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H2C-72049
Revision 0

FY24 Development of Improved Grout Waste Forms for Alternative Low Activity Waste Treatment, VSL-25R5510-1 Rev. 0

Prepared for the U.S. Department of Energy
Assistant Secretary for Environmental Management

Contractor for the U.S. Department of Energy
Hanford Field Office under Contract 89303324DEM000096

Hanford Tank Waste
Operations & Closure

P.O. Box 788
Richland, Washington 99352

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I. L. Pegg
Vitreous State Laboratory of The Catholic University of America

W. Gong
Vitreous State Laboratory of The Catholic University of America

Date Published
April 2025

DOE

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APPROVED
By Lynn M Ayers at 9:07 am, May 28, 2025

Release Approval Date

VSL-25R5510-1

Final Report

FY24 Development of Improved Grout Waste Forms for Alternative Low Activity Waste Treatment

prepared by

Weiliang Gong and Ian L. Pegg

Vitreous State Laboratory
The Catholic University of America
Washington, DC 20064

for

Atkins Energy Federal EPC, Inc.
Washington, DC 20001

and

Washington River Protection *Solutions*, LLC
Richland, WA

January 13, 2025

Rev. 0, 4/30/25

Completeness of Testing:

This report describes the results of work and testing specified by the referenced Scope of Work (SOW). The work and any associated testing followed established quality assurance requirements and were conducted as authorized. The descriptions provided in this test report are an accurate account of both the conduct of the work and the data collected. Results required by the SOW are reported. The test results and this report have been reviewed and verified.

I. L. Pegg:____________________ **Date:** 4/30/25
VSL Program Director/Principal Investigator

I. Joseph: Innocent Joseph **Date:** 04/30/2025
Atkins Sub-Contract Manager

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List of Abbreviations

AgZ	Silver Zeolite
AltLAW	Alternative Low Activity Waste
ASME	American Society of Mechanical Engineers
ASTM	ASTM International (formerly the American Society for Testing and Materials)
BBI	Best Basis Inventory
BFS	Blast Furnace Slag
BFS CP	Blast Furnace Slag Provided by Clark Pacific, CA
BFS DMI	Blast Furnace Slag Provided by Diversified Minerals Inc., CA
BFS DS	Blast Furnace Slag from Ash Grove Cement, WA
BFS SE	Blast Furnace Slag from Lafarge-Holcim’s Seattle Plant
BFS SEn	Blast Furnace Slag from Lafarge-Holcim’s Seattle Plant, New Batch
BFS SEo	Blast Furnace Slag from Lafarge-Holcim’s Seattle Plant, Old Batch
BWOS	By Weight of Slag
CASH	Calcium Aluminosilicate Hydrate
Cc	Calcium Carbonate
CHT	Calcined Hydrotacite
COCs	Constituents of Concern
CŜ	Calcium Sulfate
CSH	Calcium Silicate Hydrate
CUA	Catholic University of America
DOE	Department of Energy
ETF	Effluent Treatment Facility
EPA	Environmental Protection Agency
FA	Fly Ash
FFA	Class F Fly Ash
GUHPC	Geopolymer Ultrahigh Performance Concrete
GS	Geopolymer Solids
Hyp	Hydrophobic Admixture Eucon Hydrapel 2.5
HLW	High Level Waste
IC	Ion Chromatography
ICP-AES	Inductively Coupled Plasma – Atomic Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma – Mass Spectroscopy
IDF	Integrated Disposal Facility
IHLW	Immobilized High Level Waste
ILAW	Immobilized Low Activity Waste
LAW	Low Activity Waste
LDH	Layered Double Hydroxide
LDR	Land Disposal Restrictions
LI	Leachability Index
M	Mortar
NC	Sodium Carbonate
NQA	Nuclear Quality Assurance

NŜ	Sodium Sulfate
NSAS	Neutral Salt Activated Slag
OPC	Ordinary Portland Cement
P	Paste
PA	Performance Assessment
PC	Portland Cement
PNNL	Pacific Northwest National Laboratory
PUHPC	Portland Cement Based UHPC
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
QARD	Quality Assurance Requirements and Description
Qz	Ground Quartz Powder
SF	Silica Fume
SLAW	Supplemental Low-Activity Waste
SOW	Statement of Work
SP	Superplasticizer
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
TCLP	Toxicity Characteristic Leaching Procedure
UHPC	Ultrahigh Performance Concrete
VSL	Vitreous State Laboratory
w/dm	Water to Dry Mix Ratio
WTP	Hanford Tank Waste Treatment and Immobilization Plant
WRPS	Washington River Protection *Solutions*, LLC
XRD	X-ray Diffraction
XRF	X-ray Fluorescence Spectroscopy
ZT	Zeolite
ZT5	Zeolite Type 5A

SECTION 1.0
INTRODUCTION

1.1 Background

About 54 to 56 million gallons of radioactive mixed waste is currently stored in underground tanks at the United States Department of Energy's (DOE's) Hanford site in the State of Washington. This waste will be separated into low- and high activity waste fractions, which will then be vitrified respectively into Immobilized Low Activity Waste (ILAW) and Immobilized High Level Waste (IHLW) products for subsequent disposal. The ILAW product will be disposed of in an engineered facility at the Hanford site while the IHLW product is designed for acceptance into a national deep geological disposal facility for high level nuclear waste. Treatment of the tank waste will take place in the Hanford Tank Waste Treatment and Immobilization Plant (WTP), which is under construction.

However, since the WTP Low Activity Waste (LAW) Vitrification Facility was not designed to process the entire inventory of Hanford LAW, up to half of the retrieved Hanford LAW will require supplemental immobilization. Immobilizing LAW in a cementitious waste form known as Cast Stone has been investigated as a possible candidate supplemental immobilization technology. At this time, it is assumed that LAW stabilized/immobilized in a cementitious waste form will be disposed out-of-state even though it has been shown that onsite disposal in a facility like the Integrated Disposal Facility (IDF) would be less costly than offsite disposal [1].

In FY12, Washington River Protection *Solutions*, LLC (WRPS) began a Supplemental LAW Technology Development Program with assistance from Savannah River National Laboratory (SRNL) and Pacific Northwest National Laboratory (PNNL). That work focused on obtaining additional information on Cast Stone as a waste form for LAW immobilization and further maturing the technology for application at Hanford [2-5]. More recent work completed by PNNL in FY19 defined the chemical retention needed by grouted Alternative Low-Activity Waste (AltLAW) if it were disposed of in the IDF [6]. Performance metrics were defined for Tc, Cr, I, and NO_3^-. These constituents of concern (COCs) were chosen because they represent substantial contributors to groundwater risk in the 2017 IDF Performance Assessment. The results indicated that the estimated inventory of grouted AltLAW could meet IDF groundwater requirements if the release rates of nitrate, ^{99}Tc, and ^{129}I were reduced by a factor of approximately 3.2, 10, and 32, respectively. Current cementitious waste formulations are capable of acceptable Cr retention. In FY20, a multi-laboratory team identified and assessed possible technologies to address limitations with current retention levels [7]. There is a need for testing to assess the potential of such technologies to meet the required retention levels.

In FY21, WRPS tasked Atkins and the Vitreous State Laboratory (VSL) of The Catholic University of America (CUA) to perform testing to evaluate methods for reducing the release of COCs, particularly nitrate, ^{99}Tc, and ^{129}I, from cementitious waste forms made from aqueous LAW derived from Hanford Tank Waste [8]. In that work, a range of alternative formulations were developed and characterized. Formulations based on neutral salt activated slag (NSAS) and Portland cement ultrahigh performance concrete (PC-UHPC) exhibited good retention of the target COCs as compared to the estimated performance metric requirement. Although the waste loadings of those formulations were lower than that for the nominal cast stone formulations, the results confirmed that there was considerable scope for improvement of AltLAW waste form performance through novel formulation approaches [8].

FY22 work built on the FY21 results and further developed these formulations while targeting higher waste loadings [9]. A range of alternative formulations based on Cast Stone, Cement-Free, neutral salt activated slag, and alkali-activated slag were developed and characterized [9]. Several of the formulations, such as CSMA8S1 and CSMA3S1, met the performance metrics for Tc, Cr, and nitrate but none were able to meet the metric for iodine. In the FY23 work, these formulations were further developed and optimized with major focus on improving resistance to iodine leaching [10]. Pretreatment processes for the AltLAW were tested, targeting improved resistance to iodine leaching: Ionex Ag-400 was allowed to react with the AltLAW for 2 hrs prior to grouting and, alternatively, Ionex Ag-400 was removed after reacting for 2 hrs prior to grouting. Both pretreatment processes were successful, yielding a number of waste forms with 63-day leachability index (LI) values exceeding the estimated performance metric requirement for iodine of 10.52, such as CSMA8S2 and CSMA3S1R1 [10]. The present work, which was conducted according to the WRPS Statement of Work (SOW) [11], builds on the previous work to develop further optimized and improved grout formulations.

1.2 Objectives

The objective of this work was to perform laboratory-scale testing to further refine the most promising formulation(s) that were identified in the FY23 work. The goal of the refinement was to further reduce the release rates for ^{99}Tc, Cr, ^{129}I, and nitrate while maintaining workability of the fresh grout, and to increase waste loading. The general approach included:

- Assessment of the effect of slag compositions on properties and performance of the waste form;

- Determination of optimal formulating parameters for a waste form with further improved retention of COCs;

.

- Development and optimization of CSMA8 Series formulations with pretreatment by removing iodine from the AltLAW prior to grouting;

- Assessment of dependence of leaching resistance of COCs on the Na concentration in the AltLAW; and

- Assessment of the effect of filler content on performance and waste loading.

A phased approach, as was used in previous fiscal years, was employed to screen optimal formulations for their retention properties. Only those formulations that showed promise for improved retention of the target COCs, and in particular, for meeting the retention improvement targets were subjected to more extensive testing.

The testing included evaluation of fresh and cured properties. The primary focus was on optimization with respect to reduced leaching of the COCs, particularly rhenium (surrogate for ^{99}Tc) , iodine, and nitrate in the EPA Method 1315 test. Per the WRPS SOW [11], the simulant was spiked with land disposal restrictions (LDR) inorganics that are relevant to Hanford LAW, including arsenic, barium, cadmium, chromium, lead, nickel, selenium, silver, and thallium. The recommended grout waste forms prepared with the LDR inorganics spiked LAW (5.6 M Na) were subjected to TCLP testing (EPA Method 1311).

SECTION 2.0
TEST MATRIX

In FY23 work [10], several alternative grout formulation approaches were investigated to assess their potential to achieve the desired improvements in retentions. The objective of the present work was to perform laboratory-scale testing to refine the most promising formulations that were identified in the FY23 work. The goal of the refinements is to further reduce the release rates for ^{99}Tc, Cr, ^{129}I, and nitrate, improve workability of the fresh grout, and to increase waste loading of an optimized waste form [11].

The FY23 formulations that were used as the starting point for much of the FY24 work are listed in Tables 2.1 and 2.2 and the test results are summarized in Table 2.3. The FY23 formulations that constituted the basis for the FY24 optimization tasks were based on neutral salt activated slag (NSAS). Neutral salt activated slag belongs to the family of geopolymers or alkali activated materials. Geopolymers are cementitious materials produced by a so-called alkali activation process involving the reaction of one or more aluminosilicates in powder form with an alkaline activator solution. Examples of aluminosilicates include blast furnace slag (BFS), metakaolin, and fly ash. The activator is typically an aqueous solution of alkali hydroxide, alkali silicate, alkali carbonate or sulfate. Alkali silicate activation of metakaolin or Class F fly ash yields amorphous or partially micro-crystalline three-dimensional aluminosilicate networks, similar to those of zeolites, composed of tetrahedrally coordinated Si and Al atoms linked by oxygen atoms. Nearby alkali metal cations (typically Na^+ and/or K^+) provide charge balance for AlO_4 units. Alkali silicate activation of blast furnace slag enhances formation of calcium silicate hydrate (CSH) and highly cross-linked calcium aluminosilicate hydrate (CASH) gels and AFm/AFt phases. Blast furnace slag can be activated by near neutral and mildly alkaline solutions based on sodium carbonate (Na_2CO_3) or sodium sulfate (Na_2SO_4) [12]. The main hydration product is highly cross-linked calcium aluminosilicate hydrate (CASH) gels. Alkali sulfate activated slag yields AFt (ettringite, $Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$) as the primary secondary phase. Alkali carbonate activated slag yields layered double hydroxide (LDH) type AFm as the primary secondary phase [13]. AFm is shorthand for a family of hydrated calcium aluminate phases structurally related to hydrocalumite and occurring mainly in hydrated cement pastes. A representative formula is $[Ca_2(Al,Fe)(OH)_6]\cdot X\cdot nH_2O$ where X is an exchangeable singly-charged (e.g., chloride) or half of a doubly-charged anion (e.g., sulfate, carbonate). The anion site in the AFm/AFt phases is exchangeable for other anions including nitrate and iodine. Both the AFm and AFt phases are particularly efficient in absorbing iodine species by anion exchange [14, 15]. A range of heavy metals and radionuclides can be immobilized in the zeolitic structure or alkali substituted CASH gel that are the main gel phases in the geopolymeric materials [16, 17]. Geopolymers that employ substantial amounts of BFS have been developed to improve the immobilization of technetium via the high reduction capacity and sulfide content, which supports the reduction of Tc(VII) to Tc(IV) and precipitation either as the insoluble oxyhdroxide or sulfide [18], as in the OPC-based Savannah River Site (SRS) Saltstone. Research and development programs in geopolymers have been ongoing at VSL for over 15 years. That work has addressed low-carbon-footprint alternatives to

OPC-based construction materials as well as geopolymer technology specifically tailored to address certain radioactive waste immobilization problems.

In general, neutral salt activated slag grouts usually take longer to harden and show delayed compressive strength development as compared to alkali silicate activated slag. This delayed strength development can be mitigated by using a blended activating solution of sodium carbonate and sulfate with sodium hydroxide solution [19]. The AltLAW typically contains about 1 to 2 molar sodium hydroxide, which is advantageous to enhance setting and strength development during curing of a NSAS based grout waste form. Dimensional stability of the NSAS based waste forms can be improved by including light-burned magnesia (MgO) due to its expansive nature during the hydration process [20].

For the FY24 work, two pretreatment processes were included in developing waste forms for the AltLAW. In one approach, Ionex Ag-400 was reacted with the AltLAW simulant for 2 hrs, and the resulting suspension was mixed with the dry mix to develop CSMA8 Series waste forms. In a second approach, Ionex Ag-400 was reacted with the AltLAW simulant for 2 hrs and then the Ionex Ag-400 was removed prior to grouting; this pretreatment step was used to develop both CSMA8 and CSMA3 Series waste forms.

Reference formulations CSMA8S2 and CSMA3S1R1 were modified and further optimized by including the test variables described below.

- Slag type: Slag composition is an important factor in determining reactivity and the gel composition such as the formation of secondary phases in the cured grouts [21, 22]. For example, an increase in MgO and Al_2O_3 contents can promote hydrotalcite formation and an increase in Al_2O_3 and SiO_2 contents enhances stratlingite formation.

- Silica fume: Increasing silica fume content to test its effect on leaching resistance. The FY23 work suggested that silica fume addition improves leaching resistance [10].

- Inclusion of a plain zeolite such as zeolite Type 5, clinoptilolite, and chabazite to enhance retention of COCs.

- Hydrophobic admixture: Based on the FY23 work, a higher dosage of hydrophobic admixture may be required to further improve hydrophobicity of a waste form.

- Improvement in the rheology of the fresh grout by including a high content of silica fume and/or employing an increased water to dry mix ratio (w/dm).

- Na concentration in the LAW: Assessment of the dependence of leaching resistance on the sodium concentration in the LAW (3.5 versus 5.6 M Na). The objective was to determine whether a modest decrease in sodium concentration for an optimized NSAS formulation might improve the ability to meet the performance metrics.

- Removing inert fillers (sand and ground quartz) stepwise to increase waste loading in an optimized formulation.

Grout mix compositions based on the above-mentioned formulating variables are summarized in the test matrix (Table 2.4). The formulations proposed in this test matrix were the guide for the FY24 testing program.

SECTION 3.0
WASTE SIMULANT, MATERIALS, FORMULATIONS, AND TESTING APPROACH

3.1 Waste Simulant

The AltLAW simulant composition that was used is shown in Table 3.1. This composition is based on the "HTWOS Overall Average" used in previous Cast Stone testing [2]. We have assumed a sodium concentration of 5.6 M based on the nominal concentration for the cesium removal ion exchange process. In addition, NSAS based grout waste forms were prepared with 3.5 M Na AltLAW simulant to evaluate the effect of sodium concentration in the AltLAW on retention of COCs, in particular of iodine.

All of the simulants were spiked with iodide at 150 mg/L and Re (as a non-radioactive surrogate for Tc, added as perrhenate) at 350 mg/L to ensure detectable levels in the leachates from the EPA Method 1315 tests. It is noted that rhenium is less easily reduced than technetium and may therefore overestimate the release of technetium from reducing grouts. Chromium was added as $Na_2Cr_2O_7•2H_2O$ using a molar ratio of 0.0043 Cr/Na, which is the Best Basis Inventory (BBI) value in Table 3-3 in reference [2]; Cr in the 3.5 M Na AltLAW simulant was maintained at the same spiking level as in the 5.6 M Na AltLAW simulant.

In the simulant, sodium acetate was used to represent the total organic carbon. Much of the total organic carbon in the tank waste is unidentified, but acetate, oxalate, glycolate, and formate are common compounds found in significant amounts in most waste tanks. Acetate was chosen in these tests to represent these organic acids. The recipe for 5.6 M Na AltLAW simulant is shown in Table 3.2. The measured density was about 1.255 g/mL for the 5.6 M Na AltLAW simulant. The recipe for 3.5 M Na simulant is shown in Table 3.3 and the measured density was about 1.168 g/L.

Table 3.4 lists spiked LDR inorganics that are relevant to Hanford LAW [11]. These are antimony, arsenic, barium, cadmium, chromium, lead, nickel, selenium, silver, and thallium. The spiked chromium was prescribed with about 1250 mg/L Cr for $Na_2Cr_2O_7•2H_2O$ (Tables 3.2 and 3.3) and about 250 mg/L Cr for $Na_2CrO_4•4H_2O$. The total spiked chromium was 1500 mg/L in the AltLAW.

3.2 Raw Materials for Preparing AltLAW Waste Forms

A range of raw materials, aggregates/fillers, and additives were used to prepare grout waste forms for AltLAW, as described in the following sections.

3.2.1 Dry Mix Components

Ground granulated blast furnace slag (BFS), called NewCem, was from the Lafarge-Holcim' Seattle Plant (BFS SE). It is a grade 100 slag according to ASTM International (ASTM) C989. The slag was chosen due to the geographical proximity of the source to the Hanford Site and the fact that it was used in the sodium sulfate activated slag waste forms developed by VSL for stabilization of high-ammonia wastes from the Hanford Effluent Treatment Facility (ETF) [23-26]. Two batches of the Seattle slag were tested for performance comparison, an old batch delivered to VSL/CUA in 2020 (BFS SEo) and a newer batch in 2023 (BFS SEn). These were tested to understand whether changes in chemical composition and phase characteristics over time may affect performance of a grout waste form.

In addition to BFS SE, several alternative blast furnace slags were tested, including slag cement grade 120 from Diversified Minerals Inc. in California ((BFS DMI), DuraSlag grade 120 from Ash Grove Cement, Washington (BFS DS), and slag cement grade 120 provided by Clark Pacific in California (BFS CP). Limited testing results from the FY23 work suggested inclusion of BFS CP improved leaching resistance of sodium, nitrate and nitrite [10].

Light-burned MgO marketed under the brand name Sika Control® SC was used as an ingredient in several formulations for AltLAW. Light-burned MgO is a shrinkage compensating and reduction admixture used to produce Portland cement and geopolymeric materials with a reduced potential for drying shrinkage and cracking, which meets the requirements of ASTM C494. In addition, light-burned MgO can provide additional soluble magnesium to accelerate strength development and to promote hydrotalcite formation. Light-burned MgO alone has been tested as a chemical activator for blast furnace slag [27].

Silica fume is a byproduct of silicon metal production or ferrosilicon alloys. Silica fume consists primarily of nano particles (~2 nm) of amorphous silicon dioxide. Due to its fine particles, large surface area, and the high SiO_2 content (about 94%), silica fume is a very reactive pozzolan. Its small spherical-particle nature can be used to improve rheology and thereby achieve significant reductions of w/dm in cementitious or geopolymer mixtures. Silica fume was provided by Norchem, Inc., a wholly owned affiliate of Globe Metallurgical, Inc.

3.2.2 Sand/Fillers

Fine sand, ground quartz, and silica fume were included in waste form mixes to optimize the packing density of the resulting AltLAW waste forms. The materials used were as follows:

- Fine sand consisting mostly of quartz with a particle size of 0.05 mm to 0.6 mm with a mean diameter (d_{50}) of about 0.22 mm. Air-dry sand was used. The water absorption was about 1.25 wt%, which was included in the waste form recipes.
- Ground quartz (Qz) A25 from AGSCO Corporation, with a mean particle size of 5 microns.

- Silica fume (SF) was added as a reactive nano filler to improve rheology and particulate packing in NSAS-based waste forms. The results from the FY23 work suggests that silica fume addition improves leaching resistance particularly when calcined hydrotalcite was present in the formulation mix [10]. Silica fume likely improves the packing density and stimulates the formation of calcium aluminosilicate hydrate (CASH) gel and dense stratlingite, both of which should reduce the permeability of the waste form.

3.2.3 Additives

Various additives were used to improve the performance of the AltLAW waste forms or as getters to enhance fixation of anionic species. These additives included the following:

- EUCON Hydrapel 2.5 (Hyp) is a silicon polymer-based, plasticizing/efflorescence controlling/water-repellent admixture, provided by Euclid Chemical. EUCON Hydrapel 2.5 was estimated to contain about 55% water.
- Commercially available hydrotalcite ($Mg_6Al_2(OH)_{16}(CO_3)\cdot 4H_2O$) was calcined at 475 °C for 3 hours. The objective was for the calcined hydrotalcite (CTH) to restructure around the available anion species in the waste to enhance their retention in the waste form._Calcined hydrotalcite is well known for capturing chlorine during hydration of Portland cement and improving chemical durability of concrete [28].
- Ionex Ag-400 (AgZ) manufactured by Molecular Products Limited is a silver-exchanged zeolite with a mordenite crystalline structure. Ground Ionex Ag-400 was used as a getter for iodine in all the waste forms. Ionex Ag-400 beads were ground to 150 to 200 mesh before use. Ionex Ag-400 was selected based on its efficiency in capturing iodine in the LAW in Saltstone and geopolymer waste forms [29].
- A plain zeolite (i.e., non-silver-containing) such as zeolite Type 5 (ZT5) was included in formulations where Ionex Ag-400 was removed prior to grouting. Zeolite is well known for being a getter for COCs and it is compatible with geopolymer waste forms.

3.3 Formulations and Recipes

Two NSAS formulations developed during the FY23 work, CSMA8S2 (CSMA8-Series) and CSMA3S1R1 (CSMA3 Series), constituted the basis for the FY24 work [10]. The formulating parameters and mix compositions for the reference formulations are listed in Tables 2.1 and 2.2, respectively. In all the formulations for FY24 work, both sodium carbonate and sodium sulfate were included as activators with a mass ratio of 1:1 by Na_2O. The amounts of neutral salts (sodium carbonate and sodium sulfate) present in the AltLAW simulant were calculated as a part of the activator. The total Na_2O for neutral salts and light-burned MgO were all fixed at 5% by weight of slag (BWOS). AgZ was fixed at 5% BWOS in the CSMA8-Series formulations. Reference CSMA8S2 and CSMA3S1R1 were modified and further optimized by a set of formulating parameters.

- Blast furnace slag type: Five slag types, BFS SEo, BFS SEn, BFS DMI, BFS CP, and BFS DS, were included in the formulation testing. The effect of slag composition was systematically tested with the reference CSMA8S2 formulation only.

- EUCON Hydrapel 2.5 was included as the hydrophobic admixture at 0.75% BWOS for reference CSMA8S2 and 0.575% BWOS for reference CSMA3S1R1, respectively. The dose rates applied in the FY23 work seemed not sufficient to induce super hydrophobicity. Therefore, a higher dose of Hydrapel 2.5 was tested to further improve hydrophobicity and thus reduce permeability. In the FY24 work, Hydrapel 2.5 varied between 1.25% and 3.0% BWOS in NSAS based grout waste form formulations.

- Silica fume: The reference formulations employed 6% BWOS silica fume. In the FY24 formulations, silica fume additions were increased to 10% BWOS and 14% BWOS respectively.

- w/dm from 0.425 to 0.50. A higher w/dm was applied to improve the rheological properties. The dry mix (dm) mainly consisted of BFS, AgZ, CTH, and Zeolite Type 5 if any. Reference formulations included silica fume at about 6% BWO or 2% in the mortar mix with 39% total fillers. When silica fume increased over 6% BWOS, the amount of silica fume that exceeded 6% was included in the dry mix for w/dm calculations. In addition, the amount of water contained in Hydrapel 2.5 that exceeded either 0.75% BWOS or 0.575% BWOS for a reference formulation was also included for w/dm calculations. The moisture from sand and ground quartz powder was not part of the w/dm calculation.

- Filler contents: Typically, the mortar formulations contained 32.5 wt% fine sand and 6.5 wt% ground quartz. The total fillers amounted to 39 wt%. In the FY24 work, the total filler content varied from 0 wt% (paste) to 39 wt% (mortar) in the formulations. Reduction in the total filler content significantly increased waste loading and may have a positive impact on rheological properties of a fresh grout.

- Additives to enhance leaching resistance including calcined hydrotalcite and ground Ionex Ag-400. Ground Ionex Ag-400 was included typically at 5% BWOS in CSMA8 Series formulations to achieve a molar Ag/I ratio of about 275. Calcined hydrotalcite was the only additive to enhance leaching resistance in formulation CSAMA3S1R1 [10]. This reference formulation was modified and optimized by incorporating Zeolite Type 5, in addition to calcined hydrotalcite to test if there might be a synergistic effect on leaching resistance. The CSMA8-Series formulation was further modified assuming iodine was removed by Ionex Ag-400 prior to grouting where the Ionex Ag-400 was either replaced by zeolite Type 5A or BFS.

The formulating parameters for the CSMA8 Series waste forms with ground Ionex Ag-400 as the getter for iodine are shown in Table 3.5. These formulations, associated with a set of testing variables including BFS type, SF, Hyp, the total fillers, and w/dm ((Tables 3.6 and 3.7), and the corresponding recipes are shown in Tables 3.8 and 3.9, respectively.

The formulating parameters for the CSMA8 Series waste forms with iodine removed by ground Ionex Ag-400 prior to grouting are shown in Table 3.10. These formulations, associated with the testing variables primarily with BFS type and the total filler content, are shown in Table 3.11 and the corresponding recipes are shown in Table 3.12.

The formulating parameters for the CSMA3 Series waste forms with iodine removed by ground Ionex Ag-400 prior to grouting are shown in Table 3.13 and the corresponding grout mix compositions and recipes are shown in Table 3.14 and Table 3.15, respectively.

The formulating parameters for the waste forms with 3.5 M Na AltLAW are shown in Table 3.16 and the corresponding formulations and recipes are shown in Tables 3.17 and 3.18, respectively.

3.4 Testing Approach

The primary objective of this work was to perform laboratory-scale testing to refine the most promising formulation(s) that were identified in the FY23 work [10]. The goal of the refinements was to further reduce the release rates for ^{99}Tc, Cr, ^{129}I, and nitrate while maintaining a workable waste form. Extensive effort was made to increase waste loading by removing the total fillers in the formulations. A three-phased approach, such as was used in previous fiscal years [8-10], was employed to screen new formulations for their retention properties. Only those formulations that showed promise for improved retention of the target COCs, and in particular, for meeting the retention improvement targets, were subjected to more extensive testing. All of the waste forms developed during FY24 were subjected to the full 63-day EPA Method 1315 test along with the measurement of other properties after curing for 28 days at room temperature.

- First testing phase: The reference CSMA8S2 employed a blast furnace slag from Lafarge-Holcim's Seattle plant (BFS SE). During this testing phase, three BFS compositions, BFS CP, BFS DS and BFS DMI were tested with the reference formulation CSAM8S2 (CSMA8S2R5, CSMA8S2R6 and CSMA8S2R13). Furthermore, silica fume was increased to 10% and 14% BWOS and EUCON Hydrapel 2.5 was increased to 1.25% and 3.0% BWOS in respective formulations (CSMA8S2R4, CSMA8S2R3s, and CSMA8S2R3c). Preliminary results suggested that an optimal waste form may be formulated with 14% BWOS silica fume, 1.25% or 2.5% BWOS EUCON Hydrapel 2.5, and w/dm = 0.45 or 0.425. With these optimal parameters applied, three formulations were developed and tested: CSMA8S2R8 with a w/dm increased to 0.50 targeting rheological improvement, CSMA8S2R11a with 27.5% total filler content, and CSMA8SA2R11b with the fillers completely removed to achieve maximum waste loading. The testing results showed that BFS CP was a promising alternative to BFS SE while BFS DS exhibited excellent reducing capacity for pertechnetate in the AltLAW.

- Second testing phase. This testing stage was the primary testing phase of the present work with a focus on formulations that assumed that iodine in the AltLAW was removed prior to grouting.

    - New CSMA8 Series waste forms were developed with the optimal formulating parameters obtained during the first testing phase with addition of a pretreatment step in which Ionex Ag-400 was removed after reacting with the AltLAW simulant for 2 hours prior to grouting. CSMA8S2R12a was a mortar mix and the fillers were completely removed, yielding CSMA8S2R12d and CSMA8S2R12c. Both CSMA8S2R12a and CSMA8S2R12d were prepared with BFS SEo while CSMA8S2R12c employed BFS CP for comparison. Additional formulations with BFS DS were tested (CSMA8S2R12e and CSMA8S2R12f) by taking advantage of BFS DS for its great reduction capacity for pertechnetate. At the time when the formulations were developed and tested, the grout sample prepared with BFS DS showed very promising leaching data for nitrate and nitrite at early leaching times.

    - Three CSMA3 Series formulations were developed and tested with silica fume increased to 14% BWOS and EUCON Hydrapel 2.5 to 3.00%. CSMA3S1R3 and CSMA3S1R4 were mortar type waste forms prepared with BFS SEn and BFS CP, respectively. The fillers were completely removed to increase waste loading in CSMP3S1R1 that employed BFS CP.

    - Finally, three formulations were developed for AltLAW 3.5 M Na to test the effect of Na molarity on the properties and performance of the waste forms. The optimal formulating parameters (14% BWOS SF, 1.25% BWOS Hyp and w/dm = 0.45) were applied to formulate CSMA8S2R10, which is a mortar mix with Ionex Ag-400 included in the waste form. The fillers were removed from CSMA8S2R10, yielding CSMP8S2R2. CSMP3S2R2 was a paste formulation derived from CSMP3S1R1 that was the counterpart of AltLAW 5.6 M Na assuming iodine was removed prior to grouting. All these grout samples were prepared with BFS CP.

- Third testing phase. Nine of the better-performing formulations were selected for additional characterization with respect to rheology and dry density and porosity. More formulations than planned were tested, as steady-state leaching data were not yet available from the prior testing phase. Finally, three formulations were recommended and advanced for further testing that included isothermal calorimetry and the Toxicity Characteristic Leaching Procedure (EPA Method 1311).

Table 3.19 summarizes all the grout waste forms developed during FY24. As compared to the test matrix planned in Table 2.4, more waste form formulations were developed and tested. In particular, because of the schedule, the waste form development was a dynamic process, with changes required as new leaching data became available from the ongoing testing with the EPA Method 1315 procedure.

SECTION 4.0
TESTS AND MEASUREMENTS

This section describes the methods and procedures that were used in this work to prepare samples, and to characterize the mixing and curing process and the final waste form properties.

4.1 Sample Preparation

4.1.1 General Procedure for Grout Sample Preparation

The waste simulant was prepared by weighing the appropriate quantities of reagent grade chemicals and dissolving them in the required amount of deionized water in a plastic container. Typically, a small batch of 2 L of the AltLAW simulant was prepared with a calibrated flask and thus its density was accurately measured. Then a large batch of the simulant was prepared by scaling up according to the measured density data.

The simulant was mixed at least for 1 hr with a mechanical stirrer. For a large batch of simulant (e.g., 5L), the mixture was stirred at about 250 rpm with an IKA RW 20 Lab mixer. The simulated solution became clear. The container with the simulant was sealed and stored at room temperature for use. The simulant solution was homogenized by stirring before use to ensure no crystallization.

The appropriate quantities of simulant and blended dry mix ingredients were combined in a 7-quart planetary mixer and mixed at about 80 to 120 rpm for about 5 minutes. EUCON Hydrapel 2.5, a liquid hydrophobic admixture, was added while the mixture of the AltLAW simulant and dry ingredients became wet.

The fresh grout was often manually stirred to ensure homogeneity. Air bubbles were removed by vibration on a Vibco vibrating table. The fresh paste was poured into 2″×4″ cylindrical molds. All of the cylindrical samples were sealed with lids to prevent moisture loss and then cured in a temperature stability cabinet with curing temperature set at 22 °C. A water-bath was placed in the stability cabinet to ensure relative humidity of over 95%.

The fresh grout was sampled as needed for testing properties such as set time, rheology, isothermal calorimetry, one-day bleed, and bleed monitoring for 28 days. For initial screening purposes, rheological properties and workability of fresh grout samples were evaluated qualitatively based on observations while mixing and pouring

During all the testing phases, ground Ionex Ag-400 as the getter for iodine was mixed with AltLAW simulant for 2 hrs on a magnetic stirrer plate prior to grouting. Sodium carbonate and/or sodium sulfate were then dissolved in the AltLAW simulant toward the end of this iodine absorption process for about 10 minutes.

4.1.2 Pretreatment Step for Iodine in the AltLAW Simulant

Ground Ionex Ag-400 was mixed with AltLAW simulant for 2 hrs on a magnetic stirring plate (Cole-Parmer) at 500 to 700 rpm. The suspension of the ground Ionex Ag-400 and AltLAW simulant mixture turned black after mixing for 2 hrs (Figure 4.1), indicating iodide was captured as AgI in the nanopores of the zeolite structure. The suspension was mixed with the dry mix to prepare a grout sample that was derived from reference CSMA8S2 formulation.

In the case that the iodine was removed from the AltLAW simulant prior to grouting, about 20.7 grams of ground Ionex Ag-400 was added to 1000 grams of the AltLAW simulant (AgZ to AltLAW mass ratio of ~0.02). The molar Ag/I ratio was approximately 76. In the FY23 work, a set of iodine absorption tests were conducted with an AgZ to AltLAW (5.6 M Na) mass ratio ranging from 0.002 to 0.02 [10], equivalent to molar Ag/I ratio from 7.6 to 76, estimated by using 40% Ag_2O in the Ionex Ag-400. It was observed that 2.07 grams of AgZ per 1000 grams of 5.6 M Na AltLAW spiked with 150 mg/L iodide, equivalent to a AgZ to AltLAW mass ratio of about 0.002 (molar ratio of about 7.6), was sufficient to remove iodide in the simulant [10]. For this testing program, a higher mass ratio of AgZ to AltLAW was used to ensure adequate removal of iodine in the simulant by Ionex Ag-400.

Ground Ionex Ag-400 was allowed to react with AltLAW simulant solution for 2 hrs under constant stirring. Then the suspension was left without stirring to settle for a few hours. Though settling of the solids alone allowed for removing iodine from the simulant solution, filtration of the suspension was more efficient with residual AgI-loaded zeolite. The supernatant solution was vacuum filtered with Grade F glass microfiber filter media (0.7 μm). The filtered AltLAW simulant solution was used for preparing grout samples. Pre-settling of the suspension improved filtration efficiency greatly. It was noticed that black particles settled in the filtered AltLAW solution after a week (Figure 4.2). These were AgI loaded Ionex Ag-400 particles that passed through the 0.7 μm filter, indicating that Ionex Ag-400 loaded with AgI was not completely removed and the residual iodine would contribute to detection of iodine in leachate solutions during EPA Method 1315 testing. In this regard, iodine removal in a column format would be more efficient though at the cost of some added process complexity. Recently, Asmussen et al. conducted column performance testing on removing iodine from carbonate containing alkaline waste (180 mg/L total iodine) and their results on Ionex Ag-400 showed an 80-90% removal rate for iodide over 6000 bed volumes without breaking through [30].

The spent Ionex Ag-400 solids were washed with absolute alcohol to remove soluble salts. After drying, the solids were subjected to XRD analysis (Figure 4.3). The results showed that the dehydrated mordenite recovered its structure during reaction with the AltLAW simulant. Metallic silver, AgI, and AgCl were identified. The presence of metallic silver may be related to reduction of AgI and AgCl when exposed to light as the solids were left in the lab for a few weeks before analysis. Apparently, chloride species in the AltLAW remained a competitive species for iodine capture by Ionex Ag-400.

4.2 Tests and Analyses

Bleed Water Content: One-day bleed water content is defined herein as the water remaining unabsorbed after curing the grout in a sealed vessel for 24 hours. Specifically, the freshly prepared grouts were poured into 2″x4″ cylindrical molds, filled to within about 5mm from the top, and cured in a sealed configuration at room temperature for 24 hrs. The sealed molds were then weighed, any liquid was absorbed using tissue paper, and the samples were then weighed again. The mass loss was calculated and reported as the mass fraction of the total water contained in the sample at the time of sample preparation. When necessary, additional 2″x4″ cylindrical samples were prepared for bleed water monitoring for up to 28 days.

Hydrophobicity of cured waste forms: Hydrophobicity was evaluated qualitatively by visual wettability of a cured grout surface. A stream of water is sprayed onto the grout surface. When the water droplets are spherical and the surface is still dry after water drops are removed, the grout sample shows superhydrophobicity (Figure 4.4). When water droplets immediately spread over the grout surface, the surface shows little hydrophobicity. When water droplets become slightly flat and the surface is wet after water drops are removed, the grout sample shows some hydrophobicity. The water drop testing results on estimating hydrophobicity for all the grout samples are listed in Table 4.1.

Initial time of setting: Initial time of setting was determined by penetration resistance using the Vicat needle method described in ASTM C 191. In that test, the final set time is defined as the time required for the specimen to become impenetrable, while the initial set time is defined as the time required for a specimen to develop resistance to penetration to a depth of 25 mm. For a sample that is 40 mm high, this translates to an impenetrable depth of 15 mm. Initial set time using the 40 mm high sample can be calculated from the following formula:

$$\text{Initial Set Time} = \frac{H - E}{C - D} \times (15 - D) + E \,, \tag{4.1}$$

where E is the time in hours of the last reading smaller than 15 mm, H is the time in hours of the first reading greater than 15 mm, C is the *impenetrable* specimen height at time H, and D is the *impenetrable* height at time E.

Rheology of grouts was determined using a Haake rheometer to measure the shear stress vs. shear rate behavior, which is typically interpreted using the Bingham model for fluid flow in freshly prepared pastes [31]. The measurements were made about 15 minutes after sample preparation. The model relates shear stress and shear rate in terms of the yield stress and the plastic viscosity at a fixed time after mixing of the components.

Heat of Hydration: Heat of Hydration, including the time dependence and the quantity of the heat generated during hydration of the pastes, was measured by isothermal calorimetry using a TAM Air Isothermal Calorimeter according to the methodology described previously [32]. All the measurements were performed at 25 °C. The heat flow produced by the samples was monitored continuously during 7 days of curing.

Compressive strength: Compressive strength was measured by applying a compressive axial load to unmolded cylinders until failure occurred. The compressive strength of the specimen was calculated by dividing the maximum load attained during the test by the cross-sectional area of the specimen in accordance with ASTM C 39C /39M. Compressive strength was measured in duplicate after curing for 7 days and 28 days. The typical deviation from the mean was less than 10%.

EPA Method 1315 Leach Test: The Method 1315 test is a 63-day leach test that consists of submerging a monolithic sample in deionized water and replacing the entire leachate at fixed periods of time. The samples were 2”x4” cylinders that were cured for at least 28 days. The leachates were analyzed for key constituents. The ratio of the liquid volume to the geometric surface area of the solid sample was fixed at 9 cm^3/cm^2. At each of the nine predetermined leaching intervals, the leaching solution is replaced with fresh leachant. The standard cumulative leaching times at which solution exchanges are made are 2 hours and 1, 2, 7, 14, 28, 42, 49, and 63 days. The leachate samples were analyzed by Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES) for Ag, Na, Re, and Cr, by Ion Chromatography (IC) for NO_3^- and NO_2, and Inductively Coupled Plasma – Mass Spectroscopy (ICP-MS) for iodine. The effective diffusivity was calculated from the leachate concentration data based on a semi-infinite solid. The leachability index “LI” is a parameter derived from the test results that evaluates diffusion-controlled contaminant release over time. The data were also reported as effective diffusivity in units of cm^2/sec. The observed diffusivity for a specific species was calculated according to Eq. 4.2:

$$D = \pi\times[M_{ti}]^2/(2\times\rho\times C_0\times(\sqrt{t_i} - \sqrt{t_{i-1}}))^2 \tag{4.2}$$

where: D = observed diffusivity (m^2/s) of species for leaching interval, $t_i – t_{i-1}$,
M_{ti} = mass of species released for leaching interval i (mg/m^2),
t_i = cumulative contact time at the end of the current leaching interval, i (s),
t_{i-1} = cumulative contact time at the end of the previous leaching interval, $i-1$ (s),
ρ = cured grout density (kg/m^3), and
C_o = initial concentration of species in cured grout (mg/kg).

Toxicity Characteristic Leaching Procedure (TCLP): The TCLP leach test was performed in duplicate on selected cured samples per EPA SW-846 Method 1311. The grout waste forms for TCLP testing were prepared with an AltLAW simulant additionally spiked with LDR inorganics as showed in Table 3.4. In this test, the sample was crushed (< 3/8 inch) and placed in an acetic acid/sodium acetate buffer solution for 18 hours at room temperature (~ 22 °C) with constant end-over-end agitation. The leachate concentrations were measured by ICP-AES.

Dry Bulk Density was determined by subtracting the evaporable water present in the sample from the mass of the saturated sample; the outcome of the subtraction was then divided by the measured volume of the saturated sample. Evaporable water was estimated by subtracting the final oven-dry weight of the sample from the saturated weight of the grout. The volume of the saturated sample was determined by its geometry. It is noted that this definition of dry bulk density differs from that in [33], which here we refer to instead as the “matrix skeleton density,” as defined below.

Matrix Skeleton Density was determined by subtracting the evaporable water and the known amount of salts present in the sample from the mass of the saturated sample; the outcome of the subtraction was then divided by the measured volume of the saturated sample. Evaporable water was estimated by subtracting the final oven-dry weight of the sample from the saturated weight of the grout. The volume of the saturated sample was determined by its geometry. It is noted that this Matrix Skeleton Density is termed the “dry bulk density” in [33].

Porosity was calculated as the ratio of the simulant volume present in the cured sample to the measured saturated sample volume [34]. The simulant volume was determined by dividing the calculated simulant mass (evaporable water + estimated amount of salts present in the sample) by the density of the simulant.

Particle Density was calculated based on the matrix skeleton density and porosity values according to the formula:

$$\rho_s = \rho_m/(1-\eta), \tag{4.3}$$

where ρ_s is the particle density, ρ_m is the matrix skeleton density, and η is the porosity [33].

Apparent Density: Cured grout densities are typically determined on saturated grout samples obtained by immersing the samples in water for 24 hours to achieve saturated conditions. However, in view of the large salt content of the present grout materials an alternative method was employed. Cylindrical 2” x 4” grout samples were sealed and allowed to cure and then the density (the “apparent density”) of the cured sample was determined by measuring the sample dimensions and mass. Typically, the apparent density is slightly higher than the fresh density as a result of slight shrinkage.

SECTION 5.0
RESULTS AND DISCUSSION

5.1 Verification of Simulant Spikes

The AltLAW simulant solution was subjected to ICP-AES, IC, and ICP-MS analyses for concentrations of sodium, chromium, iodine, rhenium, nitrate, and nitrite. The results are summarized in Table 5.1, which also include the percent deviation from target (%Dev). All the measured concentrations are within 10% of the respective target values.

5.2 Characterization of Raw Materials

Analyzed chemical compositions from X-ray fluorescence spectroscopy (XRF) and X-ray Diffraction (XRD) patterns for blast furnace slags are shown in Table 5.2 and Figure 5.1, respectively. While both BFS SEo and BFS SEn showed similar compositions, BFS CP, BFS DMI, and BFS DS exhibited distinct chemical characteristics in terms of MgO and Al_2O_3 contents. The MgO content in BFS DMI was 11.54 wt%, as compared to 9.22 wt% in BFS DS, 6.88 wt% in BFS CP, and about 4-5 wt% in BFS SEs. Concurrently, CaO and SiO_2 contents decreased with increasing MgO and Al_2O_3 contents in the slags. The $(MgO+Al_2O_3)/SiO_2$ ratio was 1.10 for BFS DMI, 0.78 for BFS DS, 0.60 for BFS CP, and 0.53 for BFS SEs. Hydrotalcite yield during alkali activation is typically proportional to the $(MgO+Al_2O_3)/SiO_2$ ratio for a blast furnace slag. These slags provided an excellent opportunity to determine the effect of slag composition on fresh and cured properties of a NSAS based grout waste form. XRD analysis revealed that all slag samples are essentially glassy or amorphous, with a strong diffraction hump (2θ) between 26 and 32° (Figure 5.1). Two batches of BFS SE and BFS DMI contained mainly gypsum and bassanite as the secondary phases, while BFS CP and BFS DS contained anhydrite and bassanite as the secondary phases. All slag samples may contain calcite.

The XRF analyzed compositions for Ionex Ag-400 and Zeolite Type 5 are given in Table 5.3 and XRD patterns are shown in Figure 5.2. Both batches of Ionex Ag-400 showed a consistent chemical composition with about 40% Ag_2O. This value was used for estimating molar Ag/I ratios, which is a way to determine the dosage for Ionex Ag-400.

5.3 Phase 1a: CSMA8 Series Waste Forms with AgZ Included, Slag Types

5.3.1 Fresh and Cured Properties

Formulating parameters, mix compositions, and recipes for CSMA8 Series waste forms with different slag types are shown in Tables 3.5, 3.6, and 3.8, respectively. The test results are summarized in Table 5.4. Hydrophobicity testing results are shown in Table 4.1.

Formulation CSMA8S2 was developed for AltLAW simulant with 5.6 M Na in the FY23 work [10]. This formulation used dosages of Na_2CO_3 and Na_2SO_4 in equal amounts, with 2.5% Na_2O BWOS, EUCON Hydrapel 2.5 as the hydrophobic admixture at 0.75% BWOS, Ionex Ag-900 as the getter for iodine at 5% BWOS, silica fume at about 6% BWOS, and light-burned MgO at 5% BWOS. The w/dm ratio was 0.45 (Table 2.2). Total filler content was 39 wt%. Ionex Ag-400 was allowed to react in the AltLAW for 2 hrs prior to grouting.

Formulation CSMA8S2 used BFS SEo and that was replaced with three other BFS types: BFS CP, BFS DS and BFS DMI. The objective was to identify an alternative slag that would yield a NSAS waste form exhibiting better performance than BFS SE.

With BFS CP, the as yielded waste form, CSMA8S2R5 exhibited shorter set time and higher compressive strength values as compared to CSMA8S2 (Table 5.4). The initial set time was 19.1 hrs, as compared to over 30 hrs for CSMA8S2. The fresh grout poured slowly. The compressive strength was 6970 psi after curing for 7 days and increased to 8508 psi after 28 days. In contrast, the compressive strength for CSMA8S2 was less than 500 psi after curing for 7 days and increased to 6449 psi after 28 days.

With BFS DS, the resulting waste form, CSMA8S2R6 exhibited longer set time and significantly higher compressive strength values as compared to CSMA8S2 (Table 5.4). The initial set time was about 5 days. Surprisingly, the compressive strength was 5297 psi after curing for 7 days and increased to 10528 psi after 28 days. Including BFS DS yielded a mechanically durable waste form.

With BFS DMI, the resulting waste form, CSMA8S2R13 showed shorter set time and slightly higher compressive strength values as compared to CSMA8S2 (Table 5.4). The initial set time was about 26.0 hrs. The compressive strength was 2973 psi after curing for 7 days and increased to 7600 psi after 28 days.

5.3.2 EPA Method 1315 Leaching Results

The NRC Technical Position on Waste Form [35] provides recommendations and guidance regarding methods to demonstrate waste stability for shallow land disposal of radioactive waste. That document specifies testing using the ANSI/ANS 16.1 method and that the leachability index (LI) should be greater than 6.0 on that test; however, other (generally more stringent) requirements, including the requirement for a performance assessment to evaluate long-term performance, take precedence for the IDF. The present work, per the WRPS SOW [11], used the EPA Method 1315 test, which is derived from and is similar to the ANSI/ANS 16.1 test. A 63-day leach test was performed on most of the CSMA8 Series waste form samples per EPA Method 1315 after curing for 28 days. As noted in Section 4.2, sodium, and nitrite concentrations were measured, in addition to rhenium, iodine, chromium, and nitrate concentrations, in order to provide additional measures of the leaching behavior of soluble species to better characterize the overall retention properties of the waste form.

The measured LIs for Na, Re, Cr, I, NO_3^-, NO_2^- at 28 and 63 days are summarized in Table 5.5. The LI values at each sampling time are reported in Tables 5.6 to 5.11. These values are also plotted as functions of time and formulation type in Figures 5.3 to 5.8.

