, the strong relationship between pH and Ca release indicates that controlling leachate pH through carbonation or mixing with acidic materials can significantly reduce calcium loading in drainage. Second, the consistently high Mn concentrations across all sampling events mean that drainage from the slag stockpiles should be collected and treated before release to the environment. Thirdly, diffusion-controlled Mg release means that magnesium leaching will continue even after surface minerals are weathered. Thus, it should be monitored for a long time. Fourthly, there is no statistically significant relation between pH and S release. Therefore, sulfur management cannot rely on pH control and requires special treatment of sulfate species. Finally, the environmentally responsive leaching over a six-month period indicates that slag stockpiles should be engineered with a proper drainage system.

Appendix

Classification	Sample Name	Al	B	Ba	Ca	Cr	Fe	K	Mg	Mn	S	V
EAF	T1	0.012	1.675	0.012	38.75	0.012	0.012	0.05	11.75	1.205	0.53	0.05
	T2	0.012	0.012	0.012	172.5	0.012	0.012	128	3.255	0.12	23.1	0.05
	T3	14.4	0.012	0.012	74	0.012	0.012	130	5.9	1.27	26.95	0.05
	T4	12.15	0.012	0.012	48.4	0.012	0.012	154	9	1.47	36.45	0.05
	T5	260	1.285	24.4	203.5	0.012	0.012	138	5.05	1.12	136.5	0.05
Caster	T1	0.012	0.012	0.012	34.9	0.012	0.012	0.05	11	1.12	15.7	0.05
	T2	61.5	0.012	0.54	122	0.012	0.012	0.05	4.76	0.935	39.35	0.05
	T3	66	0.012	0.6	143.5	0.012	0.012	0.05	10.15	3.375	35.8	0.05
	T4	18.7	0.012	0.012	88	0.012	0.012	0.05	9.1	2.27	30.2	0.05
	T5	38.45	0.012	15.7	122.5	2.52	8.95	0.05	5.65	1.13	57.5	8.25

Table A.3 Supplementary leachate concentrations (mg/L) of additional elements detected by ICP-OES in EAF and Caster slag leachate across five sampling events (T1–T5) during the six-month field exposure study (December 2025 to May 2026). Values marked n.d. are below the instrument detection limit (0.01 mg/L)

CHAPTER 6- CONCLUSION

The current study investigated the environmental and engineering characteristics of Electric Arc Furnace (EAF) slag and caster slag with a view of evaluating their beneficial utilization potential in transportation infrastructures. Assessment included the physical characterization, compaction tests, SEM-EDS observations, RCRA TCLP test, pH-dependent batch testing, continuous-flow column test, and 6 months exposure test in the outdoor lysimeter. From the results, it became evident that EAF slag and caster slag possess the potential for beneficial reuse although their environmental performance varies depending on pH, particle size, mineralogy, liquid-to-solid ratio, and exposure conditions. Therefore, EAF and caster slags should be considered conditionally suitable for transportation infrastructures.

Physical characteristics of the slags differed. Specifically, EAF slag possessed high specific gravity and low water absorption, implying a dense and compact structure. On the contrary, caster slag had low specific gravity and high-water absorption, pointing to a porous and vesicular structure. Shale soil used in the study was classified as A-7-2 with plasticity index of 36.44%. This means that the soil is highly plastic subgrade requiring stabilization before pavement construction.

Addition of 10% slag resulted in different compaction performance depending on the type of slag. EAF slag-soil mixture increased the maximum dry density from 1.488 to 1.557 g/cm³ and reduced the optimum moisture content from 27.6% to 21.2%. At the same time, the caster slag-soil mixture achieved a maximum dry density of 1.471 g/cm³ and optimum moisture content of 28.3%. Thus, EAF slag and caster slag cannot be considered as similar materials for the purpose of pavement stabilization although the same percentage of incorporation.

Observations via SEM-EDS revealed that EAF slag was characterized by spherical and globular grain particles while caster slag possessed needle-like or fiber-like acicular structures and globular particles. The observation of the needle-like and globular particles in EAF and caster

slag samples both before and after leaching indicated that these features are inherent in the slags and not caused by the leaching process.