These can be compared with the leachability indices corresponding to the performance metric diffusivity values estimated by PNNL [6] for technetium (10.70; 2×10^{-11} cm^2/s), chromium (10.40; 4×10^{-11} cm^2/s), iodine (10.52; 3×10^{-11} cm^2/s), and nitrate (8.70; 2×10^{-9} cm^2/s), respectively

<u>With BFS CP (CSMA8S2R5)</u>: The 63-day LI values for Na and five COCs (Re, Cr, I, NO_3, and NO_3^-) were comparable to those for reference CSMA8S2 (Table 5.5), suggesting that BFS CP could be a good alternative to BFS SE. The 63-day LI values for Cr, I, and NO_3^- were better than the respective performance metric requirement while the 63-day LI value for Re failed to meet its performance metric requirement for rhenium of 10.70. Low Re LI values for the CSMA8 Series waste forms were related to the presence of loaded Ionex Ag-400. The sulfide species released during alkali activation of BFS is the primary reducing agent for pertechnetate or perrhenate. However, sulfide species have a great affinity for silver by precipitating Ag_2S, leaving less sulfide available for Tc or Re reduction.

<u>With BFS DS (CSMA8S2R6)</u>: The 63-day LI value for nitrate was 8.58, which failed to meet the estimated performance metric requirement for nitrate of >8.70. It is interesting that the LI values for nitrate and nitrite were significantly higher than those for the reference CSMA8S2 during early leaching times and attained its steady state condition much earlier as well, e.g., at 28 days, as observed in Figures 5.7 and 5.8. The 63-day LI value for I was only 8.86 as compared to 10.55 for CSMA8S2 with BFS SEo and 11.20 for CSMA8S2R5 with BFS CP. The 63-day LI value for Re was as high as 12.30 as compared to about 8.9 for both CSMA8S2 and CSMA8S2R5. BFS DS must have had a high reducing capacity for pertechnetate or perrhenate in the AltLAW, most likely due to a higher content of sulfide. Supply of sulfide species may be sufficient to destabilize AgI captured in the zeolite and to reduce perrhenate during alkali activation of BFS DS.

<u>With BFS DMI (CSMA8S2R13)</u>: CSMA8S2R13 had 49-day LI values for Na and COCs that were significantly lower, all about 7.4, as compared to CSMA8S2 and CSMA8S2R5 except for Cr. Mechanically, CSMA8S2R13 was quite durable with a 28-day compressive strength of 7600 psi, higher than what was obtained for CSMA8S2. The extremely low LI values for both Re and I are puzzling. If a low 49-day LI value for I was as a result of destabilization of AgI/zeolite by elevated concentrations of sulfide species in the waste form, a high LI value for Re would be expected as well. In view of the low LI values for Na, nitrate, and nitrite, it can be speculated that alkali activation of BFS DMI may yield an unfavorable gel composition and increased porosity due to its high content of MgO. Capillary pores may dominate the pore structure, increasing rates of transport for Na, nitrate and nitrite.

Preliminary test results showed that slag composition may play an important role in controlling chemical and mechanical durability of a NSAS waste form. As described in Section 5.2, BFS DMI had the highest MgO and Al_2O_3 contents and the lowest CaO and SiO_2 contents, but yielded a waste form with the lowest leaching resistance. It has been expected that high contents of MgO and Al_2O_3 in the slag could promote hydrotalcite formation during alkali activation. Abundant hydrotalcite may serve as a sink for a range of COCs including iodine, nitrate, and nitrite in the AltLAW, thus potentially resulting in improved leaching resistance. However, the leaching resistance for COCs decreased with increased contents of MgO and Al_2O_3. It is possible that the presence of silica fume may have inhibited formation of hydrotalcite. This testing phase showed that both BFS CP and BFS SE appear to have favorable slag compositions, yielding both chemically and mechanically durable waste forms for the AltLAW. BFS CP and BFS SE contained higher contents of CaO, Al_2O_3 and SiO_2, favoring stratlingite formation rather than hydrotalcite formation. Typically, stratlingite forms a highly dense gel structure that may improve impermeability of the grout waste form. Stratlingite was detected in the waste form samples where the fillers were completely removed (see Section 5.8.2).

In summary, this testing phase showed that BFS CP is a good alternative to BFS SE, yielding a NSAS waste form with comparable if not better performance than BFS SE. BFS DS had a high reducing capacity and would be particularly suitable for a NSAS waste form for targeting pertechnetate in the AltLAW more efficiently. BFS DMI was not suitable for the waste form for the AltLAW. Based on these results, BFS CP was advanced for further studies in the next testing phase, together with BFS SE.

5.4 Phase 1b: CSMA8 Series Waste Forms with AgZ Included, Varying SF, Hyp, w/dm, and Filler Content

5.4.1 Fresh and Cured Properties

Formulating parameters, mix compositions, and recipes for CSMA8 Series waste forms with varying SF, Hyp, w/dm, and filler content are shown in Tables 3.5, 3.7, and 3.9, respectively. The testing results are summarized in Table 5.4. Hydrophobicity testing results are shown in Table 4.1.

Formulation CSMA8S2 served as the starting point for modifications by varying SF, Hyp, w/dm, and filler content. Ionex Ag-400 was included in the waste form as the getter for iodine. The objective was to determine optimal formulating parameters that could be used to develop a waste form with improved performance.

Formulation CSMA8S2 used BFS SEo, 6% BWOS SF, 0.75% BWOS Hyp and w/dm at 0.45. Silica fume was increased to 10% BWOS while EUCON Hydrapel 2.5 was increased to 1.25% BWOS concurrently, yielding CSMA8S2R4. BFS SEn was the slag type for the waste form. The initial set time was 43.8 hrs, comparable to 30-48 hrs for CSMA8S2. The compressive strength was 5479 psi after curing for 7 days and increased to 8187 psi after 28 days. CSMA8S2R4 showed better performance than reference CSMA8S2 in terms of mechanical durability.

Silica fume was further increased to 14% BWOS while EUCON Hydrapel 2.5 was maintained at 1.25% BWOS, yielding CSMA8S2R3s. This mix used BFS CP. The initial set time was 11.7 hrs, as compared to 19.1 h for CSMA8S2R5 (reference formulation with BFS CP). The compressive strength was as high as 7860 psi after curing for 7 days and increased to 9530 psi after 28 days. CSMA8S2R3s showed improved performance over CSMA8S2R5 in terms of mechanical durability, likely due to the increased silica fume content in the formulation.

The w/dm ratio was lowered to 0.425 and EUCON Hydrapel 2.5 further increased to 3% BWOS while silica fume was maintained at 14% BWOS, yielding CSMA8S2R3c. BFS CP was the slag type. The initial set time was 18.1 hrs, as compared to 11.7 h for CSMA8S2R3s. The compressive strength was 7515 psi after curing for 7 days and increased to 9607 psi after 28 days. CSMA8S2R3c showed comparable performance to CSMA8S2R3s in terms of mechanical durability when w/dm was decreased to 0.425.

Due to schedule constraints, successive formulation decisions often had to be made based on early leaching data, before steady state LI values became available. Optimal formulating parameters were determined according to compressive strength and short-term leaching data. The tests conducted above showed that silica fume definitely benefited mechanical durability and likely leaching resistance for COCs and that 14% BWOS SF is likely adequate to yield a more durable waste form. 1.25% BWOS Hyp was sufficient to induce super-hydrophobicity, as reported in Table 4.1. EUCON Hydrapel 2.5 as high as 3% BWOS did not show negative impacts on mechanical durability. Therefore, 14% BWOS SF, 1.25% to 3% BWOS Hyp, and w/dm of 0.45 or 0.425 were considered as optimal formulating parameters for further formulation testing. Both BFS SE and BFS CP were suitable slag compositions for the waste forms for the AltLAW.

While EUCON Hydrapel 2.5 was maintained at 1.25% BWOS and silica fume at 14% BWOS, w/dm was raised to 0.50, yielding CSMA8S2R8. This mix used BFS CP and the objective was to test the effect of high w/dm on fresh and cured properties of the waste form. The fresh grout was thin and pourable. The initial set time was 16.0 hrs, increased slightly from 11.7 h for CSMA8S2R3s that was formulated with a w/dm of 0.45, as would be expected. The compressive strength was 7023 psi after curing for 7 days and increased to 9030 psi after 28 days. An increased w/dm had an insignificant impact on mechanical durability of the waste form as compared to CSMA8S2R3s.

CSMA8S2R11a was formulated with 1.25% BWOS Hyp, 14% BWOS SF, and w/dm at 0.425. The total filler content was decreased to 27.5% from 39%, which was used for CSMA8S2R3s, representing about 15% increase in waste loading over CSMA8S2. BFS CP was the slag type. The fresh grout was thinner than CSMA8S2R3s, suggesting that removal of the fillers improved workability. The initial set time was 20.9 hrs, increased significantly from 11.7 hrs for CSMA8S2R3s. The compressive strength was 8907 psi after curing for 7 days and increased to 10823 psi after 28 days.

CSMA8S2R11a was modified by removing the fillers completely and increasing EUCON Hydrapel to 2.5% BWOS to further improve super-hydrophobicity, yielding CSMA8S2R11b. The waste loading was increased by 55.2% over CSMA8S2. Without the fillers in the grout mix, the fresh grout was thinner and became pourable. The initial set time was about 16.7 hrs. The compressive strength was 8239 psi after curing for 7 days, but only 8972 psi after 28 days. A lower

28d compressive strength value may be due to presence of higher waste solids content and higher %BWOS for hydrophobic admixture per solids (Table 4.1) as a result of removing the fillers in CSMA8S2R11b.

5.4.2 EPA Method 1315 Leaching Results

The measured LIs for Na, Re, Cr, I, NO_3^-, and NO_2^- at 28 and 63 days are summarized in Table 5.5. The LI values at each sampling time are reported in Tables 5.6 to 5.11. These values are also plotted as functions of time and formulation type in Figures 5.9 to 5.14.

LI values for Na: The 63-day LI values for Na varied from formulation to formulation in a narrow range of 8.97 to 9.13 (Table 5.5, Figure 5.9), as compared to 8.67 for reference CSMA8S2. Better performance for the waste forms developed in this testing phase was most like due to improved impermeability by increased silica fume content and super-hydrophobicity in the respective formulations.

LI values for Re: The 63-day LI values for Re were quite low, between 8.8 and 9.0 (Tables 5.5 and 5.7; Figure 5.10). As expected, all the waste forms failed to meet the estimated performance metric requirement for rhenium of 10.70 owing to the inclusion of 5% BWOS Ionex Ag-400. The sulfide species released during alkali activation of BFS was the primary reducing agent for pertechnetate or perrhenate. However, sulfide species have a great affinity for silver by precipitating Ag_2S, leaving less sulfide available for Tc or Re reduction.

LI values for Cr: All of the formulations tested during this testing phase showed excellent resistance to Cr leaching. The 63-day LI values for Cr were between 13.0 and 13.5 (Tables 5.5 and 5.8; Figure 5.11). Steady state was reached rapidly, within about 14 days, indicating that Cr^{6+} was fully reduced and likely hydrolyzed to precipitate highly insoluble $Cr(OH)_3$. As can be seen in Figure 5.11 and Table 5.8, all of the waste forms had Cr LI values better than the estimated performance metric requirement for chromium of 10.40.

LI values for I: The 63-day LI values for I ranged from about 10.47 to 14.30 for the formulations tested during this phase. All of the waste forms included 5% Ionex Ag-400 as the getter for iodine in the AltLAW, equivalent to a molar Ag/I ratio of ~275. The waste forms prepared with BFS CP had LI values significantly better than the estimated performance metric requirement for iodine of 10.52 (Table 5.5 and Figure 5.12). It is worth noting that the waste forms prepared with BFS CP showed significantly higher LI values for I than these with BFS SE (Figure 5.12). For example, 63-day LI values for I ranged between 11.9 and 14.3 for the waste forms with BFS CP, whereas the LI values for CSMA8S2 and CSMA8S2R4 prepared with BFS SE were on the order of about 10.5 (Table 5.5). It can be speculated that BFS SE has a higher reducing capacity or sulfide concentration than BFS CP. Although Ionex Ag-400 is known to be an efficient getter for iodine in the alkaline AltLAW simulant by precipitating AgI in the nanopores of the zeolitic structure, this process can be disrupted by the release of sulfide during alkali activation of BFS [37]. AgI in the zeolite destabilizes the precipitated AgI in the cured grout. Precipitated AgI may react with sulfide from the slag over time to form the very stable Ag_2S, thereby releasing the captured iodine [36]. Sulfide from the slag destabilizes the AgI captured in the zeolite structure, releasing more iodine during leaching process. For example, the majority of the AgI captured in the zeolite was most likely destabilized in the waste form prepared with BFS DS, resulting in its LI value for I being far below the estimated performance metric requirement of 10.40 (Table 5.5).

LI values for NO_3^-, NO_2^-: As can be seen in Tables 5.5, 5.10 and 5.11 as well as in Figures 5.13 and 5.14, the 63-day LI values ranged from 8.71 to 8.89 for nitrate, better than the estimated performance metric requirement for nitrate of 8.70 (diffusivity = 2×10^{-9} cm^2/s) [6] in all of the waste forms. The 63-day LI values for nitrite closely tracked nitrate (Figure 5.14). It is interesting to note that for waste forms prepared with BFS CP, the LI values for nitrate and nitrite reached their steady states much earlier, within about 28 days, whereas the LI values constantly increased with increasing leaching time for the waste forms prepared with BFS SE.

Testing results showed that formulating parameters 14% BWOS SF and 1.25% to 3% BOWS Hyp are adequate for optimizing CSMA8 Series formulations for the AltLAW with Ionex Ag-400 included. 5% BWOS Ionex Ag-400 was sufficient to yield 63-day LI values exceeding the estimated performance metric requirement for iodine of 10.40. All the waste forms with BFS CP showed LI values better than estimated performance metric requirements for all COCs, except for Re, with significantly improved mechanical durability over the reference CSMA8S2. In addition, testing results suggest that a higher waste loading is achievable without impairing mechanical durability and leaching resistance. As high as 55% waste loading increase over reference CSMA8S2 was attained in CSMA8S2R11b. BFS CP was an excellent alternative to BFS SE in developing waste forms with AgZ included for the AltLAW. A new batch of BFS SE yielded a waste form with fresh and cured properties and leaching resistance comparable to the one made with the old batch of BFS SE.

5.5 Phase 2a: CSMA8 Series Waste Forms with Iodine Removed

5.5.1 Fresh and Cured Properties

Formulating parameters, mix compositions, and recipes for CSMA8 Series formulations are shown in Tables 3.10, 3.11, and 3.12, respectively. The test results are summarized in Table 5.12. All the waste forms showed superhydrophobicity (Table 4.1).

CSMA8 Series formulations developed during the previous testing phase served as the starting point for further modifications by replacing Ionex Ag-400 with Type 5 zeolite or BFS and addition of a pretreatment step by which Ionex Ag-400 was removed by filtration after reacting with the AltLAW for 2 hrs prior to grouting. The optimal formulating parameters obtained from previous testing phase were applied to waste form development. The fillers were removed partially or completely to increase waste loading for the AltLAW. Both BFS CP and BFS SEo were included for this testing phase.

CSMA8S2R12a was formulated with a set of optimal formulating parameters including 14% BWOS SF, 2.5% BWOS Hyp, 5% BWOS Zeolite Type 5, and w/dm at 0.425. Ionex Ag-400 was allowed to react with the AltLAW for 2 hrs and was then removed by filtration prior to grouting. BFS SEo was the slag type. The fresh grout was a thick paste and slow to pour. Vibration caused liquefaction. The initial set time was about 46 hrs, characteristic of fresh grouts prepared with BFS SE. The compressive strength was 5155 psi after curing for 7 days and increased to 8511 psi after 28 days.

CSMA8S2R12a was modified by lowering Hyp to 1.25% and increasing w/dm to 0.45 and completely removing the fillers, yielding CSMA8S2R12d. BFS SEo was the slag type. The fresh grout was thick and slow to pour. The initial set time was 27.5 hrs. The compressive strength was 4407 psi after curing for 7 days and increased to 6967 psi after 28 days. CSMA8S2R12d showed less mechanical durability than CSM8S2R12a, most likely caused by an increased waste solids content in the waste form. The waste solids content in CSMA8S2R12a was about 5.88% and it increased to 10.21% in CSMA8S2R12d. The presence of waste solids, mostly sodium nitrate and nitrite, may interfere with the alkali activation process and internal hydrophobic membrane formation and increase the proportion of capillary pores in the gel structure.

CSMA8S2R12c had the same mix composition as CSMA8S2R12d but the slag type was BFS CP. The fresh grout was thin and pourable. The initial set time was 8.7 hrs, significantly shorter as compared to the waste forms with Ionex Ag-400 included and BFS CP (Table 5.5). The compressive strength was 6628 psi after curing for 7 days and increased to 7107 psi after 28 days. CSMA8S2R12c showed slightly improved mechanical durability over CSMA8S2R12d, its counterpart with BFS SE.

CSMA8S2R12c was modified by replacing zeolite Type 5A with blast furnace slag and including BFS DS, yielding CSMA8S2R12e. BFS DS was chosen because BFS DS has a high reducing capacity, which may benefit improvement in leaching resistance for Tc/Re. At the time when this formulation was developed, only early leaching data were available for CSMA8S2R6 (Table 5.5). The early leaching data showed rather good leaching resistance for nitrate and nitrite as compared to CSM8S2R4 made with BFS SEn (Table 5.10). It was expected that the LI value for nitrate could increase over 8.70 towards end of the 63-day leaching procedure. The fresh grout was thin and pourable. The initial set time was 39.4 hrs. The compressive strength was 4350 psi after curing for 7 days and increased to 6533 psi after 28 days.

CSMA8S2R12e was modified by adding 27.5% fillers to the formulation, yielding CSMA8S2R12f. Increase in the filler content lowers the waste solids concertation in a grout mix and could improve performance of the waste form. The fresh grout was thin and pourable. The initial set time was about 36 hrs, comparable to its paste counterpart, CSMA8S2R12e. The compressive strength was 6643 psi after curing for 7 days and increased to 9151 psi after 28 days. CSMA8S2R12f showed a significantly increased mechanical durability over CSMA8S2R12e, its paste version.

For a waste form with 27.5% and 0% fillers, the waste loading increased by 26.2% and 73.0% respectively, over the one with 39% fillers (CSMA8S2R12a). While a waste form with maximum waste loading is always desirable and economically advantageous, completely removing the fillers in a formulation may yield a waste form with significantly impacted mechanical and chemical durability. The waste solids content in the waste form played an important role in determining mechanical durability. The waste solids content was about 5.9 wt% in CSMA8S2R12a (39% fillers), increased to 7.1% in CSMA8S2R12f (27.5% fillers), and further increased to 10.21% in CSMA8S2R12d (without fillers). Per specification for EUCON Hydrapel 2.5, overdosing usually impacts mechanical properties of a grout or concrete. EUCON Hydrapel 2.5 was prescribed by weight of slag in all the formulations. When a grout mix includes the fillers, the actual Hyp dosage is lower in terms of by weight of total solids whereas, it could become overdosed in the paste mix (Table 4.1), which may also contribute to impaired mechanical durability.

5.5.2 EPA Method 1315 Leaching Results

The measured LIs for Na, Re, Cr, I, NO_3^-, and NO_2^- at 28 and 63 days are summarized in Table 5.13. The LI values at each sampling time are reported in Tables 5.14 to 5.19. These values are also plotted as functions of time and formulation type in Figures 5.15 to 5.20.

LI values for Na: Three waste forms prepared with BFS SE (CSMA8S2R12a and CSMA8S2R12d) and BFS CP (CSMA8S2R12c) showed excellent leaching resistance for sodium. The 63-day LI values for Na varied in a narrow range from of 8.91 to 9.29, as compared to 8.83 for reference CSMA3S1R1 (Tables 5.13, Figure 5.15). In contrast, other two waste forms prepared with BFS DS (CSMA8S2R12e and CSMA8S2R12f) showed poor leaching resistance. The 63-day LI value for Na was 8.40 for CSMA8S2R12e (without fillers) and increased to 8.67 for CSMA8S2R12f (27.5% fillers). Apparently, leaching resistance was affected mostly by the fillers content or waste loading and slag type. The 63-day LI value for Na was as high as 9.29 for CSMA8S2R12a, which incorporated BFS SEo as the slag type and the nominal filler content of 39% in its formulation, whereas the value decreased to 8.91 for CSMA8S2R12d that was the paste counterpart.

LI values for Re: The 63-day LI values for Re varied from formulation to formulation, between 9.97 and 12.26 (Tables 5.13 and 5.15, Figure 5.16). Again, leachability indices for Re were mostly determined by the slag type and the filler content or waste loading. Two waste forms prepared with BFS DS exhibited excellent resistance to Re leaching owing to its superior reduction capacity. The 63-day LI values for Re was as high as 12.26 for CSMA8S2R12f (27.5% fillers), whereas the 63-day LI values for Re was 11.53 for CSMA8S2R12e due to increased waste solids content in the waste form. The waste forms prepared with BFS CP showed relatively low resistance to Re leaching owing to its lower reduction capacity. The 63-day LI value was 9.88 for CSMA8S2R12c, below the estimated performance metric requirement for rhenium of 10.7. The impact of waste loading or waste solids content in the waste form can be better illustrated by the data from two waste forms prepared with BFS SEo. The steady state LI value for Re was 12.33 for CSMA8S2R12a (39% fillers and 5.88 wt% waste solids) and this value was lowered to 9.97 for CSMA8S2R12d. Note that steady state Re LI values were used instead for both of the waste forms due to data scatter towards the end of the leaching procedure. Waste solids content as high as 10.21% in CSMA8S2R12d may have resulted in its LI value being below the estimated performance metric requirement of 10.7 for rhenium.

LI values for Cr: All of the formulations tested during this testing phase showed excellent resistance to Cr leaching. The 63-day LI values for Cr were between 13.16 and 13.52 (Tables 5.13 and 5.16, Figure 5.17). Steady state was reached rapidly, within about 7 days, indicating that Cr^{6+} was fully reduced and likely hydrolyzed to precipitate highly insoluble $Cr(OH)_3$. As can be seen in Figure 5.16, LI values for Cr typically reached maximum at about 7 days and then decreased slightly with increasing leaching time, probably caused by re-oxidization of precipitated reduced chromium in the waste form. All of the waste forms had Cr LI values better than the estimated performance metric requirement of 10.40 for chromium. It is noted that Cr concentrations in the leachate solutions were often below detection limit (~0.002 mg/L) for ICP-AES; in such cases, detection limit value was used for the LI calculations.

LI values for I: The 63-day LI values for I varied from 12.50 to 12.98 for the formulations tested during this testing phase, all much better than the estimated performance metric requirement of 10.52 for iodine (Tables 5.13 and 5.17, Figure 5.18). Note that the steady state LI value for I was used instead for CSMA8S2R12a, due to data scatter towards the end of the leaching procedure (Figure 5.18). All of the waste forms were prepared by employing a pretreatment step, as described in Section 4.1.2, and with this pretreatment step, the vast majority of the iodine in the AltLAW was removed prior to grouting, which would result in a significantly better resistance to iodine leaching. The leachability indices were calculated based on the original iodine concentration in the AltLAW before contacting with Ionex Ag-400. The residual iodine release is due to incomplete removal of iodine by the Ionex Ag-400 and incomplete removal of the loaded Ionex Ag-400 from the AltLAW solution by filtration, as evidenced by black particles settling in the filtered solution after a week (Figure 4.2).

LI values for NO_3^-, NO_2^-: As can be seen in Tables 5.13 and 5.18 as well as in Figure 5.19, the 63-day LI values for nitrate varied from formulation to formulation, ranging from 8.27 to 9.06. Leachability indices for nitrate and nitrite depended on the slag type and the filler content or waste loading. Among the formulations tested during this testing phase, only CSMA8S2R12a (BFS SEo and 39% fillers) showed a 63-day LI value better than the estimated performance metric requirement for nitrate of 8.70 (diffusivity = 2×10^{-9} cm^2/s) [6]. The 63-day LI value was as high as 9.06 for nitrate and 9.12 for nitrite, respectively. When the fillers were removed and w/dm increased to 0.45 in CSMA8S2R12d, the waste solids content increased from 5.89% to 10.21%. The 63-day LI value decreased to 8.66 for nitrate and 8.74 for nitrite, respectively. BFS SEo in the formulation CSMA8S2R12d was replaced with BFS CP, yielding CSMA8S2R12c. Its 63-day LI value for nitrate was 8.61. Two other waste forms prepared with BFS DS (CSMA8S2R12e and CSMA8S2R12f) showed much lower LI values for nitrate. The 63-day LI value for nitrate was 8.27 for CSMA8S2R12e (without fillers) and increased to 8.52 for CSMA8S2R12f (27.5% fillers). Both waste forms prepared with BFS DS gave 63-day LI values far below the estimated performance metric requirement of 8.7 for nitrate.

In summary, pretreatment with Ionex Ag-400 followed by removal of the loaded Ionex Ag-400 represents a promising alternative processing strategy that results in all the waste forms with 63-day LI values better than the estimated performance metric requirement of 10.52 for iodine. All the waste forms, independent of slag type and filler content showed 63-day LI values for Cr about two units higher than the estimated performance metric requirement of 10.40 for chromium. The LI values for technetium and nitrate were more dependent on slag type and the total filler content or waste solids content in waste forms. Again, the waste forms with BFS DS (CSMA8S2R12e and CSMA8S2R12f) showed good resistance to rhenium leaching but significantly lower resistance to nitrate leaching as compared to the waste forms prepared with BFS SE and BFS CP. CSMA8S2R12a made with BFS SE represents the best-performing waste form in terms of both mechanical and chemical durability. The 63-day LI values were better than the estimated performance requirements for all COCs including rhenium, chromium, iodine and nitrate. CSMA8S2R12d represents a waste form with the highest waste loading. The steady-state LI values for nitrate were marginal, around 8.70 (Figures 5.19 and 5.20). CSMA8S2R12d had a steady state LI value of about 10 for rhenium. Rhenium is less easily reduced than technetium, often resulting in over estimation of the release of technetium from the waste form. Grout waste forms that included both technetium and rhenium have showed that LI values for technetium are typically one or more units higher than those for rhenium [38, 39]. Therefore, it is expected that the LI value for Tc may be much higher, likely better than the estimated performance metric requirement for technetium of 10.7. If higher waste loading is deemed desirable, CSMA8S2R12d is a candidate for further formulation optimization.

5.6 Phase 2b: CSMA3 Series Waste Forms with Iodine Removed

5.6.1 Fresh and Cured Properties

Formulating parameters, mix compositions, and recipes for CSMA3 Series formulations with iodine removed are shown in Tables 3.13, 3.14, and 3.15, respectively. The test results are summarized in Table 5.12. All of the waste forms showed superhydrophobicity (Table 4.1).

CSMA3S1R1 was a reference formulation that employed a pretreatment step in which iodine was removed from the AltLAW prior to grouting. The formulation used EUCON Hydrapel 2.5 as the hydrophobic admixture at 0.575% BWOS, calcined hydrotalcite at 10% BWOS and silica fume at about 6% BWOS. The w/dm ratio was 0.425 (Table 2.1).

CSMA3S1R1 was modified by increasing SF to 14% BWOS and Hyp to 3%, yielding CSMA3S1R3. The slag type was BFS SEn. The fresh grout was thick and slow to pour. The initial set time was 25.3 hrs, comparable to CSMA3S1R1 prepared with BFS SEo (Table 2.3). The compressive strength was 6409 psi after curing for 7 days and increased to 9039 psi after 28 days.

CSMA3S1R3 was further modified by including equal amounts of ZT5 and CTH at 5%, yielding CSMA3S1R4. The slag type was BFS CP. The initial set time was 10.8 hrs. The fresh grout was thick and not pourable. The compressive strength was 7883 psi after curing for 7 days and increased to 9440 psi after 28 days (Table 5.12). It is worth noting that the early compressive strength, i. e., 7883 psi at 7 days, was significantly higher than the value of 6628 psi for CSMA8S2R12c (Table 5.12), probably due to acceleration by calcined hydrotalcite that was included in CSMA3S1R4.

CSMA3S1R4 was modified by removing all of the fillers and including 3% ZT5 and 7% CTH, yielding a paste waste form CSMP3S1R1. BFS CP was the slag type. The formulation for CSMP3S1R1 was developed before the lower reduction capacity for BFS CP than for BFS SE was identified. The fresh grout was thick and slow to pour. Initial set time was 4.7 hrs. Faster setting observed in CSMP3S1R1 was due to its higher content of calcined hydrotalcite than in CSMA3S1R4. The compressive strength was 6474 psi after curing for 7 days and increased to 8233 psi after 28 days. As compared to its mortar counterparts, 28-day compressive strength was lower owing to the higher waste solids content in the waste form.

5.6.2 EPA Method 1315 Leaching Results

A 63-day leach test was performed on all CSMA3 Series waste forms per EPA Method 1315 after curing for 28 days. The measured LIs for Na, Re, Cr, I, NO_3^-, NO_2^- at 28 and 63 days are summarized in Table 5.13. The LI values at each sampling time are reported in Tables 5.14 to 5.19. These values are also plotted as functions of time and formulation type in Figures 5.21 to 5.26.

<u>LI values for Na:</u> Three CSMA3 Series waste forms prepared with BFS SE (CSMA3S1R3) and BFS CP (CSMA3S1R4 and CSMP3S1R1) showed excellent leaching resistance for Na. LI values at 63 days for Na were all about 9.07, as compared to 8.83 for reference CSMA3S1R1 (Tables 5.13 and 5.14; Figure 5.21).

<u>LI values for Re:</u> The 63-day LI value for Re was 11.33 for CSMA3S1R3 prepared with BFS SEo whereas the 63-day LI values for Re were lower for two waste forms prepared with BFS CP. The 63-day LI value for Re was 10.03 for CSMA3S1R4 and 10.27 for CSMP3S1R1 respectively (Tables 5.13 and 5.15; Figure 5.22). The test data showed again that BFS CP may have a lower reduction capacity than BFS SE.

<u>LI values for Cr:</u> All of the CSMA3 Series waste forms showed excellent resistance to Cr leaching. The 63-day LI values for Cr were between 13.12 and 14.15 (Tables 5.13 and 5.16, Figure 5.23). Steady state was reached rapidly, within about 7 days in the waste forms and LI values were slightly lower towards the end of the leaching procedure. All of the waste forms had Cr LI values better than the estimated performance metric requirement for chromium of 10.40.

<u>LI values for I:</u> All of the CSMA3 Series formulations showed excellent resistance to I leaching. The 63-day LI values for I were between 12.14 and 13.06 (Table 5.13 and 5.17, Figure 5.24), far better than the estimated performance metric requirement of 10.52 for iodine.

<u>LI values for NO_3^-, NO_2^-:</u> The 63-day LI value for nitrate was 8.77 for CSMA3S1R3 prepared with BFS SE and 8.88 for CSMA3S1R4 with BFS CP (Tables 5.13, 5.18, 5.19, Figures 5.25 and 5.26), better than the estimated performance metric requirement for nitrate of 8.70 (diffusivity = 2×10^{-9} cm^2/s) [6]. Both waste forms were the mortar type with 39% fillers content. CSMP3S1R1 was a paste type waste form with the fillers removed. Steady state was reached much earlier, within about 14 days (Figure 5.25). The LI value for NO_3^- was as high as 8.67 at 14 days,

increased to 8.75 at 49 days, and decreased to 8.67 at 63 days (Table 5.18). The calculated LI value at steady state was about 8.70. LI values for nitrite followed those for nitrate. Lower LI values for nitrate were associated with higher waste solids content (~9.61%) in CSMP3S1R1.

Pretreatment with Ionex Ag-400 to remove iodine in the AltLAW was used to prepare CSMA3 Series waste forms. Only one waste form, CSMA3S1R3 prepared with BFS SE, had 63-day LI values better than the estimated performance metric requirements for all the COCs, including technetium, chromium, iodine and nitrate. Increased SF content and Hyp dose yielded a waste form with improved leaching resistance over CSMA3S1R1 [9]. CSMA3S1R4, prepared with BFS CP, had 63-day LI values exceeding the estimated performance metric requirements for chromium, iodine, and nitrate, whereas the 63-day Re LI value was 10.03, below the estimated performance metric requirement of 10.7 for rhenium. CSMP3S1R1, prepared with BFS CP, had 63-day LI values exceeding the estimated performance metric requirements for chromium and iodine. The steady state nitrate LI value was marginal, close to the estimated performance metric of 8.7 for nitrate. Yet, the 63-day Re LI value (10.27) failed to meet the estimated performance metric requirement for rhenium of 10.70. The LI value for Tc would be much better as Re is less easily reduced than Tc. Formulation CSMP3S1R1 could be a good candidate for further waste form development to achieve higher waste loading. The waste loading for CSMP3A1R1 increased by about 68% over reference CSMA3S1R1.

5.7 Phase 2c: Waste Forms for 3.5 M Na AltLAW

5.7.1 Fresh and Cured properties

The objective of this testing phase was to test the effect of Na molarity on the properties and performance of the waste forms and to explore the feasibility for increasing waste loading by removing the fillers in the formulation.

Formulating parameters, mix compositions, and recipes for the waste forms with 3.5 M Na AltLAW are shown in Tables 3.16, 3.17 and 3.18 respectively. The test results are summarized in Table 5.20. All the waste forms showed superhydrophobicity (Table 4.1).

CSMA8S2R10 was formulated with 14% BWOS SF, 1.25% BWOS Hyp, and w/dm = 0.45. BFS CP was used as the slag type, owing to its excellent performance in the waste forms developed during Phase 1. The formulation included 5% Ionex Ag-400 as the getter for iodine. The fresh grout was thick and slow to pour. The initial set time was 11.3 hrs, very close to 11.7 hrs for its counterpart at 5.6 M Na, CSMA8S2R3s (Table 5.4). The compressive strength was 6585 psi after curing for 7 days and increased to 8268 psi after 28 days.

The fillers were totally removed from CSMA8S2R10, yielding CSMP8S2R2. The slag type was BFS CP. The initial set time was 11.7 hrs, almost identical to the value for its mortar counterpart CSMA8S2R10. The fresh grout was thick and slow to pour. The compressive strength was 5955 psi after curing for 7 days and increased to 7669 psi after 28 days (Table 5.20).

CSMP3S1R1 was a paste type waste form for 5.6 M Na AltLAW. The same formulating parameters for CSMP3S1R1 were used to formulate CSMP3S1R2 with 3.5 M Na AltLAW. BFS CP was the slag type. The fresh grout became thin and pourable. Initial set time was about 5 hrs, very close to 4.7 hrs for its counterpart with 5.6 M Na AltLAW. The compressive strength was 6124 psi after curing for 7 days and increased to 7209 psi after 28 days.

5.7.2 EPA Method 1315 Leaching Results

A 63-day leach test was performed on three waste forms for 3.5 M Na AltLAW per EPA Method 1315 after curing for 28 days. The measured LIs for Na, Re, Cr, I, NO_3^-, and NO_2^- at 28 and 63 days are summarized in Table 5.21. The LI values at each sampling time are reported in Tables 5.22 to 5.27. These values are also plotted as functions of time and formulation type in Figures 5.27 to 5.31.

LI values for Na: Three 3.5 M Na waste forms showed excellent resistance to Na leaching (Tables 5.21 and 5.22; Figure 5.27). The 63-day LI value for Na was as high as 9.29 for CSMA8S2R10 whereas the value was 9.07 for CSMP8S2R2, a paste version of CSMA8S2R10. The 63-day LI values for Na was 9.28 for CSMP3S1R2 with iodine removed prior to grouting. As can been seen in Figure 5.27, the LI value rapidly increased within 7 days, indicating that sodium in the pores, most likely in sodium nitrate and sodium nitrite, was vulnerable to leaching and the LI value continued to increase at a lower rate, suggesting that sodium in the gel matrix was resistant to leaching.

LI values for Re: All three 3.5 M Na waste forms failed to meet the estimated performance metric requirement for rhenium of 10.7 (Tables 5.21 and 5.23, Figure 5.28). The 63-day LI value for Re was 9.07 for CSMA8S2R10 and 8.16 for its paste counterpart, CSMP8S2R2. Lower LI values for Re were due to presence of Ionex Ag-400 in both CSMA8 Series waste forms. The 63-day Re LI value for CSMP3SR1R2 was 9.60, slightly improved as AgZ was removed prior to grouting. Again, low LI values for Re were caused by a lower reducing capacity for BFS CP as compared to BFS SE.

LI values for Cr: All of the 3.5 M Na waste forms showed excellent resistance to Cr leaching (Tables 5.21 and 5.24, Figure 5.29). The 63-day Cr LI value was 12.81 for CSMA8S2R10 and 12.21 for its paste counterpart, CSMP8S2R2. The 63-day Cr LI value was 13.71 for CSMP3S1R2; it reached steady state rapidly within 7 days and the LI value decreased slightly towards the end of the leaching period. Two CSMA8 Series waste forms showed lower LI values at early leaching times and a continual increase over time (Figure 5.29). It is possible that the chromium was mostly reduced in CSMP3R1R2 while some chromium remained unreduced during curing of two CSMA8 Series waste forms as silver released from the immobilized AgI/zeolite competed for sulfide species that were released during alkali activation of slag.

LI values for I: All three 3.5 M Na waste forms showed excellent resistance to I leaching. The 63-day LI values for I were between 12.49 and 13.02 (Table 5.21 and 5.25, Figure 5.30), far better than the estimated performance metric requirement for iodine of 10.52. The LI values for I reached maximum at 28 days and then decreased with increasing leaching time, as observed in all the waste forms.

LI values for NO_3^-, NO_2^-: The measured LI values for nitrate and nitrite are reported in Tables 5.21 and 5.26 and Figures 5.31 and 5.32. The 63-day LI value for nitrate was 8.92 for CSMA8S2R10, significantly higher than 8.76 for its counterpart at 5.6 M Na, CSMA8S2R3s (Table 5.5). The 63-day LI value for nitrate was only 8.67 for CSMP8S2R2, the paste composition derived from CSMA8S2R3s. The 63-day LI value for nitrate was as high as 8.89 for CSMP3S1R2, significantly higher than its counterpart at 5.6 M Na, CSMP3S1R1 (Table 5.13). CSMP3S1R2 was the only paste waste form with iodine removed prior to grouting, showing 63-day LI value better than the estimated performance metric requirement for nitrate of 8.7. LI values for nitrite largely tracked those for nitrate.

Both CSMA8S2R10 and CSMP2R1R2 showed 63-day LI values better than the estimated performance metric requirements for chromium, iodine, and nitrate. All three waste forms failed to meet the estimated performance metric requirement for rhenium of 10.7. Lower 63-day Re LI values was due to BFS CP included in the formulations. BFS CP has less reduction capacity than BFS SE. In general, lower molar Na in the AltLAW improved mechanical durability and resistance to leaching of COCs.

5.8 Formulations Recommended for Further Characterization

This section summarizes the results from the first and second testing phases, describes the formulations recommended for additional characterization, and presents the results of that additional testing.

5.8.1 Testing Summary

The objective of this work was to perform laboratory-scale testing to further optimize and demonstrate methods to reduce the release rates of nitrate, iodine, and technetium from grouted AltLAW waste forms. Additional tests were conducted with formulations without fillers to maximize waste loading, with a focus on the CSMA8 Series formulations with a pretreatment step to remove iodine. Sections 5.4 to 5.7 report test results during the first and second testing phases. The results are summarized as follows:

- Initial set time ranged from 4.7 hrs to about 5 days. The slag compositions had significant effects on set time. The initial set times ranged from 25 hrs to 48 hrs for fresh grouts prepared with BFS SE while the initial set times ranged from 4.7 hrs to 20.9 hrs for fresh grouts prepared with BFS CP. Set time was also affected by mix composition. Calcined hydrotalcite was known to accelerate setting and promote earlier strength development of a curing waste form. In some waste forms, increasing waste loading by removing the fillers from the formulation caused accelerated setting, owing to increased amounts of neutral salts and sodium hydroxide, which causes enhanced alkali activation during early cuing times.

- 7-day compressive strength varied from 2973 to 8907 psi and 28-day compressive strength varied from 6533 to 10823 psi. Slag types and the filler content were two key factors on determining compressive strength. BFS SE, BFS CP, and BFS DS were suitable slags for yielding a mechanically durable waste form. BFS CP often yielded a waste form with a higher 7-day compressive strength than the one with BFS SE. Decrease in the filler content in a formulation decreased both 7-day and 28-day compressive strength. A mortar formulation typically contained about 6 wt% waste solids (5.6 M Na). When the fillers were completely removed, waste loading increased by 55 to 73%, with the waste solids content increased to about 10 wt%, yielding a paste type waste form. Increased concentrations of sodium nitrate/nitrite caused increased interference with alkali activation of slag. In addition, since EUCON Hydrapel 2.5 was prescribed by weight of slag, it could become overdosed in the paste type waste form, which can also contribute to impaired mechanical strength.

- Cracking caused by expansion or contraction was not observed for any of the grout samples subjected to 63-day leaching per EPA Method 1315.

- All of the waste forms showed excellent resistance to chromium leaching with 63-day LI values varying from 12.21 to 14.14, far exceeding the estimated performance metric requirement for chromium of 10.40 (4×10^{-11} cm^2/s). LI values for Cr increased rapidly with leaching time and attained steady state typically within 7 to 14 days and then decreased slightly with increasing leaching time. Likely, oxidative leaching occurred during the late leaching times.

- 63-day LI values for rhenium varied from formulation to formulation, ranging from 7.4 to 12.3 for the various waste forms.
    - Including Ionex Ag-400 as the getter for iodine in waste forms for the AltLAW often yielded a low 63-day LI value for rhenium, ranging from 7.4 to 9.07, below the estimated performance metric requirement for rhenium of 10.7, except for the waste form made with BFS DS. A low 63-day LI value for Re was expected for the waste form with Ionex Ag-400 as the getter. The sulfide species released during alkali activation of BFS is the primary reducing agent for pertechnetate or perrhenate. However, sulfide species have a great affinity for silver by precipitating Ag_2S, leaving less sulfide available for Tc or Re reduction. In the present work, the AltLAW was spiked with 150 mg/L iodide whereas the maximum iodine was projected to be 3.55 mg/L in the West Area feed [11]. Therefore, much less Ionex Ag-400 may be included in a formulation to meet the estimated performance metric requirement for iodine of 10.40. This will leave more sulfide species available for reduction of pertechnetate or perrhenate and thus improve resistance to Re/Tc leaching.

  - The 63-day LI values for rhenium highly depended on the slag type. BFS DS yielded the highest 63-day LI value for Re (Tables 5.5 and 5.13). The reducing capacity of BFS DS was so high that perrhenate in the AltLAW was greatly reduced while AgI-loaded zeolite in the waste form was vastly destabilized, resulting in a 63-day LI value for Re as high as 12.30 whereas the value for I was as low as 8.86 (Table 5.5). The reduction capacity for BFS DS was so strong that reduction of perrhenate in the AltLAW was hardly affected by increased waste solids content, as demonstrated by two waste forms made with BFS DS with iodine removed prior to grouting (Table 5.13). BFS SE had an intermediate reduction capacity. When Ionex Ag-400 was removed prior to grouting, and sulfide species released during alkali activation were sufficient to reduce perrhenate in the AltLAW, this yielded a waste form with 63-day LI values exceeding the estimated performance requirement for rhenium of 10.7, as observed in CSMA3S1R3 (Table 5.13). BFS CP had a reduction capacity lower than that of BFS SE, yielding a 63-day LI value slightly lower than the estimated performance metric requirement for rhenium of 10.7, as shown in CSMA3S1R4 (Table 5.13). It is noted that rhenium is less easily reduced than technetium, often resulting in over estimation of the release of technetium from the waste form, typically by an order of magnitude or more. Therefore, it is expected that the LI value for Tc may be much higher, likely better than the estimated performance metric for Tc [32, 33].

  - LI values for Re were affected by the increased waste solids content in a formulation made by BFS SE and BFS CP. The 63-day LI values were below the estimated performance metric requirement for rhenium of 10.7 for all the paste type waste forms with iodine removed prior to grouting (Table 5.13). Waste solids in a waste form may interfere with not only alkali activation of slag but also with reduction of perrhenate in the AltLAW.

- Pretreatment of the AltLAW with Ionex Ag-400 to remove iodine followed by separation of the loaded Ag-400 prior to grouting of the pretreated AltLAW was demonstrated as a promising alternative treatment strategy. The waste forms made using this approach including both CSMA8 and CSMA3 Series formulations showed 63-day LI values for I that varied from about 11.99 to 13.06, all better than the estimated performance metric requirement for iodine of 10.52. These values are dependent in part on the effectiveness of the solid-liquid separation process used for Ag-400 removal.

- For the waste forms with 5% BWOS Ionex Ag-400, LI values for I varied in a large range from 7.94 to 14.32, highly dependent on the slag type. BFS DMI and BFS DS yielded waste forms with a 63-day LI value for I lower than 9. BFS CP yielded waste forms with 63-day LI values ranging from 11.20 to 14.32, much better than the estimated performance metric requirement for iodine of 10.52. BFS CP is an excellent alternative to BFS SE for waste forms with Ionex Ag-400 included as the getter for iodine.

- For the waste forms with 5% BWOS Ionex Ag-400 included, LI values for nitrate varied from 7.40 to 8.89. 63-day LI values for the waste forms made with BFS DMI and BFS DS failed to meet the estimated performance metric requirement for nitrate of 8.7. Lower LI values for nitrate were probably associated with unfavorable gel compositions due to high MgO contents in both BFS DMI and BFS DS. 63-day LI values for waste forms made with BFS CP and BFS SE were between 8.73 and 8.89, all exceeding the estimated performance metric requirement for nitrate of 8.7. Na molarity in the AltLAW played an important role in resistance to nitrate leaching. For example, the 63-day LI value for nitrate was 8.76 for CSMA8S2R3s (5.6 M Na) and the value increased to 8.92 for CSMA8S2R10 (3.5 M Na).

- For the waste forms with iodine removed from the AltLAW prior to grouting, 63-day LI values for nitrate ranged from 8.27 to 9.06. Waste loading or waste solids content played an important role in affecting LI values for nitrate and nitrite. The waste forms made with 39% fillers and BFS CP or BFS SE yielded 63-day LI values ranging from 8.77 to 9.06, better than the estimated performance metric requirement for nitrate of 8.70. When the fillers were completely removed, the 63-day LI values became lower, usually near or slightly below 8.70 (Tables 5.13 and 5.21). For example, the 63-day LI value for nitrate was 9.06 for CSMA8S2R12a and the value decreased to about 8.66 for its paste counterpart, CSMA8S2R12d. In addition, on decreasing the Na molarity from 5.6 to 3.5 M, 63-day LI values for nitrate increased owing to the decreased waste solids content in the waste form. The 63-day LI value for nitrate was about 8.70 for CSMP3S1R1 (5.6 M Na) and the value increased to 8.89 for CSMP3R1R2 (3.5 M Na).

- The slag compositions played a crucial role in determining fresh and cured properties and leaching resistance of a waste form. Five slag sources were tested, including two batches of BFS SE, BFS CP, BFS DS, and BFS DMI. All of the slag types were composed essentially of a CaO-MgO-Al_2O_3-SiO_2 glass phase, with a distinct $(MgO+Al_2O_3)/SiO_2$ ratio. BFS SE and BFS CP had a low $(MgO+Al_2O_3)/SiO_2$ ratio, about 0.5 to 0.6, yielding a NSAS waste form with excellent mechanical strength and leaching resistance. BFS DMI had the highest $(MgO+Al_2O_3)/SiO_2$ ratio (1.05) with MgO as high as 11.54%, yielding a waste form with the least resistance to leaching. Therefore, BFS DMI is not suitable for the waste forms developed for the AltLAW. Silica fume, an essential component of a NSAS formulation, may inhibit hydrotalcite formation and the high MgO content in the slag glass phase may retard stratlingite formation during alkali activation of BFS DMI. BFS DS had a $(MgO+Al_2O_3)/SiO_2$ ratio of 0.78, yielding a waste form with leaching resistance between the ones prepared with BFS DMI and BFS SE or BFS CP. The reduction capacity of a blast furnace slag determined resistance to Re/Tc leaching. The reduction capacity increased in the order of BFS CP, BFS SE, and BFS DS.

- Formulating parameters of 14% BWOS silica fume and 1.25% to 3% BWOS EUCON Hydrapel 2.5 were adequate for developing an optimal formulation for the AltLAW. Further increased content of silica fume may improve particulate packing density of a waste form mixture and enhance stratlingite and CASH formation during alkali activation of a blast furnace slag. 1.25% BWOS EUCON Hydrapel 2.5 was sufficient to induce superhydrophobicity in a waste form. Synergistic use of optimal formulating parameters for silica fume and EUCON Hydrapel 2.5 and either BFS SE or BFS CP often yielded a waste form with improved 63-day LI values for Na (>9.0) as compared to CSMA8S2 or CSMA3S1R1 recommended in the FY23 work. The LI value for Na can be considered an overall index for diffusive leaching resistance of a waste form matrix since there is little holdup in secondary phases. As shown in Figure 5.33, LI values for Na were proportional to LI values for nitrate, indicating that sodium nitrate was a mobile species in the pores and the LI values were determined essentially by the impermeability of the gel matrix in the waste form. Likely, both silica fume and hydrophobic admixture improved impermeability of the waste form.

- BFS CP was an excellent alternative to BFS SE in developing CSMA8 Series waste forms with Ionex Ag-400 included as the getter. The waste forms with BFS CP showed LI values better than estimated performance metric requirements for all COCs, including chromium, iodine, and nitrate, except for rhenium. As high as 55% waste loading increase over the reference CSMA8S2 was attained in CSMA8S2R11b without impairing mechanical strength and leaching resistance. Increasing w/dm to 0.50 did not affect mechanical strength and leaching resistance of CSMA8S2R8, showing robustness of the formulation for the AltLAW. However, BFS CP had a lower reduction capacity than BFS SE. The maximum ^{99}Tc in the AltLAW feed vector was projected to be about 16 mg/L [29]. However, the present leaching data for Re were acquired with the AltLAW spiked with 350 mg/L Re. Therefore, the sulfide species released during alkali activation of BFS CP may be sufficient to fully reduce all the technetium actually present in the AltLAW and thus improve leaching resistance for technetium significantly.

- Slag compositions, filler content, or waste solids content, and Na molarity for the AltLAW are important factors that affect fresh and cured properties of a waste form for the AltLAW and play profound roles in leaching resistance of COCs, in particular, rhenium and nitrate.

5.8.2 Interpretation of Leaching Results from EPA Method 1315

The cumulative release of a species in Method 1315 can be analyzed using the analytical solution for simple radial diffusion from a cylinder into an infinite bath (EPA Method 1315):

$$Mt = 2\times\rho\times C_0\times (D_{obs}\times t/\pi)^{1/2} \tag{5.1}$$

where:

M_t = cumulative mass released during the leaching time, t (mg/m^2),
D_{obs} = observed diffusivity of species (m^2/s)
t = cumulative contact time (s),
ρ = cured grout density (kg/m^3), and
C_o = initial concentration of species in cured grout (mg/kg).

Taking the logarithm of Eq. 5,1 yields:

$$\log[M_t] = \log[2\times\rho\times C_0\times (D_{obs}/\pi)^{1/2}] + \tfrac{1}{2}\, t. \qquad (5.2)$$

Eq. 5.2 shows that cumulative mass released should be proportional to the square root of leaching time with a slope of 0.5 based on a "perfect" simple diffusion model. In this work, cumulative mass released values for COCs were plotted against leaching time on a log-log scale; these plots are presented in Figures A1 to A20 in the Appendix. The slope values were calculated and are reported in Table A1 in the Appendix. The slope values were correlated with percentage of the cumulative mass released during early leaching times, e.g., 2 days vs. the total mass release (Figure A21). The slope values decreased with increasing %cumulative mass release at 2 days. The majority of the slope values for sodium, nitrate, and nitrite ranged from 0.35 to 0.50, indicating that these species followed close to a simple diffusion behavior during leaching. Sodium, nitrate, and nitrite are mobile and mainly physically immobilized in the gel matrix. Some fraction of the sodium, nitrate, and nitrite may be comparatively "immobile" due to chemical bonding in the gel matrix, which could cause the observed deviations from slope values of ½. This is the case where sodium is chemically incorporated in the calcium aluminosilicate hydrate, which is the main gel phase of neutral salt activated slag. In contrast, the slope values for Re, Cr, and I varied over a large range, from 0.15 to 0.50 and the majority of the slope values were lower than 0.35, indicating that another retardation mechanism must be present in addition to simple diffusion. Iodine was either removed or immobilized in the Ionex Ag-400 before grouting. Iodine becomes mobile only when the AgI that is formed is disrupted by the release of sulfide during alkali activation of BFS [37]. Both rhenium and chromium become relatively immobile as Cr^{6+} and Re^{7+} are reduced to their insoluble forms by sulfide species released during neutral salt activation of slag. During early leaching times, unreduced Cr and Re species in the grout waste forms contribute to a large %cumulative release (2 days). At later leaching times, when mobile species are leached out, oxidative leaching may take place but at a much lower rate.

LI values for Na were roughly proportional to LI values for nitrate, as shown in Figure 5.33. Comparison of Na, nitrate, and nitrite was further explored by accounting for the differences in the diffusion of each species in water. The retardation factor represents the ability of a grout matrix to retain a specific constituent relative to a non-sorbing/non-reactive constituent[1] in the same sample. The parameter is an empirical representation that reflects the cumulative effect of all retarding phenomena that occur over the duration of a leach test [40]. Note that if a compound such as the dissolved sodium ion is assumed to not be retarded by the matrix (i.e., $R_{Na} = 1$) then the retardation coefficient for another species (denoted "*x*") can be derived from leach data according to the following equation:

$$R_x = (D_{obs,Na}/D_{obs,x})\times(D_x/D_{Na}) \qquad (5.3)$$

where: $D_{obs,x}$ = Observed diffusivity of species "x" (cm^2/s)
$D_{obs,Na}$ = Observed diffusivity of Na (cm^2/s)
D_x = Diffusivity of "x" in water (cm^2/s)

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[1] This is an important assumption that is likely not valid for sodium in these binder systems, as discussed below.

D_{Na} = Diffusivity of Na in water (cm^2/s).

Observed diffusivity values and retardation factors from the present work for sodium, iodine, nitrate, and nitrite are summarized in Table A2 in the Appendix and observed diffusivity values for nitrate and nitrite are plotted against $D_{obs,Na} \times (D_x/D_{Na})$ in Figure A22. The diffusivity (D_x) of sodium, nitrate, nitrite, and iodine in water that were used to estimate the retardation factors were 1.33E-5, 1.90E-5, 1.91E-5, and 2.045E-5 cm^2/s, respectively [41]. The majority of the data points for nitrate and nitrite fall above the straight line for $R_{Na} = 1$, as shown in Figure A22. The calculated retardation factors for nitrate ranged from 0.55 to 1.75 and the majority of the values fell between 0.55 and 1.06. The calculated retardation factors for nitrite ranged from 0.53 to 1.64 and the majority of the values fell between 0.53 and 1.15 (Table A2). Most of the formulations have a high retention of iodine, suggesting that Ionex Ag-400 was efficient in fixing iodine (Table A2).

For comparison, observed nitrate and nitrite diffusivity values for the NSAS waste forms developed prior to FY24 are plotted against $D_{obs,Na} \times (D_x/D_{Na})$ in Figure A23 and the observed diffusivity values and retardation factors for nitrate and nitrite are summarized in Table A3 in the Appendix. In contrast to the results from the present work (Figure A22), all of the data points for nitrate and nitrite fall below the straight line that is $R_{Na} = 1$, as shown in Figure A23. The calculated retardation factors for nitrate varied in a large range, from 0.95 to 5.99 while the calculated retardation factors for nitrite range from 0.92 to 7.32 (Table A3). In addition to the large variation, the values are in general significantly higher than those for the NSAS waste forms developed in FY24 (Table A2). The results suggest that transport of nitrate and nitrite were more retarded by the matrix *relative to sodium* for the waste forms developed prior to FY24. It is important to note that this could reflect changes in transport behavior of nitrate/nitrite, or the transport behavior of sodium; or, more likely, both.

In an effort to better understand the distinct behaviors of nitrate and nitrite shown in Figures A22 and A23 the composition variations of the matrices were reviewed which led to the identification of silica fume as one of the more significant differences between the pre-FY24 work and the FY24 work. To investigate this, the deviation from the $R_{Na} = 1$ lines in Figures A22 and A23 was plotted against the silica fume content (BWOB) of the waste form. The deviation was calculated by taking the ratio of the ordinate to the abscissa in Figures A22 and A23 (that is $D_{obs,x}$ divided by $D_{obs,Na} \times (D_x/D_{Na})$, which is just the reciprocal of the retardation factor). In this way, the 45-degree lines in Figures A22 and A23 become horizontal lines at unity and points above the 45-degree lines fall above the unity line, and vice versa in Figures A24 and A25. Although there is significant scatter, both plots show clear trends with silica fume content in the grout mix compositions. Furthermore, most of the FY24 compositions had higher silica fume contents than formulations from previous years, which is consistent with the differences in behavior in Figures A22 and A23.

It is well known that neutral salt activation of blast furnace slag yields abundant layered double hydroxide-type phases (AFm and/or AFt) as the major secondary phases in addition to highly cross-linked sodium-substituted calcium aluminosilicate hydrate (CNASH) gels [12]. Furthermore, the addition of silica fume can greatly enhance the incorporation of sodium into the

CNASH gels [42]. This would decrease the retardation factors for nitrate and nitrite *relative to sodium*, as is observed in this work. In addition, since the AFm and/or AFt secondary phases are considered possible host phases for nitrate and nitrite [43], it is expected that a certain proportion of nitrate or nitrite can be fixed in these secondary phases, leading to a higher retardation factor relative to sodium. However, introduction of silica fume into a NSAS system suppresses the formation of AFm/AFt secondary phases in favor of CNASH and NASH gel formation [42]. This may provide further explanation for a lower retardation factor for nitrate or nitrite in the waste forms with high silica fume content. Other factors that may affect retardation factors for nitrate and nitrite include molar Na in the AltLAW, w/dm, and addition of calcium hydrotalcite and/or zeolite. For example, the retardations factors for nitrate for CSM0.40A4S and CSM0.40A8S were as high as 4.11 and 5.99, respectively (Table A3). Both waste forms were prepared with 1 M Na AltLAW and w/dm of 0.40. A lower w/dm will often yield a denser gel matrix with low porosity while incorporation of calcined hydrotalcite will enhance formation of LDH phases that provide the host sites for nitrate or nitrite. CSMA3S3.5M1 used a w/dm of 0.40 and 3.5M Na AltLAW and the mix contained calcined hydrotalcite but without silica fume. Yet the retardation factor for nitrate was as high as 4.64 for nitrate and 7.32 for nitrite (Table A3). This suggests that there could be synergistic effects of w/dm, molar Na, silica fume, and other additives such as calcined hydrotalcite and zeolite, that may yield high retardation factors for nitrate and nitrite relative to sodium.

As noted above, the definition of retardation factors for nitrate and nitrite in Eq. 5.3 assumes that the dissolved sodium is not retarded by the matrix. However, particularly in the geopolymer-type waste forms, a significant proportion of the sodium is incorporated and immobilized in calcium aluminosilicate hydrate, a primary gel phase formed during neutral salt activation of slag. Therefore, retardation factors calculated by Eq. 5.3 evaluate retardation for nitrate and nitrite relative to sodium, but sodium is *also* subject to retardation by the matrix.

5.8.3 Formulations Recommended for Further Characterization

Based on the results from the first and second testing phases, and the later availability of the leaching data, a rather broad range of formulations (CSMA8S2R3s, CSMA8S2R8, CSMA8S2R11a, CSMA8S2R11b, CSMA8S2R12a, CSMA8S2R12c, CSMA8S2R12d, CSMA8S2R12f, CSMA3S1R3, and CSMP3SR2 were subjected to more extensive characterization for rheology, dry bulk density, matrix skeleton density, and XRD (Tables 5.28 and 5.29; Figures 5.34 to 5.40).

Table 5.28 provides a summary of the set time, compressive strength, and rheological properties of the selected formulations. During rheological testing, a short cycling time was used since the fresh grouts can contain relatively coarse particles. Figures 5.34, 5.36, and 5.38 show that the shear stress increased to a maximum during shearing between 10 s^{-1} and 40 s^{-1} and then decreased slowly to attain a steady state condition to complete the upper flow curve. The shear stress was continually measured at a constant shear rate of 200 s^{-1} and then a linear down curve was obtained. The total testing duration was 3 min. These flow curves were typical of cement pastes and mortars at a cycling time of a few minutes [44]. Structural breakdown due to shear occurs while the paste or mortar is being tested, which produces the flow curve. The down curve data were fitted with Bingham model to calculate dynamic yield stress and plastic viscosity of fresh grout samples. The dynamic yield stress ranged from 159.5 and 468.3 Pa. As a comparison, the yield stress ranged from 10 and 400 Pa for typical cement pastes and mortars [44]. For CSMA8 Series waste forms, fresh pastes showed lower yield stress values (159.5 Pa ~ 231.3 Pa) than the mortar samples (270.7 ~ 468.3 Pa). Fresh pastes were often thin and became pourable whereas fresh mortars were thick and often harder to pour. Figures 5.35. 5.37, and 5.39 show viscosity versus shear rates (upper curves only). Viscosity decreased with increasing shear rate with a steady state value between 19 Poise and 54 Poise, characteristic of thixotropic behavior, as evidenced as well by Figures 5.34. 5.36, and 5.38 where shear stress decreased at a constant shear rate of 200 s^{-1}. A thick grout became fluid after vibration for a few seconds, also indicating thixotropic behavior.

Table 5.29 summarizes the measured values of apparent density, matrix skeleton density, particle density, and porosity. The apparent densities ranged from 1.90 to 2.10 g/cm^3 for the cured mortars and from 1.90 to 1.96 g/cm^3 for the cured pastes. The matrix skeleton densities ranged from 1.69 to 1.79 g/cm^3 for the cured mortars and from 1.38 to 1.51 for the cured pastes. The porosities ranged from 0.24 to 0.30 for the cured mortars and from 0.35 to 0.42 for the cured pastes. The particle densities of all of the cured grouts range from 2.37 to 2.57 g/cm^3. Cured pastes always had lower apparent density and matrix skeleton density and higher porosity as compared to their mortar counterparts.

Figure 5.40 shows XRD patterns for the paste-type waste forms after curing for at least 28 days. The strong humps between 28 and 32 2θ are characteristic of calcium aluminosilicate gel, most likely sodium substituted (C,N)ASH, overlapped with calcite ($CaCO_3$) and nitratine ($NaNO_3$). Thenardite, $NaSO_4$, was a residual neutral salt, indicating alkali activation of slag had not yet been completed. The expansion caused by massive thenardite crystallization during early curing times as seen in some grout samples for ETF brine [45] was not observed in any of the waste forms for AltLAW. As adequate curing condition is met and neutral salts are mostly consumed during early curing times, crystallization of thenardite at late curing times will not cause any dimensional instability. Instead, sodium sulfate will continue to react with slag to densify the gel matrix, which will provide long-term strength development. Periclase, from the light-burned magnesia, remained after curing for months, indicating that it hydrated at a lower rate, which may benefit mitigating long-term shrinkage of the waste form. Zeolite was identified in all the waste form samples in which either Ionex Ag-400 was added as the getter for iodine in CSMA8 Series formulations or zeolite Type 5 was included in the waste forms when iodine was removed from the AltLAW prior to grouting. Stratlingite, a silicate layered double hydroxide was present in all of the waste forms. Increasing silica fume in the formulation definitely promotes formation of stratlingite. While ettringite may be present, hydrotalcite was not positively identified either due to its low concentration in the waste form or because its formation was inhibited by increased silica fume content in a formulation. During the neutral salt activation process, CO_3^{2-} and SO_4^{2-} species supplied by the activator react with the dissolved Ca^{2+} from the slag to form calcite and gypsum, resulting in an increase in the alkalinity of the pore solution, and the reaction proceeds similarly to the process observed when using NaOH as alkaline activator [12]. During the late curing times, silica fume may dissolve in the NaOH pore solution and thus sodium silicate may participate during alkali activation of slag. Gypsum may be consumed by formation of ettringite.

Finally, three formulations, CSMA8S2R11b, CSMA8S2R12a, and CSMP3S1R2, representing the best performing waste forms in terms of mechanical and chemical durability and waste loading were recommended for further testing. Table 5.30 provides a summary of the set time, compressive strength, and 63-day LI values for sodium and all COCs for the selected waste forms with two reference formulations included for comparison. LI values are plotted as functions of time and formulation type in Figures 5.41 to 5.46. These waste forms were further subjected to isothermal calorimetry and TCLP testing. CSMA8S2R11b was chosen due to its high waste loading, better workability, mechanical strength, and comparable LI values for rhenium, chromium, iodine, and nitrate to reference CSMA8S2 (Table 5.30). CSMA8S2R12a represents a new CSMA8 Series waste form with a pretreatment step to remove iodine in the AltLAW prior to grouting. This formulation was selected due to its significantly improved 63-day LI values for all the COCs over the reference CSMA3S1R1. CSMP3S1R2 was recommended for its high waste loading and significantly improved 63-day LI values for Na and COCs over the reference CSMA3S1R1, except for rhenium. This formulation used BFS CP that had a lower reduction capacity than BFS SE. BFS SE may be used instead in the formulation to improve the 63-day LI value for rhenium.

Additional formulations, CSMA8S2R12d and CSMP3S1R1 are proposed for further optimization if higher waste loading becomes an important factor in the future (Table 5.30). Both formulations are of the paste type, where the fillers are removed completely and with waste loading increased by 60-70% as compared to its mortar counterpart. The 63-day LI values for Na were about 9, indicating an excellent overall resistance to leaching. The 63-day LI values for nitrate were marginal, around 8.7, and the values for Re were lower. Both formulations may be subjected to optimization in order to develop a waste form with 63-day LI values exceeding the estimated performance metric requirements for all the COCs including rhenium, chromium, iodine, and nitrate while still maintaining high waste loading. For CSMA8S2R12d, reducing w/dm to 0.425 and increasing the filler content may yield a waste form with improved 63-day LI values for rhenium and nitrate. For CSMP3R1R1, BFS CP may be replaced with BFS SE to improve the 63-day LI value for Re. Increasing the filler content and reducing the dosage of EUCON Hydrapel 2.5 may yield a waste form with improved 63-day LI values for nitrate and rhenium with a relatively high waste loading.

Isothermal calorimetry measurements were made at 25°C on the three formulations, CSMA8S2R11b, CSMA8S2R12a, and CSMP3SR2. Sand and ground quartz were included in the recipe for CSMA8S2R12a. The normalized heat flow results are shown in Figure 5.47 and the normalized heat release results are shown in Figure 5.48. The results are summarized in Tables 5.31 and 5.32. Normalization was done with respect to the mass of wet grout. The tests were run for about 200 hrs.

Heat flows associated with dissolution were clearly identified for CSMA8S2R11b and CSMP3S1R2. The heat flow was 1.08 mW/g at 0.42 hrs for CSMA8S2R11b and it was as high as 16.4 mW/g at 0.10 hrs for CSMP3S1R2. The dissolution peak for CSMA8S2R12a was partially recorded. The dissolution stage was followed by a dormant or induction period where a very low rate of heat release was detected. The duration of the induction period varied from formulation to formulation. A main heat flow indicative of alkali activation with massive precipitation of gel products such as (C,N)ASH was observed between 10 and 70 hours. CSMA8S2R12a showed the lowest heat flow (0.37 mW/g), which occurred after reacting for 69.37 hrs. Dilution effects due to the 39% filler content contributed at least partially to the low heat flow. CSMA8S2R11b showed the highest heat flow (2.41 mW/g), which occurred after reacting for 17.10 hrs. The heat flow was 1.71 mW/g for CSMA3S1R2 but the main peak occurred at much earlier time (10.37 hrs). Occurrence of this main peak was related to initial setting of the curing grout, as seen in Table 5.31. Typically, initialization of an accelerating stage often precedes initial setting

The cumulative heat release curves for all grout samples are presented in Figure 5.48. The induction period corresponds to the relatively flat regions at the early stage of reaction in the cumulative heat release curves. A rapid increase in heat release is associated with the main heat flow peak when massive precipitation of gel products occurred. 7-day heat release was 107.16 J/g for CSMA8S2R11b, 55.21 J/g for CSMA8S2R12a, and 89.37 J/g for CSMP3S1R2. Since heat release is indicative of reaction progress, 7-day heat release was well correlated with 7-day compressive strength. For example, CSMA8S2R11b had the highest 7-day heat release (107.16 J/g) and the highest compressive strength after curing for 7 days (8289 psi). Dilution effects due to the presence of the inert fillers (39%) in CSMA8S2R12a contributed in part to lower heat releases during curing of the waste form. Lower heat release was observed for CSMP3S1R2 with 3.5 M Na than for CSMA8S2R11b with 5.6M Na. Both formulations were the paste type prepared with BFS CP. It is clear that calcined hydrotalcite affected only the early stages of reaction, resulting in accelerated setting. Reaction progress in the late curing times may be affected by the presence of a higher dosage of EUCON Hydrapel 2.5, which is a retarder for neutral salt activation of slag.

TCLP results for three grout samples are reported in Table 5.33. Ag, As, Ba, Cd, Cr, Hg, Ni, Pb, Sb, Se, and Tl were spiked into the simulant according to Table 3.4. Retention factors were calculated as 1 minus the amount leached divided by the amount initially present for each species. Table 5.33 shows that leachate concentrations for all species except Ag are below their respective UTS limits. The concentrations of silver in the TCLP leachate are high simply due to the high concentration of silver in the Ag-400, which makes the retention factors based on the spike amount negative; for comparison, previous work has shown that silver concentrations in leachates from TCLP Method 1315 are often extremely low [10]. Among eleven species tested, retentions for As, Cd, Cr, Ni, Pb, and Sb were between 0.95 and 1.00. The retention for Tl was over 0.93. High retentions observed for these heavy metals may be related to the presence of sulfide species released during the neutral salt activation of blast furnace slag. Heavy metals such as Cd, Ni, Pb, Sb, and Tl tend to form highly insoluble sulfide compounds during neutral salts activation of blast furnace slag. Cr^{6+} may be reduced by sulfide species to Cr^{3+} that may subsequently hydrolyze to precipitate insoluble $Cr(OH)_3$. The retentions for Se for two paste-type grout samples (CSMA8S2R11b and CSMP3R1R2) were around 0.66, significantly lower than the value of 0.95 for the mortar-type grout sample (CSMA8S2R12a). Both selenite and arsenate may be immobilized in the ettringite or AFm phase structures [46, 47]. However, it is also plausible that selenite and arsenate could be reduced by sulfide species released during neutral salt activation of slag. For example, arsenate may undergo reductive precipitation to form As_2S_3 [48]. Determination of the exact mechanisms for immobilization of selenite and arsenate in the neutral salt activated slag would require further investigation. As noted above, the retention values for Ag are negative in all the grout samples simply due to the presence of Ionex Ag-400 (either as the getter or residue in grout samples), which added an additional inventory of silver. The negative retention values for Ba may be related to the slag activation process since blast furnace slag often contains some BaO (see Table 5.2) and to the presence of barium as an impurity in other chemicals.

SECTION 6.0
SUMMARY AND CONCLUSIONS

The primary objective of this work was to perform laboratory-scale testing to refine the most promising formulations that were identified in the FY23 work. The goal of the refinements was to further reduce the release rates for ^{99}Tc, Cr, ^{129}I, and nitrate while maintaining a workable waste form. Efforts were also made to develop waste forms with increased waste loading. A three-phased approach, such as was used in previous fiscal years, was employed to screen for optimal formulations primarily for 5.6 M Na AltLAW. Only those formulations that showed promise for improved retention of the target COCs, and in particular, for meeting the retention improvement targets, were subjected to more extensive testing. All of the waste forms developed during the FY24 work were subjected to the full 63-day EPA Method 1315 test along with measurement of other properties after curing for 28 days at room temperature. Based on these results, a smaller set of formulations was selected for additional characterization including isothermal calorimetry and TCLP testing.

In the first testing phase, three BFS types, BFS CP, BFS DS, and BFS DMI were tested with the reference formulation CSMA8S2 that included Ionex Ag-400 as the getter for iodine. The effect of slag compositions on fresh and cured properties and retention of COCs was explored. Only BFS CP, BFS SE, and BFS DS were subjected to further testing with silica fume up to 14% BWOS, EUCON Hydrapel 2.5 from 1.25% to 3% BWOS, and w/dm up to 0.50. The test results suggested that an optimal waste form could be formulated with 14% BWOB silica fume, 1.25% or 2.5% BWOB EUCON Hydrapel 2.5, and w/dm = 0.45 or 0.425. With these optimal parameters, formulations with higher waste loading were developed, yielding 63-day LI values exceeding the estimated performance metric requirements for all COCs, except for rhenium. For example, the waste loading for formulation CSMA8S2R11b increased by over 55% as compared to reference CSMA8S2 developed in the FY23 work.

The second testing period was the primary testing phase of the present work with a focus on further improving leaching performance and waste loading assuming that iodine in the AltLAW was removed prior to grouting. This testing period proceeded in three sub-tasks. Task 1: A CSMA8 Series waste form formulated with optimal formulating parameters derived from the first testing phase, yielding CSMA8S2R12a made with BFS SE, which showed significantly improved retentions of all COCs over reference CSMA3A1R1 developed in the FY23 work. Furthermore, the fillers were partially or completely removed for increased waste loading. Three slag types were tested including BFS SE, BFS CP, and BFS DS. BFS DS was chosen owing to its excellent capacity for reducing perrhenate/pertechnetate in the AltLAW. Task 2: Reference formulation CSMA3S1R1 was further modified by increasing silica fume to 14% BWOS and EUCON Hydrapel 2.5 to 3.00% and including zeolite Type 5A as the getter for COCs. Both BFS SE and BFS CP were included for CSMA3 Series formulation testing. A CSMA3 Series formulation was assessed for performance by removing the fillers completely for increased waste loading. Task 3: Three waste forms were formulated for testing with 3.5 M Na AltLAW by using optimal formulating parameters and BFS CP. Two CSMA8A Series waste forms included Ionex Ag-400 as the getter for iodine, with and without the fillers, and one CSMA3 Series waste form was formulated with the fillers completely removed.

In the third phase of testing, eight better-performing formulations were selected for additional characterization with respect to rheology, dry density, and porosity (Table 5.29). Finally, the three best performing formulations (CSMA8S2R11b, CSMA8S2R12a, and CSMP3S1R2) were recommended and advanced for further testing including isothermal calorimetry and the TCLP. Two additional formulations (CSMA3S1R3 and CSMP3R1R1) are proposed for future optimization for higher waste loading.

The results from the present work show that many of the formulations that were developed exhibit improved performance as compared to the two reference formulations developed in the FY23 work in terms of waste loading and retention of the target COCs. Moreover, the retention performance of many of the new formulations is better than the respective requirements for the COCs based on estimated performance metrics [6]. An important conclusion from the present work is, therefore, that there is considerable scope for improvement of AltLAW waste form performance through these novel formulation approaches.

Key results with respect to the AltLAW waste form performance metrics are:

- Thirteen of the twenty formulations have nitrate LI values that are better than the estimated performance metric requirement for nitrate of 8.70 (diffusivity = 2×10^{-9} cm^2/s) [6]. The highest measured LI value for nitrate of 9.06 corresponds to a diffusivity of 8.73×10^{-10} cm^2/s.

- Five of the twenty formulations have rhenium LI values that are better than the estimated performance metric requirement for technetium of 10.70 (diffusivity = 2×10^{-11} cm^2/s) [6]. The highest measured LI value for rhenium of 12.3 corresponds to a diffusivity of 5.03×10^{-13} cm^2/s. It is noted that rhenium is less easily reduced than technetium, often resulting in over estimation of the release of technetium from the waste form, typically by an order of magnitude or more. Therefore, it is expected that the LI value for Tc may be much higher, likely better than the estimated performance metric for Tc [38, 39].

- Seventeen of the twenty formulations tested have iodine LI values that are better than the estimated performance metric requirement for iodine of 10.52 (diffusivity = 3×10^{-11} cm^2/s) [6]. The highest measured LI value for iodine of 14.30 corresponds to a diffusivity of 5.01×10^{-15} cm^2/s.

- All of twenty formulations have chromium LI values that are better than the estimated performance metric requirement for chromium of 10.40 (diffusivity = 4×10^{-11} cm^2/s) [6]. The highest measured LI value for chromium of over 14.14 corresponds to a diffusivity of $>7.21\times 10^{-15}$ cm^2/s.

- Only two formulations (CSMA8S2R12a and CSMA3S1R3) have LI values that are better than the estimated performance metric requirement for all COCs, including technetium, iodine, chromium, and nitrate. In both formulations, Ionex Ag-400 was removed after reacting it with the AltLAW for 2 hrs before the pretreated AltLAW was grouted. The static fresh grout for CSMA8S2R12a was a relatively thick paste that was slow to pour; it set in about 46 hrs. The static fresh grout for CSMA3R1R3 was also thick and not easily pourable; it set in 15.8 hrs. However, both fresh grouts liquefied and became very fluid under the influence of vibration or mixing. The emphasis of the present work was on improving leaching performance for formulations with reasonable workability. Based on these results, further improvements in workability should be achievable depending on the particular requirements of the processing system that is ultimately selected

Future work would be useful to continue these efforts to improve the leaching performance of these prospective waste forms and further increase waste loadings.

SECTION 7.0
QUALITY ASSURANCE

This work was conducted under a quality assurance program compliant with the applicable criteria of 10 CFR 830.120; the American Society of Mechanical Engineers (ASME), Quality Assurance Requirements for Nuclear Facility Applications, ASME NQA-1-2008 and NQA-1a-2009 Addenda; and DOE Order 414.1 D, Quality Assurance. These quality assurance (QA) requirements were implemented through a Quality Assurance Project Plan (QAPP) for WRPS work that is conducted at VSL [49]. Test and procedure requirements by which the testing activities were planned and controlled were also defined in that plan. The program was supported by VSL standard operating procedures that was used for this work [50].

This work did not include any high level waste (HLW) waste form affecting activities and therefore the requirements of DOE/RW-0333P, Office of Civilian Waste Management Quality Assurance Requirements and Description (QARD), were not applicable.

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Table 2.1. Formulation Parameters for the Two Reference Formulations [10].

Grout ID	w/dm	Na_2O as in NC	Na_2O as in NŚ	MgO	AgZ	CTH	SF	Hyp	Type BFS
		%BWOS							
CSMA8S2	0.45	2.5	2.5	5.0	5.0	-	6.0	0.75	SEo
CSMA3S1R1*	0.425	2.5	2.5	5.0	-	8.6	6.0	0.575	SEo

NC = sodium carbonate anhydrous; NŚ = sodium sulfate anhydrous; AgZ = Ionex Ag-400; CTH = calcined hydrotalcite; SF = Silica fume; Hyp = Hydrapel 2.5; SEo = Old batch of BFS from Lafarge-Holcim's Seattle plant.
* Ionex Ag-400 was removed after iodine absorption with the same amount of BFS added.

Table 2.2. Grout Mix Compositions the Two Reference Formulations in wt% [10].

Grout ID	BFS SEo	NC	NŚ	MgO	Sand	QZ	SF	CTH	AgZ	Hyp	AltLAW
CSMA8S2	31.88	0.81	1.60	1.59	32.50	6.50	2.00	-	1.59	0.24	21.29
CSMA3S1R1*	31.48	0.79	1.78	1.55	32.50	6.50	2.00	2.69	-	0.18	20.53

BFS SEo = from Seattle Plant, old batch; NC = sodium carbonate anhydrous; NŚ = sodium sulfate anhydrous ; QZ = ground quartz powder; SF = silica fume; CTH = calcined hydrotalcite; AgZ = ground Ionex Ag 400; Hyp = Eucon Hydrapel 2.5; AltLAW = Alternative Low Activity Waste (5.6 M Na).
* Ionex Ag-400 was removed after iodine absorption with the same amount of BFS added.

Table 2.3. Two Reference Formulations: Properties and Leaching Performance [10].

Grout I.D.	Set Time	Plastic Viscosity	Yield Strength	Compressive Strength (psi)		Leachability Index at Steady State					
		cP	Pa	7d	28d	**Na**	**Re**	**I**	**Cr**	**NO_3^-**	**NO_2^-**
CSMA8S2	30-48h	5348	264	<500	6449	8.67	8.90	10.55	11.90	8.79	8.69*
CSMA3S1R1	28.1h	9342	558	6460	10028	8.83	11.55	13.19	13.74	8.73	8.76*
Performance Metric						-	>10.7	>10.52	>10.40	>8.70	-

* New measurements

Table 2.4. Test Matrix for Formulation Refinement and Optimization.

Test	Grout ID	Formulation Type	Molar Na	AgZ	Variables	Absorbent	Mortar or paste
-	Reference [10]	CSMA8S2	5.6 M	5%	BFS SE/SF@6.0% (FY23)	Included	Mortar
#1	CSMA8S2R2	CSMA8S2	5.6 M	5%	BFS SE/SF@ 10.0%	Included	Mortar
#2	CSMA8S2R3	CSMA8S2	5.6 M	5%	BFS SE/SF@ 14.0%	Included	Mortar
#3	CSMA8S2R4	CSMA8S2	5.6 M	5%	BFS SE/Hyp@1.25%	Included	Mortar
#4	CSMA8S2R5	CSMA8S2	5.6 M	5%	BFS CP/SF@6.0%	Included	Mortar
#5	CSMA8S2R6	CSMA8S2	5.6 M	5%	BFS DS/SF@6.0%	Included	Mortar
#6	CSMA8S2R7	CSMA8S2	5.6 M	5%	Optimal mix*	Included	Mortar
#7	CSMA8S2R8	CSMA8S2	5.6 M	5%	Optimal mix*/w/dm = 0.50	Included	Mortar
#8	CSMA8S2R9	CSMA8S2	5.6 M	5%	Optimal mix*/w/dm = 0.40	Included	Mortar
#9	CSMA8S2R10	CSMA8S2	3.5 M	5%	Optimal mix*	Included	Mortar
#10	CSMA8S2R11	CSMA8S2	5.6 M	5%	Optimal mix*/50%fillers removed	Included	Mortar
#11	CSMP8S2R1	CSMA8S2	5.6 M	5%	Optimal mix*/100%fillers removed	Included	Paste
#12	CSMP8S2R2	CSMA8S2	3.5 M	5%	Optimal mix*/100%fillers removed	Included	Paste
#13	CSMA8S2R12	CSMA8S2	5.6 M	None	Optimal mix*/ZT for AgZ	Removed	Mortar
-	Reference [10]	CSMA3S1R1	5.6 M	None	BFS SE/CTH@8.6%	Removed	Mortar
#14	CSMA3S1R2	CSMA3S1R1	5.6 M	None	BFS SE/Hyp/ZT&CTH@5.0%	Removed	Mortar
#15	CSMA3S1R3	CSMA3S1R1	5.6 M	None	BFS SE/Hyp/ZT&CTH@5.0%	Removed	Mortar
#16	CSMA3S1R4	CSMA3S1R1	5.6 M	None	BFS CP/NC/Hyp/ZT&CTH@5.0%	Removed	Mortar
#17	CSMP3S1R1	CSMA3S1R1	5.6 M	None	Optimal mix*/100%fillers removed	Removed	Paste
#18	CSMP3S1R2	CSMA3S1R1	3.5 M	None	Optimal mix*/100%fillers removed	Removed	Paste

% = percent by weight of slag (BWOS).

*An optimal mix to be developed by including all variables that yield positive effect on leaching resistance. These variables may include SF, Hyp, BFS type, and ZT.

BFS SE = BFS from Seattle Plant; BFS CP = BFS from Clark Pacific; BFS DS = DuraSlag from Ash Grove; NC = sodium carbonate anhydrous; SF = silica fume; Hyp = Hydrapel 2.5; CTH = calcined hydrotalcite; ZT = plain zeolite; AgZ = Ionex Ag-400; Fillers = Combined ground quartz and fine sand in mass ratio of 1 : 5.

Table 3.1. Composition of AltLAW Simulant; "HTWOS Overall Average" from [1].

Constituent	Moles per Mole of Na	Mol/L at 5.6 M Na	Mol/L at 3.5 M Na
Na	1.000	5.600	3.500
K	0.007	0.039	0.025
Al	0.061	0.342	0.214
Cl	0.008	0.045	0.028
F	0.006	0.034	0.021
SO_4	0.017	0.095	0.060
PO_4	0.01	0.056	0.035
NO_2	0.113	0.633	0.396
NO_3	0.324	1.814	1.134
CO_3	0.055	0.308	0.193
TOC	0.015	0.084	0.053

Note: The simulant is spiked with I, Re, and Cr – see text and Table 3.2.

Table 3.2. Recipe for One Liter of Hanford AltLAW Waste Simulant (5.6 M Na).

Analyte	Target (Moles)	Reagent	Molecular Weight	Assay	Target Masses (g)
Al	0.3416	$NaAlO_2$	81.97	1.000	28.001
OH^-	1.7136	NaOH	40.01	0.995	69.114
SO_4^{2-}	0.0952	Na_2SO_4	142.04	0.998	13.550
Cl^-	0.0448	NaCl	58.443	1.000	2.618
NO_3^-	1.8144	$NaNO_3$	84.995	0.997	151.337
NO_2^-	0.6328	$NaNO_2$	68.995	0.997	43.792
CO_3^{2-}	0.3080	Na_2CO_3	105.99	0.998	32.710
K	0.0392	KNO_3	101.11	0.997	3.975
PO_4^{3-}	0.0560	Na_3PO_4	163.94	0.992	9.255
TOC	0.0840	$CH_3COONa \cdot 3H_2O$	136.08	0.987	11.581
F	0.0336	NaF	41.99	0.990	1.425
Re	350 mg/L	$HReO_4$ (Re)	186.21	0.500*	0.7000
I	150 mg/L	NaI	149.89	0.999	0.1774
Cr	0.0241	$Na_2Cr_2O_7 \cdot 2H_2O$	298.00	1.000	3.5879
H_2O	-	DI H_2O	18.02	1.000	882.99
Total, g/L					1254.604

* 50% metal contained in $HReO_4$ solution

Table 3.3. Recipe for One Liter of Hanford AltLAW Waste Simulant (3.5 M Na).

Analyte	Target (Moles)	Reagent	Molecular Weight	Assay	Target Masses (g)
Al	0.2135	$NaAlO_2$	81.97	1.000	17.501
OH^-	1.0710	NaOH	40.01	0.995	43.066
SO_4^{2-}	0.0595	Na_2SO_4	142.04	0.998	8.468
Cl^-	0.0280	NaCl	58.443	1.000	1.636
NO_3^-	1.1340	$NaNO_3$	84.995	0.997	94.585
NO_2^-	0.3955	$NaNO_2$	68.995	0.997	27.370
CO_3^{2-}	0.1925	Na_2CO_3	105.99	0.998	20.440
K	0.0245	KNO_3	101.11	0.997	2.485
PO_4^{3-}	0.0350	Na_3PO_4	163.94	0.992	5.784
TOC	0.0525	$CH_3COONa \bullet 3H_2O$	136.08	0.987	7.238
F	0.0210	NaF	41.99	0.990	0.891
Re	350 mg/L	$HReO_4$ (Re)	186.21	0.500*	0.7000
I	150 mg/L	NaI	149.89	0.999	0.1774
Cr	0.0241**	$Na_2Cr_2O_7 \bullet 2H_2O$	298.00	1.000	3.5879
H_2O	-	DI H_2O	18.02	1.000	933.570
Total, g/L					1167.50

* 50% metal contained in $HReO_4$ solution; ** The same spiking level as in AltLAW 5.6 M Na

Table 3.4. Spiked LDR Inorganics in the AltLAW for Preparing TCLP Grout Samples.

LDR species	Spiking level, mg/L	Chemicals
Sb^{5+}	17.9	$SbCl_3$
As^{5+}	13.0	$Na_2HAsO_4 \bullet 7H_2O$
Ba^{2+}	1.65	$Ba(NO_3)_2$
Cd^{2+}	10.3	$Cd(NO_3)_2 \bullet 4H_2O$
Cr	1500	$Na_2CrO_4 \bullet 4H_2O$
Pb^{2+}	35.4	$Pb(NO_3)_2$
Hg^{2+}	1.19	$Hg(NO_3)_2 \bullet H_2O$
Ni^{2+}	27.9	$Ni(NO_3)_2 \bullet 6H_2O$
Se^{6+}	21.6	Na_2SeO4
Ag^{1+}	1.75	$AgNO_3$
Tl^{1+}	14.9	$TlNO_3$

Table 3.5. Grout Formulating Parameters for NSAS Waste Forms Based on Reference CSMA8S2 with AgZ (5.6 M Na).

Grout ID	w/dm	Na_2O in NC	Na_2O in NŚ	MgO	AgZ	SF	Hyp	Fillers in mix	Type BFS	Testing Variables
		%BWOS								
CSMA8S2 [10]	0.45	2.5	2.5	5.0	5.0	6.0	0.75	39.0%	SEo	Reference
CSMA8S2R5	0.45	2.5	2.5	5.0	5.0	6.0	0.75	39.0%	CP	BFS Type
CSMA8S2R6	0.45	2.5	2.5	5.0	5.0	6.0	0.75	39.0%	DS	
CSMA8S2R13	0.45	2.5	2.5	5.0	5.0	6.0	0.75	39.0%	DMI	
CSMA8S2R4	0.45	2.5	2.5	5.0	5.0	10.0	1.25	39.0%	SEn	w/dm, SF, Hyp,
CSMA8S2R3s	0.45	2.5	2.5	5.0	5.0	14.0	1.25	39.0%	CP	
CSMA8S2R3c	0.425	2.5	2.5	5.0	5.0	14.0	3.00	39.0%	CP	
CSMA8S2R8	0.50	2.5	2.5	5.0	5.0	14.0	1.25	39.0%	CP	
CSMA8S2R11a	0.425	2.5	2.5	5.0	5.0	14.0	1.25	27.5%	CP	%Fillers
CSMA8S2R11b	0.425	2.5	2.5	5.0	5.0	14.0	2.50	0%	CP	

NC = sodium carbonate anhydrous; NŚ = sodium sulfate anhydrous; AgZ = ground Ionex Ag 400; SF = silica fume; Hyp = Eucon Hydrapel 2.5; Fillers = Combined ground quartz and fine sand in mass ratio of 1 : 5; SEo = BFS from Seattle Plant old batch; SEn = BFS from Seattle Plant, new batch; CP = BFS from Clark Pacific; DS = DuraSlag from Ash Grove Cement; DMI = from Diversified Minerals Inc.

Table 3.6. Mortar Formulations for CSMA8 Series Waste Forms with AgZ (in wt%): Varying Slag Compositions (5.6 M Na).

Grout ID	BFS Type	BFS	NC	NŚ	MgO	Sand	QZ	SF	AgZ	Hyp	AltLAW
CSMA8S2 [10]	SEo	31.88	0.81	1.60	1.59	32.50	6.50	2.00	1.59	0.24	21.29
CSMA8S2R5	CP	31.89	0.81	1.60	1.59	32.50	6.50	2.00	1.59	0.24	21.28
CSMA8S2R6	DS	31.89	0.81	1.60	1.59	32.50	6.50	2.00	1.59	0.24	21.28
CSMA8S2R13	DMI	31.89	0.81	1.60	1.59	32.50	6.50	2.00	1.59	0.24	21.28

SEo = BFS from Seattle Plant, old batch; CP = BFS from Clark Pacific; DS = DuraSlag from Ash Grove Cement; DMI = from Diversified Minerals Inc.; NC = sodium carbonate anhydrous; NŚ = sodium sulfate anhydrous; QZ = ground quartz; SF = silica fume; AgZ = ground Ionex Ag 400; Hyp = Eucon Hydrapel 2.5.

Table 3.7. Mortar Formulations for CSMA8 Series Waste Forms with AgZ (in wt%): Varying w/dm and %Fillers (5.6 M Na).

Grout ID	BFS Type	BFS	NC	NŚ	MgO	Sand	QZ	SF	AgZ	Hyp	AltLAW
CSMA8S2R4	SEn	30.86	0.77	1.54	1.54	32.50	6.50	3.09	1.54	0.39	21.28
CSMA8S2R3s	CP	29.90	0.72	1.48	1.49	32.50	6.50	4.19	1.49	0.37	21.34
CSMA8S2R3c	CP	30.40	0.78	1.52	1.52	32.50	6.50	4.26	1.52	0.91	20.09
CSMA8S2R8	CP	28.64	0.63	1.40	1.43	32.50	6.50	4.01	1.69	0.36	22.84
CSMA8S2R11a	CP	36.17	0.91	1.81	1.81	22.91	4.58	5.06	1.81	0.45	24.48
CSMA8S2R11b	CP	49.94	1.28	2.51	2.50	-	-	6.99	2.50	1.25	33.04

SEn = BFS from Seattle Plant, new batch; CP = BFS from Clark Pacific; NC = sodium carbonate anhydrous; NŚ = sodium sulfate anhydrous; QZ = ground quartz; SF = silica fume; AgZ = ground Ionex Ag 400; Hyp = Eucon Hydrapel 2.5.

Table 3.8. Recipes for CSMA8 Series Formulations with AgZ: Varying Slag Compositions.

Grout ID		CSMA8S2R5	CSMA8S2R6	CSMA8S2R13
BFS Type		**BFS CP**	**BFS DS**	**BFS DMI**
Order	**Component**	**Mass, grams**		
6	Eucon Hydrapel 2.5	9.77	9.77	9.77
5	BFS	1302.14	1302.14	1302.14
5	Sika SC MgO	65.11	65.11	65.11
5	Silica Fume	81.68	81.68	81.68
5	AGSCO Silica A-25	265.45	265.45	265.45
5	Yellow Sand, Air Dry	1327.26	1327.26	1327.26
4	Moisture from Sand	15.93	15.93	15.93
3	Na_2CO_3 (99.8%)	33.19	33.19	33.19
3	Na_2SO_4 (99.8%)	65.39	65.39	65.39
2	Ground Ionex Ag-400	65.11	65.11	65.11
1	AltLAW 5.6 M Na	868.98	868.98	868.98
Total batch, g		4100.00	4100.00	4100.00

CP = BFS from Clark Pacific; DS = DuraSlag from Ash Grove Cement; DMI = from Diversified Minerals Inc.

Table 3.9. Recipes for CSMA8 Series Formulations with AgZ: Varying w/dm, Hyp and %Fillers.

Grout ID		CSMA8S2R4	CSMA8S2R3s	CSMA8S2R3c	CSMA8S2R8	CSMA8S2R11a	CSMA8S2R11b
Variable	w/dm	0.45	0.45	0.425	0.50	0.425	0.425
	Fillers	39.0%	39.0%	39.0%	39.0%	27.5%	0%
Order	**Component**	**Mass in grams**					
6	Eucon Hydrapel 2.5	15.93	15.26	37.24	14.62	18.49	51.18
5	BFS CP	-	1221.05	1241.30	1169.72	1478.87	2047.40
5	BFS SEn	1260.12	-	-	-	-	-
5	Sika SC MgO	63.01	61.05	62.07	58.49	73.94	102.37
5	Silica Fume	126.01	170.95	173.78	163.76	207.04	286.64
5	AGSCO Silica A-25	265.45	265.45	265.45	265.45	187.36	-
5	Yellow Sand, Air Dry	1327.26	1327.26	1327.26	1327.27	936.79	-
4	Moisture from Sand	15.93	15.93	15.93	15.93	11.24	-
3	Na_2CO_3 (99.8%)	31.38	29.64	31.84	25.85	37.33	52.48
3	Na_2SO_4 (99.8%)	62.98	60.71	62.42	57.11	74.12	102.95
2	Ground Ionex Ag-400	63.01	61.05	62.07	69.01	73.94	102.37
1	AltLAW 5.6 M Na	869.10	871.64	820.65	932.78	1000.88	1354.61
	Total batch	4100.00	4100.00	4100.00	4100.00	4100.00	4100.00

CP = BFS from Clark Pacific; SEn = BFS from Seattle Plant, new batch.

Table 3.10. Grout Formulating Parameters for NSAS Waste Forms Based On Reference CSMA8S2 with Iodine Removed (5.6 M Na).

Grout ID	w/dm	Na_2O in NC	Na_2O in NŚ	MgO	ZT5	SF	Hyp	Fillers in mix	Type BFS	Testing Variables
		%BWOS								
CSMA8S2R12a	0.425	2.5	2.5	5.0	5.0	14.0	2.50	39.0%	SEo	BFS Type, Zeolite Type 5A, and %Fillers
CSMA8S2R12c	0.45	2.5	2.5	5.0	5.0	14.0	1.25	0%	CP	
CSMA8S2R12d	0.45	2.5	2.5	5.0	5.0	14.0	1.25	0%	SEo	
CSMA8S2R12e	0.45	2.5	2.5	5.0	-	14.0	1.25	0%	DS	
CSMA8S2R12f	0.45	2.5	2.5	5.0	-	14.0	1.25	27.5%	DS	

NC = sodium carbonate anhydrous; NŚ = sodium sulfate anhydrous; ZT5 = zeolite Type 5A; SF = silica fume; Fillers = Hyp = Eucon Hydrapel 2.5; Fillers = Combined ground quartz and fine sand in mass ratio of 1 : 5; SEo = BFS from Seattle Plant, old batch; CP = BFS from Clark Pacific; DS = DuraSlag from Ash Grove Cement.

Table 3.11. Formulations for CSMA8 Series Waste Forms with Iodine Removed (wt%): Varying Slag Compositions, Zeolite Type, and %Fillers (5.6 M Na).

Grout ID	BFS Type	BFS	NC	NŚ	MgO	Sand	QZ	SF	ZT5	Hyp	AltLAW
CSMA8S2R12a	SEo	30.41	0.78	1.53	1.52	32.50	6.50	4.26	1.52	0.76	20.22
CSMA8S2R12c	CP	49.02	1.19	2.43	2.45	-	-	6.86	2.45	0.61	34.99
CSMA8S2R12d	SEo	49.02	1.19	2.43	2.45	-	-	6.86	2.45	0.61	34.99
CSMA8S2R12e	DS	51.47	1.19	2.43	2.45	-	-	6.86	-	0.61	34.99
CSMA8S2R12f	DS	37.20	0.85	1.76	1.77	22.91	4.58	4.96	-	0.44	25.53

SEo = BFS from Seattle Plant, old batch; CP = BFS from Clark Pacific; DS = DuraSlag from Ash Grove Cement; NC = sodium carbonate anhydrous; NŚ = sodium sulfate anhydrous; QZ = ground quartz; SF = silica fume; ZT5 = ground zeolite Type 5A; Hyp = Eucon Hydrapel 2.5.

Table 3.12. Formulations for CSMA8 Series Waste Forms with Iodine Removed: Varying Slag Compositions and %Fillers.

Grout ID		**CSMA8S2R12a**	**CSMA8S2R12c**	**CSMA8S2R12d**	**CSMA8S2R12e**	**CSMA8S2R12f**
Variable	**BFS Type**	SEo	CP	SEo	DS	DS
	Fillers	39.0%	0%	0%	0%	27.50%
Order	**Component**	**Mass in grams**				
5	Eucon Hydrapel 2.5	31.05	25.12	25.12	25.12	18.11
4	BFS	1242.10	2009.47	2009.47	2109.94	1520.87
4	Ground Zeolite Type 5A	62.11	100.47	100.47	-	-
4	Sika SC MgO	62.11	100.47	100.47	100.47	72.42
4	Silica Fume	173.89	281.33	281.33	281.33	202.78
4	AGSCO Silica A-25	265.45	-	-	-	187.36
4	Yellow Sand, Air Dry	1327.26	-	-	-	936.79
3	Moisture from Sand	15.93	-	-	-	11.24
2	Na_2CO_3 (99.8%)	31.73	48.78	48.78	48.78	34.91
2	Na_2SO_4 (99.8%)	62.41	99.91	99.91	99.91	71.91
1	AltLAW simulant 5.6 M Na	825.96	1434.45	1434.45	1434.45	1043.61
Total batch		4100.00	4100.00	4100.00	4100.00	4100.00

SEo = BFS from Seattle Plant, old batch; CP = BFS from Clark Pacific; DS = DuraSlag from Ash Grove Cement

Table 3.13. Grout Formulating Parameters for CSMA3 Series Waste Forms with Iodine Removed (w/dm = 0.425).