EDS mapping revealed calcium-silicon-rich and iron-manganese-magnesium-rich domains on the surface of EAF and caster slag samples. The mineralogical inhomogeneity of the slag samples correlates well with different leaching results obtained in the column experiments including the dissolution of calcium-silicon-rich phases and exposing of iron-manganese-magnesium-rich phases. Nevertheless, EDS mapping alone cannot determine exact mineralogical phases. Since the analysis was performed in secondary electron mode without identical-particle tracking, backscattered electron imaging, spot EDS confirmation, and direct XRD analysis of test residues, the phase assignment should be considered as mineralogical inference rather than precise identification.

According to the TCLP results, all three replicates of EAF and caster slag samples did not exceed RCRA toxicity characteristic limits for eight metals being tested. Thus, based on EPA method 1311, EAF and caster slags did not have toxicity characteristics of hazardous wastes and can be considered as non-hazardous according to RCRA criteria. Small amounts of barium, chromium, and selenium were observed in some of the extracts but did not exceed RCRA limits.

Nevertheless, TCLP results do not determine the safety of slags under any conditions of transportation infrastructure utilization. TCLP is a single-point extraction test and cannot evaluate all effects related to changes in pH, particle size, long-term percolation, mineral dissolution, or seasonal weathering. More detailed method 1313 results showed that the slags can release constituents in concentrations exceeding drinking-water screening benchmarks depending on specific acidic and alkaline conditions.

According to the results obtained during pH-dependent testing, the calcium was released at all pH values due to the dissolution of calcium oxide, portlandite, larnite, and other calcium-containing silicates. Magnesium, barium, and iron were usually released at acidic conditions, while aluminum possessed amphoteric behavior and its concentrations were lowest at moderately alkaline conditions. Boron release followed the oxyanionic leaching pattern and exceeded the

EPA health reference level of 1.4 mg/L for pH values ranging from 6 to 11 across the evaluated particle sizes. The maximum concentration of boron for the EAF 19 mm fraction was 8.05 mg/L at pH 5.19.

The highest individual pH-dependent concentrations revealed considerable environmental release under unfavorable conditions. Specifically, iron reached the concentration of 1,585 mg/L in the caster 19 mm fraction at pH 5.24, and manganese reached 1,075 mg/L in the EAF 19 mm fraction at pH 5.56. Other high concentrations were detected for nickel in the EAF 5 mm fraction, lead in the caster 19 mm fraction, and zinc in the caster 19 mm fraction. These results show that coarse aggregate fractions can release a notable number of constituents at acidic pH values, although the results should be interpreted cautiously due to lack of independence between particle size, pH, and contact time in the modified test.

Particle size had a considerable effect on the achieved pH and chemical composition of the leachate. The finer fraction possesses a larger reactive surface and thus consumes more acid to achieve a certain pH value, maintaining alkaline conditions even if a strongly acidic target pH value is applied. As particle size increases, the difference between target and achieved pH becomes smaller, and the concentrations of several constituents increase at acidic pH values. This means that the leaching behavior cannot be determined by only the elemental composition of the slags; the physical properties of the slags, including gradation, should be taken into consideration, especially for unbound coarse aggregate.

The results of the continuous-flow column test represented more realistic situation of the usage of slags in the subgrade layer of pavement construction. In both cases of EAF and caster slag-soil mixture, the alkaline buffer was established during the experiment, and the leachate pH value varied from neutral to the stable value in the range from 8.6 to 8.8 despite the application of pH 5 synthetic precipitation. The unamended soil sample did not exhibit buffer behavior and tended to decrease pH. This fact shows that both EAF and caster slags can significantly change the chemical properties of the amended soil.

Calcium release in both slag-amended columns was characterized by initial release followed by stabilization. The calcium concentrations varied in the range from 510 to 846 mg/L in the caster slag column and from 552 to 600 mg/L in the EAF slag column. At the final cumulative liquid-to-solid ratio of 10.9, the cumulative calcium release was 6,390 mg/kg for the caster slag and 6,200 mg/kg for the EAF slag sample, indicating calcium dissolution and alkaline buffer action.

Other constituents were released in a different manner. For instance, the magnesium was released at the initial stage and then depleted, which corresponds to the removal of readily soluble magnesium-bearing phases. The boron concentration showed a peak-and-decline pattern, reaching the concentration of 0.972 mg/L in the caster slag column at the cumulative liquid-to-solid ratio of 2.01 and 0.984 mg/L in the EAF slag column at the cumulative liquid-to-solid ratio of 9.05. The vanadium concentration increased steadily in both columns reaching the maximum value of 0.208 mg/L in the EAF column and 0.109 mg/L in the caster column. The steady increase of vanadium indicates its dissolution under the established alkaline conditions.