Grout ID	Molar Na	Fillers in mix	Na_2O in NC	Na_2O in NŚ	MgO	SF	ZT5	CTH	Hyp	Type BFS
			%BWOS							
CSMA3S1R1 [10]	5.6	39.0%	2.5	2.5	5.0	6.0	-	8.6	0.6	SEo
CSMA3S1R3	5.6	39.0%	2.5	2.5	5.0	14.0	-	10.0	3.0	SEn
CSMA3S1R4	5.6	39.0%	2.5	2.5	5.0	14.0	5.0	5.0	3.0	CP
CSMP3S1R1	5.6	0%	2.5	2.5	5.0	14.0	5.0	7.0	3.0	CP

Fillers = Combined ground quartz and fine sand in mass ratio of 1 : 5; NC = sodium carbonate anhydrous; NŚ = sodium sulfate anhydrous; SF = silica fume; ZT5 = zeolite Type 5A; CTH = Calcined hydrotalcite; Hyp = Eucon Hydrapel 2.5; SEo = BFS from Seattle Plant, old batch; SEn = BFS from Seattle Plant, new batch; CP = BFS from Clark Pacific;

Table 3.14. Formulations for CSMA3 Series Waste Forms with Iodine Removed (wt%).

Grout ID	BFS Type	BFS	NC	NŚ	MgO	Sand	QZ	SF	ZT5	CTH	Hyp	AltLAW
CSMA3S1R1 [10]	SEo	31.48	0.79	1.78	1.55	32.50	6.50	2.00	-	2.69	0.18	20.53
CSMA3S1R3	SEn	29.33	0.73	1.46	1.47	32.50	6.50	4.11		2.93	0.88	20.09
CSMA3S1R4	CP	29.33	0.73	1.46	1.47	32.50	6.50	4.11	1.47	1.47	0.88	20.09
CSMP3S1R1	CP	48.08	1.20	2.40	2.40	-	-	6.73	1.44	3.37	1.44	32.93

SEo = BFS from Seattle Plant, old batch; SEn = BFS from Seattle Plant, new batch; CP = BFS from Clark Pacific; NC = sodium carbonate anhydrous; NŚ = sodium sulfate anhydrous; QZ = ground quartz; SF = silica fume; ZT5 = ground zeolite Type 5A; CTH = calcined hydrotalcite; Hyp = Eucon Hydrapel 2.5.

Table 3.15. Recipes for CSMA3 Series Formulations with Iodine Removed.

Grout ID		CSMA3S1R3	CSMA3S1R4	CSMP3S1R1
Variable	**Total Fillers**	39.0%	39.0%	0%
	BFS Source	SEn	CP	CP
Order	**Component**	**Mass in grams**		
5	Eucon Hydrapel 2.5	35.94	35.94	59.14
4	BFS	1197.88	1197.88	1971.28
4	Sika SC MgO	59.89	59.89	98.56
4	Calcined Hydrotalcite	119.79	59.89	137.99
4	Silica Fume	167.70	167.70	275.98
4	Ground Zeolite Type 5A	0.00	59.89	59.14
4	AGSCO Silica A-25	265.45	265.45	-
4	Yellow Sand, Air Dry	1327.26	1327.26	-
3	Moisture from Sand	15.93	15.93	-
2	Na_2CO_3 (99.8%)	29.96	29.96	49.30
2	Na_2SO_4 (99.8%)	59.91	59.91	98.59
1	AltLAW Simulant 5.6 M Na	820.30	820.30	1350.02
Total Batch		4100.00	4100.00	4100.00

SEn = BFS from Seattle Plant, new batch; CP = BFS from Clark Pacific

Table 3.16. Grout Formulating Parameters for NSAS Based Waste Forms with 3.5 M Na AltLAW Simulant and BFS CP.

Grout ID	AgZ	w/dm	Fillers in mix	Na_2O in NC	Na_2O in NŚ	MgO	SF	ZT5	CTH	AgZ	Hyp
				%BWOS							
CSMA8S2R10	Included.	0.45	39.0%	2.5	2.5	5.0	14.0	-	-	5.0	1.25
CSMP8S2R2		0.45	0%	2.5	2.5	5.0	14.0	-	-	5.0	1.25
CSMP3S1R2	Removed	0.425	0%	2.5	2.5	5.0	14.0	3.0	7.0	-	3.0

Fillers = Combined ground quartz and fine sand in mass ratio of 1 : 5; NC = sodium carbonate anhydrous; NŚ = sodium sulfate anhydrous; SF = silica fume; ZT5 = zeolite Type 5A; CTH = Calcined hydrotalcite; AgZ = Ionex Ag-400; Hyp = Eucon Hydrapel 2.5.

Table 3.17. Formulations for NSAS Waste Forms with 3.5 M Na AltLAW Simulant and BFS CP (wt%).

Grout ID	BFS	NC	NŚ	MgO	Sand	QZ	SF	ZT5	CTH	AgZ	Hyp	AltLAW
CSMA8S2R10	31.00	0.98	1.63	1.55	32.50	6.50	4.34	-	-	1.55	0.39	19.56
CSMP8S2R2	50.82	1.61	2.68	2.54	-	-	7.11	-	-	2.54	0.64	32.06
CSMP3S1R2	49.75	1.60	2.63	2.49	-	-	6.96	1.49	3.48	-	1.49	30.10

NC = sodium carbonate anhydrous; NŚ = sodium sulfate anhydrous; QZ = ground quartz; SF = silica fume; ZT5 = ground zeolite Type 5A; CTH = calcined hydrotalcite; AgZ = Ionex Ag-400; Hyp = Eucon Hydrapel 2.5.

Table 3.18. Recipes for NSAS Waste Forms with 3.5 M Na AltLAW Simulant.

Grout ID		**CSMA8S2R10**	**CSMP8S2R2**	**CSMP3S1R2**
Variable	**Fillers**	39.0%	0%	0%
	Formulation Type	CSMA8 Series		CSMA3 Series
Order	**Component**	**Mass in grams**		
6	Eucon Hydrapel 2.5	15.82	26.04	61.18
5	BFS CP	1265.88	2083.34	2039.38
5	Sika SC MgO	63.29	104.17	101.97
5	Calcined Hydrotalcite	-	-	142.76
5	Silica Fume	177.22	291.67	285.51
5	Ground Zeolite Type 5A	-	-	61.18
5	AGSCO Silica A-25	265.45	-	-
5	Yellow Sand, Air Dry	1327.25	-	-
4	Moisture from Sand	15.93	-	-
3	Na_2CO_3 (99.8%)	40.24	66.23	65.75
3	Na_2SO_4 (99.8%)	66.88	110.07	108.13
2	Ground Ionex Ag-400	63.29	104.17	-
1	AltLAW Simulant 3.5 M Na	798.73	1314.32	1234.14
	Total Batch	4100.00	4100.00	4100.00

CP = BFS from Clark Pacific.

Table 3.19. Waste Form Formulations Developed during Respective Testing Phases.

Testing Phase	Grout I.D.	Key Variable	w/dm	BFS Type	By Weight of Slag					Fillers in mix	AgZ
					SF	Hyp	AgZ	CTH	ZT5		
FY23	CSMA8S2 [10]	Reference formulation	0.45	SEo	6%	0.75%	5.0%	-	-	39.0%	Included
Phase 1	CSMA8S2R5	BFS Type	0.45	CP	6%	0.75%	5.0%	-	-	39.0%	Included
	CSMA8S2R6	BFS Type	0.45	DS	6%	0.75%	5.0%	-	-	39.0%	Included
	CSMA8S2R13	BFS Type	0.45	DMI	6%	0.75%	5.0%	-	-	39.0%	Included
	CSMA8S2R4	SF, Hyp	0.45	SEn	10%	1.25%	5.0%	-	-	39.0%	Included
	CSMA8S2R3s	SF, Hyp	0.45	CP	14%	1.25%	5.0%	-	-	39.0%	Included
	CSMA8S2R3c	SF, Hyp	0.425	CP	14%	3.00%	5.0%	-	-	39.0%	Included
	CSMA8S2R8	Optimal: w/dm	0.50	CP	14%	1.25%	5.9%	-	-	39.0%	Included
	CSMA8S2R11a	Optimal: Fillers	0.425	CP	14%	1.25%	5.0%	-	-	27.5%	Included
	CSMA8S2R11b	Optimal: Fillers	0.425	CP	14%	2.50%	5.0%	-	-	0%	Included
FY23	CSMA3S1R1 [10]	Reference formulation	0.425	SEo	6%	0.575%	-	8.60%	-	39.0%	Removed
Phase 2a	CSMA8S2R12a	Optimal: ZT5/BFS Type	0.425	SEo	14%	2.50%	-	-	5.00%	39.0%	Removed
	CSMA8S2R12d	Optimal: ZT5/BFS Type	0.45	SEo	14%	1.25%	-	-	5.00%	0%	Removed
	CSMA8S2R12c	Optimal: ZT5/BFS Type	0.45	CP	14%	1.25%	-	-	-	0%	Removed
	CSMA8S2R12f	Optimal: BFS Type	0.45	DS	14%	1.25%	-	-	-	27.5%	Removed
	CSMA8S2R12e	Optimal: BFS Type	0.45	DS	14%	1.25%	-	-	-	0%	Removed
Phase 2b	CSMA3S1R3	SF, Hyp, ZT5	0.425	SEn	14%	3.00%	-	10.00%	-	39.0%	Removed
	CSMA3S1R4	SF, Hyp, ZT5	0.425	CP	14%	3.00%	-	5.00%	5.00%	39.0%	Removed
	CSMP3S1R1	Fillers	0.425	CP	14%	3.00%	-	7.00%	3.00%	0%	Removed
Phase 2c	CSMA8S2R10	Optimal: 3.5M Na	0.45	CP	14%	1.25%	5.0%	-	-	39.0%	Included
	CSMP8S2R2	Optimal: 3.5M Na	0.45	CP	14%	1.25%	5.0%	-	-	0%	Included
	CSMP3S1R2	Optimal: 3.5M Na	0.425	CP	14%	3.00%	-	7.00%	3.00%	0%	Removed
Phase 3	CSMA8S2R3s	Rheology/dry porosity	0.45	CP	14%	1.25%	5.0%	-	-	39.0%	Included
	CSMA8S2R8	Rheology/dry porosity	0.50	CP	14%	1.25%	5.9%	-	-	39.0%	Included
	CSMA8S2R11a	Rheology/dry porosity	0.425	CP	14%	1.25%	5.0%	-	-	27.5%	Included
	CSMA8S2R11b	Rheology/dry porosity	0.425	CP	14%	2.50%	5.0%	-	-	0%	Included
	CSMA8S2R12a	Rheology/dry porosity	0.425	SEo	14%	2.50%	-	-	5.00%	39.0%	Removed
	CSMA8S2R12f	Rheology/dry porosity	0.45	DS	14%	1.25%	-	-	-	27.5%	Removed
	CSMA8S2R12d	Rheology/dry porosity	0.45	SEo	14%	1.25%	-	-	5.00%	0%	Removed
	CSMA3S1R3	Rheology/dry porosity	0.425	SEn	14%	3.00%	-	10.00%	-	39.0%	Removed
	CSMP3S1R2	Rheology/dry porosity	0.425	CP	14%	3.00%	-	7.00%	3.00%	0%	Removed

SEo = BFS from Seattle Plant, old batch; SEn = BFS from Seattle Plant, new batch; CP = BFS from Clark Pacific; DS = Duraslag from Ash Grove Cement; DMI = Diversified Minerals Inc.; SF = silica fume; AgZ = Ionex Ag-400; ZT5 = zeolite Type 5A; CTH = calcined hydrotalcite; Hyp = Eucon Hydrapel 2.5.

Table 4.1. Water Drop Qualitative Test Results for Hydrophobicity.

Grout I.D.	BFS Type	AgZ	Hyp %BWOS	Hyp %BWOTS*	Water Drop Testing	Hydro-phobicity
CSMA8S2R5	CP	Included	0.75	0.31	Flat water drop, wet surface	Some
CSMA8S2R6	DS	Included	0.75	0.31	Flat water drop, wet surface	Some
CSMA8S2R13	DMI	Included	0.75	0.31	Flat water drop, wet surface	Some
CSMA8S2R4	SEn	Included	1.25	0.51	Spherical water drop, dry surface	Super
CSMA8S2R3s	CP	Included	1.25	0.49	Spherical water drop, dry surface	Super
CSMA8S2R3c	CP	Included	3.00	1.19	Spherical water drop, dry surface	Super
CSMA8S2R8	CP	Included	1.25	0.48	Spherical water drop, dry surface	Super
CSMA8S2R11a	CP	Included	1.25	0.62	Spherical water drop, dry surface	Super
CSMA8S2R11b	CP	Included	2.50	2.02	Spherical water drop, dry surface	Super
CSMA8S2R12a	SEo	Removed	2.50	0.99	Spherical water drop, dry surface	Super
CSMA8S2R12c	CP	Removed	1.25	1.01	Spherical water drop, dry surface	Super
CSMA8S2R12d	SEo	Removed	1.25	1.01	Spherical water drop, dry surface	Super
CSMA8S2R12e	DS	Removed	1.25	1.01	Spherical water drop, dry surface	Super
CSMA8S2R12f	DS	Removed	1.25	0.62	Spherical water drop, dry surface	Super
CSMA3S1R3	SEn	Removed	3.00	1.15	Spherical water drop, dry surface	Super
CSMA3S1R4	CP	Removed	3.00	1.15	Spherical water drop, dry surface	Super
CSMP3S1R1	CP	Removed	3.00	2.33	Spherical water drop, dry surface	Super
CSMA8S2R10	CP	Included	1.25	0.50	Spherical water drop, dry surface	Super
CSMP8S2R2	CP	Included	1.25	1.01	Spherical water drop, dry surface	Super
CSMP3S1R2	CP	Removed	3.00	2.33	Spherical water drop, dry surface	Super

* By weight of total solids. Total solids included blast furnace slag, zeolite, silica fume, MgO, sand, and ground quartz. CP = BFS from Clark Pacific; DS = Duraslag from Ash Grove Cement; DMI = Diversified Minerals Inc; SEo = BFS from Seattle Plant, old batch; SEn = BFS from Seattle Plant, new batch; Hyp = Hydrapel 2.5.

Table 5.1. Target and Measured Concentrations of Na, Cr, and NO_3^- in AltLAW Simulant 5.6 M Na (mg/L).

Species	Target	Measured	%Dev
Sodium	129323	127140	-1.69
Chromium	1252	1135.5	-9.31
Rhenium	350	341.75	-2.36
Nitrate	112502	120396	+7.02
Nitrite	29112	29976	+2.97
Iodine	150	ND	NC

.

Table 5.2. XRF Analyzed Compositions of Blast Furnace Slags.

-	BFS DMI	BFS DS	BFS CP	BFS SEo	BFS SEn
$(MgO+Al_2O_3)/SiO_2$	1.01	0.78	0.60	0.53	0.53
Al_2O_3	16.82	15.64	12.30	12.19	13.08
BaO	-	0.05	-	-	0.09
CaO	35.62	36.16	41.71	43.11	40.50
Fe_2O_3	0.48	0.35	1.58	0.78	0.88
K_2O	0.29	0.40	0.32	0.53	0.54
MgO	11.54	9.22	6.88	4.85	4.92
MnO	0.33	0.33	0.16	0.15	0.14
Na_2O	0.47	0.47	0.22	0.24	0.40
P_2O_5	0.03	0.01	0.02	0.01	0.02
SiO_2	28.15	31.84	32.20	32.38	33.92
SO_3	4.20	4.39	4.03	5.03	4.75
SrO	0.05	0.07	0.06	0.06	0.07
TiO_2	1.91	0.95	0.47	0.51	0.54
ZrO_2	0.05	0.04	0.03	0.04	0.04
Others	0.09	0.08	0.03	0.11	0.12
Sum*	100.00	100.00	100.00	100.00	100.00

* LOI is not included.

DMI = Diversified Minerals Inc.; DS = Duraslag from Ash Grove Cement; CP = BFS from Clark Pacific; SEo = BFS from Seattle Plant, old batch; SEn = BFS from Seattle Plant, new batch

Table 5.3. XRF Analyzed Compositions of Ionex Ag-400 and Zeolite Type A.

Oxide	**Ionex Ag400 B3**	**Ionex Ag400 B3**	**Zeolite Type 5A**
	Old batch	New batch	
Ag_2O	40.76	40.29	0.01
Al_2O_3	21.01	21.17	29.69
BaO	-	0.02	0.09
CaO	0.39	0.27	12.73
Fe_2O_3	0.40	0.37	1.14
K_2O	0.08	0.11	0.61
MgO	1.33	0.84	3.12
Na_2O	0.13	0.20	4.42
P_2O_5	0.15	0.07	0.04
SiO_2	35.65	36.59	47.91
SO_3	0.01	0.01	0.01
TiO_2	0.06	0.05	0.15
Others	0.03	0.02	0.04
Sum*	100.00	100.00	100.00

* LOI is not included

Table 5.4. Summary of Fresh and Cured Properties of Waste Forms, AgZ Included (Phase 1a).

Grout I.D.	**Formulating Parameters (SF/Hyp/w/dm/M or P/Fillers)**	**BFS Source**	**24 h Bleed**	**Set Time**	**Compressive Strength (psi)**	
					7d	28d
CSMA8S2 [10]	Reference A8 Series	SEo	0%	30-48 h	<500	6449
CSMA8S2R5	Reference A8 Series	CP	0%	19.1 h	6970	8508
CSMA8S2R6	Reference A8 Series	DS	0%	~5d	5297	10528
CSMA8S2R13	Reference A8 Series	DMI	0%	26.0 h	2973	7600
CSMA8S2R4	SF10%/Hyp1.25%/0.45/M	SEn	0%	43.8 h	5479	8187
CSMA8S2R3s	SF14%/Hyp1.25%/0.45/M	CP	0%	11.7 h	7861	9530
CSMA8S2R3c	SF14%/Hyp3%/0.425/M	CP	0%	18.1 h	7515	9607
CSMA8S2R8	SF14%/Hyp1.25%/0.50/M	CP	0%	16.0 h	7023	9030
CSMA8S2R11a	SF14%/Hyp1.25%/0.425/Fillers27.5%	CP	0%	20.9 h	8907	10823
CSMA8S2R11b	SF14%/Hyp2.5%/0.425/P	CP	0%	16.7 h	8239	8972

M = Mortar type waste form; P = Paste type waste form; SEo = BFS from Seattle Plant, old batch; DS = Duraslag from Ash Grove Cement; DMI = Diversified Minerals Inc.; SEn = BFS from Seattle Plant, new batch; CP = BFS from Clark Pacific; SF = silica fume; Hyp = Hydrapel 2.5.; Fillers = combined ground quartz and fine sand in mass ratio of 1:5.

Table 5.5. Summary of Results of EPA 1315 Leaching Tests (Phase 1).

Grout I.D. (BFS)	Set Time	Compressive Strength (psi)		Days Leached	Leachability Index					
		7d	28d		Na	Re	Cr	I	NO_3^-	NO_2^-
CSMA8S2 (SEo)[$]	30-48 h	<500	6449	28d	8.40	8.62	11.33	10.55	8.39	8.37
				63d	8.67	8.90	11.90	10.55	8.79	8.69
CSMA8S2R5 (CP)	19.1 h	6970	8508	28d	8.59	8.79	12.41	10.39	8.56	8.58
				63d	8.69	8.98	12.46	11.20	8.78	8.75
CSMA8S2R6 (DS)	~5 d	5297	10528	28d	8.54	10.60	13.11	8.74	8.61	8.52
				63d	8.75	12.30	13.41	8.86	8.58	8.54
CSMA8S2R13 (DMI)	26.0 h	2973	7600	28d	7.61	7.46	12.47	8.11	7.33	7.35
				49d	7.44	7.40	12.35	7.94	7.40	7.40
CSMA8S2R4 (SEn)	43.8 h	5479	8187	28d	8.61	8.68	13.59	10.16	8.56	8.53
				63d	8.97	8.87	13.41	10.47	8.73	8.71
CSMA8S2R3s (CP)	11.7 h	7861	9530	28d	8.83	8.73	12.90	11.97	8.68	8.63
				63d	9.06	8.88	13.42	11.94	8.76	8.68
CSMA8S2R3c (CP)	18.1 h	7515	9607	28d	9.00	8.93	13.56	11.88	8.79	8.76
				63d	9.07	8.99	13.38	12.29	8.88	8.87
CSMA8S2R8 (CP)	16.0 h	7023	9030	28d	9.02	8.96	13.44	12.47	8.77	8.73
				63d	9.02	8.98	13.01	12.22	8.89	8.97
CSMA8S2R11a (CP)	20.9 h	8907	10823	28d	8.84	8.82	13.23	12.40	8.71	8.73
				63d	9.13	8.92	13.09	12.49	8.84	8.83
CSMA8S2R11b (CP)	16.7 h	8239	8972	28d	8.93	8.79	14.18	12.97	8.66	8.65
				63d	8.97	8.86	13.49	14.30	8.78	8.78
Performance Metric				-	-	>10.7	>10.40	>10.52	>8.70	-

[$] Reference formulation [10]

SEo = BFS from Seattle Plant, old batch; CP = BFS from Clark Pacific; DS = Duraslag from Ash Grove Cement; DMI = Diversified Minerals Inc.; SEn = BFS from Seattle Plant, new batch.

Table 5.6. Sodium Leachability Indices for AltLAW Waste Forms (Phase 1).

Leach Time, days	Leach Time, hrs	BFS Source			Silica Fume, Hydrapel 2.5, and w/dm				Fillers	
		CSMA 8S2R5	CSMA 8S2R6	CSMA8S 2R13	CSMA 8S2R4	CSMA8 S2R3s	CSMA8 S2R3c	CSMA 8S2R8	CSMA8 S2R11a	CSMA8 S2R11b
0.08	2	7.99	7.60	7.22	8.02	8.42	8.60	8.03	8.20	8.30
1	24	8.32	7.87	7.33	8.30	8.47	8.49	8.42	8.43	8.56
2	48	8.42	8.04	7.40	8.30	8.62	8.53	8.47	8.57	8.60
7	168	8.60	8.35	7.53	8.51	8.81	8.70	8.64	8.72	8.63
14	336	8.61	8.52	7.48	8.61	8.80	8.80	8.77	8.93	8.86
28	672	8.59	8.54	7.61	8.61	8.83	9.00	9.02	8.84	8.93
42	1008	8.61	8.53	7.49	8.73	8.90	9.03	9.15	9.00	9.02
49	1176	8.65	8.55	7.44	8.72	8.89	9.14	9.16	8.96	8.89
63	1512	8.69	8.75	ND	8.97	9.06	9.03	9.02	9.13	8.97

ND: Not determined as the testing ceased at 49 days

Table 5.7. Rhenium Leachability Indices for AltLAW Waste Forms (Phase 1).

Leach Time, days	**Leach Time, hrs**	**BFS Source**			**Silica Fume, Hydrapel 2.5, and w/dm**				**Fillers**	
		CSMA 8S2R5	CSMA 8S2R6	CSMA8S 2R13	CSMA 8S2R4	CSMA8 S2R3s	CSMA8 S2R3c	CSMA 8S2R8	CSMA8 S2R11a	CSMA8 S2R11b
0.08	2	8.13	7.53	7.09	7.87	8.37	8.44	8.03	8.11	8.36
1	24	8.46	7.95	7.22	8.22	8.43	8.42	8.57	8.40	8.55
2	48	8.57	8.25	7.24	8.15	8.57	8.44	8.58	8.55	8.54
7	168	8.70	8.84	7.43	8.38	8.74	8.66	8.71	8.64	8.66
14	336	8.76	9.57	7.39	8.58	8.73	8.80	8.73	8.77	8.76
28	672	8.79	10.60	7.46	8.68	8.73	8.93	8.96	8.82	8.79
42	1008	8.76	11.90	7.47	8.77	8.83	8.94	9.02	8.87	8.83
49	1176	8.94	12.14	7.40	8.75	8.92	8.99	9.11	8.87	8.95
63	1512	8.98	12.30	ND	8.87	8.88	9.07	8.98	8.92	8.86

ND: Not determined as the testing ceased at 49 days

Table 5.8. Chromium Leachability Indices for AltLAW Waste Forms (Phase 1).

Leach Time, days	**Leach Time, hrs**	**BFS Source**			**Silica Fume, Hydrapel 2.5, and w/dm**				**Fillers**	
		CSMA 8S2R5	CSMA 8S2R6	CSMA8S 2R13	CSMA 8S2R4	CSMA8 S2R3s	CSMA8 S2R3c	CSMA 8S2R8	CSMA8 S2R11a	CSMA8 S2R11b
0.08	2	10.52	11.65	9.71	10.99	11.79	11.40	11.38	11.17	11.51
1	24	10.74	12.56	10.58	11.77	11.72	11.53	11.81	11.38	12.37
2	48	11.40	12.70	11.20	12.10	12.26	12.07	12.49	12.08	13.03
7	168	11.99	13.39	12.15	13.20	12.92	12.66	13.09	12.72	13.38
14	336	12.24	13.10	11.80	13.29	12.95	13.07	13.14	13.06	13.63
28	672	12.41	13.11	12.47	13.59	12.90	13.56	13.44	13.23	14.18
42	1008	12.24	12.88	12.66	13.97	12.89	13.58	13.21	13.74	13.51
49	1176	12.35	12.89	12.35	12.89	12.90	13.22	13.29	13.37	13.58
63	1512	12.46	13.41	ND	13.41	13.42	13.38	13.01	13.09	13.49

ND: Not determined as the testing ceased at 49 days

Table 5.9. Iodine Leachability Indices for AltLAW Waste Forms (Phase 1).

Leach Time, days	**Leach Time, hrs**	**BFS Type**			**Silica Fume, Hydrapel 2.5, and w/dm**				**Fillers**	
		CSMA 8S2R5	CSMA 8S2R6	CSMA8S 2R13	CSMA 8S2R4	CSMA8 S2R3s	CSMA8 S2R3c	CSMA 8S2R8	CSMA8 S2R11a	CSMA8 S2R11b
0.08	2	8.96	7.82	8.40	8.98	9.97	9.66	10.22	9.64	9.65
1	24	9.11	7.85	8.11	9.23	9.62	9.58	10.11	9.79	9.80
2	48	9.43	7.93	7.88	8.87	9.25	9.75	10.62	10.14	10.01
7	168	9.86	8.37	8.13	9.35	10.54	10.34	11.96	10.74	10.97
14	336	10.31	8.53	8.05	9.84	10.92	11.01	13.17	11.52	12.01
28	672	10.39	8.74	8.11	10.16	11.97	11.88	12.47	12.40	12.97
42	1008	11.43	8.74	8.22	10.40	11.96	12.22	12.53	12.69	13.24
49	1176	11.16	8.67	7.94	10.10	11.62	11.88	12.07	12.15	12.43
63	1512	11.20	8.86	ND	10.47	11.94	12.29	12.22	12.49	14.30

ND: Not determined as the testing ceased at 49 days

Table 5.10. Nitrate Leachability Indices for AltLAW Waste Forms (Phase 1).

Leach Time, days	**Leach Time, hrs**	**BFS Type**			**Silica Fume, Hydrapel 2.5, and w/dm**				**Fillers**	
		CSMA 8S2R5	CSMA 8S2R6	CSMA8S 2R13	CSMA 8S2R4	CSMA8 S2R3s	CSMA8 S2R3c	CSMA 8S2R8	CSMA8 S2R11a	CSMA8 S2R11b
0.08	2	7.90	7.41	7.00	7.73	8.12	8.33	7.83	7.98	8.21
1	24	8.29	7.81	7.10	8.14	8.29	8.35	8.34	8.33	8.43
2	48	8.35	7.96	7.14	8.09	8.39	8.39	8.41	8.45	8.43
7	168	8.51	8.37	7.28	8.32	8.99	8.56	8.54	8.54	8.51
14	336	8.56	8.49	7.28	8.47	8.64	8.73	8.67	8.69	8.63
28	672	8.56	8.61	7.33	8.56	8.68	8.79	8.77	8.71	8.66
42	1008	8.65	8.61	7.39	8.66	8.77	8.82	8.90	8.75	8.75
49	1176	8.76	8.61	7.40	8.69	8.84	8.92	8.88	8.75	8.71
63	1512	8.78	8.58	ND	8.73	8.76	8.88	8.89	8.84	8.78

ND: Not determined as the testing ceased at 49 days

Table 5.11. Nitrite Leachability Indices for AltLAW Waste Forms (Phase 1).

Leach Time, days	**Leach Time, hrs**	**BFS Source**			**Silica Fume, Hydrapel 2.5, and w/dm**				**Fillers**	
		CSMA 8S2R5	CSMA 8S2R6	CSMA8S 2R13	CSMA 8S2R4	CSMA8 S2R3s	CSMA8 S2R3c	CSMA 8S2R8	CSMA8 S2R11a	CSMA8 S2R11b
0.08	2	7.89	7.44	6.99	7.74	8.20	8.16	7.75	8.11	8.16
1	24	8.29	7.77	7.06	8.15	8.29	8.25	8.31	8.32	8.43
2	48	8.37	7.97	7.13	8.11	8.44	8.40	8.29	8.39	8.40
7	168	8.53	8.26	7.26	8.28	8.98	8.95	8.50	8.52	8.51
14	336	8.57	8.45	7.28	8.49	8.65	8.61	8.64	8.64	8.63
28	672	8.58	8.52	7.35	8.53	8.63	8.76	8.73	8.73	8.65
42	1008	8.59	8.52	7.34	8.63	8.69	8.81	8.83	8.73	8.74
49	1176	8.64	8.54	7.40	8.65	8.76	8.83	8.79	8.67	8.70
63	1512	8.75	8.54	ND	8.71	8.68	8.87	8.97	8.83	8.78

ND: Not determined as the testing ceased at 49 days

Table 5.12. Summary of Fresh and Cured Properties of Waste Forms Based on CSMA8 and CSMA3 Series Formulations with Iodine Removed (Phases 2a and 2b).

Grout I.D.	**Formulating Parameters (SF/Hyp/ZT/CTH/w/dm/M or P/Fillers)**	**BFS Type**	**24 h Bleed**	**Set Time**	**Compressive Strength (psi)**	
					7d	28d
CSMA8S2R12a	SF14%/Hyp2.5%/ZT5%/0.425/M	SEo	0%	~46 h	5155	8511
CSMA8S2R12d	SF14%/Hyp1.25%/ZT5%/0.45/P	SEo	0%	27.5 h	4407	6967
CSMA8S2R12c	SF14%/Hyp1.25%/ZT5%/0.45/P	CP	0%	8.7 h	6628	7107
CSMA8S2R12f	9SF14%/Hyp1.25%/0.45/Fillers27.5%	DS	0%	~36 h	6643	9151
CSMA8S2R12e	SF14%/Hyp1.25%/0.45/P	DS	0%	39.4 h	4350	6533
CSMA3S1R1 [10]	Reference CSMA3 Series	SEo	0%	28.1 h	6460	10028
CSMA3S1R3	SF14%/Hyp3%/CTH10%/0.425/M	SEn	0%	25.3 h	6409	9039
CSMA3S1R4	SF14%/Hyp3%/ZT5%/CTH5%/0.425/M	CP	0%	10.8 h	7883	9440
CSMP3S1R1	SF14%/Hyp3%/ZT3%/CTH7%0.425/P	CP	0%	4.7 h	6476	8233

SF = silica fume; Hyp = Hydrapel 2.5; ZT = zeolite Type 5; CTH = calcined hydrotalcite; Fillers = combined ground quartz and fine sand in mass ratio of 1 : 5; M = Mortar type waste form; P = Paste type waste form; SEo = BFS from Seattle Plant, old batch; CP = BFS from Clark Pacific; DS = Duraslag from Ash Grove Cement; SEn = BFS from Seattle Plant, new batch.

Table 5.13. Summary of Results of Leaching Tests with Iodine Removed (Phases 2a and 2b).

Grout I.D. (BFS)	Set Time	Compressive Strength (psi)		Days Leached	Leachability Index					
		7d	28d		Na	Re	Cr	I	NO_3^-	NO_2^-
CSMA3S1R1 [SEo]$	28.1h	6460	10028	28d	8.60	10.69	13.32	13.22	8.61	8.60
				63d	8.83	11.55	13.74	13.19	8.73	8.76
CSMA8S2R12a (SEo)	~46 h	5155	8511	28d	8.97	10.54	13.55	13.04	8.80	8.78
				63d	9.29	12.33*	13.36	12.50*	9.06	9.12
CSMA8S2R12d (SEo)	27.5 h	4407	6967	28d	8.87	9.87	13.46	12.42	8.56	8.54
				63d	8.91	9.97*	13.16	12.55	8.66	8.74
CSMA8S2R12c (CP)	8.7 h	6628	7107	28d	8.84	9.95	13.95	13.51	8.63	8.62
				63d	9.03	9.88	13.52	12.98	8.61	8.59
CSMA8S2R12f (DS)	~36 h	6643	9151	28d	8.63	12.12	14.92	12.44	8.46	8.36
				49d	8.67	12.26	13.37	11.99	8.52	8.57
CSMA8S2R12e (DS)	39.4 h	4350	6533	28d	8.40	10.67	13.60	12.36	8.18	8.12
				63d	8.59	11.53	13.16	12.52	8.27	8.34
CSMA3S1R3 (SEo)	25.3 h	6409	9039	28d	8.86	10.61	14.16	12.55	8.73	8.69
				63d	9.07	11.31	13.12	12.14	8.82	8.86
CSMA3S1R4 (CP)	10.8 h	7883	9440	28d	8.98	9.44	14.15	13.02	8.77	8.74
				63d	9.07	10.03	>13.72	12.37	8.88	8.89
CSMP3S1R1 (CP)	4.7 h	6474	8233	28d	8.77	9.88	14.17	15.21	8.67	8.65
				64d	9.05	10.27	14.14	13.06	8.70*	8.69*
Performance Metric				-	-	>10.7	>10.40	>10.52	>8.70	-

* Steady state value for better representation as data scattered toward end of the leaching procedure.

$ Reference formulation [10]

SEo = BFS from Seattle Plant, old batch; CP = BFS from Clark Pacific; DS = Duraslag from Ash Grove Cement.

Table 5.14. Sodium Leachability Indices for AltLAW Waste Forms with Iodine Removed (Phases 2a and 2b).

Leach Time, days	Leach Time, hrs	CSMA8 Series					CSMA3 Series		
		CSMA8 S2R12a	CSMA8 S2R12d	CSMA8 S2R12c	CSMA8 S2R12f	CSMA8 S2R12e	CSMA3 S1R3	CSMA3 S1R4	CSMP3S 1R1
0.08	2	CSMA8	CSMA8	CSMA8	CSMA8	CSMA8	7.97	8.35	8.62
1	24	7.99	8.04	8.39	7.92	7.80	8.15	8.42	8.56
2	48	8.12	8.16	8.35	8.12	7.98	8.35	8.46	8.79
7	168	8.31	8.23	8.42	8.21	8.13	8.55	8.67	8.61
14	336	8.40	8.54	8.56	8.22	8.19	8.70	8.90	8.88
28	672	8.59	8.62	8.66	8.59	8.62	8.86	8.98	8.77
42	1008	8.97	8.87	8.84	8.63	8.40	8.96	9.16	8.98
49	1176	9.02	8.92	8.82	8.73	8.53	8.89	8.91	8.89
63	1512	9.05	8.97	8.99	8.67	8.62	9.07	9.07	9.05

Table 5.15. Rhenium Leachability Indices for AltLAW Waste Forms with Iodine Removed (Phases 2a and 2b).

Leach Time, days	**Leach Time, hrs**	**CSMA8 Series**					**CSMA3 Series**		
		CSMA8 S2R12a	CSMA8 S2R12d	CSMA8 S2R12c	CSMA8 S2R12f	CSMA8 S2R12e	CSMA3 S1R3	CSMA3 S1R4	CSMP3S 1R1
0.08	2	8.06	8.11	8.57	8.53	8.17	8.04	8.39	8.78
1	24	8.33	8.40	8.50	8.91	8.44	8.29	8.46	8.70
2	48	8.79	8.67	8.64	9.95	9.00	8.64	8.56	8.87
7	168	9.21	9.23	9.01	10.97	9.49	9.20	8.81	9.04
14	336	9.84	9.77	9.53	11.43	12.05	9.85	9.13	9.44
28	672	10.54	9.87	9.95	12.12	10.67	10.61	9.44	9.88
42	1008	13.42	10.04	10.37	12.19	11.13	11.13	9.58	10.11
49	1176	12.70	10.11	9.97	12.26	11.29	12.70	9.69	10.14
63	1512	10.86	9.76	9.88	ND	11.53	11.31	10.03	10.27*

ND: Not determined; * 64 days

Table 5.16. Chromium Leachability Indices for AltLAW Waste Forms with Iodine Removed (Phases 2a and 2b).

Leach Time, days	**Leach Time, hrs**	**CSMA8 Series**					**CSMA3 Series**		
		CSMA8 S2R12a	CSMA8 S2R12d	CSMA8 S2R12c	CSMA8 S2R12f	CSMA8 S2R12e	CSMA3 S1R3	CSMA3 S1R4	CSMP3S 1R1
0.08	2	12.69	13.09	13.10	12.86	13.09	12.70	12.69	13.06
1	24	13.48	13.52	13.88	13.64	13.87	13.48	13.12	13.85
2	48	13.01	13.41	13.41	12.57	13.40	13.01	13.01	13.38
7	168	13.95	13.40	14.36	13.52	13.26	13.36	13.16	14.32
14	336	13.85	13.16	14.26	13.22	13.45	13.86	13.85	14.22
28	672	13.55	13.46	13.95	14.92	13.60	14.16	14.15	14.17
42	1008	13.32	13.53	13.97	13.49	13.97	13.32	13.32	14.29
49	1176	13.20	13.60	13.61	13.37	13.60	13.21	13.20	13.22
63	1512	13.36	13.16	13.52	ND	13.16	13.12	13.72	14.14*

ND: Not determined; * 64 days

Table 5.17. Iodine Leachability Indices for AltLAW Waste Forms with Iodine Removed (Phases 2a and 2b).

Leach Time, days	**Leach Time, hrs**	**CSMA8 Series**					**CSMA3 Series**		
		CSMA8 S2R12a	CSMA8 S2R12d	CSMA8 S2R12c	CSMA8 S2R12f	CSMA8 S2R12e	CSMA3 S1R3	CSMA3 S1R4	CSMP3S 1R1
0.08	2	10.11	12.19	11.39	13.51	12.52	12.26	12.71	11.88
1	24	10.82	12.47	13.41	14.29	12.77	12.48	13.33	12.91
2	48	11.56	12.35	12.51	13.82	12.72	12.34	13.52	12.65
7	168	12.39	12.93	13.54	14.77	14.75	12.40	13.68	12.52
14	336	11.38	13.75	12.49	11.98	13.34	12.04	13.58	13.81
28	672	13.04	12.42	13.51	12.44	12.36	12.55	13.02	15.21
42	1008	13.27	12.21	15.09	12.42	12.49	12.67	13.58	12.81
49	1176	12.45	12.38	12.54	11.99	12.24	12.24	12.49	12.71
63	1512	11.79	12.55	12.98	ND	12.52	12.26	12.37	13.06*

ND: Not determined; * 64 days

Table 5.18. Nitrate Leachability Indices for AltLAW Waste Forms with Iodine Removed (Phases 2a and 2b).

Leach Time, days	**Leach Time, hrs**	**CSMA8 Series**					**CSMA3 Series**		
		CSMA8 S2R12a	CSMA8 S2R12d	CSMA8 S2R12c	CSMA8 S2R12f	CSMA8 S2R12e	CSMA3 S1R3	CSMA3 S1R4	CSMP3S 1R1
0.08	2	7.67	7.83	8.27	7.73	7.65	7.82	8.25	8.49
1	24	7.92	8.09	8.24	8.06	7.75	8.08	8.36	8.47
2	48	8.19	8.16	8.31	8.10	7.94	8.19	8.42	9.00
7	168	8.28	8.37	8.47	8.21	8.06	8.43	8.56	8.51
14	336	8.53	8.52	8.56	8.35	8.07	8.54	8.68	8.67
28	672	8.80	8.56	8.63	8.46	8.18	8.73	8.77	8.67
42	1008	8.93	8.67	8.67	8.59	8.28	8.86	8.88	8.67
49	1176	9.03	8.70	8.64	8.52	8.35	8.83	8.77	8.75
63	1512	9.06	8.66	8.61	ND	8.27	8.82	8.88	8.67*

ND: Not determined; * 64 days

Table 5.19. Nitrite Leachability Indices for AltLAW Waste Forms with Iodine Removed (Phases 2a and 2b).

Leach Time, days	Leach Time, hrs	CSMA8 Series					CSMA3 Series		
		CSMA8 S2R12a	CSMA8 S2R12d	CSMA8 S2R12c	CSMA8 S2R12f	CSMA8 S2R12e	CSMA3 S1R3	CSMA3 S1R4	CSMP3S 1R1
0.08	2	7.61	7.77	8.17	7.75	7.60	7.78	8.17	8.36
1	24	7.88	8.08	8.22	7.99	7.74	8.06	8.33	8.44
2	48	8.08	8.14	8.25	8.06	7.93	8.11	8.36	8.88
7	168	8.29	8.37	8.45	8.13	7.99	8.39	8.56	8.50
14	336	8.49	8.48	8.55	8.25	8.06	8.51	8.65	8.66
28	672	8.78	8.54	8.62	8.36	8.12	8.69	8.74	8.65
42	1008	8.95	8.58	8.65	8.52	8.17	8.80	8.89	8.72
49	1176	9.03	8.74	8.71	8.57	8.30	8.85	8.76	8.70
63	1512	9.12	8.74	8.59	ND	8.34	8.86	8.89	8.64*

ND: Not determined; * 64 days

Table 5.20. Summary of Fresh and Cured Properties of Waste Forms with 3.5 M Na AltLAW Simulant and BFS CP (Phase 2c).

Grout I.D.	Formulating Parameters (SF/Hyp/ZT/CTH/w/dm/M or P)	AgZ	24 h Bleed	Set Time	Compressive Strength (psi)	
					7d	28d
CSMA8S2R10	SF14%/Hyp1.25%/0.45/M	Included	0%	11.3 h	6585	8268
CSMP8S2R2	SF14%/Hyp1.25%/0.45/P	Included	0%	11.7 h	5955	7669
CSMP3S1R2	SF14%/Hyp3%,/ZT3%/CTH7%/0.425/P	Removed	0%	~5 h	6124	7209

SF = silica fume; Hyp = hydrapel 2.5; ZT = zeolite Type 5; CTH = calcined hydrotalcite; M = Mortar type waste form; P = Paste type waste form; AgZ = Ionex Ag-400.

Table 5.21. Summary of Results on Leaching Tests for AltLAW Waste Forms with 3.5 M Na AltLAW (Phase 2c).

Grout I.D.	Set time	Compressive Strength (psi)		Days Leached	Leachability Index					
		7d	28d		Na	Re	Cr	I	NO_3^-	NO_2^-
CSMA8S2R10	11.3 h	6585	8268	28d	8.88	8.90	11.88	13.75	8.80	8.78
				63d	9.29	9.07	12.81	12.49	8.92	8.88
CSMP8S2R2	11.7 h	5955	7669	28d	8.80	8.04	11.31	15.31	8.64	8.62
				63d	9.07	8.16	12.21	13.02	8.67	8.69
CSMP3S1R2	~5 h	6124	7209	28d	8.99	9.45	13.90	15.26	8.84	8.82
				63d	9.28	9.60	13.71	12.79	8.89	8.85
Performance Metric				-	-	>10.7	>10.40	>10.52	>8.70	-

Table 5.22. Sodium Leachability Indices for AltLAW Waste Forms with 3.5 M Na AltLAW (Phase 2c).

Leach Time, days	**Leach Time, hrs**	**CSMA8S2R10**	**CSMP8S2R2**	**CSMP3S1R2**
		AgZ Included, Mortar	AgZ Included, Paste	AgZ Removed; Paste
0.08	2	8.10	8.24	8.13
1	24	8.54	8.58	8.48
2	48	8.84	8.70	8.24
7	168	8.93	8.82	8.82
14	336	8.89	8.72	9.02
28	672	8.88	8.80	8.99
42	1008	9.10	9.01	9.14
49	1176	9.06	9.01	9.22
63	1512	9.29	9.07	9.28

Table 5.23. Rhenium Leachability Indices for AltLAW Waste Forms with 3.5 M Na AltLAW (Phase 2c).

Leach Time, days	**Leach Time, hrs**	**CSMA8S2R10**	**CSMP8S2R2**	**CSMP3S1R2**
		AgZ Included, Mortar	AgZ Included, Paste	AgZ Removed; Paste
0.08	2	8.03	7.57	8.33
1	24	8.65	7.88	8.69
2	48	8.77	7.94	8.65
7	168	8.89	8.03	9.18
14	336	8.97	8.03	9.38
28	672	8.90	8.04	9.45
42	1008	9.00	8.03	9.53
49	1176	9.02	8.09	9.56
63	1512	9.07	8.16	9.60

Table 5.24. Chromium Leachability Indices for AltLAW Waste Forms with 3.5 M Na AltLAW (Phase 2c).

Leach Time, days	**Leach Time, hrs**	**CSMA8S2R10**	**CSMP8S2R2**	**CSMP3S1R2**
		AgZ Included, Mortar	AgZ Included, Paste	AgZ Removed; Paste
0.08	2	10.28	10.17	12.24
1	24	10.61	10.09	12.02
2	48	10.86	10.28	13.35
7	168	11.12	10.63	13.70
14	336	11.54	10.94	13.85
28	672	11.88	11.31	13.90
42	1008	12.28	11.60	13.67
49	1176	12.90	11.85	13.55
63	1512	12.81	12.21	13.71

Table 5.25. Iodine Leachability Indices for AltLAW Waste Forms with 3.5 M Na AltLAW (Phase 2c).

Leach Time, days	**Leach Time, hrs**	**CSMA8S2R10**	**CSMP8S2R2**	**CSMP3S1R2**
		AgZ Included, Mortar	AgZ Included, Paste	AgZ Removed; Paste
0.08	2	9.51	11.31	12.24
1	24	10.01	10.97	13.13
2	48	10.59	11.44	12.55
7	168	11.71	12.88	13.58
14	336	12.21	13.08	13.92
28	672	13.75	15.31	15.26
42	1008	12.35	13.48	13.17
49	1176	12.01	12.39	13.03
63	1512	12.49	13.02	12.79

Table 5.26. Nitrate Leachability Indices for AltLAW Waste Forms with 3.5 M Na AltLAW (Phase 2c).

Leach Time, days	**Leach Time, hrs**	**CSMA8S2R10**	**CSMP8S2R2**	**CSMP3S1R2**
		AgZ Included, Mortar	AgZ Included, Paste	AgZ Removed; Paste
0.08	2	7.88	7.98	8.00
1	24	8.46	8.38	8.47
2	48	8.64	8.52	7.95
7	168	8.70	8.55	8.70
14	336	8.69	8.53	8.88
28	672	8.80	8.64	8.84
42	1008	8.92	8.69	8.89
49	1176	8.84	8.65	8.90
63	1512	8.92	8.67	8.89

Table 5.27. Nitrite Leachability Indices for AltLAW Waste Forms with 3.5 M Na AltLAW (Phase 2c).

Leach Time, days	**Leach Time, hrs**	**CSMA8S2R10**	**CSMP8S2R2**	**CSMP3S1R2**
		AgZ Included, Mortar	AgZ Included, Paste	AgZ Removed; Paste
0.08	2	7.82	7.91	7.89
1	24	8.42	8.38	8.41
2	48	8.51	8.45	7.89
7	168	8.64	8.53	8.68
14	336	8.66	8.53	8.85
28	672	8.78	8.62	8.82
42	1008	8.80	8.63	8.22
49	1176	8.75	8.53	8.93
63	1512	8.88	8.69	8.85

Table 5.28. Data Summary for Selected AltLAW Grout Formulations*.

Formulation ID	**Formulation Characteristics**	**w/dm**	**Set Time**	**Compressive Strength (psi)**		**Plastic Viscosity (cP)**	**Yield Stress (Pa)**
				7d	28d		
CSMA8S2R3s	AgZ incl., M, CP	0.45	11.7 h	7861	9530	1416	375.8
CSMA8S2R8	AgZ incl., M, CP	0.50	16.0 h	7023	9030	1022	431.2
CSMA8S2R11a	AgZ incl.; 27.5%Fillers, CP	0.425	20.9 h	8907	10823	714	456.1
CSMA8S2R11b	AgZ incl., P, CP	0.425	16.7 h	8239	8972	927	231.3
CSMA8S2R12a	AgZ remv., M, SEo	0.425	~46 h	5155	8511	2750	468.3
CSMA8S2R12d	AgZ remv., P, SEo	0.45	27.5 h	4407	6967	757	159.5
CSMA8S2R12c	AgZ remv., P, CP	0.45	8.7 h	6628	7107	1062	181.0
CSMA8S2R12f	AgZ remv., M, DS	0.45	~36 h	6643	9151	1069	270.7
CSMA3S1R3	AgZ remv., M, SEo	0.425	25.3 h	6409	9039	2308	274.3
CSMP3S1R2	AgZ remv., P, CP	0.425	~ 5 h	6124	7209	1197	413.3

* All grout samples prepared with 5.6 M Na AltLAW except for CSMP3S1R2, which was made with 3.5 M Na AltLAW

AgZ = Ionex Ag-400; M = Mortar type waste form; P = Paste type waste form; Fillers = combined ground quartz and fine sand in mass ratio of 1:5; CP = BFS from Clark Pacific; SEo = BFS from Seattle Plant, old batch; DS = Duraslag from Ash Grove Cement.

Table 5.29. Apparent Density, Matrix Skeletal Density, Porosity, and Particle Density of NSAS Based Grout Samples.

Sample ID	Formulation Characteristics	Apparent Density (g/cm^3)	Matrix Skeletal Density (g/cm^3)	Porosity	Particle Density (g/cm^3)
CSMA8S2R3s-1	5.6 M Na; 5% AgZ; w/dm = 0.45, Mortar; CP	2.10	1.76	0.27	2.41
CSMA8S2R3s-2		2.09	1.76	0.27	2.39
CSMA8S2R3s-3		2.08	1.75	0.26	2.37
Average		2.09	1.76	0.27	2.39
CSMA8S2R11a-1	5.6 M Na; 5% AgZ; w/dm = 0.425; Mortar, 27.5% Fillers; CP	2.07	1.69	0.30	2.42
CSMA8S2R11a-2		2.07	1.70	0.30	2.42
CSMA8S2R11a-3		2.05	1.69	0.29	2.38
Average		2.06	1.69	0.30	2.41
CSMA8S2R11b-1	5.6 M Na; 5% AgZ; w/dm = 0.425; Paste; CP	1.97	1.49	0.42	2.57
CSMA8S2R11b-2		1.96	1.48	0.41	2.50
CSMA8S2R11b-3		1.95	1.47	0.42	2.54
Average		1.96	1.48	0.42	2.54
CSMA8S2R8-1	5.6 M Na; 5% AgZ; w/dm = 0.50; Mortar; CP	2.06	1.70	0.28	2.37
CSMA8S2R8-2		2.04	1.70	0.28	2.34
CSMA8S2R8-3		2.05	1.70	0.28	2.36
Average		2.05	1.70	0.28	2.36
CSMA8S2R12a-1	5.6 M Na; AgZ removed; w/dm = 0.425; Mortar; SEo	2.08	1.75	0.26	2.37
CSMA8S2R12a-2		2.08	1.75	0.26	2.37
CSMA8S2R12a-3		2.08	1.75	0.26	2.37
Average		2.08	1.75	0.26	2.37
CSMA8S2R12d-1	5.6 M Na; AgZ removed; w/dm = 0.45; Paste; SEo	1.91	1.38	0.41	2.36
CSMA8S2R12d-2		1.89	1.38	0.41	2.32
CSMA8S2R12d-3		1.89	1.38	0.41	2.34
Average		1.90	1.38	0.41	2.34
CSMA3S1R3-1	5.6 M Na; AgZ removed; w/dm = 0.425; Mortar; SEo	2.11	1.80	0.25	2.39
CSMA3S1R3-2		2.10	1.79	0.24	2.37
CSMA3S1R3-3		2.09	1.79	0.24	2.35
Average		2.10	1.79	0.24	2.37
CSMP3S1R2-1	3.5 M Na; AgZ removed; w/dm = 0.425; Paste; CP	1.92	1.51	0.36	2.33
CSMP3S1R2-2		1.92	1.51	0.35	2.33
CSMP3S1R2-4		1.93	1.51	0.35	2.34
Average		1.92	1.51	0.35	2.34

AgZ = Ionex Ag-400; CP = BFS from Clark Pacific; SEo = BFS from Seattle Plant, old batch; Fillers = combined ground quartz and fine sand in mass ratio of 1 : 5.

Table 5.30. Recommended NSAS Based Waste Forms, Properties, and Leaching Performance.

Grout I.D (BFS)	**Set time**	**Compressive Strength (psi)**		**Leachability Index at 63 days**					
		7d	28d	**Na**	**Re**	**Cr**	**I**	**NO_3^-**	**NO_2^-**
CSMA8S2 [10]	30-48 h	<500	6449	8.67	8.90	11.90	10.55	8.79	8.69
CSMA8S2R11b (CP)	16.7 h	8239	8972	8.97	8.86	13.49	14.32	8.78	8.78
CSMA8S2R12a (SEo)	~46 h	5155	8511	9.29	12.33*	13.36	12.50*	9.06	9.12
CSMP3S1R2 (CP)	~5 h	6124	7209	9.28	9.60	13.71	12.79	8.89	8.85
CSMA3S1R3 (SEn)	25.3 h	6409	9039	9.07	11.31	13.12	12.14	8.82	8.86
CSMA8S2R12d (SEo)	27.5 h	4407	6967	8.91	9.97*	13.16	12.55	8.66	8.74
CSMP3S1R1 [10]	4.7 h	6474	8233	9.05	10.27	14.14	13.06	8.70*	8.69*
Performance Metric				-	>10.7	>10.52	>10.40	>8.70	-

* Steady state value

CP = BFS from Clark Pacific; SEo = BFS from Seattle Plant, old batch; SEn = BFS from Seattle Plant, new batch

Table 5.31. Heat Flow Data for Three AltLAW Grout Samples.

Grout ID (BFS)	**Dissolution Peak**		**Main Peaks Indicating Endothermic Reaction**	
	Time. Min, hrs	Heat Flow (mW/g)	Time, hrs	Heat Flow (mW/g)
CSMA8S2R11b (CP)	0.42	1.08	17.10	2.41
CSMA8S2R12a (SEo)	<0.18	>0.43	69.37	0.37
CSMP3S1R2 (CP)	0.10	16.46	10.37	1.71

Table 5.32. Heat Release and Compressive Strength Data for Four AltLAW Grout Samples.

Grout ID (BFS)	**Initial set time**	**Normalized Heat Release, J/g paste**				**Compressive Strength, psi**	
		6 hrs	12 hrs	24 hrs	7 days (168 hrs)	7 days	28 days
CSMA8S2R11b (CP)	16.7 hrs	5.18	8.35	72.44	107.12	8239	8972
CSMA8S2R12a (SEo)	46 hrs	1.45	2.23	3.30	55.21	5155	8511
CSMP3S1R2 (CP)	5 hrs	9.15	36.87	62.13	89.37	6124	7209

Table 5.33. TCLP Leachate Concentrations and Retention Factors for Selected AltLAW Grout Sampless (mg/L).

Grout ID (BFS)	Ag	As	Ba	Cd	Cr	Hg	Ni	Pb	Sb	Se	Tl
CSMA8S2R11b (CP)	0.153	0.009	0.359	0.001	<0.002	0.004	<0.001	0.019	0.006	0.092	0.013
Retention Factor	*	0.95	*	0.99	1.00	0.75	1.00	0.96	0.97	0.68	0.93
CSMA8S2R12a (SE)	0.185	0.006	0.381	0.001	<0.002	0.004	<0.001	0.012	0.053	0.087	0.008
Retention Factor	*	0.94	*	>0.99	1.00	0.58	1.00	1.00	0.96	0.95	0.93
CSMP3S1R2 (CP)	0.140	0.009	0.291	<0.001	<0.002	0.003	<0.001	0.020	0.006	0.099	0.005
Retention Factor	*	0.95	*	>0.99	1.00	0.80	1.00	0.96	0.98	0.64	0.97
EPA UTS Limit	0.14	5.0	21	0.11	0.60	0.025	11	0.75	1.15	5.7	0.20

* Negative value

Figure 4.1. Color change before and after reacting ground Ionex Ag-400 with AltLAW simulant for 2 hours (Left: Before; Right: After).

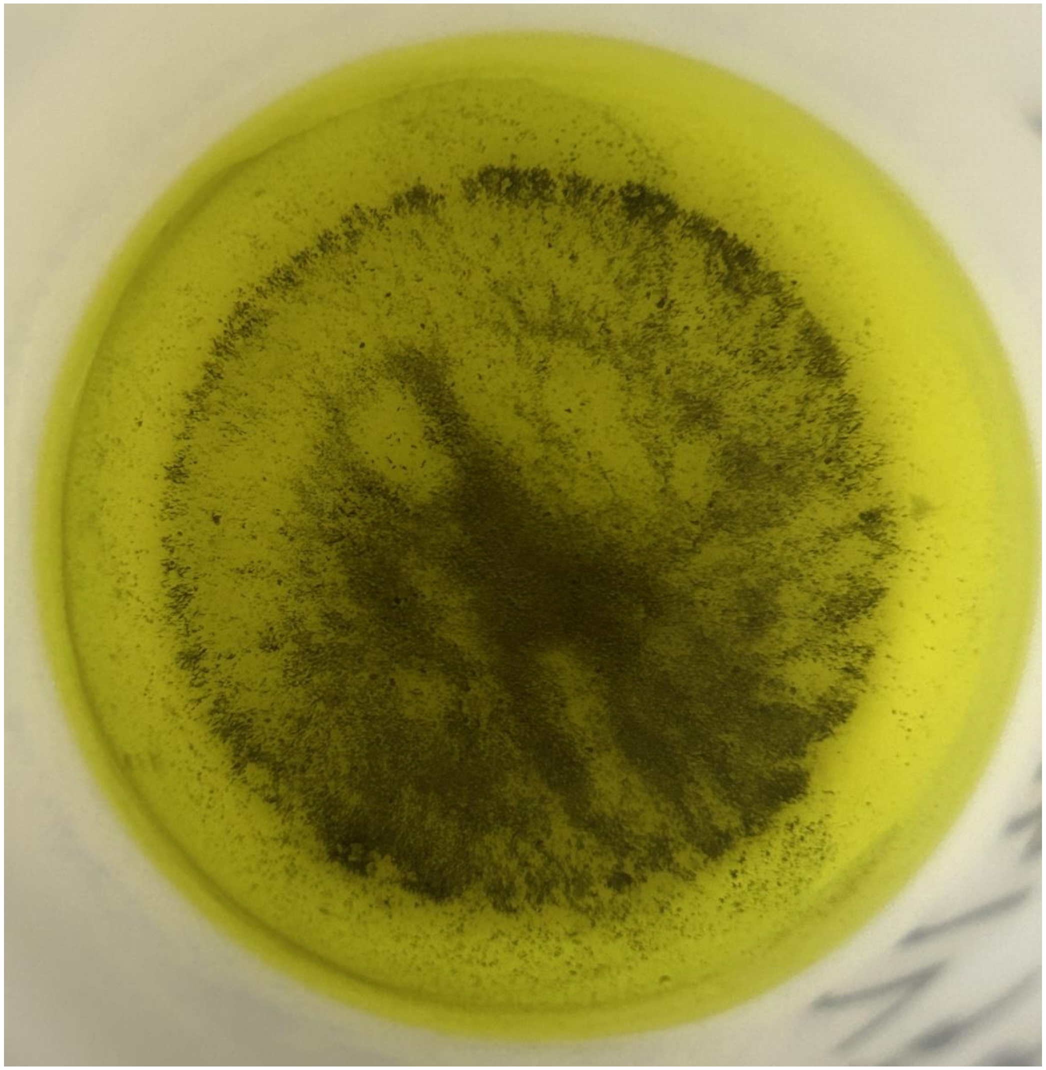

Figure 4.2. Settling of AgI loaded Ionex Ag-400 particles in the 100-ml filtered AltLAW simulant solution.

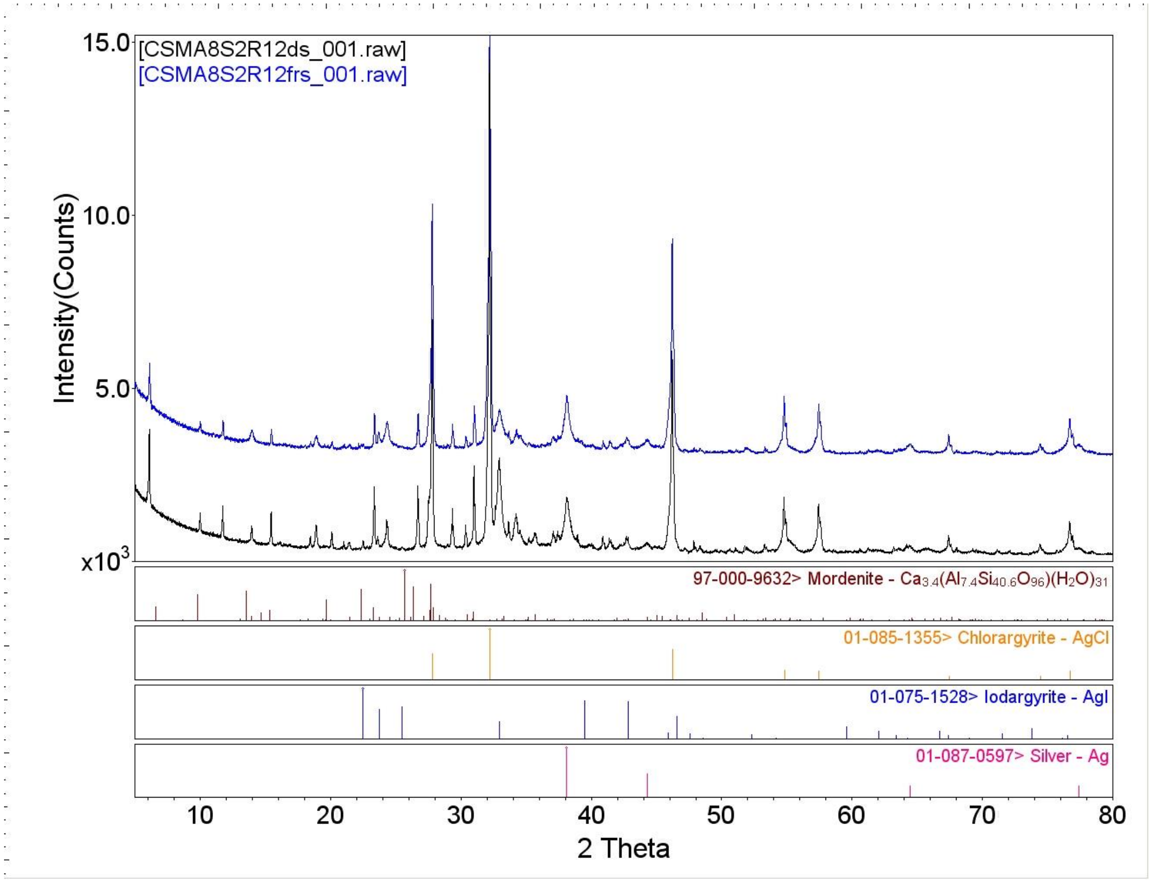

Figure 4.3. XRD patterns of spent Ionex Ag-400 particles.

Figure 4.4. Super hydrophobicity of a grout waste form induced by EUCON Hydrapel 2.5.

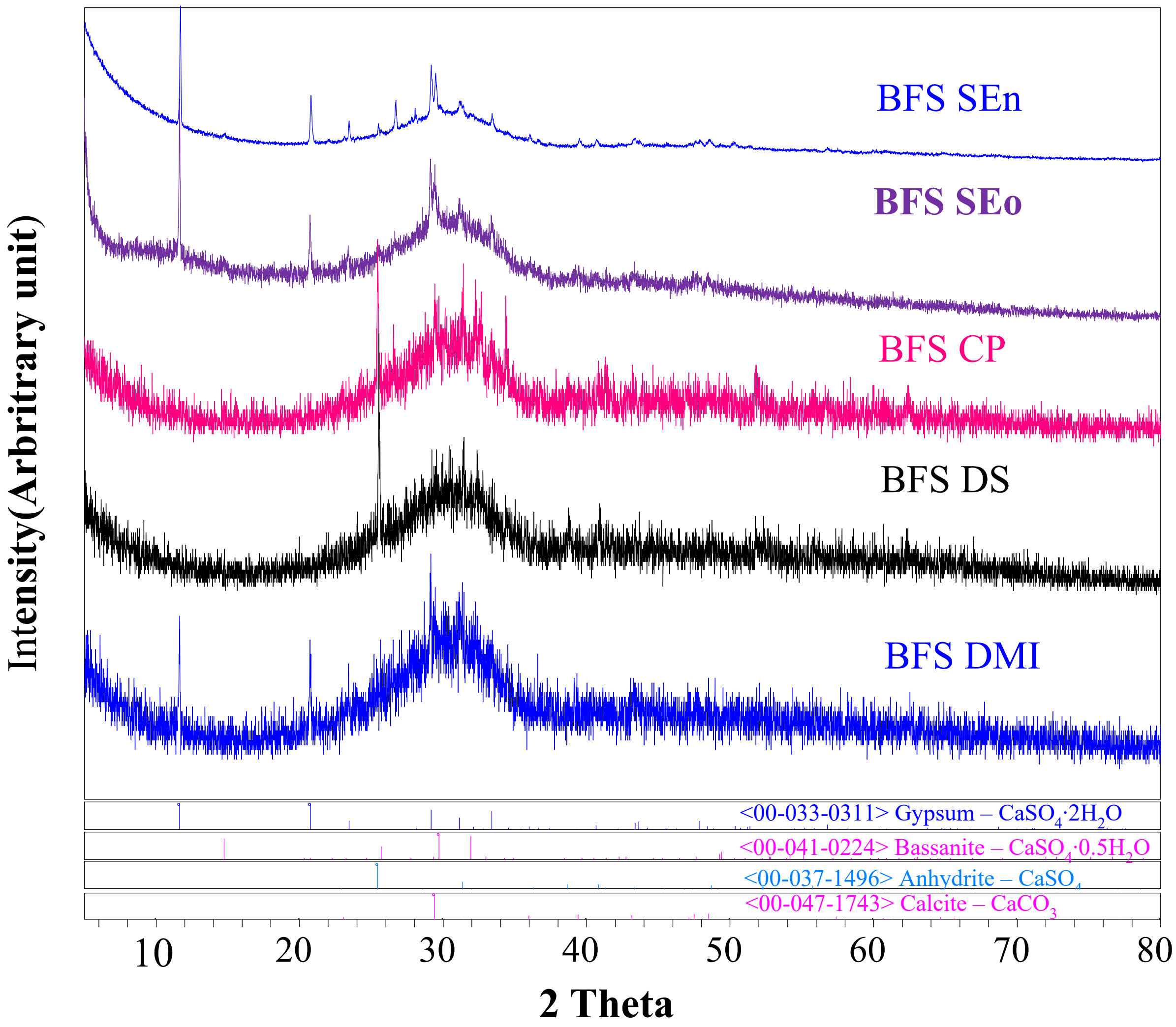

Figure 5.1. XRD patterns of five slag types used for formulation testing.

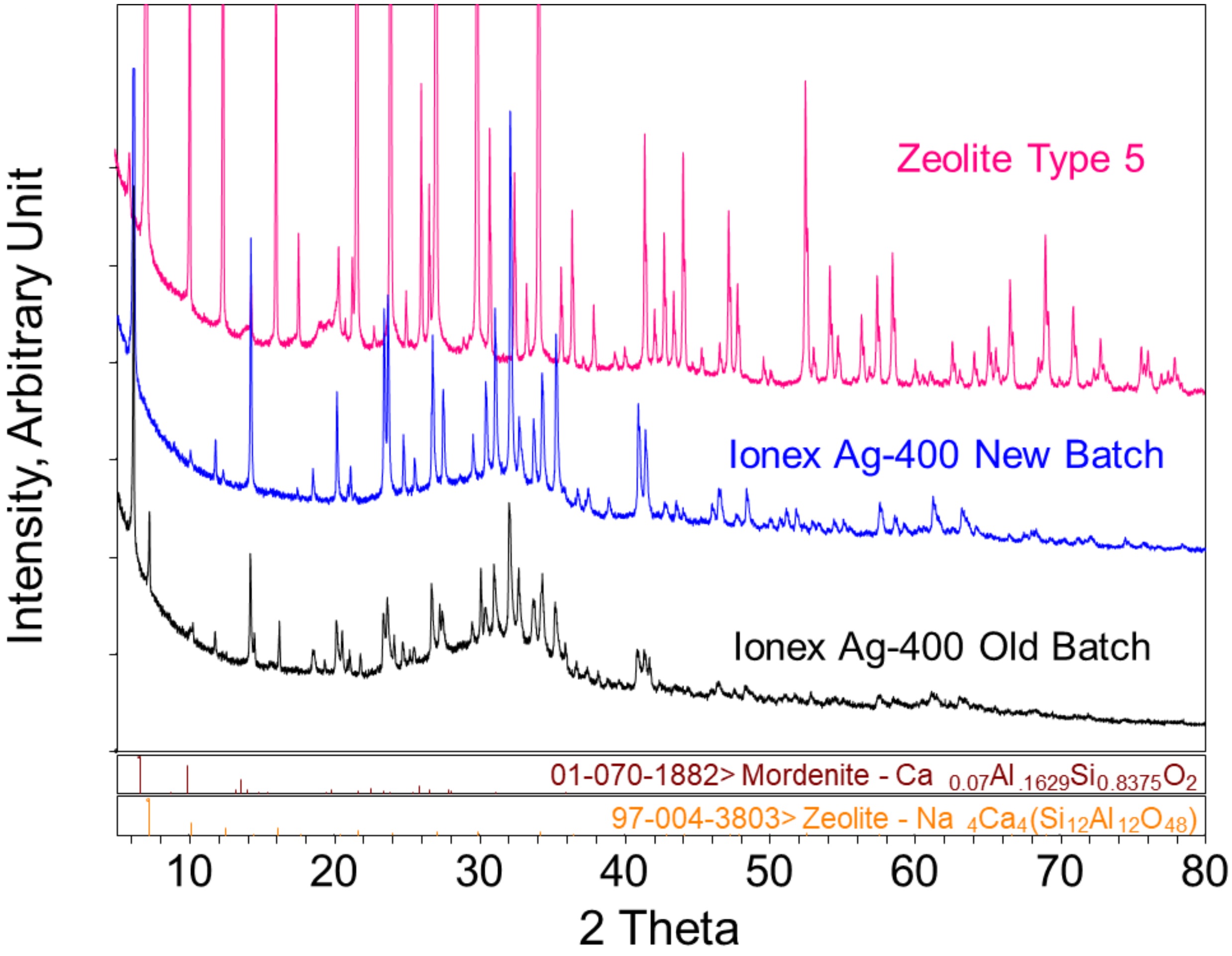

Figure 5.2. XRD patterns of Ionex Ag-400 and Zeolite Type 5.

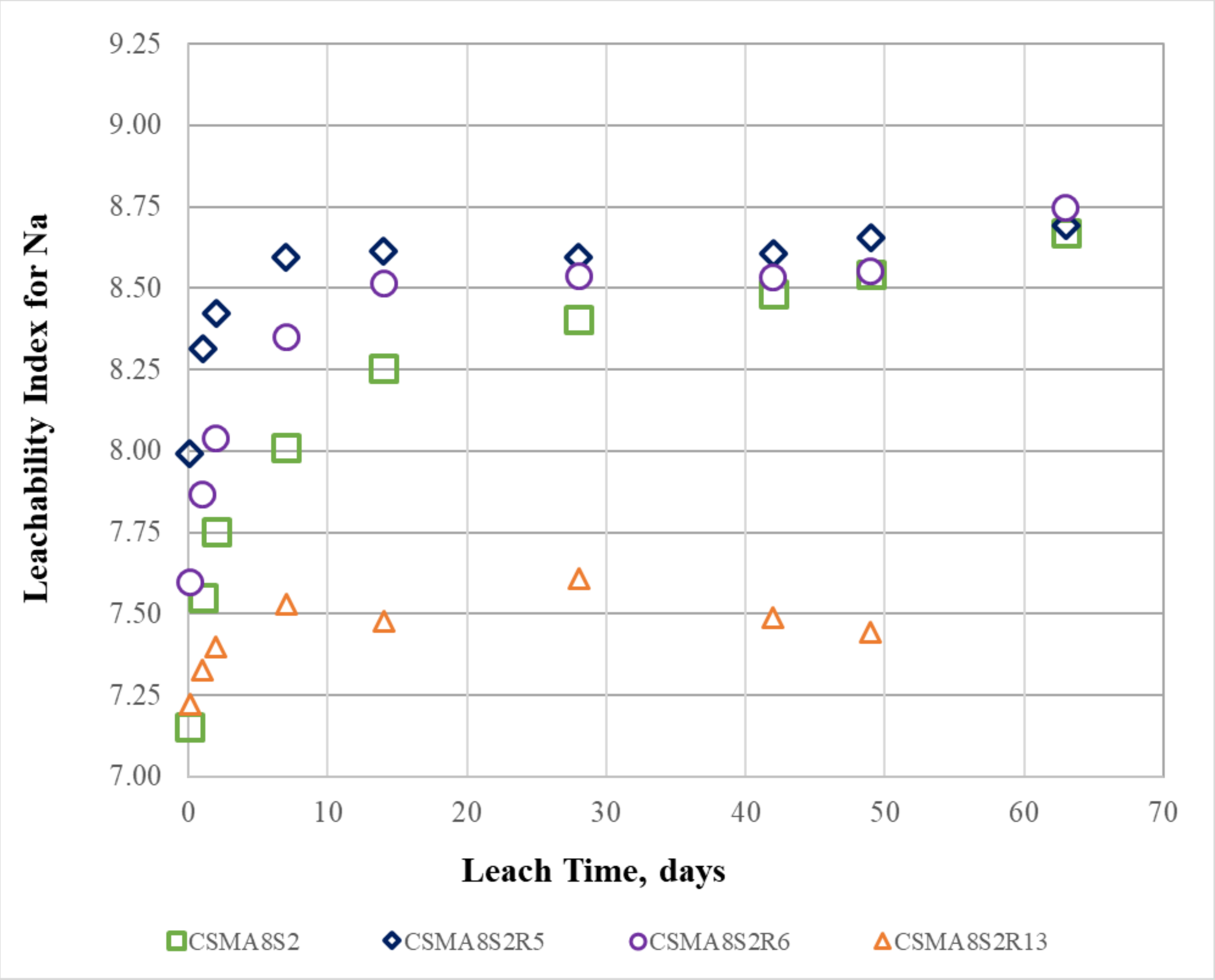

Figure 5.3. Leachability Index values for sodium as functions of time and formulation; Slag type: SEo for CSMA8S2; CP for CSMA8S2R5; DS for CSMA8S2R6; DMI for CSMA8S2R13.

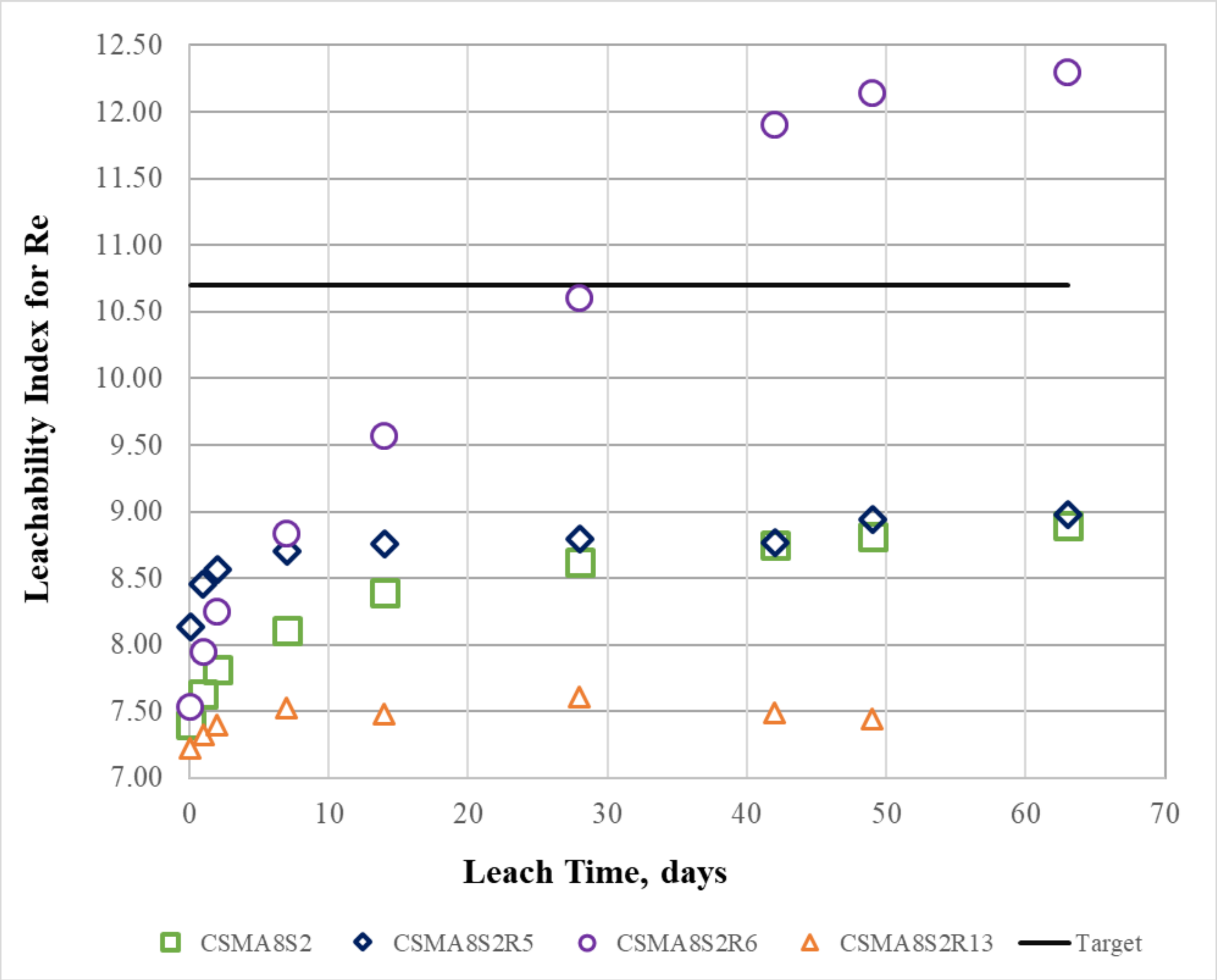

Figure 5.4. Leachability Index values for rhenium as functions of time and formulation: Slag type: SEo for CSMA8S2; CP for CSMA8S2R5; DS for CSMA8S2R6; DMI for CSMA8S2R13.

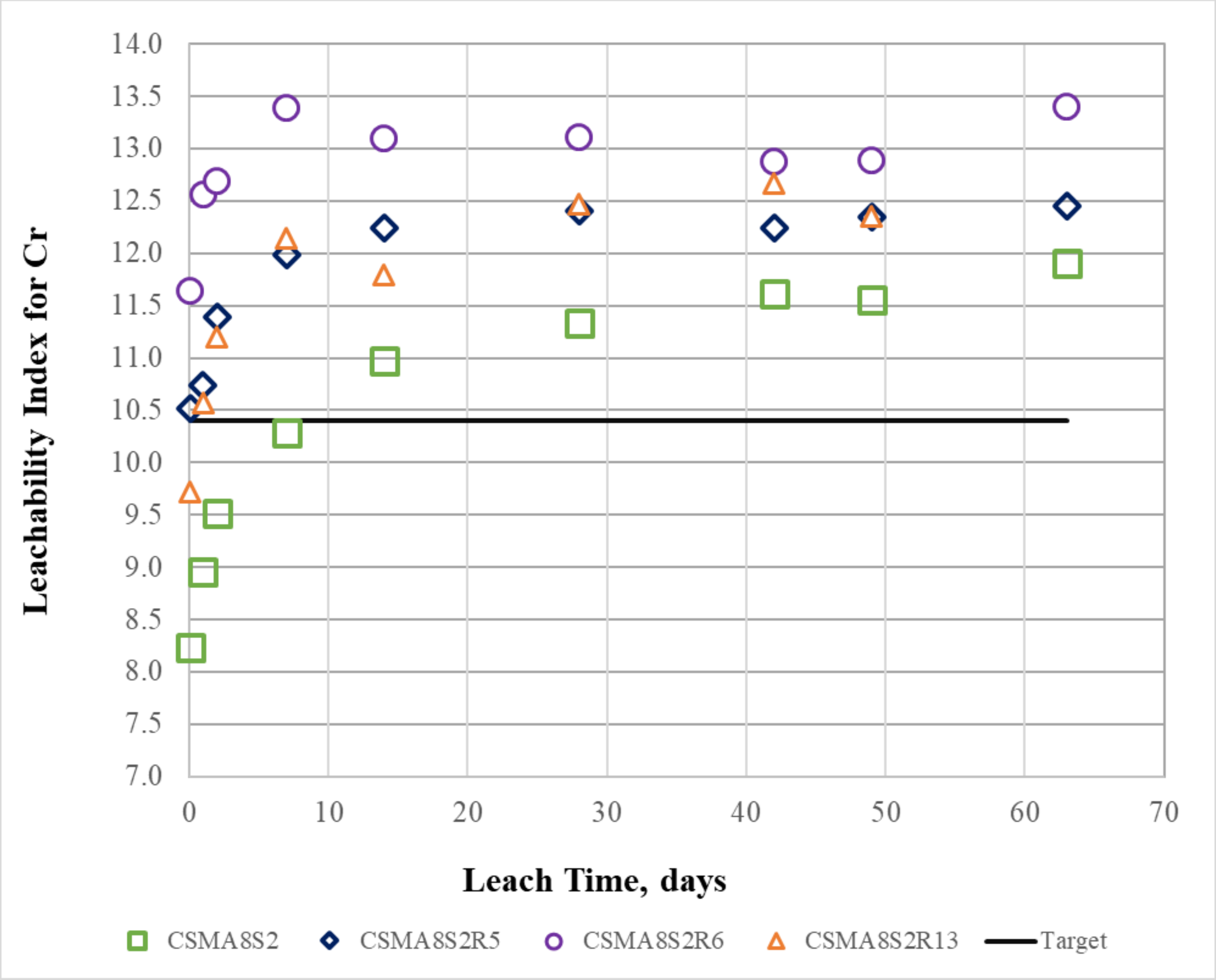

Figure 5.5. Leachability Index values for chromium as functions of time and formulation: Slag type: SEo for CSMA8S2; CP for CSMA8S2R5; DS for CSMA8S2R6; DMI for CSMA8S2R13.

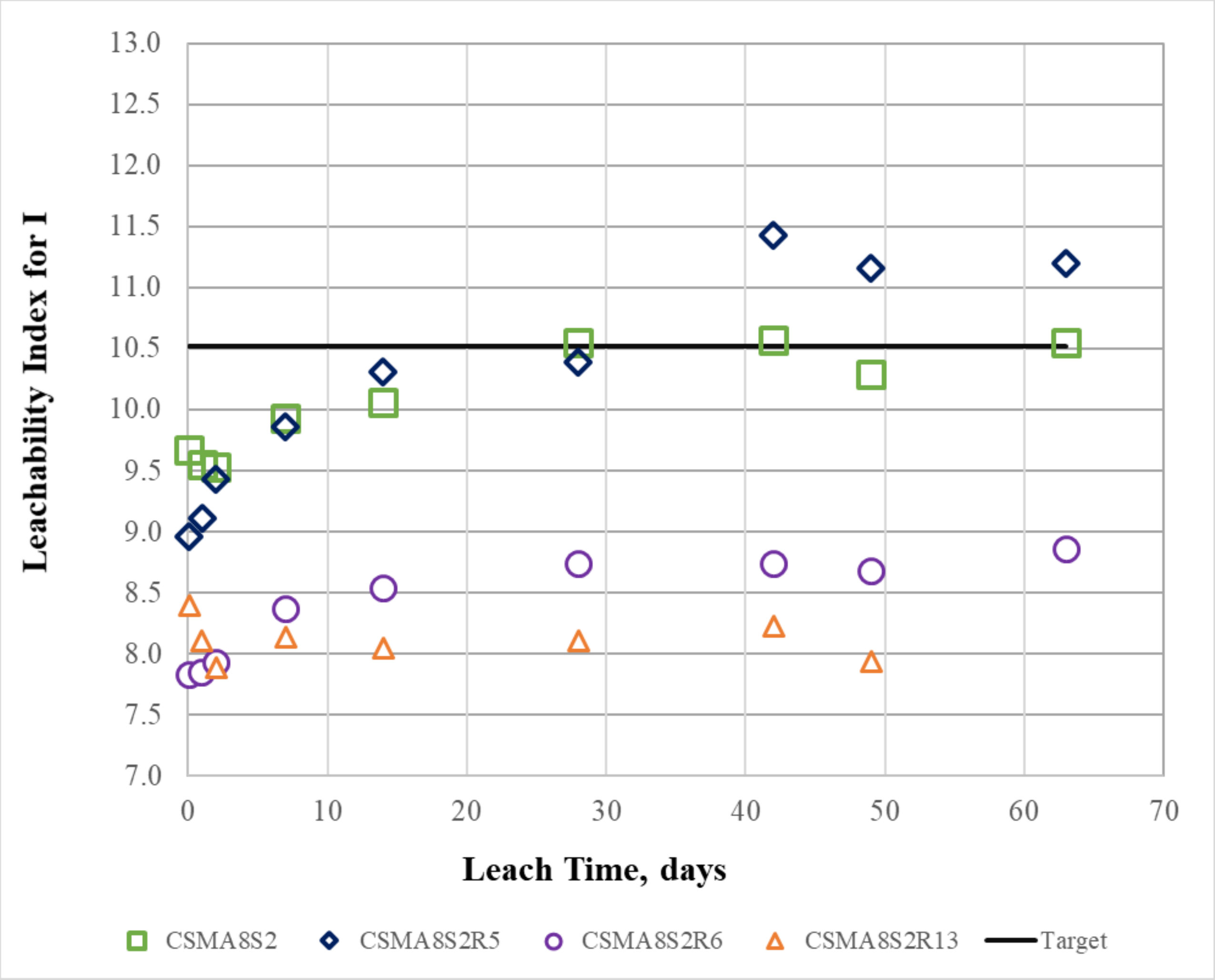

Figure 5.6. Leachability Index values for iodine as functions of time and formulation: Slag type: SEo for CSMA8S2; CP for CSMA8S2R5; DS for CSMA8S2R6; DMI for CSMA8S2R13.

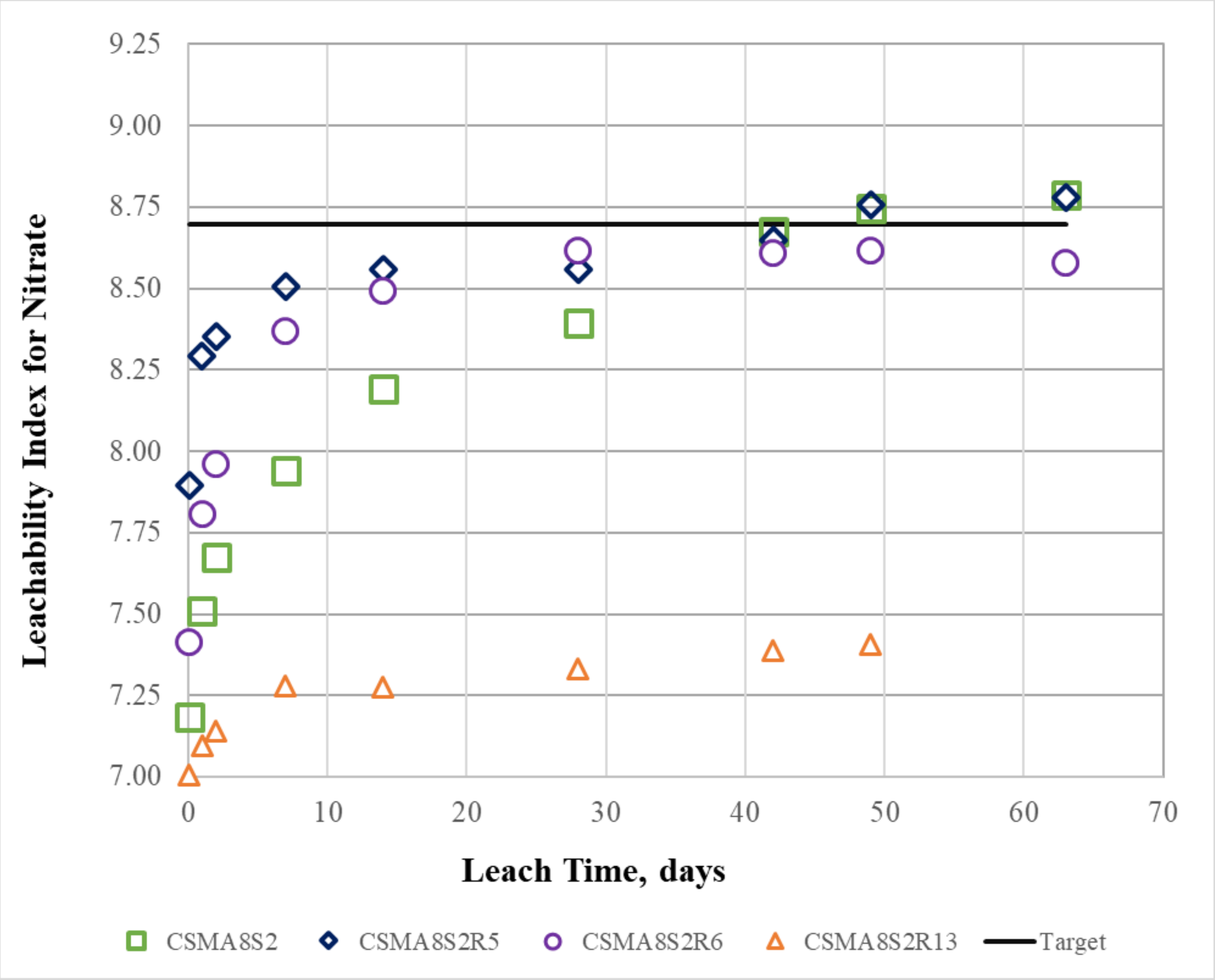

Figure 5.7. Leachability Index values for nitrate as functions of time and formulation: Slag type: SEo for CSMA8S2; CP for CSMA8S2R5; DS for CSMA8S2R6; DMI for CSMA8S2R13.

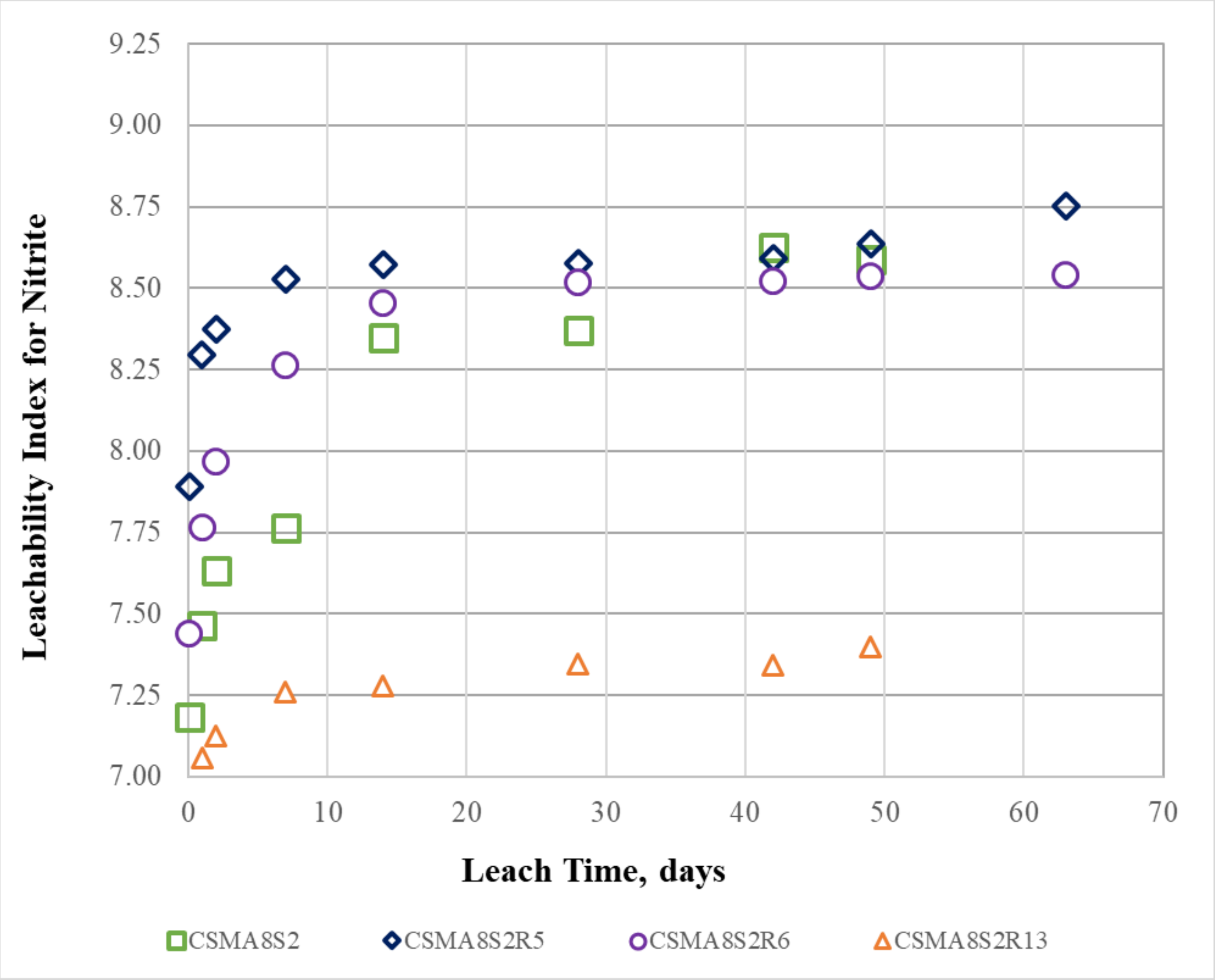

Figure 5.8. Leachability Index values for nitrite as functions of time and formulation: Slag type: SEo for CSMA8S2; CP for CSMA8S2R5; DS for CSMA8S2R6; DMI for CSMA8S2R13.

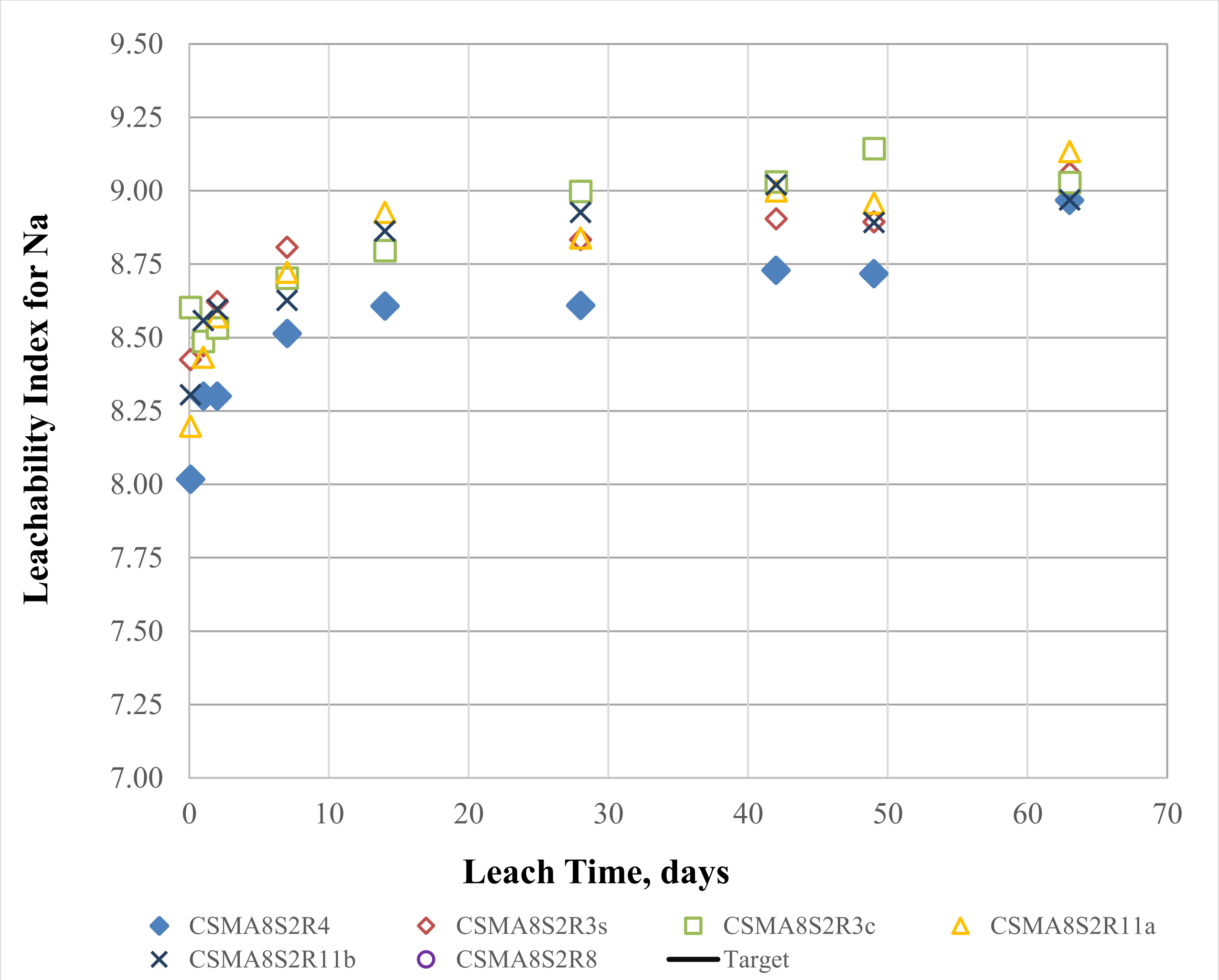

Figure 5.9. Leachability Index values for sodium as functions of time and formulation: Varying silica fume, Hydrapel 2.5 and fillers content.