According to the results of the outdoor lysimeter experiment, the leaching under natural weathering is environmentally variable rather than constant phenomenon. This conclusion is based on five sampling events over 6 months with the influence of precipitation, snowfall, temperature, humidity, pH, and dilution on the leachate composition. The calcium concentration varied from 38.75 to 203.50 mg/L in EAF slag and from 34.90 to 143.50 mg/L in caster slag. Calcium release corresponded to the dissolution process while the magnesium concentration decreased with the increase of pH.

The most important constituent that was found to cause the regulatory concern in outdoor exposure was manganese. The manganese concentration exceeded the USEPA secondary maximum contaminant level of 0.05 mg/L during each sampling event for both slags. EAF leachate manganese concentration varied from 0.12 to 1.47 mg/L, while caster slag ranged from 0.94 to 3.38 mg/L with the maximum value for caster slag being 67.6 times higher than the screening limit. The manganese showed high variability and did not have statistically significant correlation with environmental parameters due to sensitivity to redox, dissolution, precipitation, and sorption processes.

Sulfur was the constituent behaving differently from calcium, magnesium, and manganese. It did not correlate with pH meaning that the sulfur management is not possible with pH adjustment only. During the conversion into sulfate, the EAF leachate reached the concentration of 409.5 mg/L during the final sampling event exceeding the USEPA secondary maximum contaminant level of 250 mg/L. The maximum concentration of caster slag sulfate was 172.5 mg/L which is lower than screening level. The precipitation and temperature variability during six months could affect the sulfate interpretation because the aging effects could not be separated from the seasonal variations.

Overall, the results do not allow concluding that either EAF or caster slags are suitable for beneficial utilization in unencapsulated road-base or subbase under TCLP results. Even though both slags passed RCRA hazardous waste screening, they showed the pH-dependent leaching, particle size effects, persistent alkalinity, continuing calcium dissolution, increase of vanadium concentration during percolation, and exceedance of manganese concentration during outdoor exposure. The only conclusion that can be made is the conditional suitability of EAF and caster slags for beneficial reuse provided that their beneficial reuse will be carried out considering the environmental characterization of the site and monitoring.

Before beneficial utilization, the chosen slag should be assessed using several methods of leaching test. As a minimum, the assessment should include the regulatory screening, pH-dependent test, particle size assessment, and continuous-flow percolation using the conditions like those of intended application. The drainage controls are necessary due to the persistence of elevated manganese concentration. The results also support the need for long-term vanadium and magnesium monitoring and sulfate release management.

Several limitations of the study are identified. The method 1313 pH and particle size combinations were not replicated, the modified fractions did not correspond to the field gradation, and some of the target pH values were not achieved due to high buffering capability of the fine fraction. Only single column per each condition was used during the column experiment lasting for 2.5 weeks. The outdoor experiment included only single basin per each slag type, five

sampling events, one climatic location, and 6 months monitoring period. No hydrologic mass balance and transport-attenuation modeling were performed, and no XRD characterization of slag and column residues was performed.

The SEM-EDS analysis is limited by secondary-electron imaging, variable fields of views and working distances, different coating, and the absence of identical-particle tracking. Therefore, only globular, acicular, calcium-silicon-rich, and iron-manganese-magnesium-rich features can be used as qualitative evidence but cannot be considered as the proof of the selective dissolution and identification of exact mineral phases causing the release of certain constituent.

Future work should include replicated columns, long-term field monitoring, direct XRD or microanalytical characterization of slag before and after leaching, hydrologic transport modeling, and testing under wet-dry and freeze-thaw cycles.

In conclusion, EAF slag and caster slag are not classified as hazardous under the RCRA TCLP criteria and possess the physical and chemical properties that justify further investigation of their beneficial utilization in transportation infrastructures. However, the environmental performance of EAF and caster slags is not static and cannot be determined by single-point test only. The beneficial reuse should be carried out considering the application-specific conditions including particle size, drainage, exposure, and monitoring with particular emphasis on manganese, vanadium, boron, sulfate, and persistent alkalinity.

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