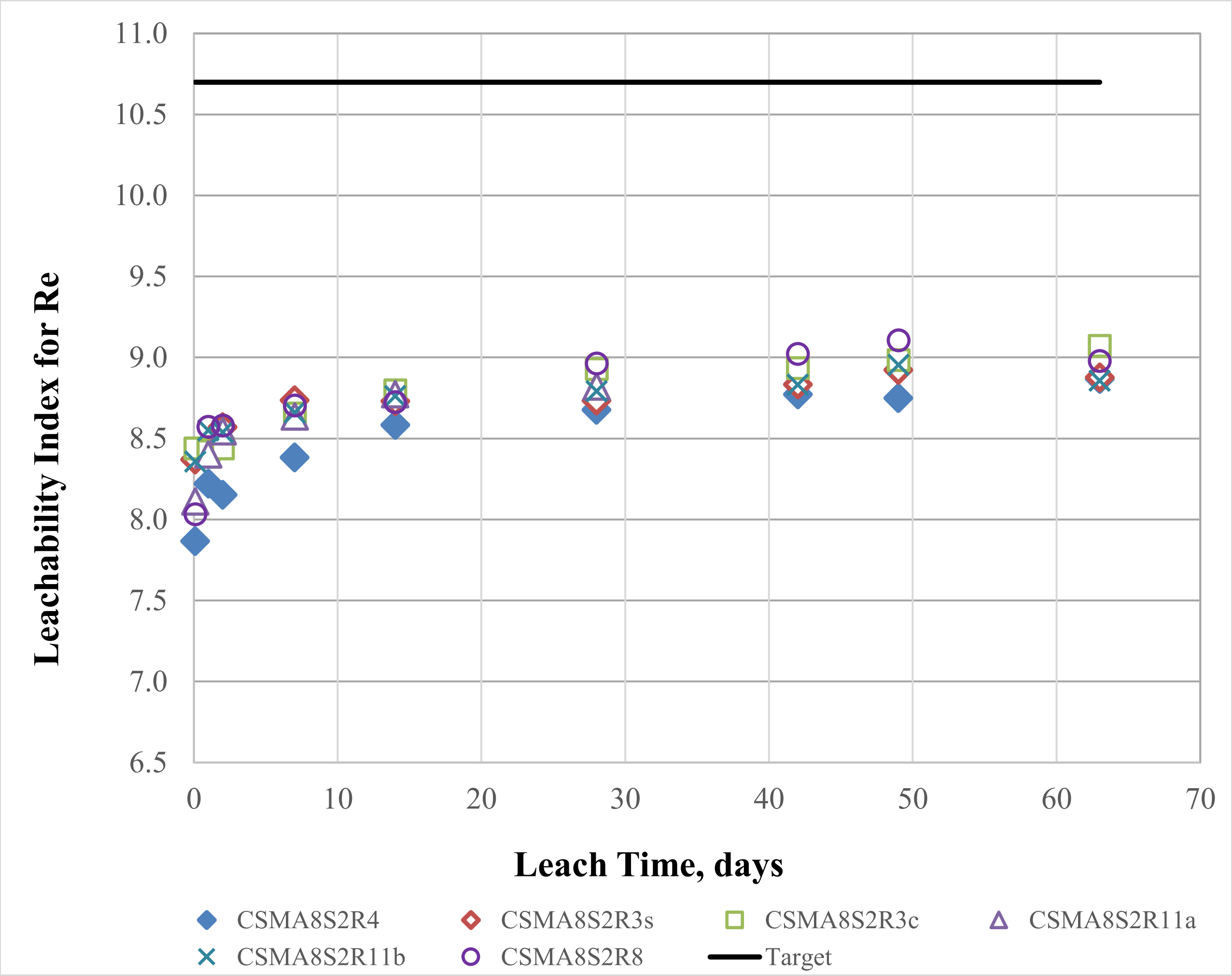

Figure 5.10. Leachability Index values for rhenium as functions of time and formulation: Varying silica fume, Hydrapel 2.5 and fillers content.

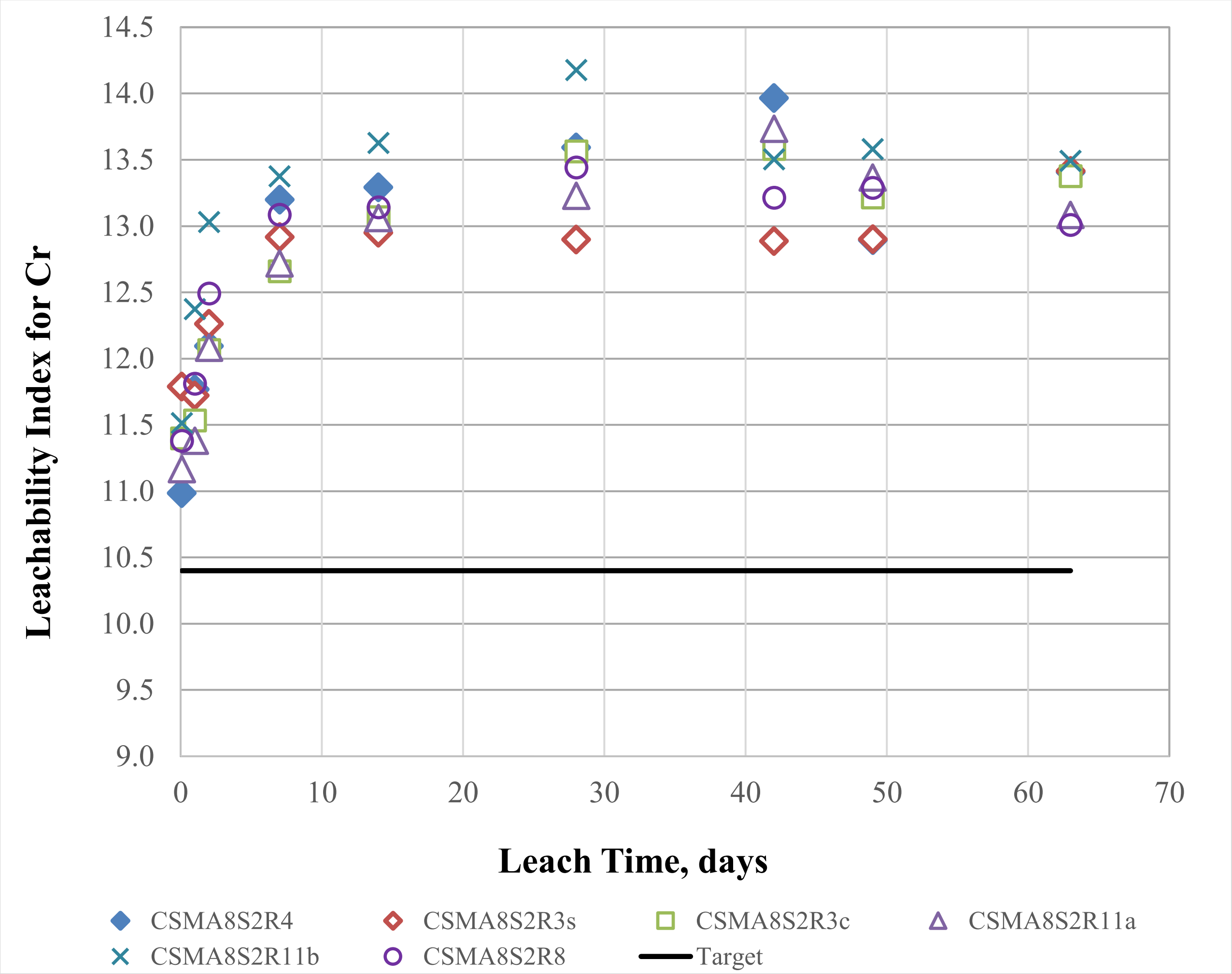

Figure 5.11. Leachability Index values for chromium as functions of time and formulation: Varying silica fume, Hydrapel 2.5 and fillers content.

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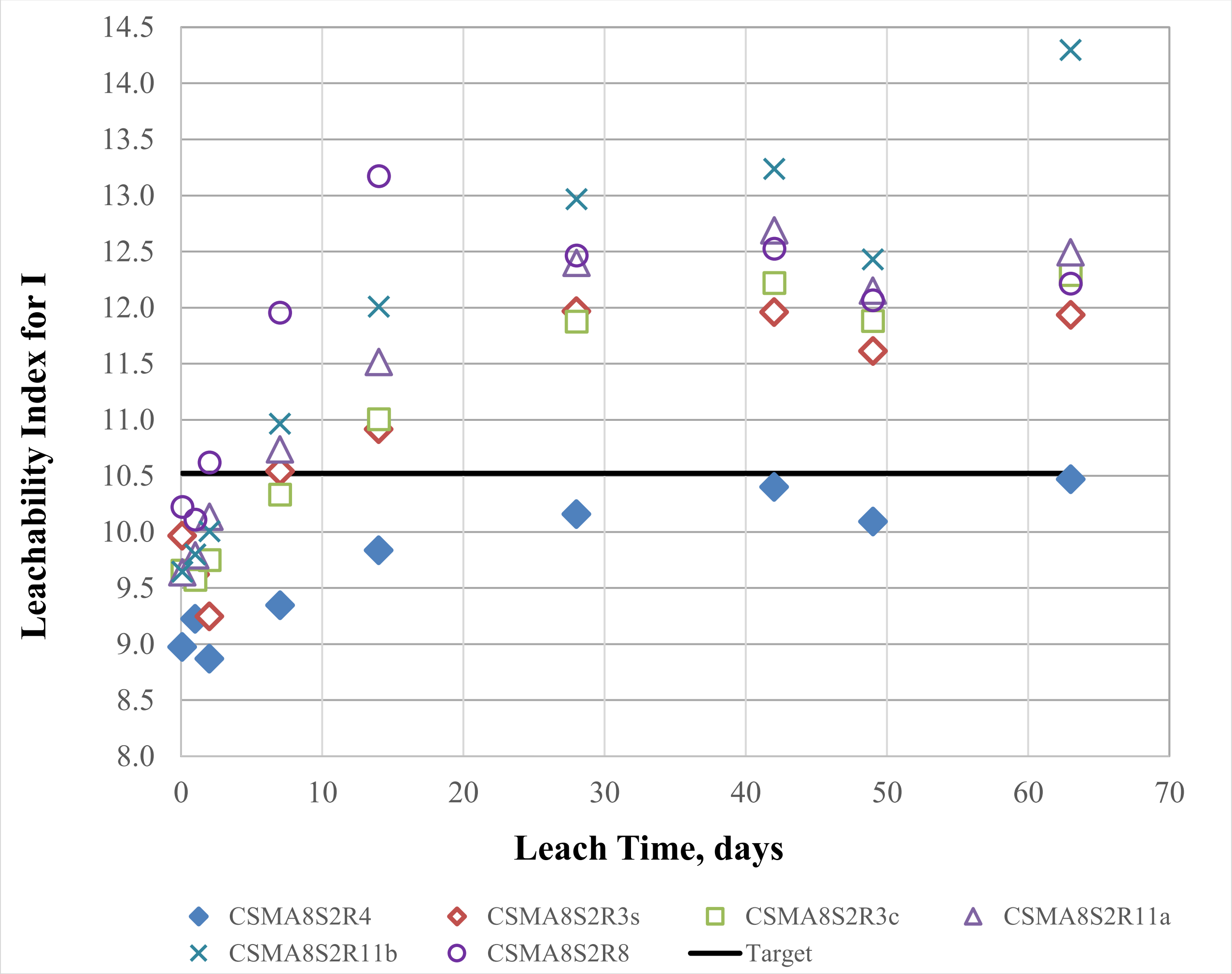

Figure 5.12. Leachability Index values for iodine as functions of time and formulation: Varying silica fume, Hydrapel 2.5 and fillers content.

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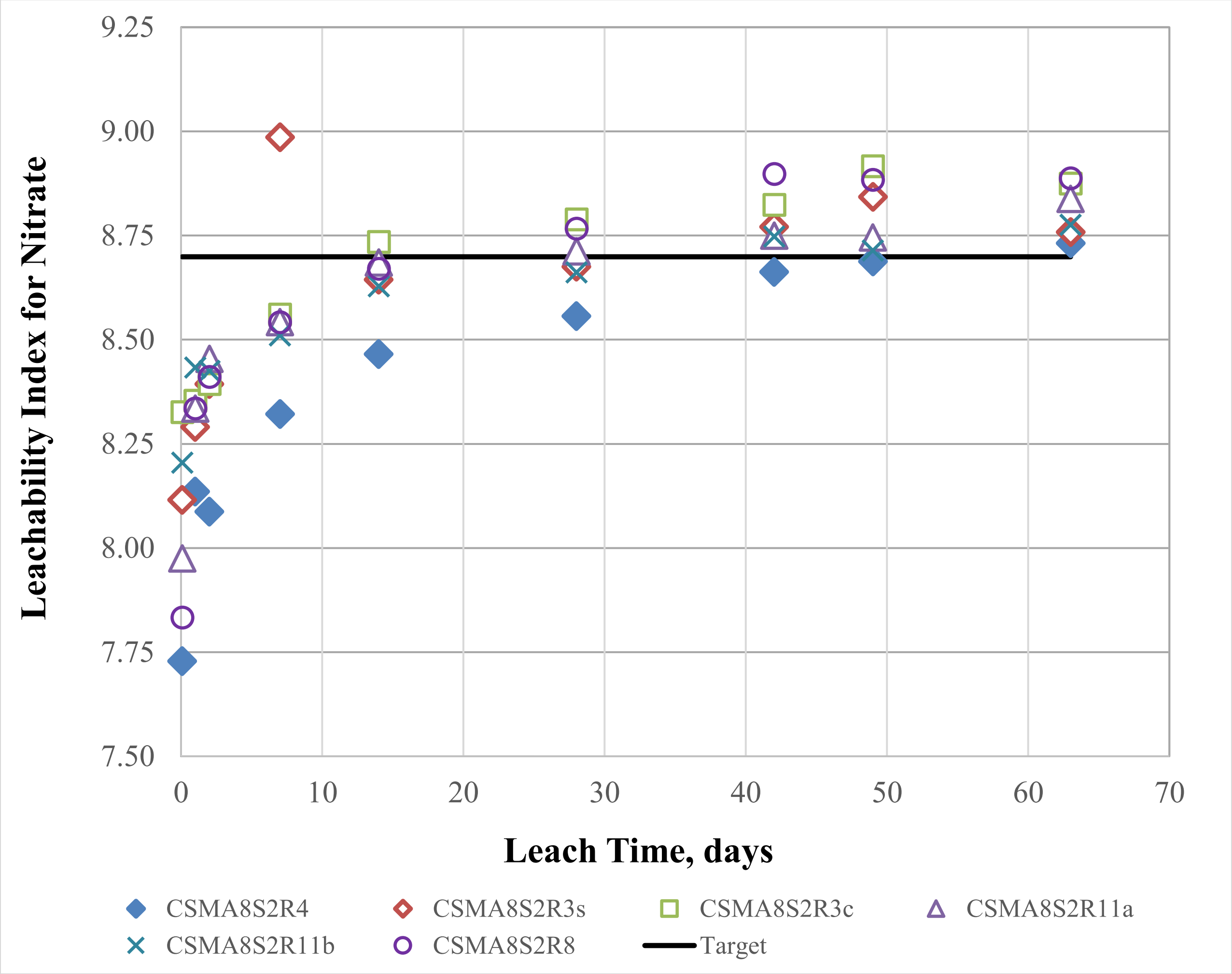

Figure 5.13. Leachability Index values for nitrate as functions of time and formulation: Varying silica fume, Hydrapel 2.5 and fillers content.

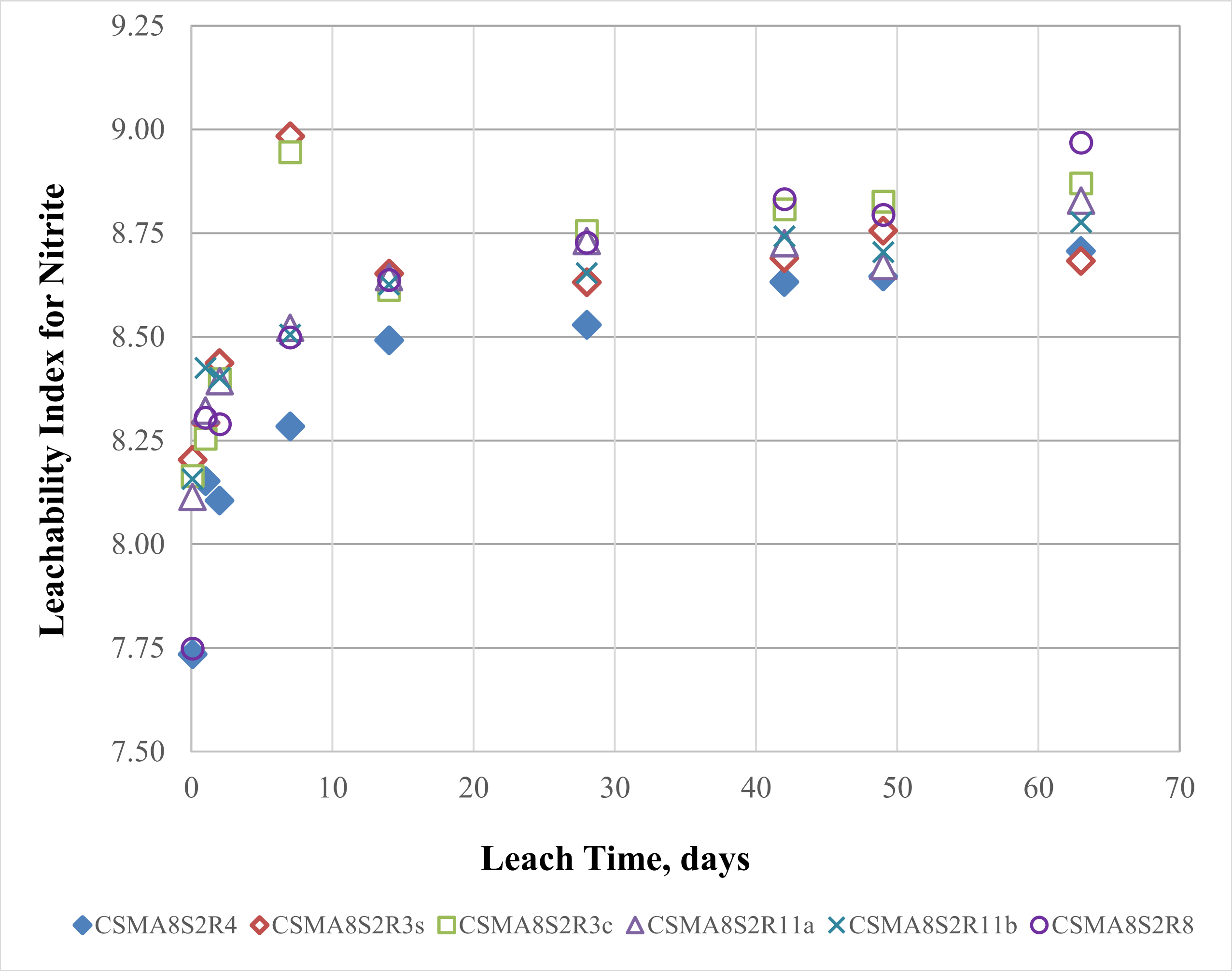

Figure 5.14. Leachability Index values for nitrite as functions of time and formulation: Varying silica fume, Hydrapel 2.5 and fillers content.

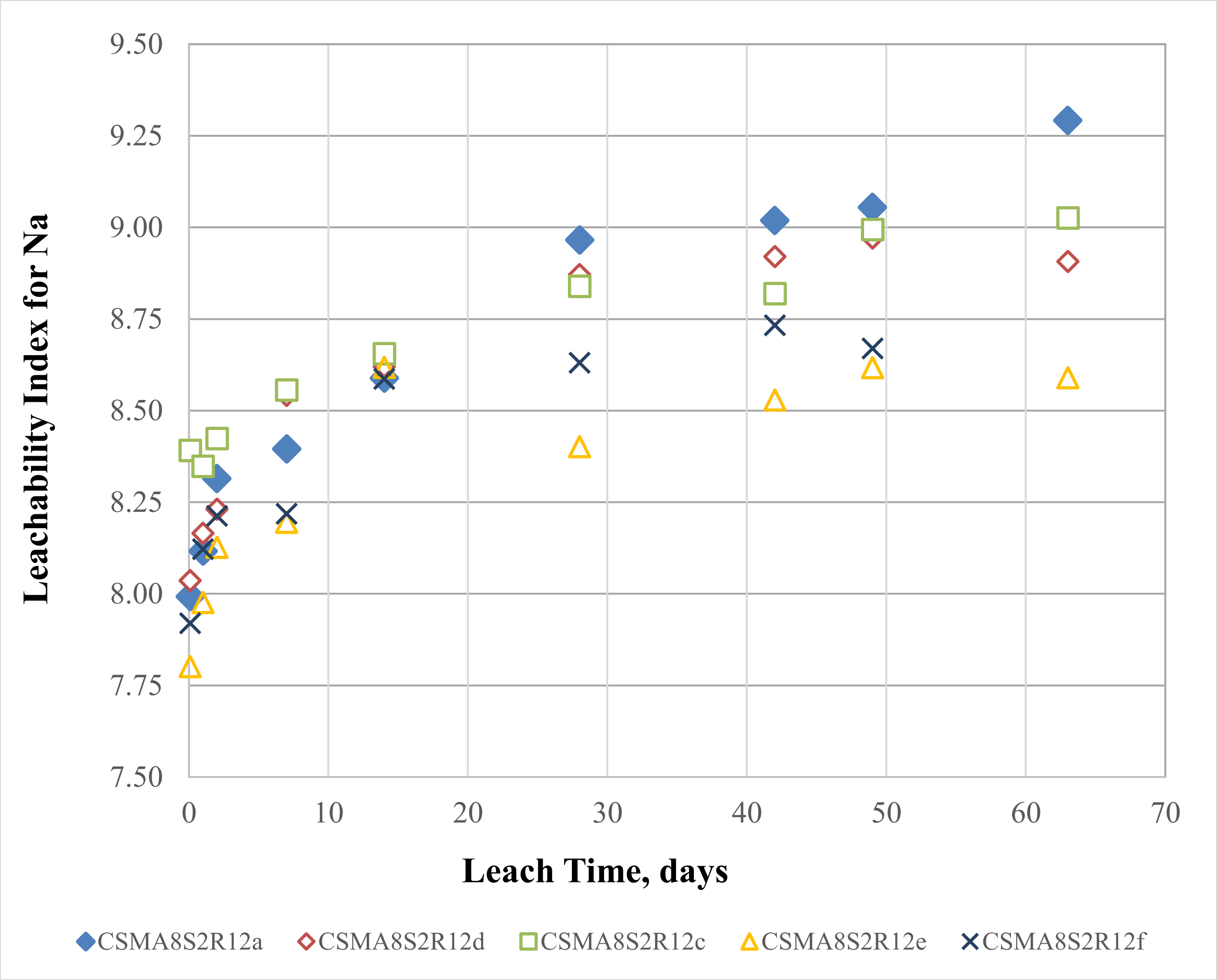

Figure 5.15. Leachability Index values for sodium as functions of time and formulation: CSMA8 Series with iodine removed.

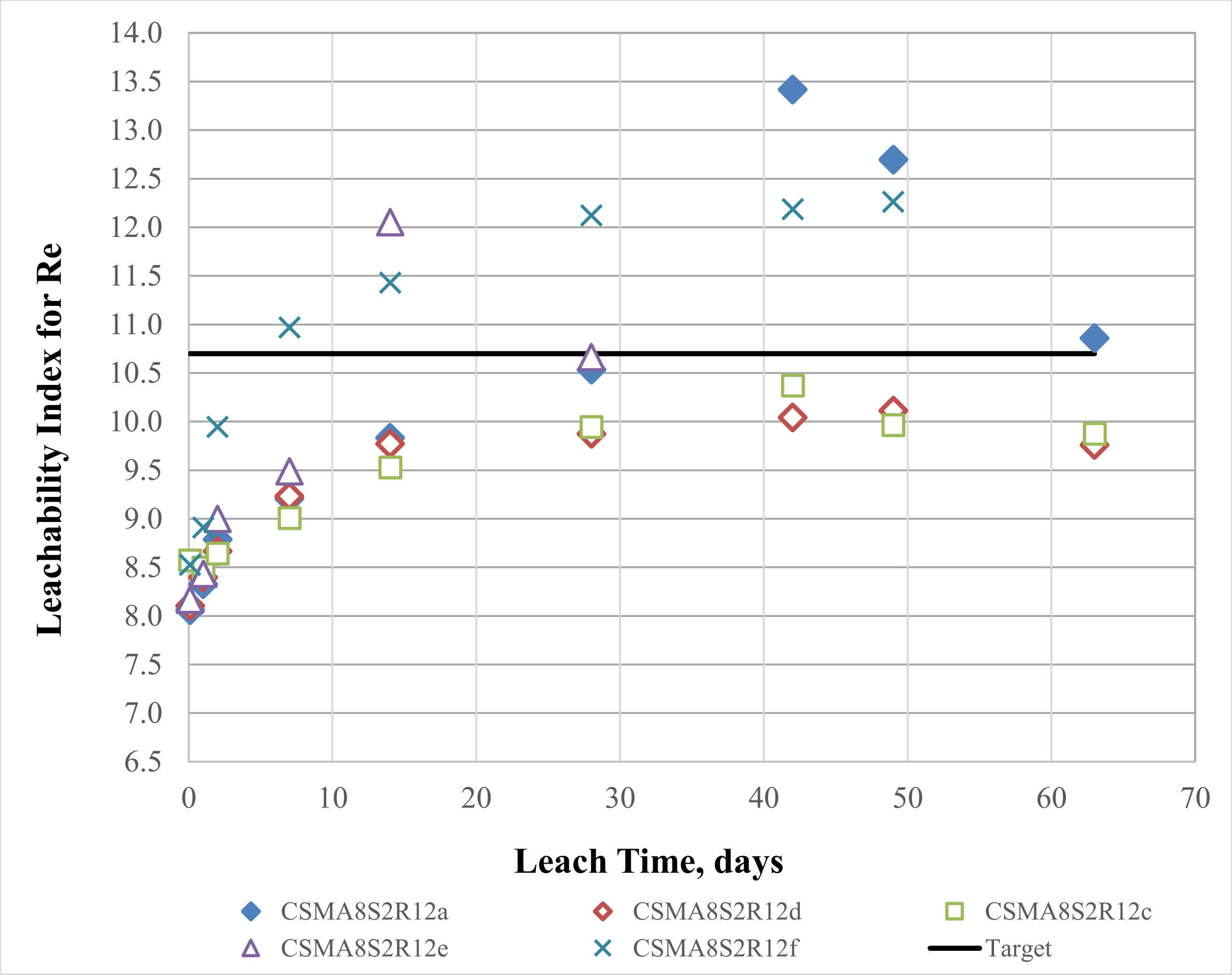

Figure 5.16. Leachability Index values for rhenium as functions of time and formulation: CSMA8 Series with iodine removed.

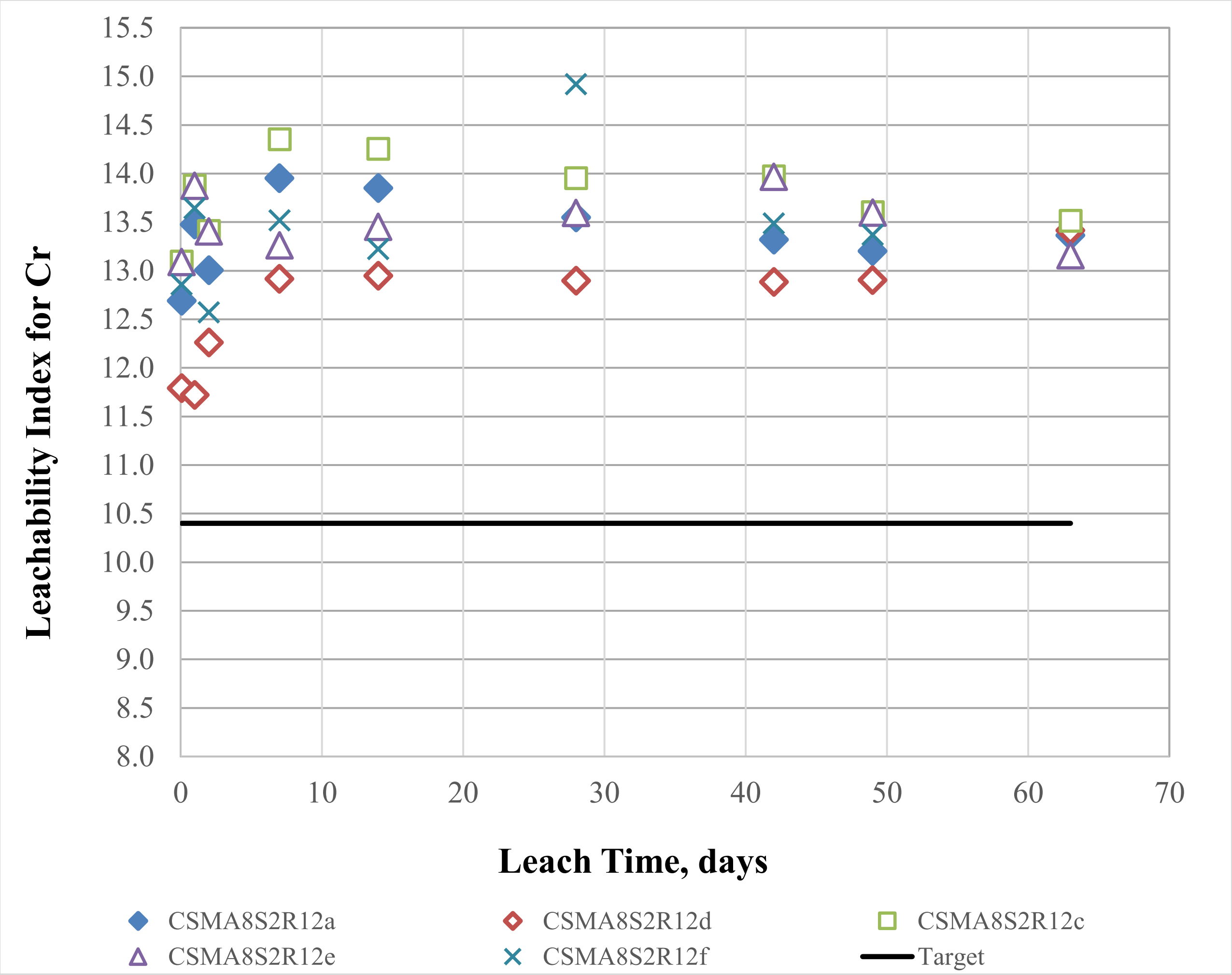

Figure 5.17. Leachability Index values for chromium as functions of time and formulation: CSMA8 Series with iodine removed.

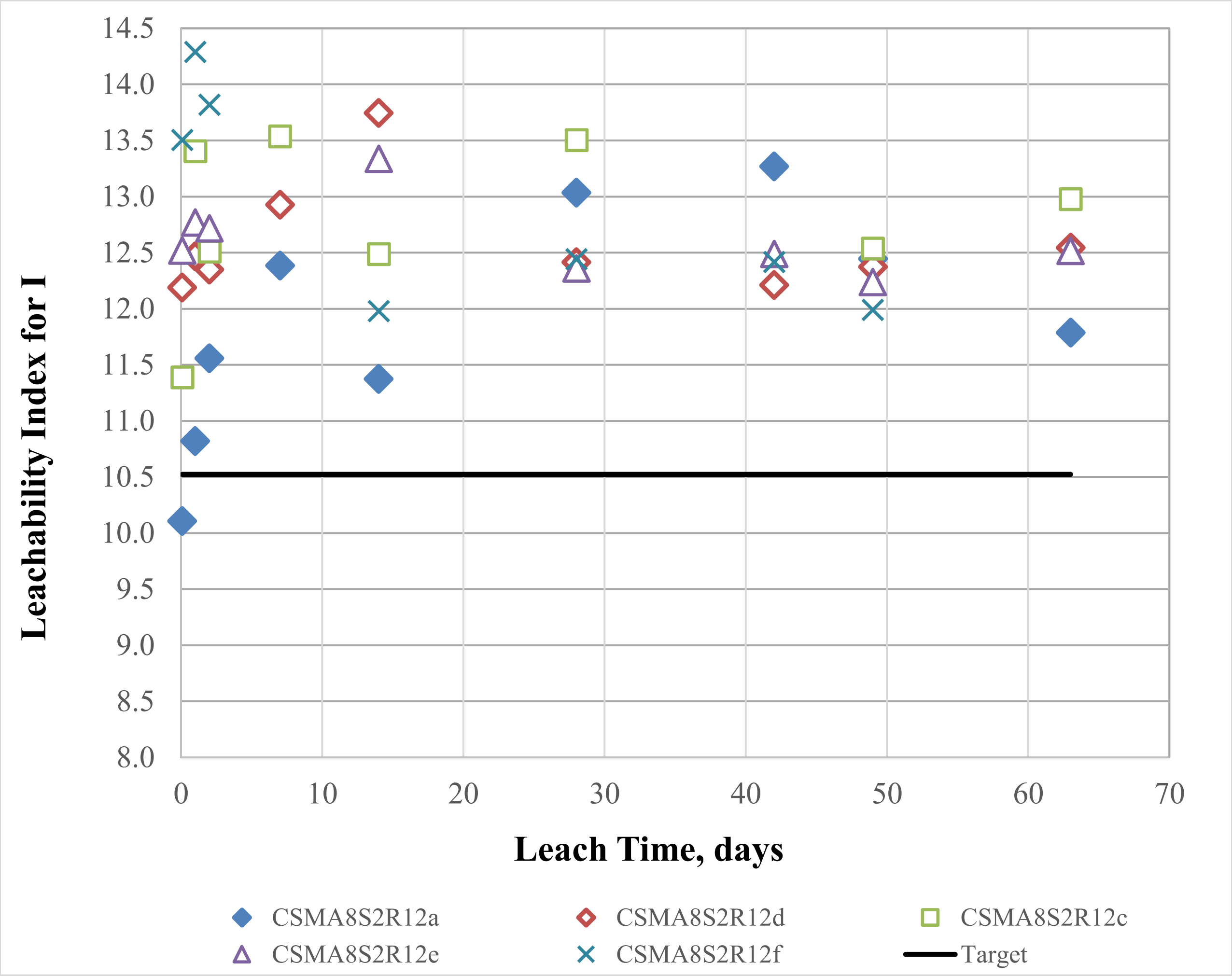

Figure 5.18. Leachability Index values for iodine as functions of time and formulation: CSMA8 Series with iodine removed.

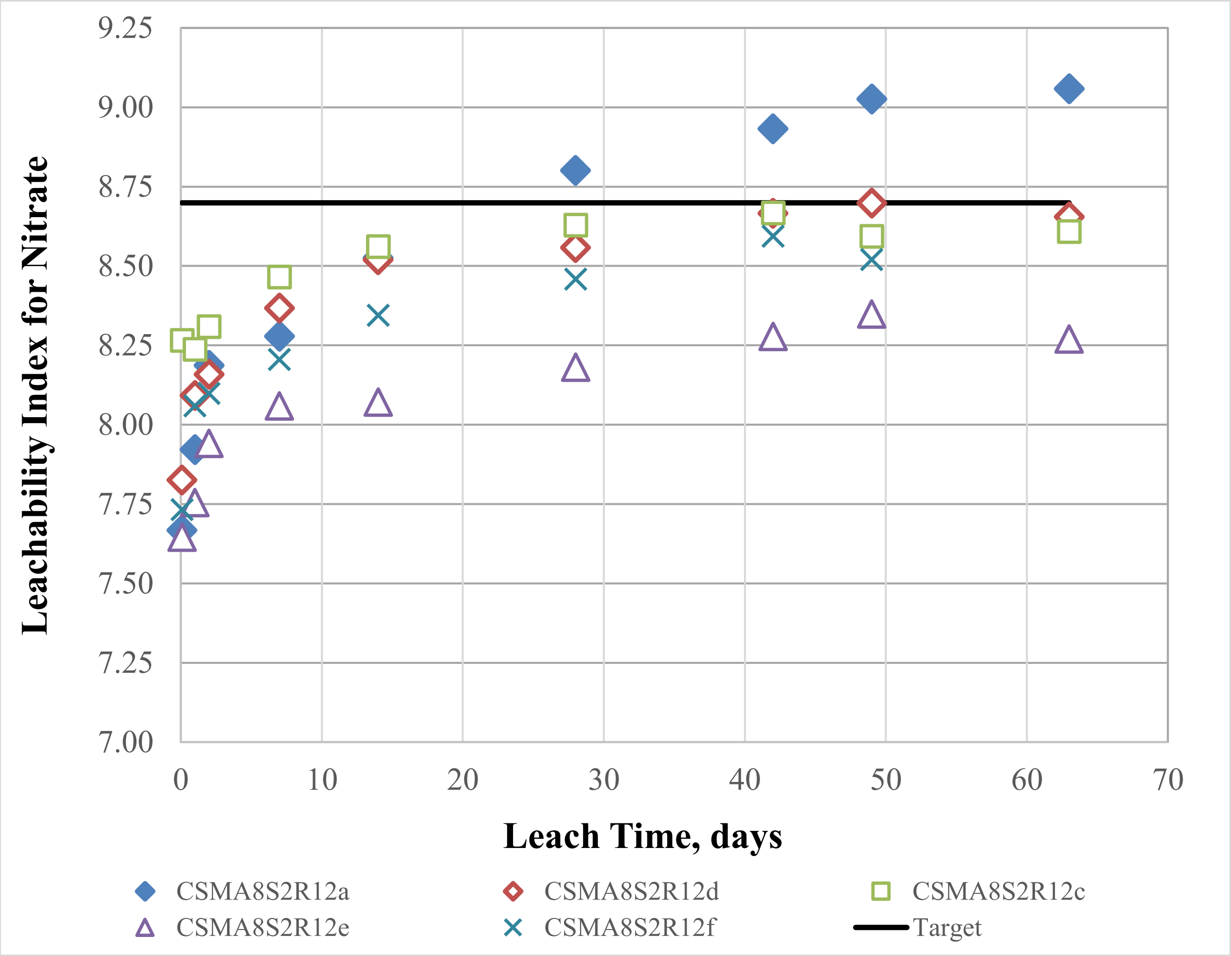

Figure 5.19. Leachability Index values for nitrate as functions of time and formulation: CSMA8 Series with iodine removed.

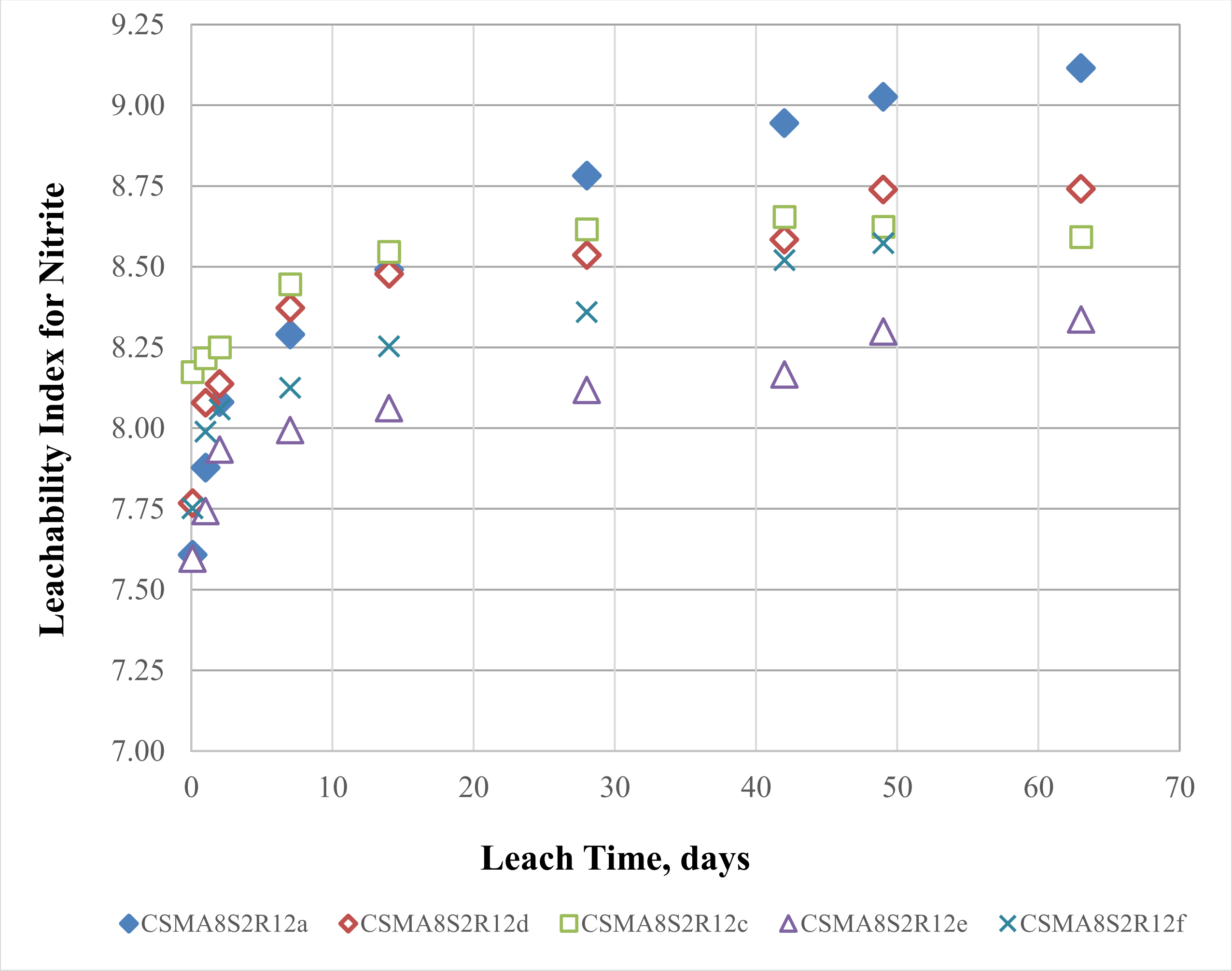

Figure 5.20. Leachability Index values for nitrite as functions of time and formulation: CSMA8 Series with iodine removed.

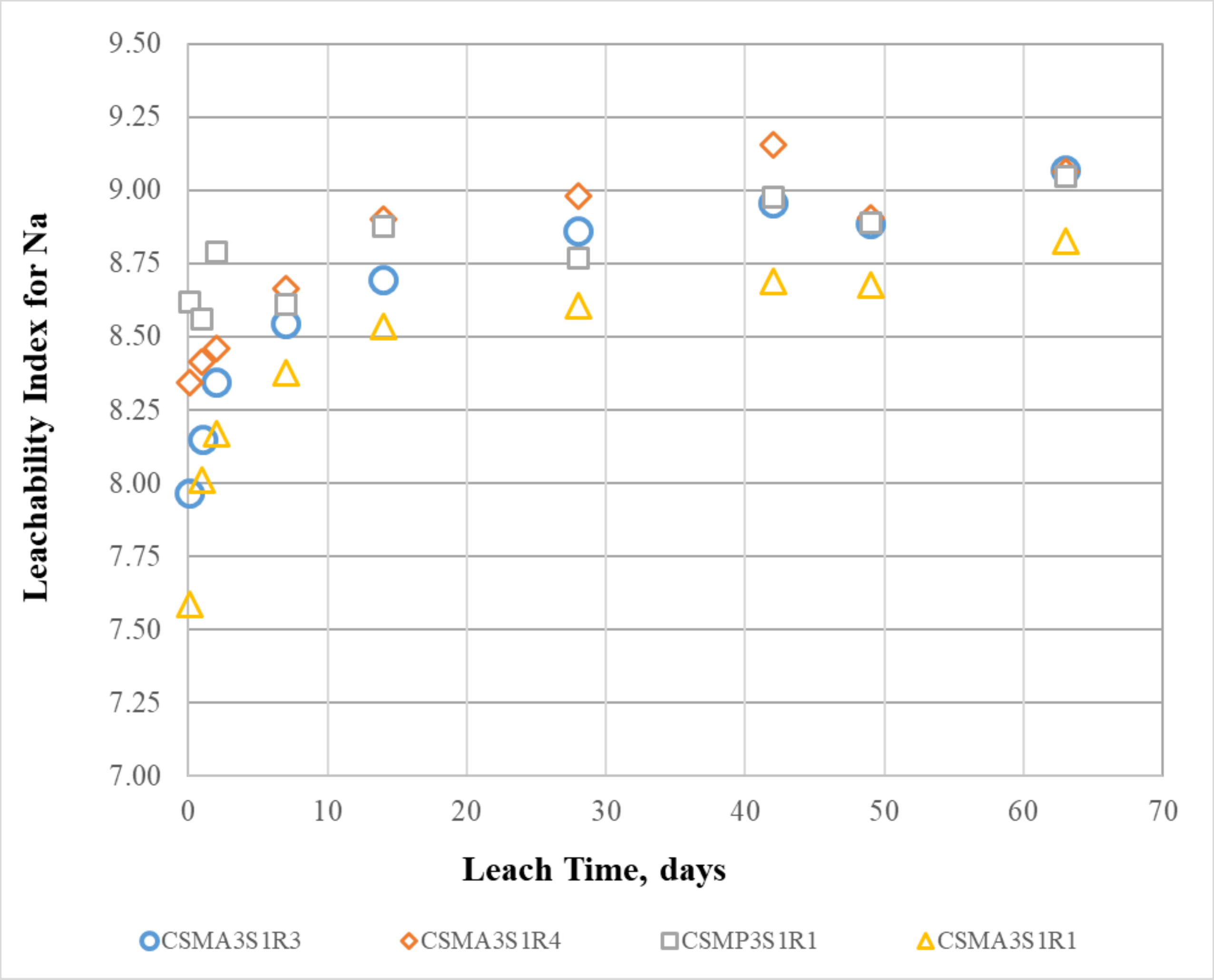

Figure 5.21. Leachability Index values for sodium as functions of time and formulation: CSMA3 Series with iodine removed.

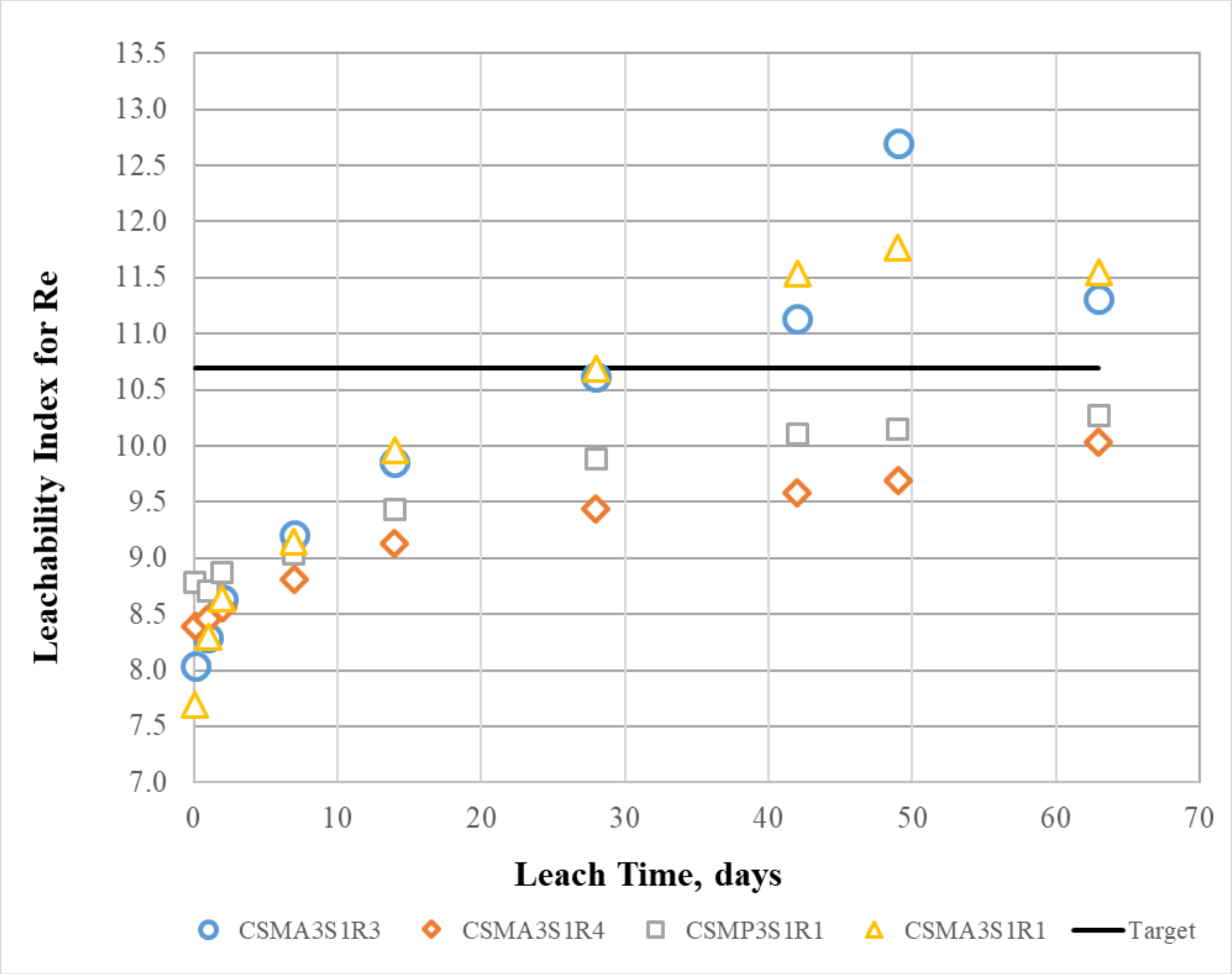

Figure 5.22. Leachability Index values for rhenium as functions of time and formulation: CSMA3 Series with iodine removed.

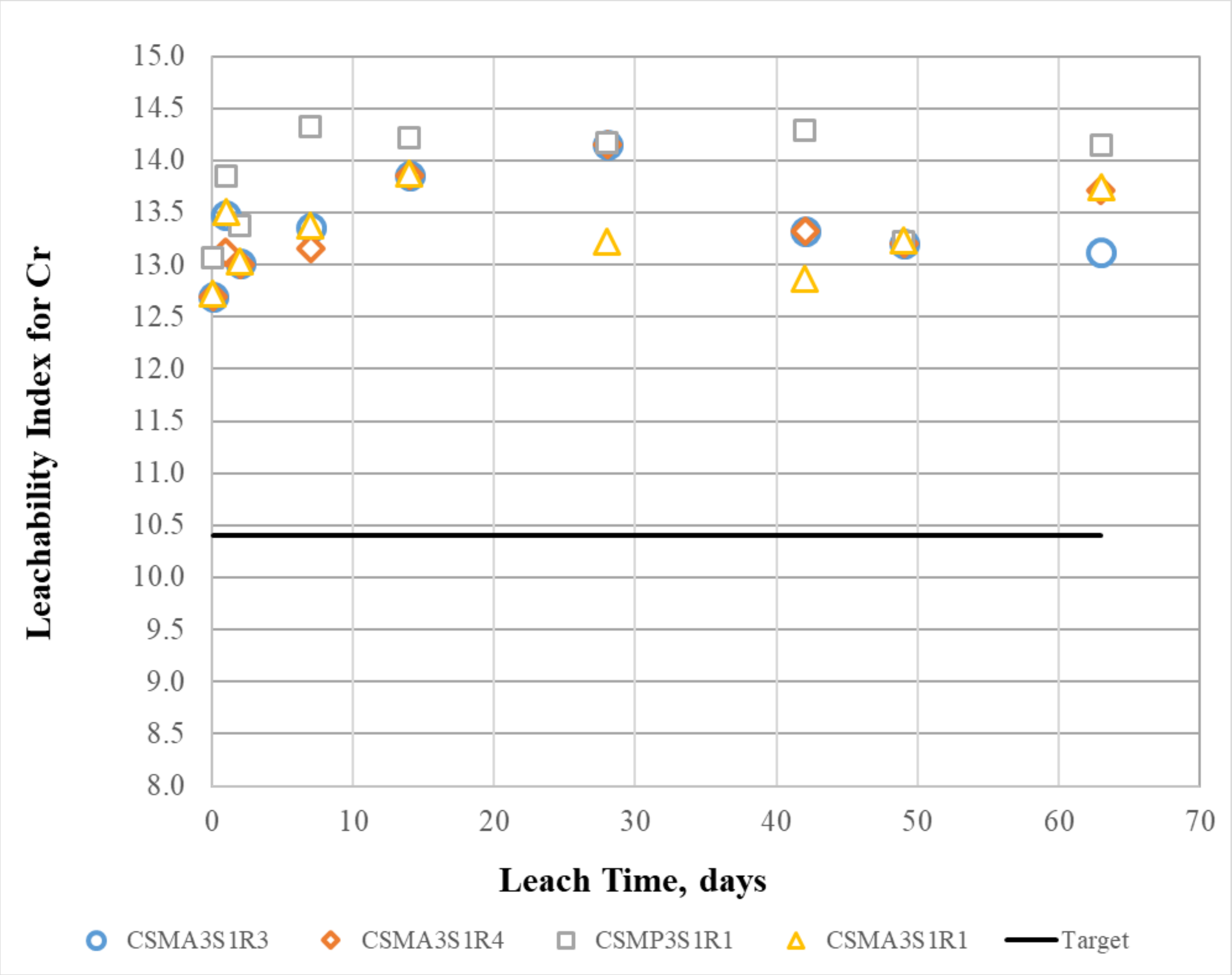

Figure 5.23. Leachability Index values for chromium as functions of time and formulation: CSMA3 Series with iodine removed.

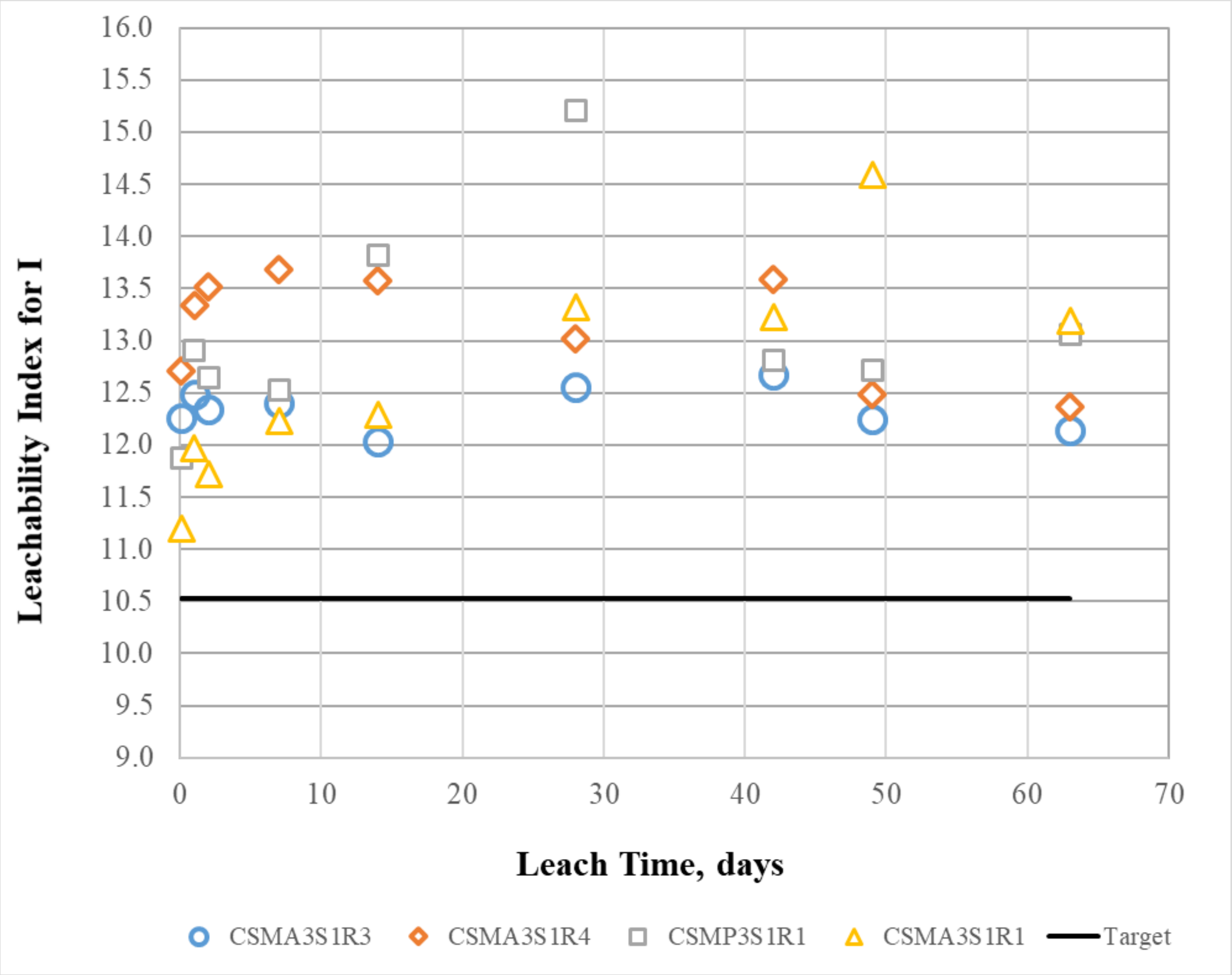

Figure 5.24. Leachability Index values for iodine as functions of time and formulation: CSMA3 Series with iodine removed.

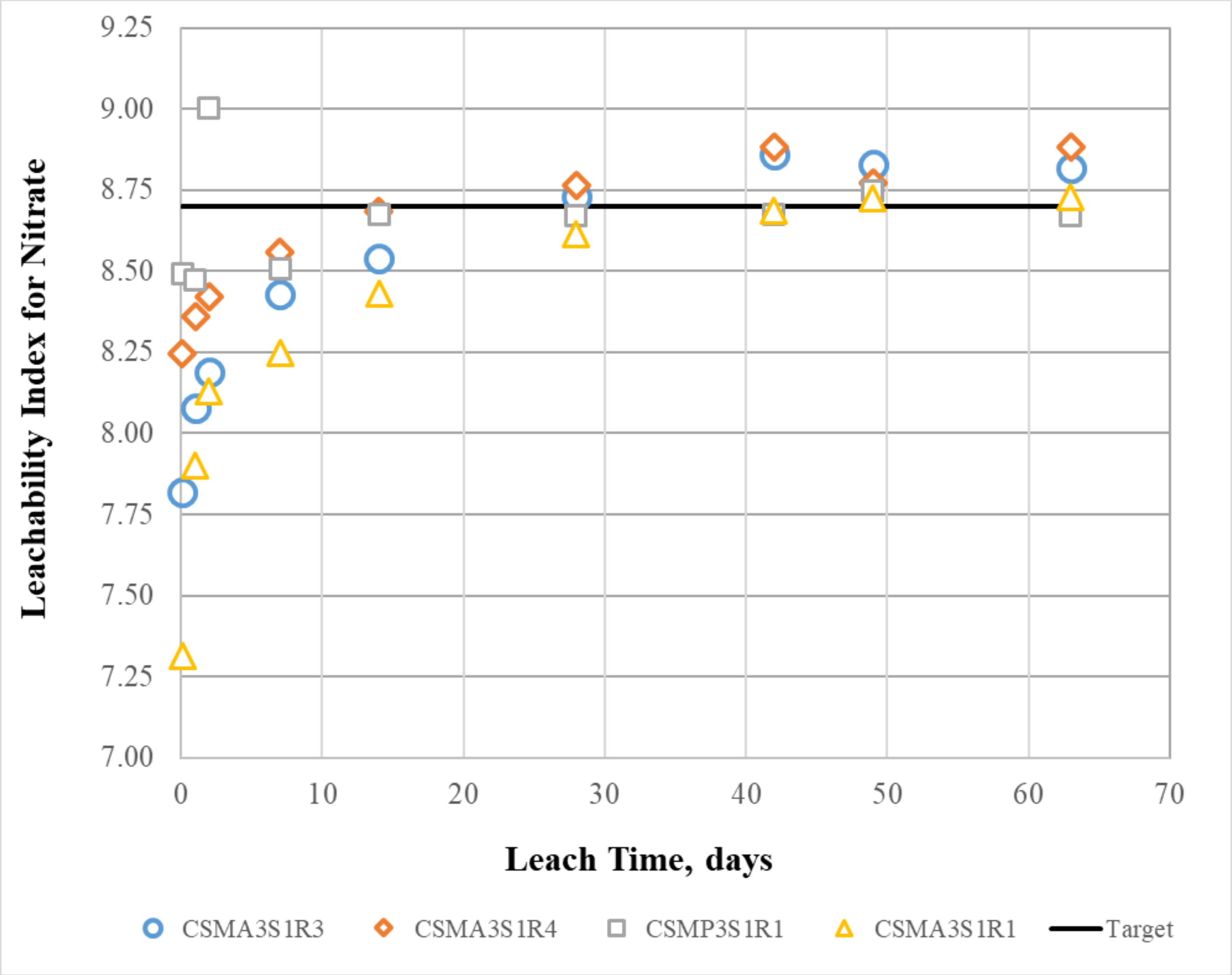

Figure 5.25. Leachability Index values for nitrate as functions of time and formulation: CSMA3 Series with iodine removed.

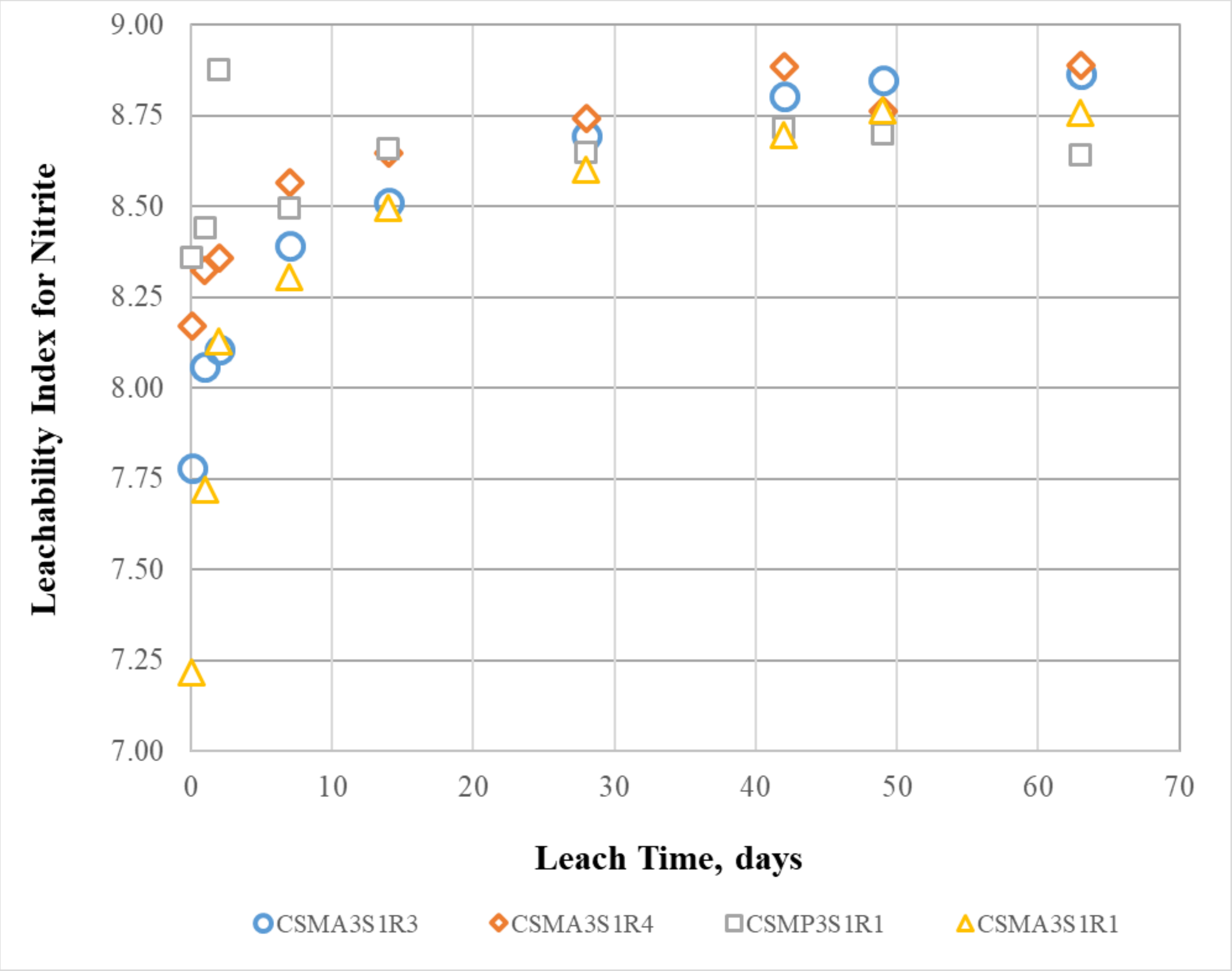

Figure 5.26. Leachability Index values for nitrite as functions of time and formulation: CSMA3 Series with iodine removed.

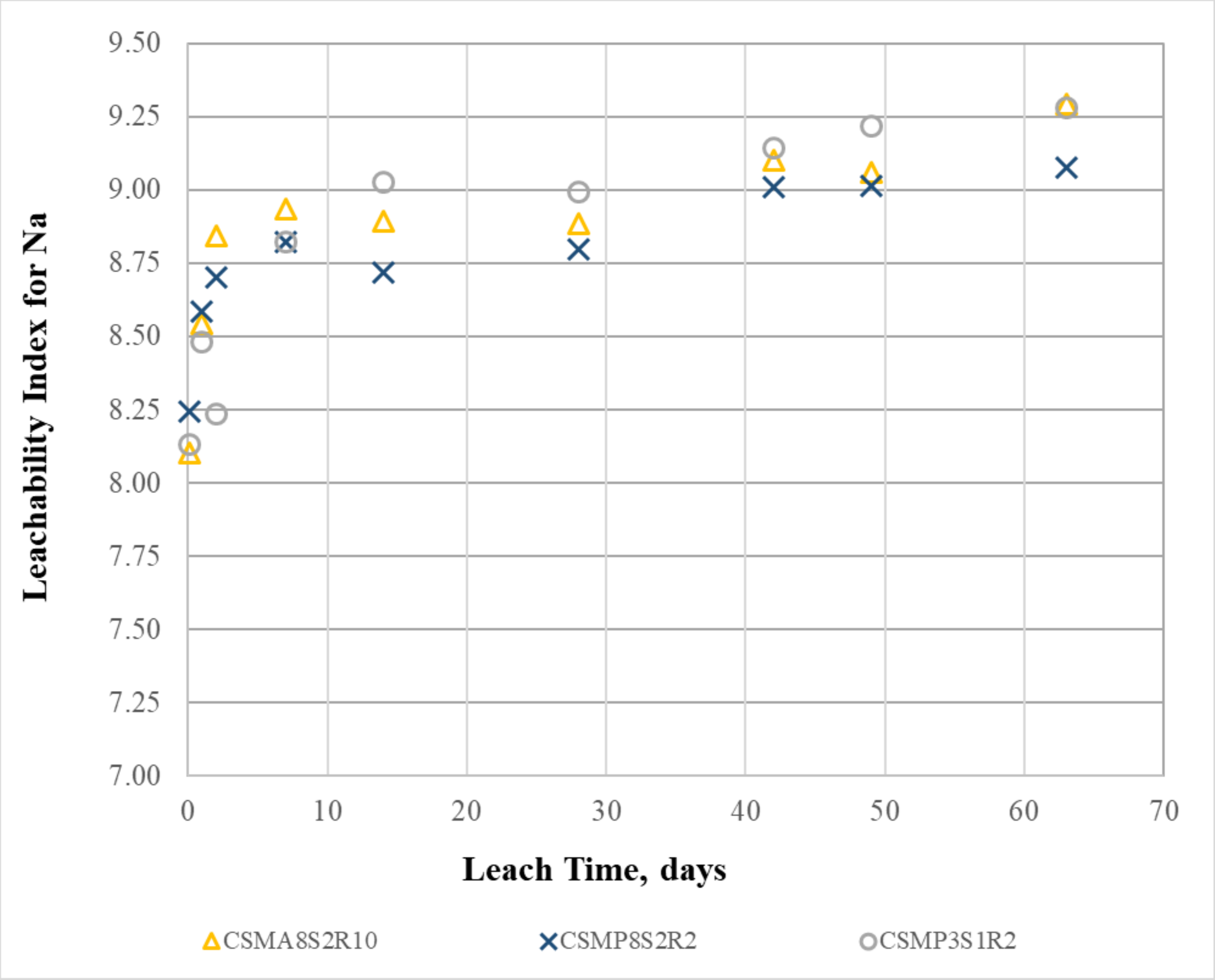

Figure 5.27. Leachability Index values for sodium as functions of time and formulation: 3.5 M Na.

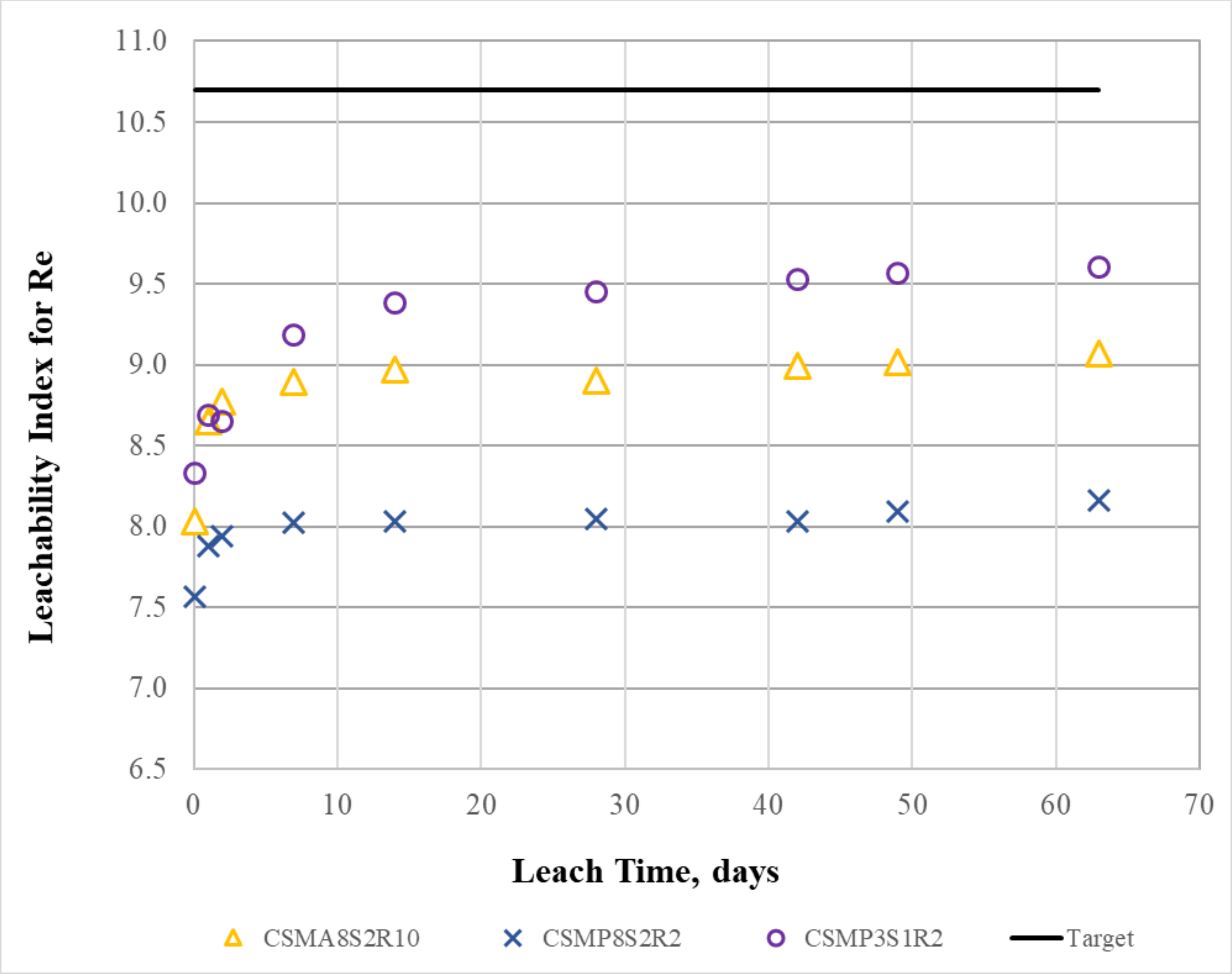

Figure 5.28. Leachability Index values for rhenium as functions of time and formulation: 3.5 M Na.

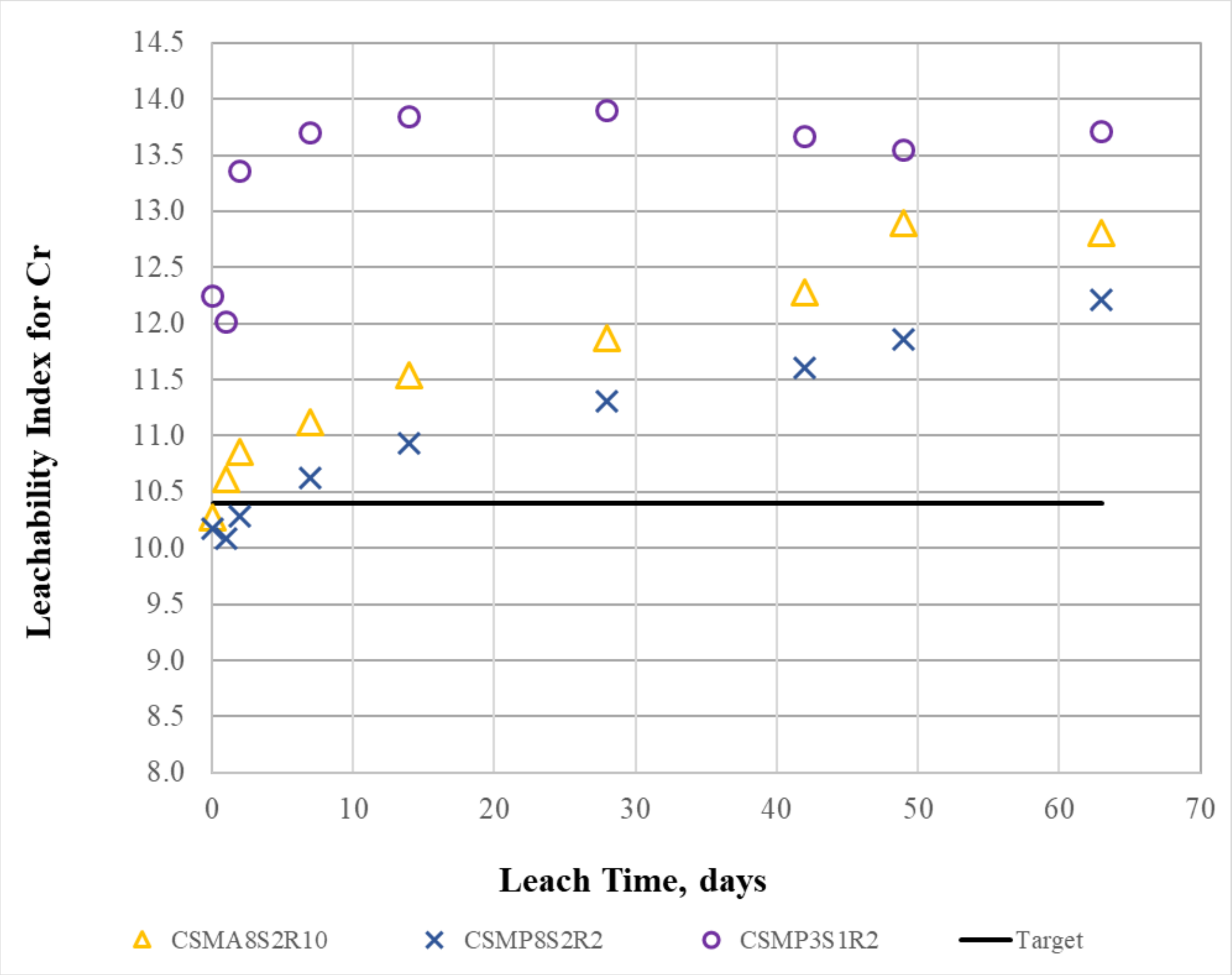

Figure 5.29. Leachability Index values for chromium as functions of time and formulation: 3.5 M Na.

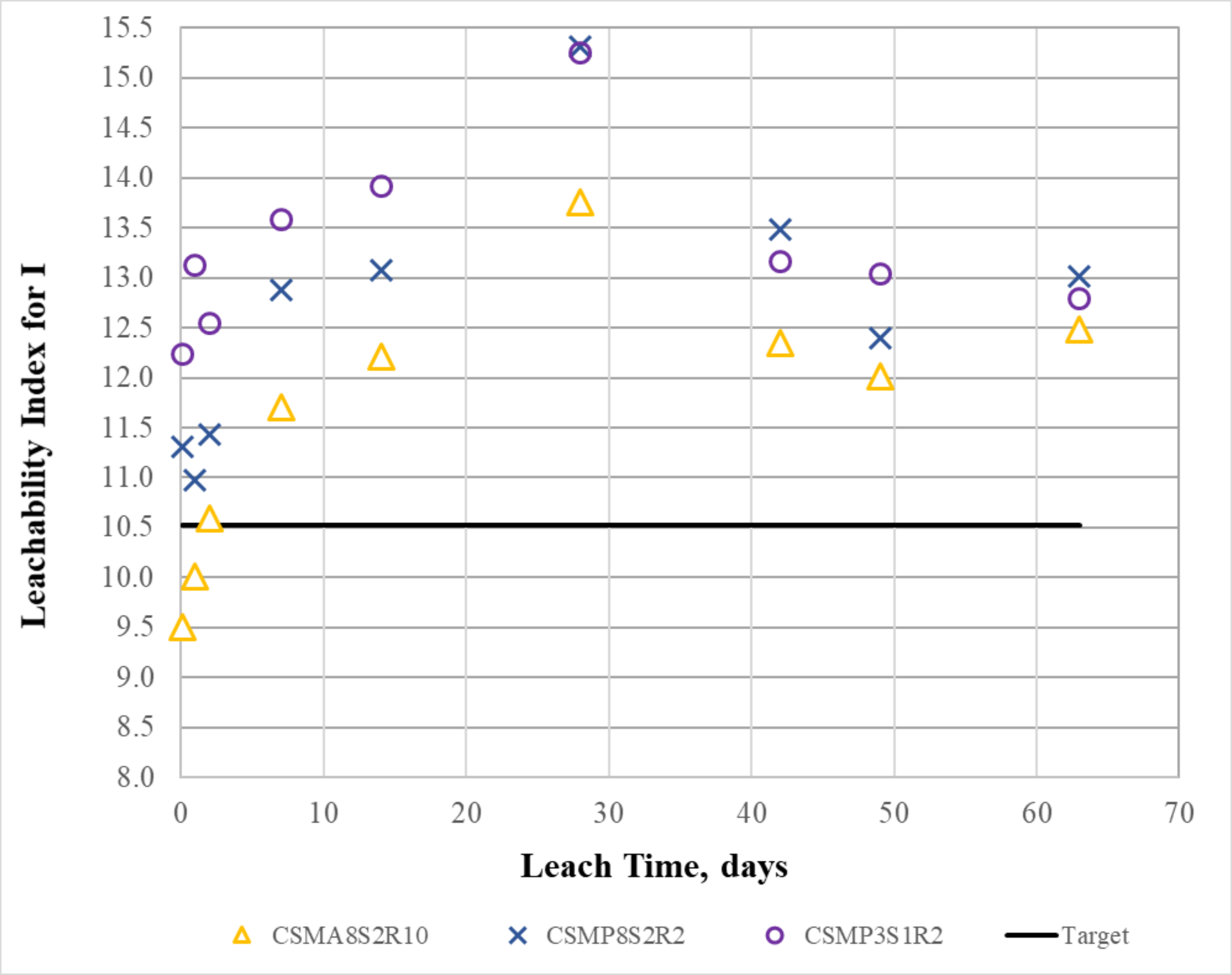

Figure 5.30. Leachability Index values for iodine as functions of time and formulation: 3.5 M Na.

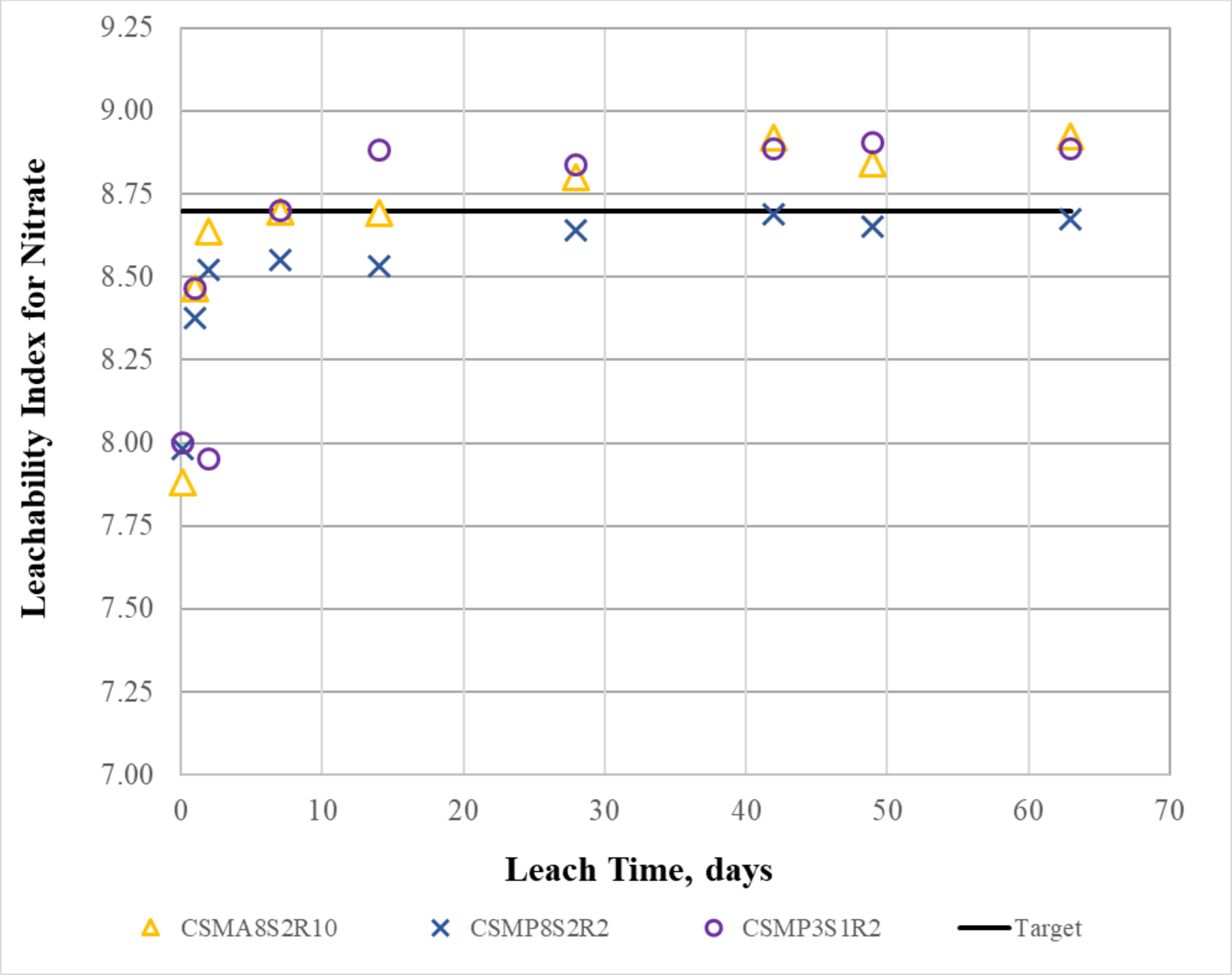

Figure 5.31. Leachability Index values for nitrate as functions of time and formulation: 3.5 M Na.

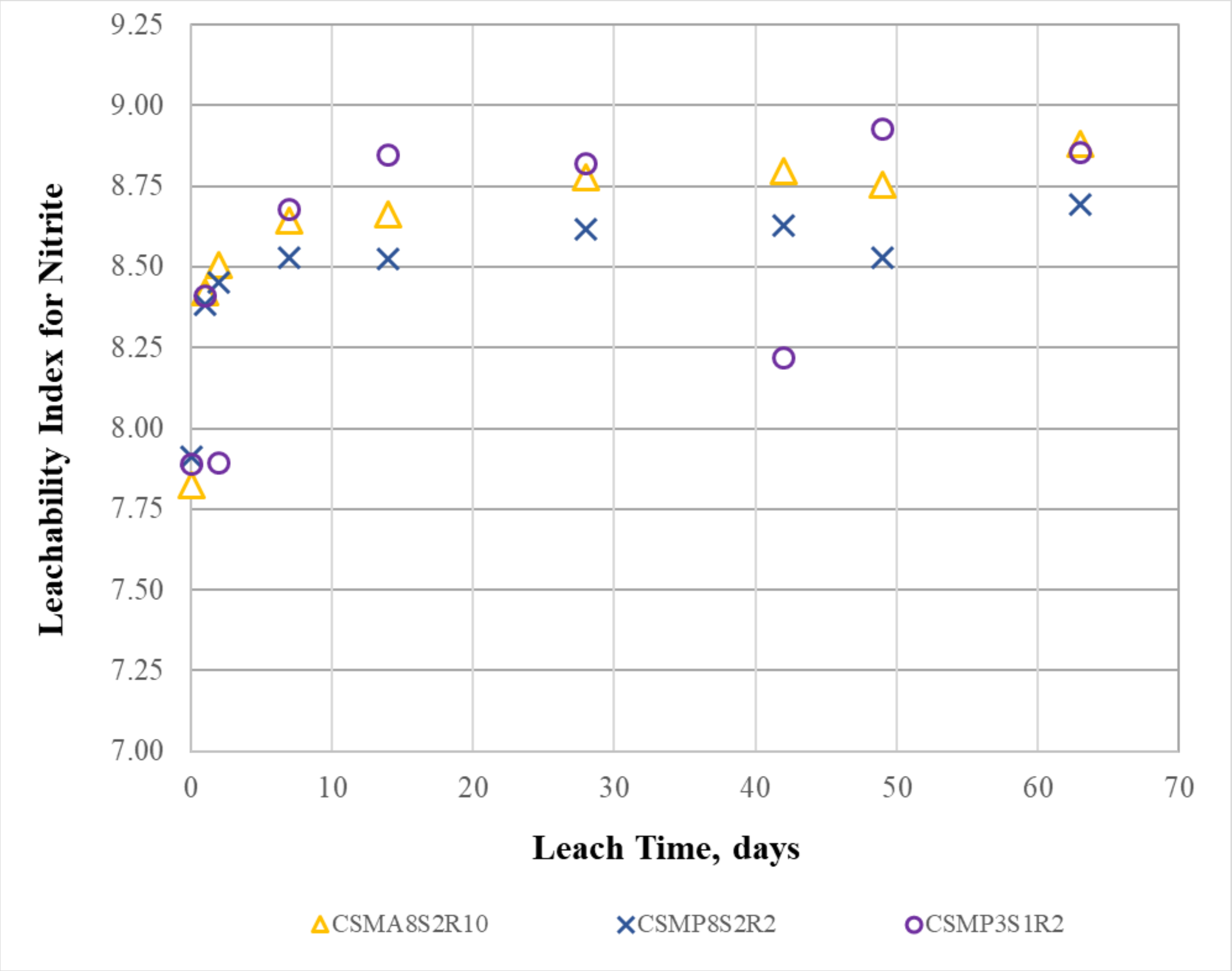

Figure 5.32. Leachability Index values for nitrite as functions of time and formulation: 3.5 M Na.

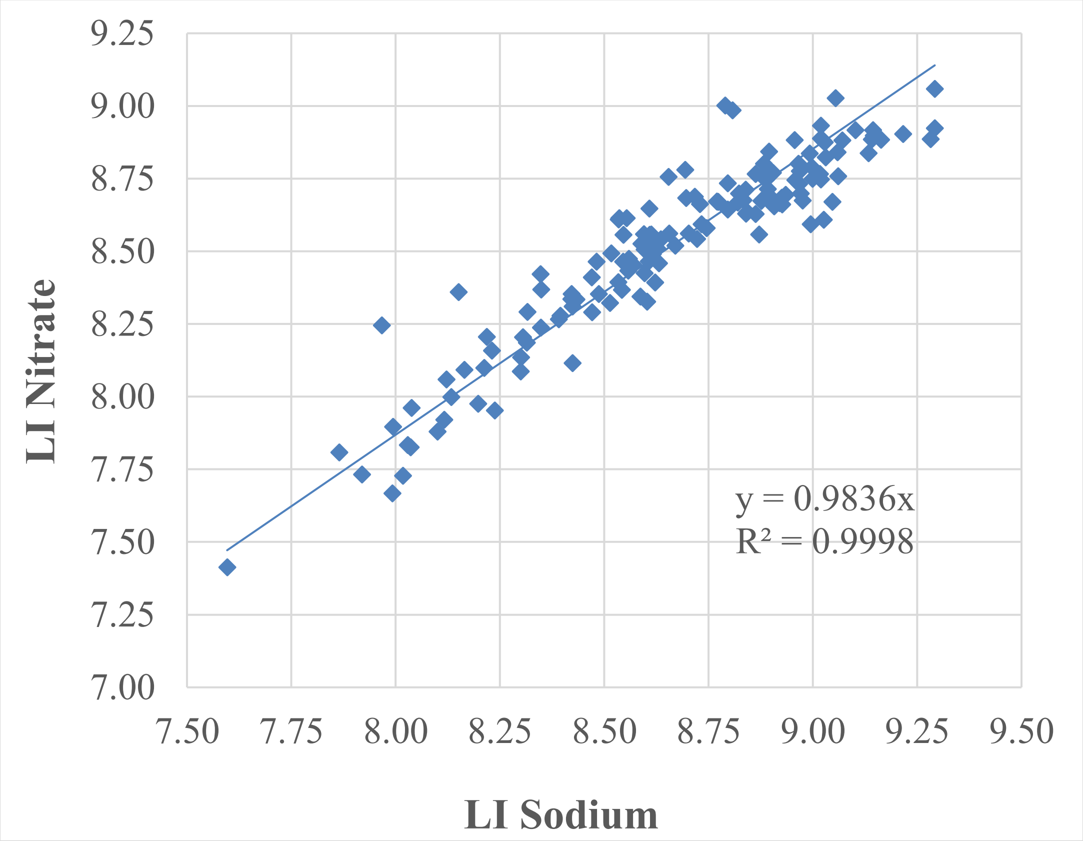

Figure 5.33. Relationship between Leachability indexes for nitrate and sodium in NSAS based waste forms.

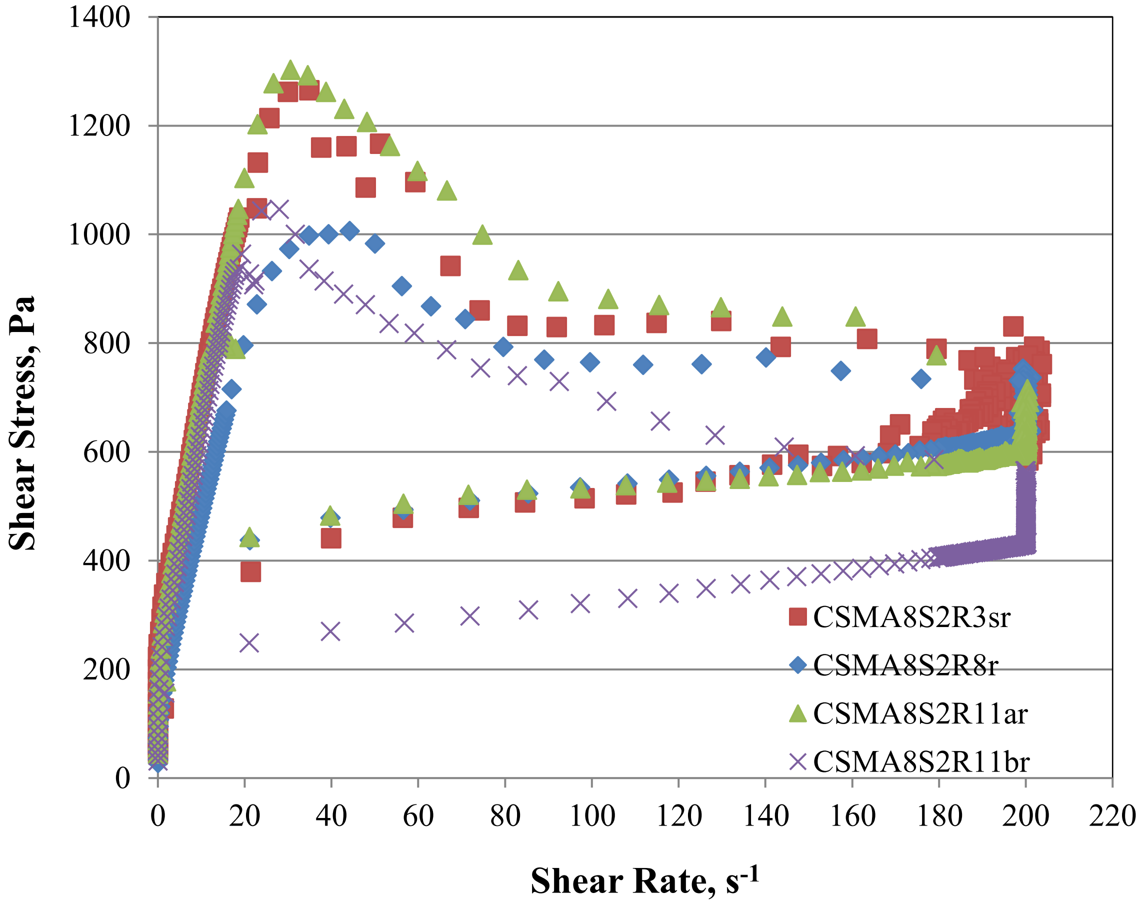

Figure 5.34. Flow curves for fresh grout samples selected (CSMA8 Series with AgZ included).

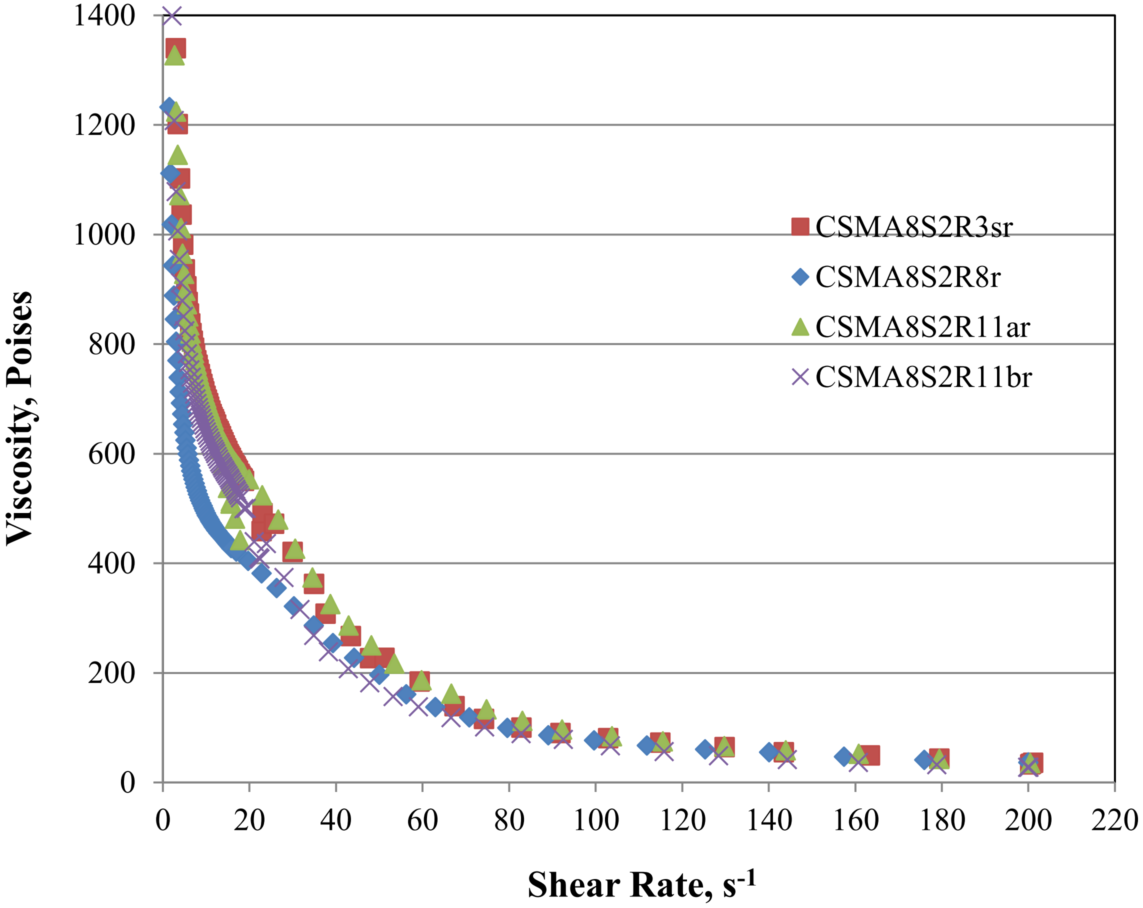

Figure 5.35. Viscosity versus shear rate (increasing) for fresh grout samples selected (CSMA8 Series with AgZ included).

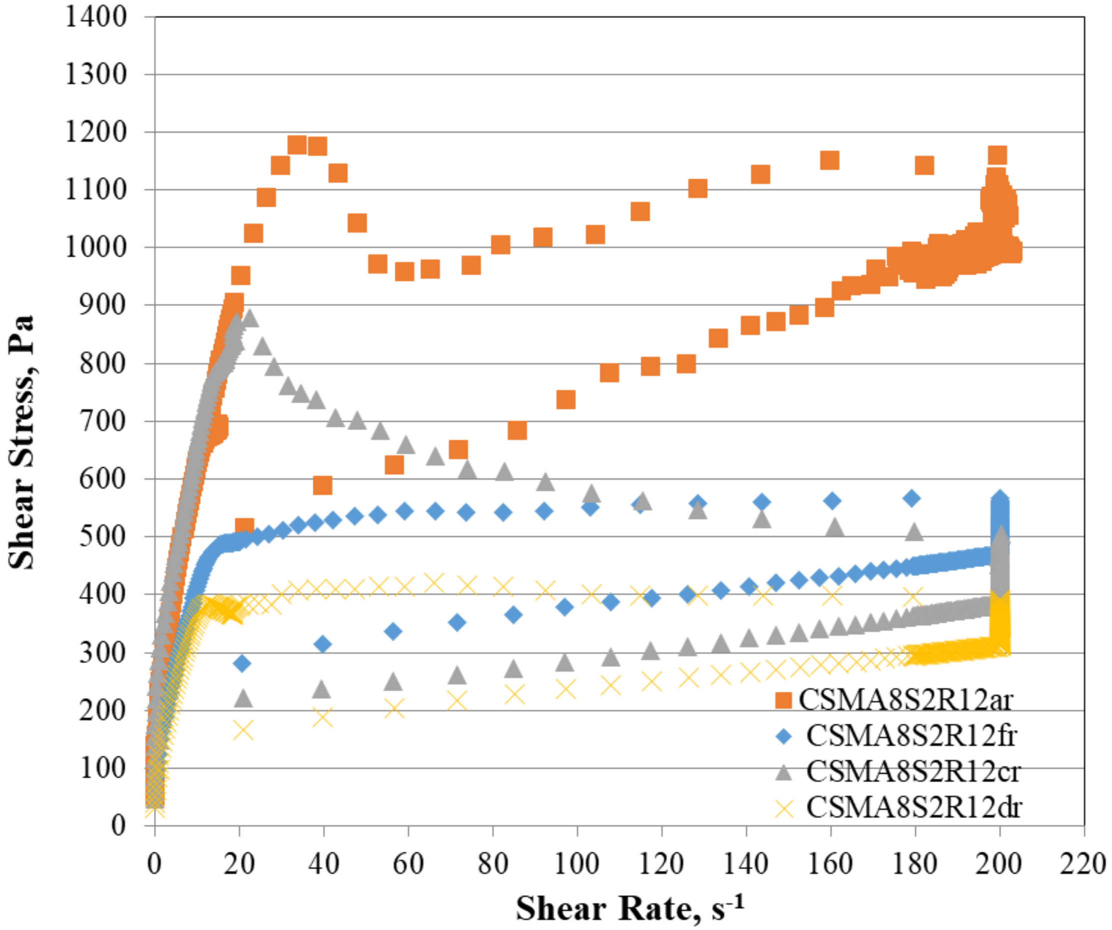

Figure 5.36. Flow curves for fresh grout samples selected (CSMA8 Series with iodine removed).

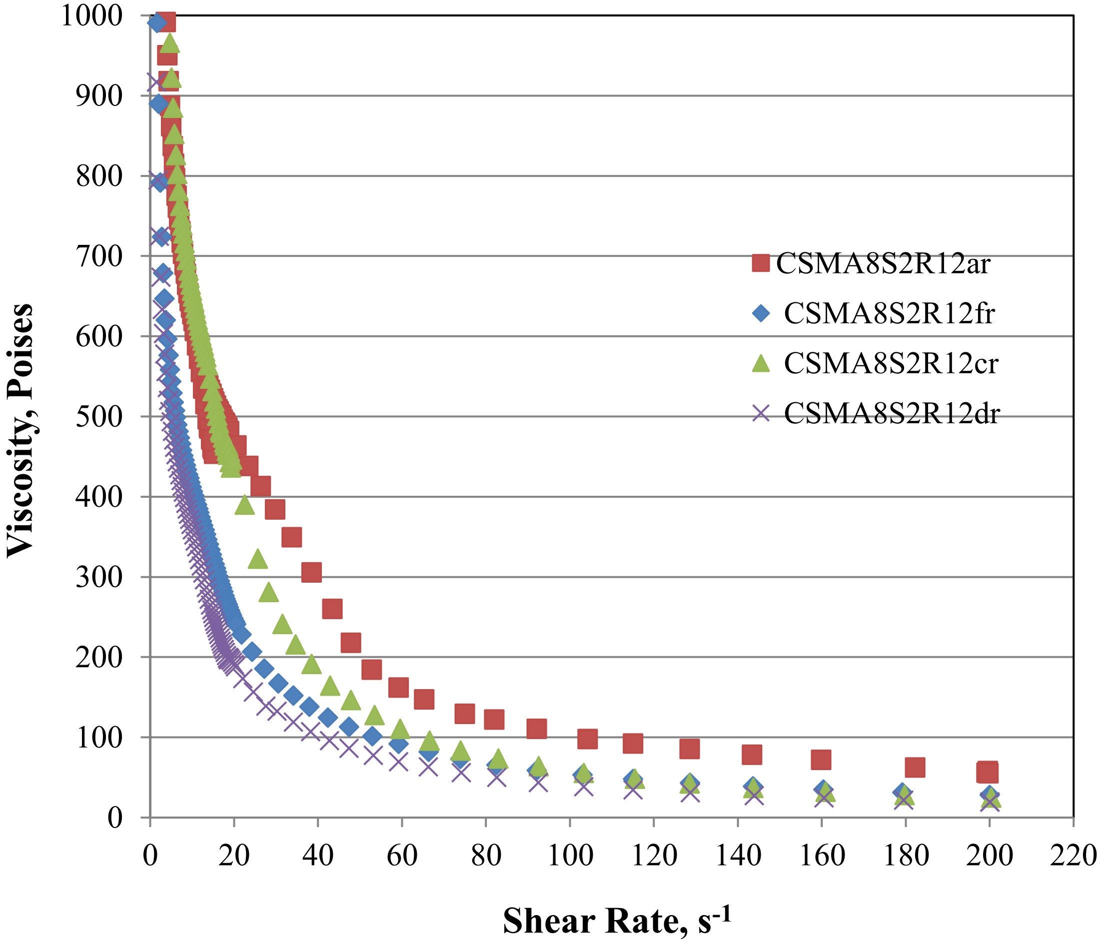

Figure 5.37. Viscosity versus shear rate (increasing) for fresh grout samples selected (CSMA3 Series with iodine removed).

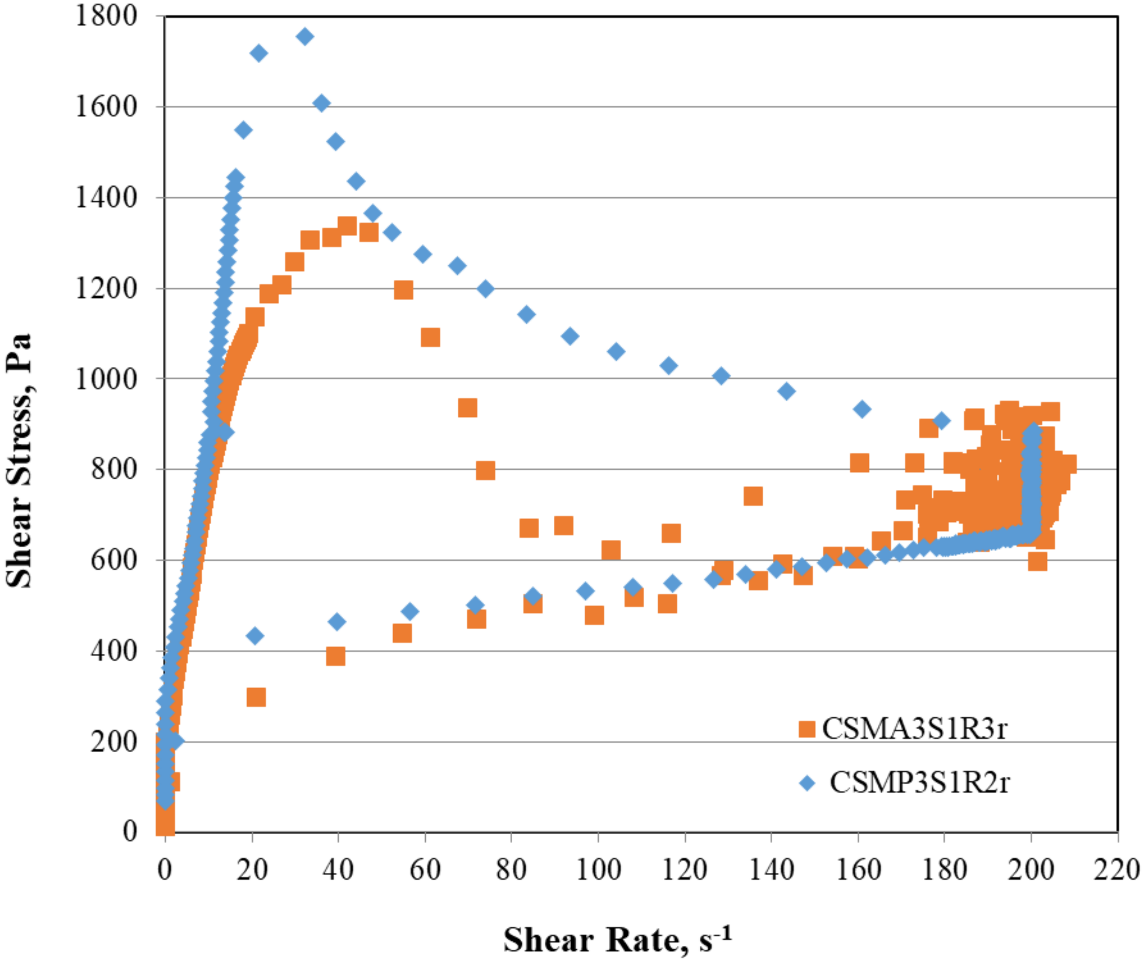

Figure 5.38. Flow curves for fresh grout samples selected (CSMA3 Series with iodine removed).

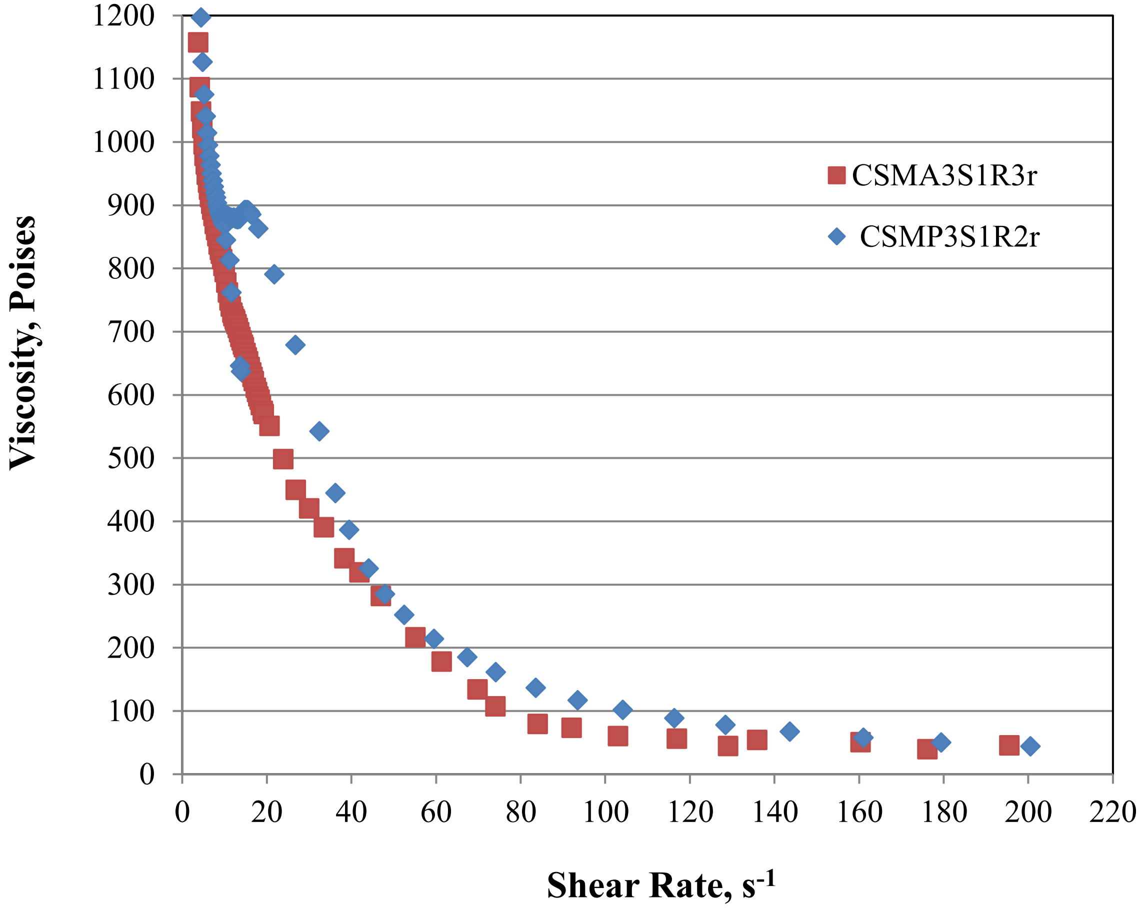

Figure 5.39. Viscosity versus shear rate (increasing) for fresh grout samples selected (CSMA3 series with iodine removed).

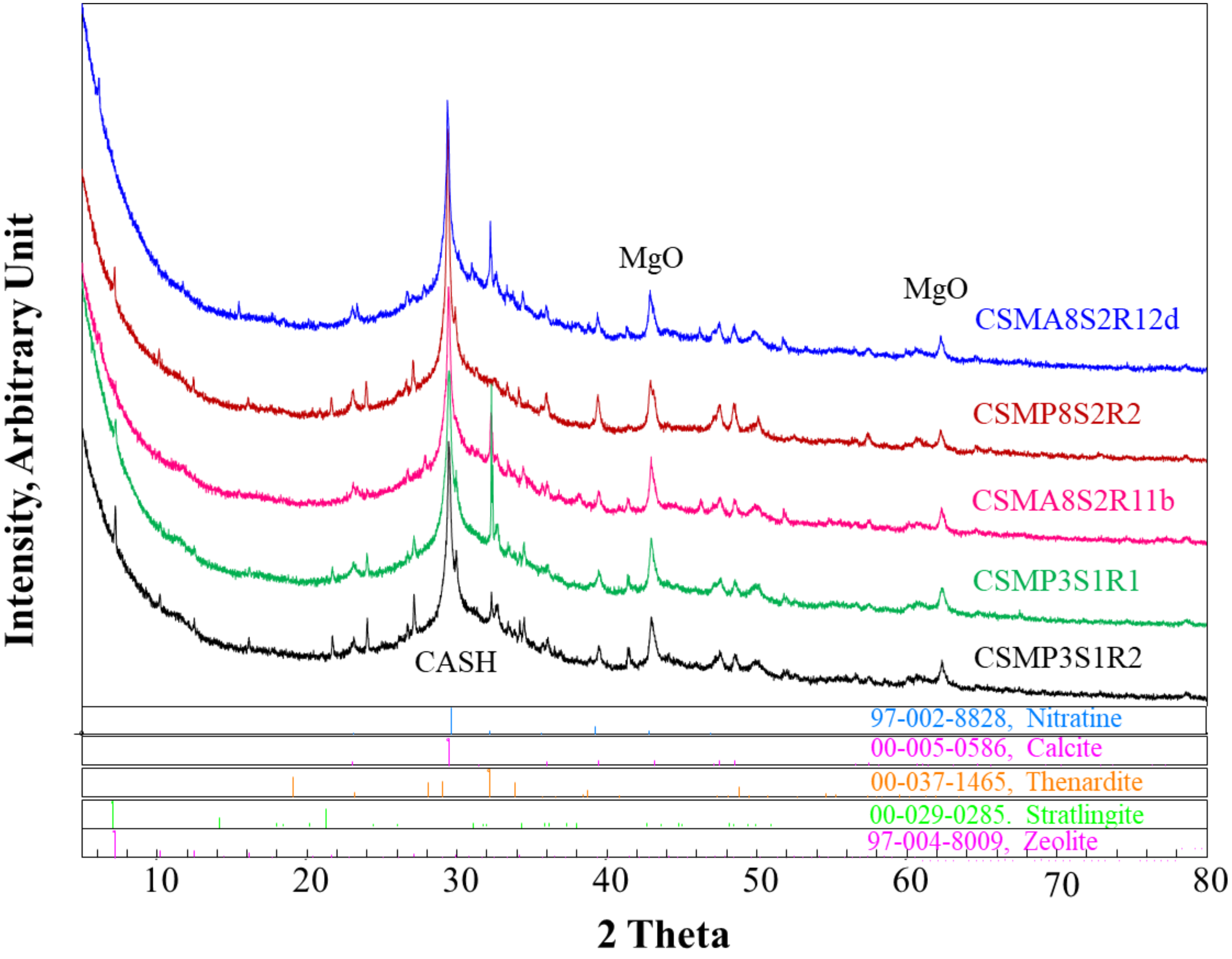

Figure 5.40. XRD patterns of NSAS waste forms (paste only).

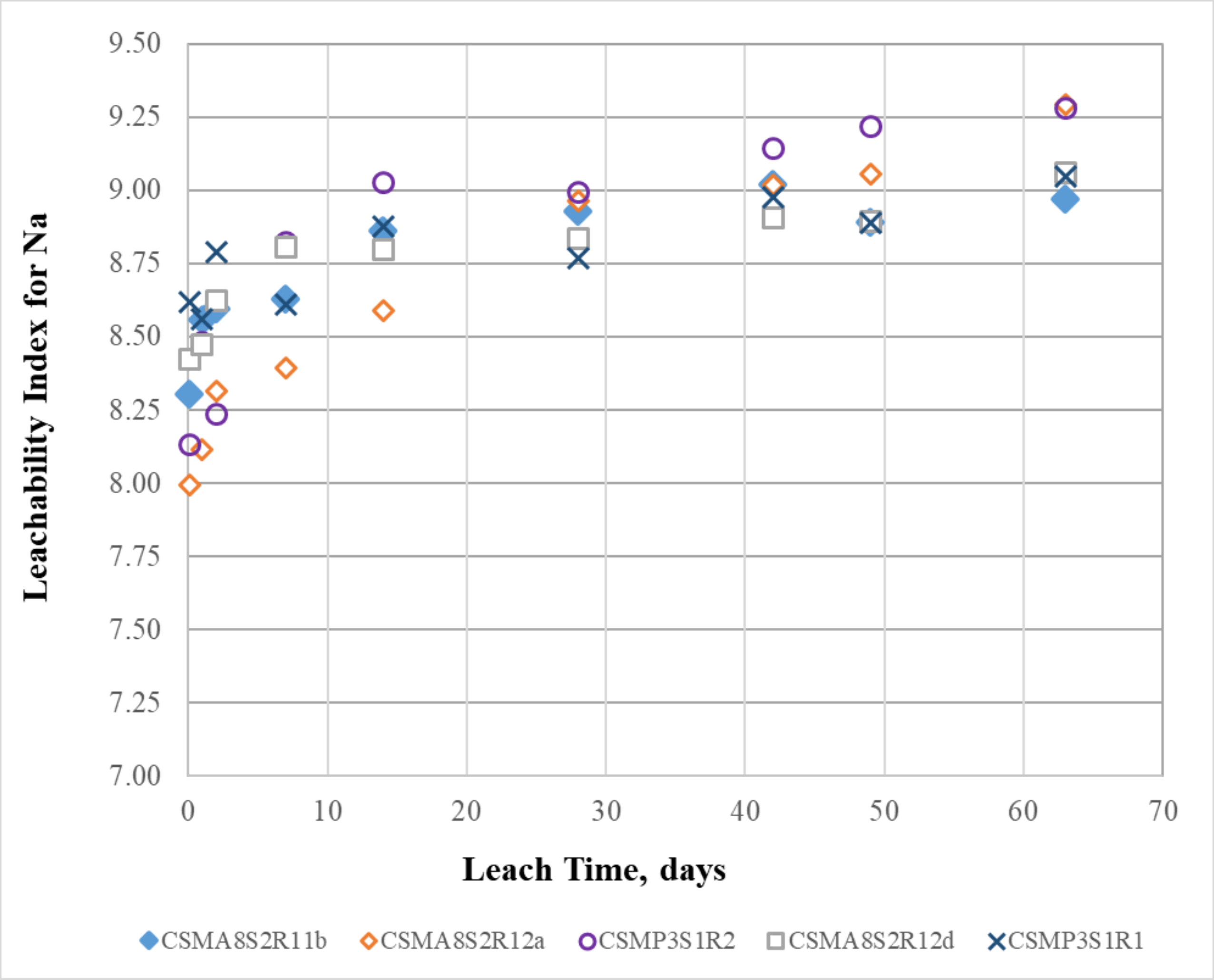

Figure 5.41. Leachability Index values for sodium as functions of time for recommended formulations.

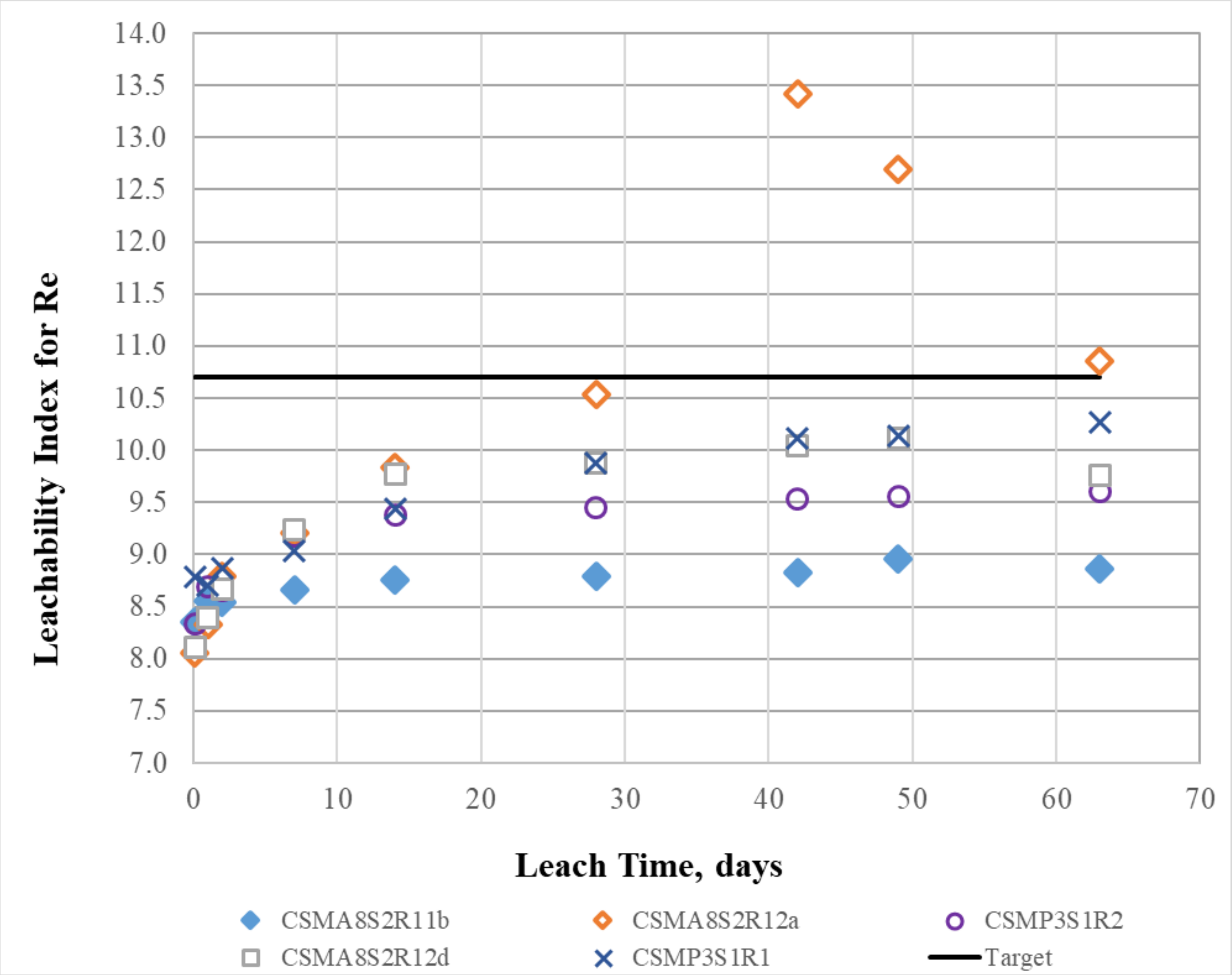

Figure 5.42. Leachability Index values for rhenium as functions of time for recommended formulations.

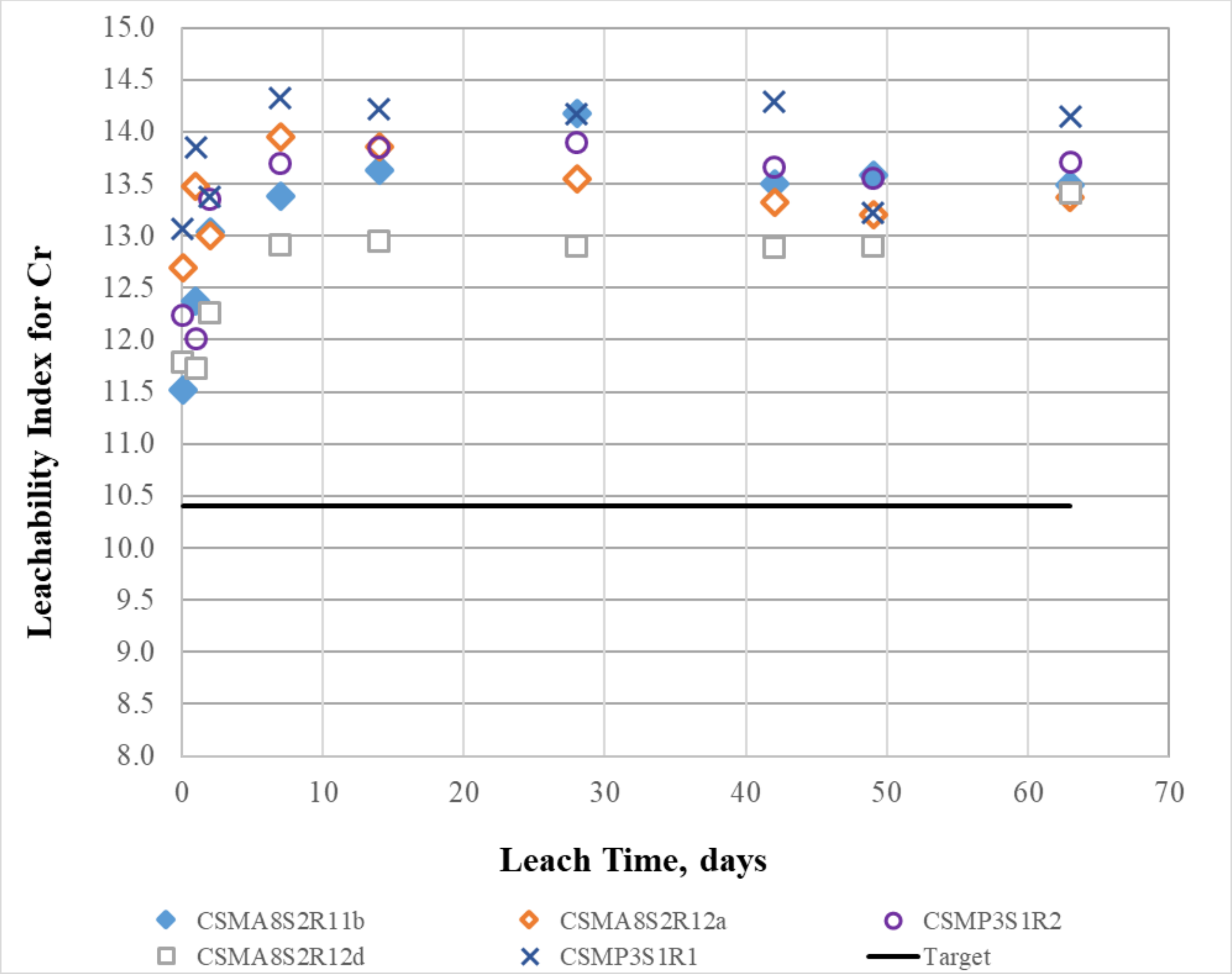

Figure 5.43. Leachability Index values for chromium as functions of time for recommended formulations.

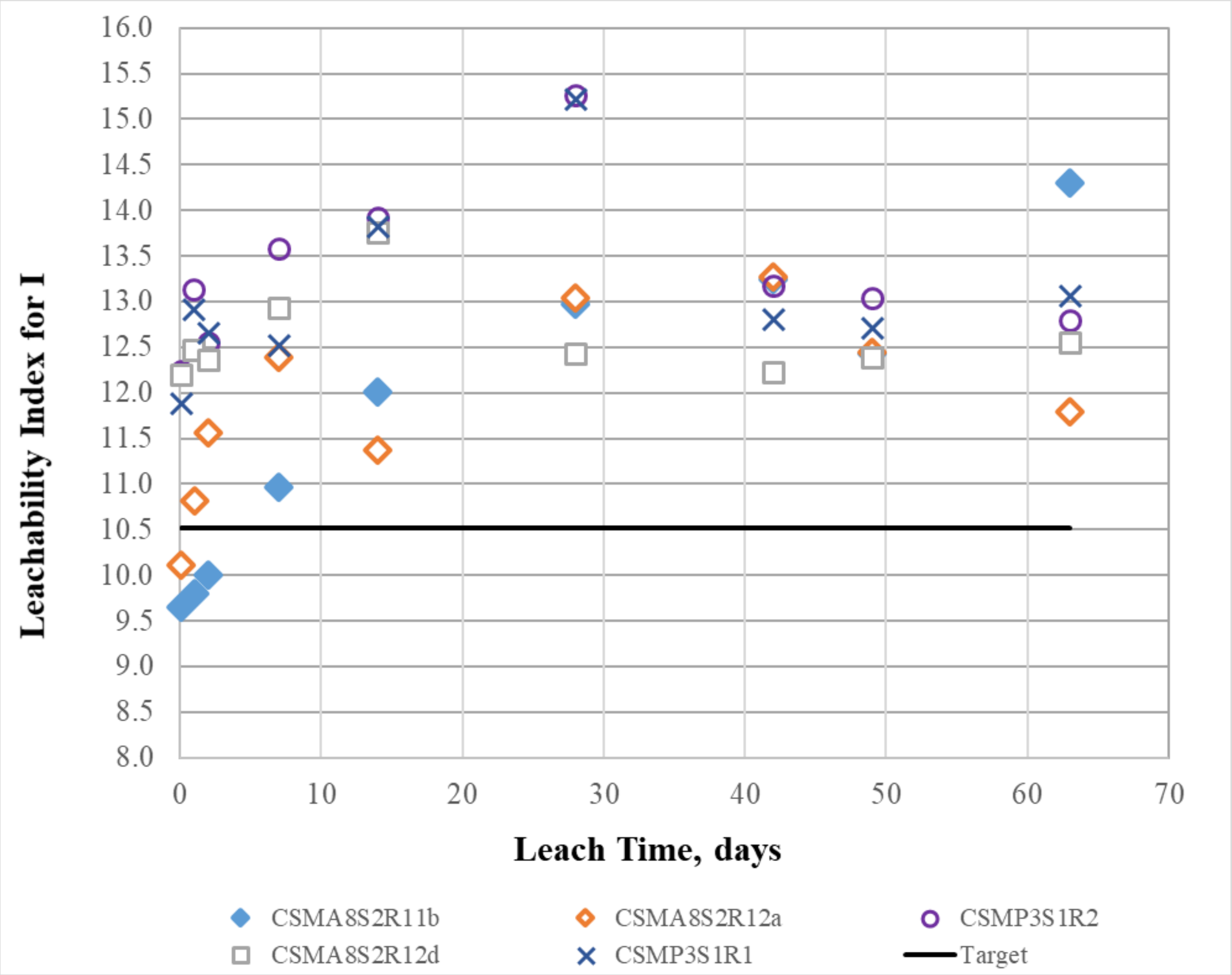

Figure 5.44. Leachability Index values for iodine as functions of time for recommended formulations.

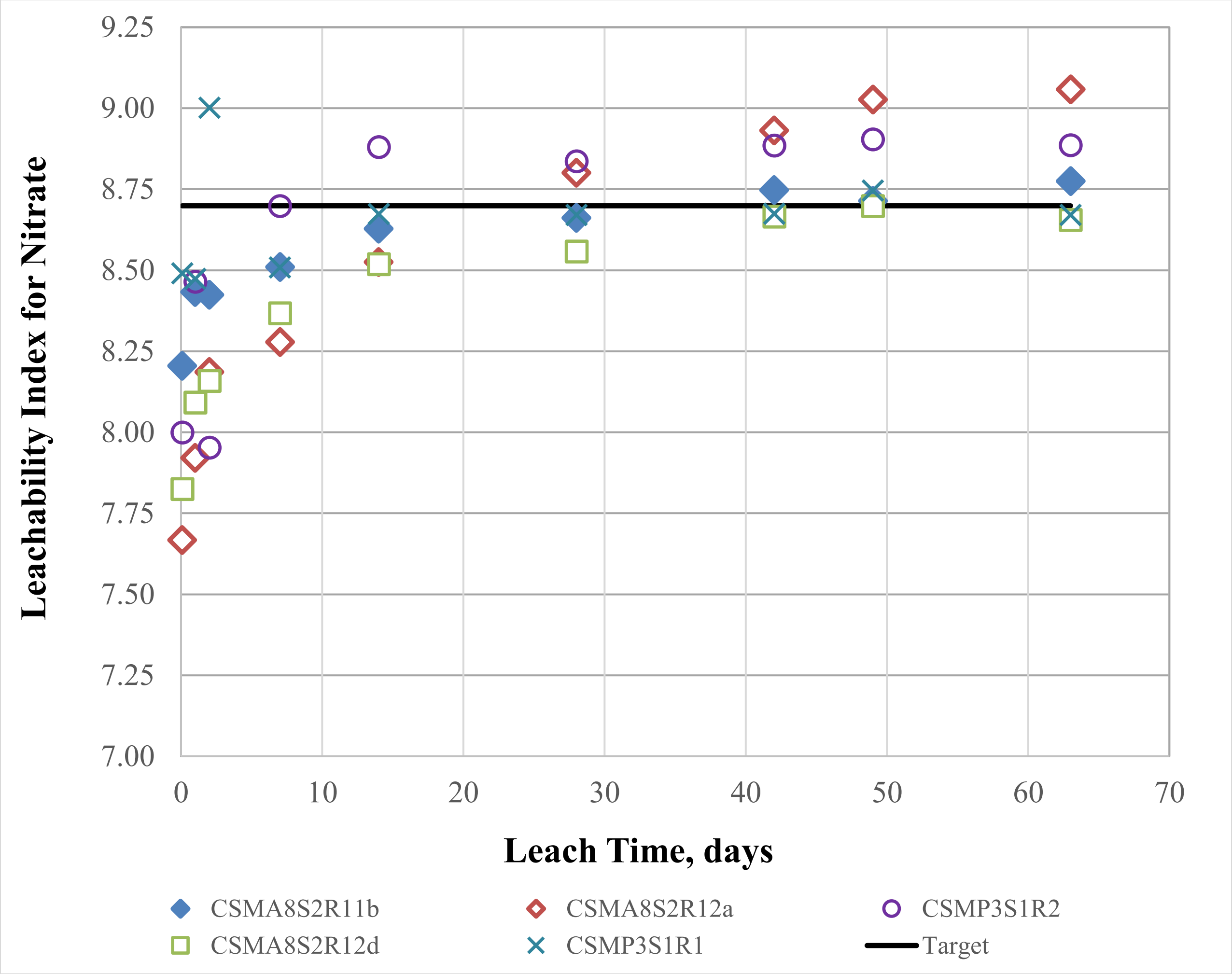

Figure 5.45. Leachability Index values for nitrate as functions of time for recommended formulations.

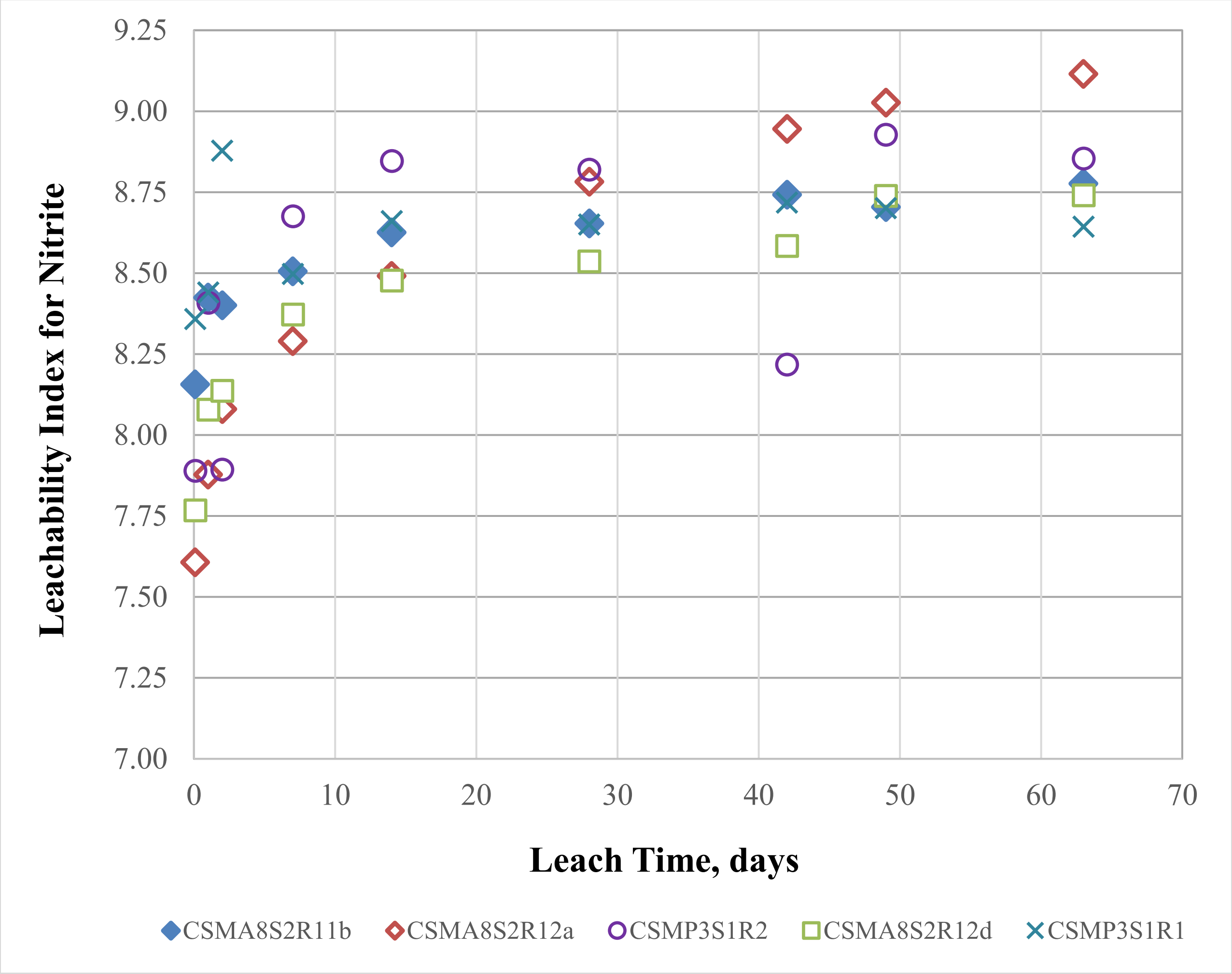

Figure 5.46. Leachability Index values for nitrite as functions of time for recommended formulations.

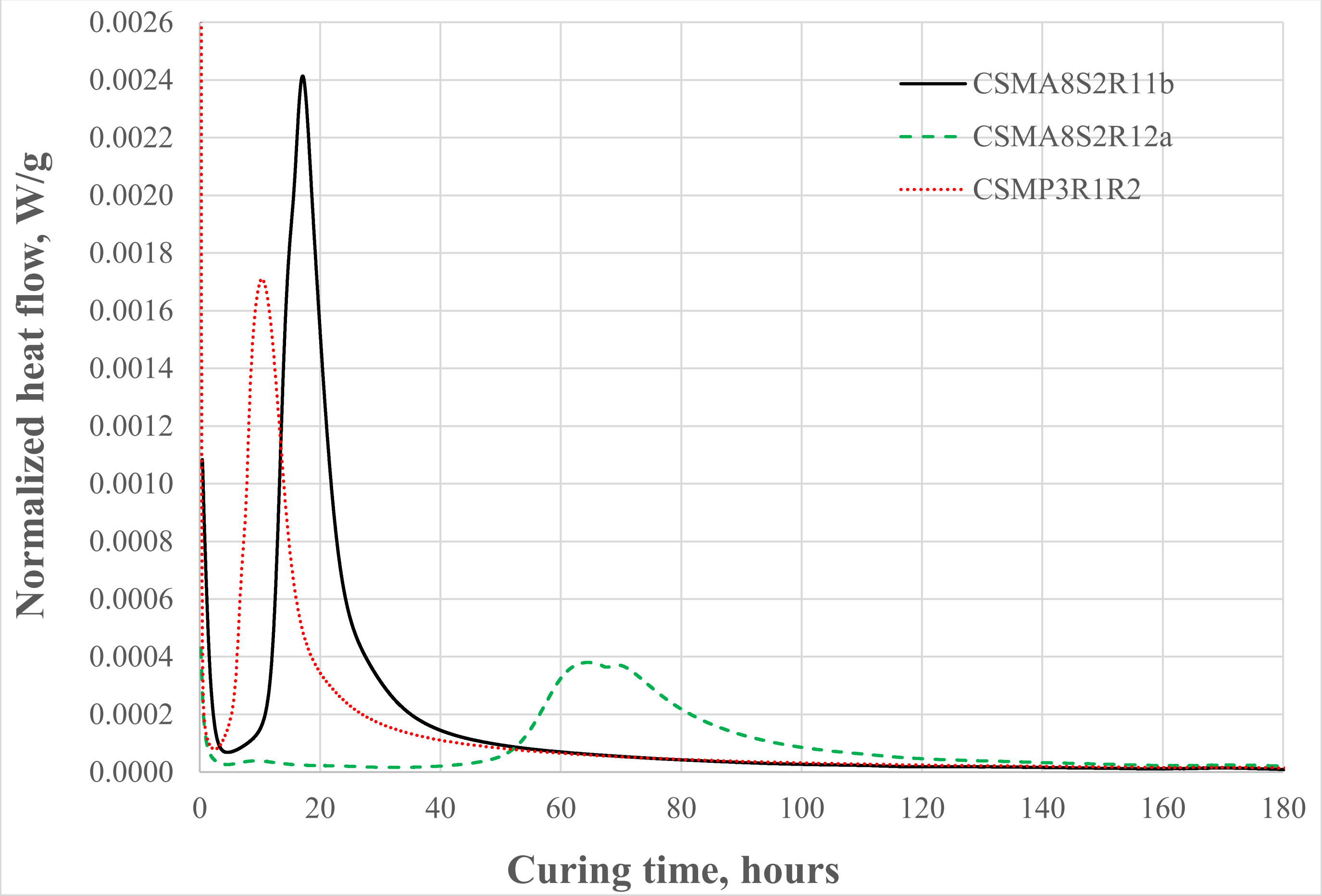

Figure 5.47. Normalized heat flows as function of curing time for recommended formulations.

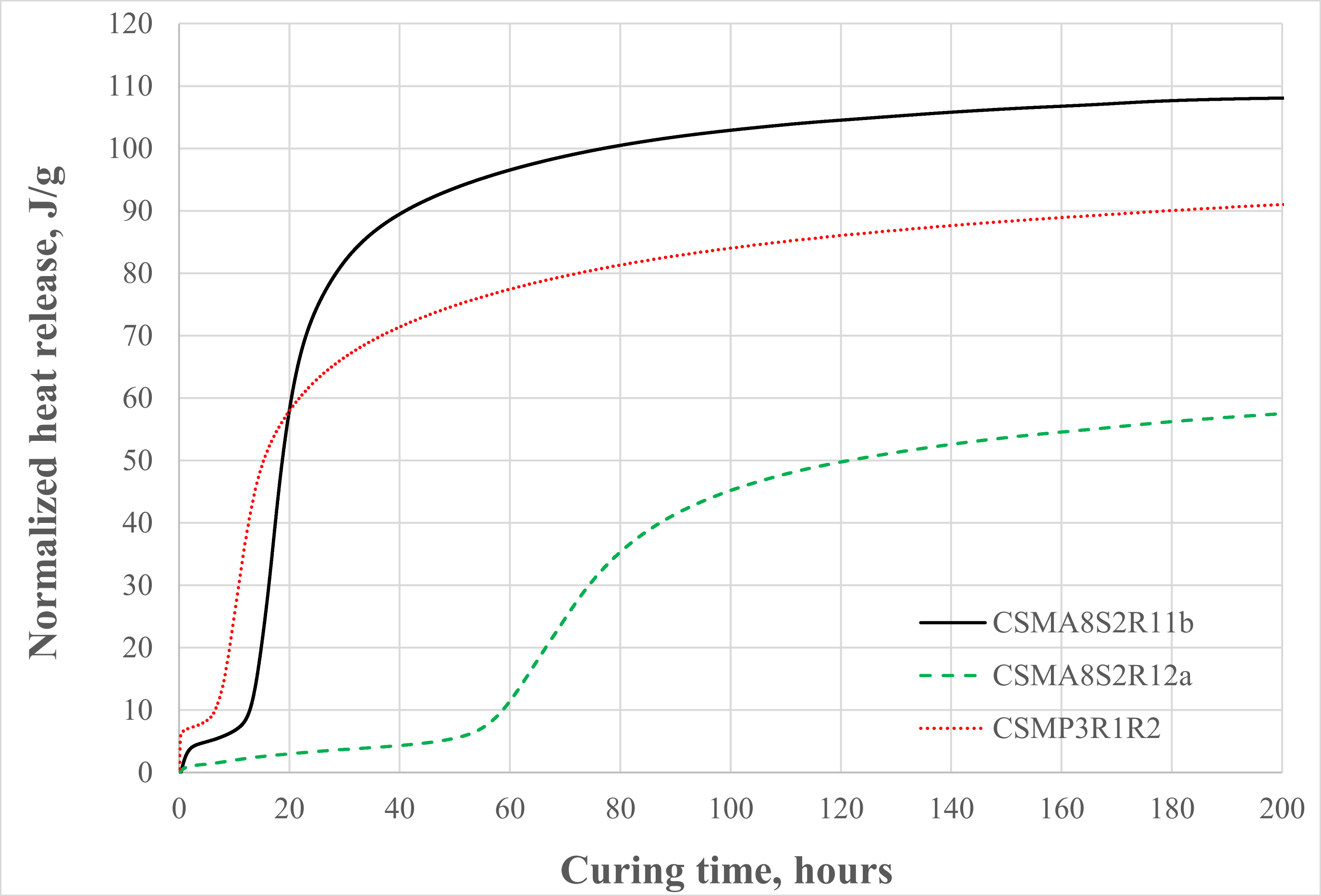

Figure 5.48. Normalized heat release as function of curing time for recommended formulations.

APPENDIX

Analysis of Leaching Data from EPA Method 1315 Tests

Table A1. Slope Values from Plots of Logarithm of Cumulative Releases versus Logarithm of Leaching Time.

Grout ID	BFS Type	AgZ	Na	Re	Cr	I	NO_3^-	NO_2^-
CSMA8S2R5	CP	Included	0.403	0.400	0.257	0.300	0.394	0.394
CSMA8S2R6	DS	Included	0.360	0.219	0.279	0.379	0.331	0.345
CSMA8S2R13	DMI	Included	0.449	0.443	0.172	0.547	0.449	0.448
CSMA8S2R4	SEn	Included	0.389	0.387	0.184	0.370	0.381	0.385
CSMA8S2R3s	CP	Included	0.389	0.275	0.463	0.426	0.396	0.413
CSMA8S2R3c	CP	Included	0.450	0.434	0.259	0.302	0.400	0.385
CSMA8S2R8	CP	Included	0.369	0.375	0.239	0.242	0.364	0.359
CSMA8S2R11a	CP	Included	0.393	0.395	0.237	0.250	0.390	0.413
CSMA8S2R11b*	CP	Included	0.415	0.435	0.201	0.231	0.433	0.426
CSMA8S2R12a*	SEo	Removed	0.382	0.240	0.365	0.208	0.351	0.344
CSMA8S2R12c	CP	Removed	0.442	0.349	0.359	0.243	0.447	0.436
CSMA8S2R12d*	SEo	Removed	0.389	0.275	0.453	0.426	0.390	0.385
CSMA8S2R12e	DS	Removed	0.442	0.349	0.359	0.243	0.447	0.436
SMA8S2R12f	DS	Removed	0.400	0.216	0.451	0.453	0.417	0.418
CSMA3S1R3*	SEn	Removed	0.374	0.243	0.370	0.490	0.373	0.372
CSMA3S1R4	CP	Removed	0.410	0.370	0.370	0.420	0.424	0.415
CSMP3S1R1*	CP	Removed	0.467	0.379	0.341	0.312	0.473	0.455
CSMA8S2R10$^{\$}$	CP	Included	0.366	0.361	0.297	0.172	0.362	0.362
CSMP8S2R2$^{\$}$	CP	Included	0.407	0.426	0.358	0.269	0.403	0.398
CSMP3S1R2*$^{\$}$	CP	Removed	0.370	0.341	0.280	0.296	0.380	0.387

* Formulations selected for further consideration

$ Grout samples prepared with 3.5 M Na; all other samples were prepared with 5.6 M Na AltLAW

Table A2. Data Summary of Observed Diffusivity and Retardation Factors (FY24).

Grout ID	Additives	SF (BWOS)	D_{obs}, cm^2/s				Retardation Factor		
			NO_3^-	NO_2^-	Na	I	NO_3^-	NO_2^-	I
CSMA8S2R5	AgZ	0.06	1.66E-09	1.77E-09	2.02E-09	6.35E-12	1.75	1.64	490
CSMA8S2R6	AgZ	0.06	2.63E-09	2.87E-09	1.80E-09	1.38E-09	0.98	0.90	2.00
CSMA8S2R13	AgZ	0.06	3.94E-08	3.99E-08	3.61E-08	1.15E-08	1.31	1.30	4.81
CSMA8S2R4	AgZ	0.10	1.85E-09	1.96E-09	1.08E-09	3.37E-11	0.83	0.79	49.21
CSMA8S2R3s	AgZ	0.14	1.74E-09	2.07E-09	8.70E-10	1.15E-12	0.71	0.60	1159.
CSMA8S2R3c	AgZ	0.14	1.33E-09	1.35E-09	9.37E-10	5.09E-13	1.01	1.00	2820
CSMA8S2R8	AgZ	0.14	1.29E-09	1.07E-09	9.56E-10	6.06E-13	1.06	1.28	2425
CSMA8S2R11a	AgZ	0.14	1.45E-09	1.48E-09	7.36E-10	3.20E-13	0.72	0.71	3533
CSMA8S2R11b*	AgZ	0.14	1.67E-09	1.67E-09	1.07E-09	5.01E-15	0.92	0.92	329631
CSMA8S2R12a*	#	0.14	8.73E-10	7.67E-10	5.11E-10	1.63E-12	0.84	0.96	482
CSMA8S2R12c	#	0.14	2.46E-09	2.56E-09	9.41E-10	1.05E-13	0.55	0.53	13846
CSMA8S2R12d*	#	0.14	2.21E-09	1.81E-09	1.24E-09	1.34E+13	0.80	0.98	6683
CSMA8S2R12e	#	0.14	5.36E-09	4.60E-09	2.57E-09	3.04E-13	0.68	0.80	12981
CSMA8S2R12f	#	0.14	3.02E-09	2.67E-09	2.14E-09	1.02E-12	1.01	1.15	3211
CSMA3S1R3*	#	0.14	1.52E-09	1.37E-09	8.50E-10	7.26E-13	0.80	0.89	1803
CSMA3S1R4	#	0.14	1.31E-09	1.29E-09	8.60E-10	4.31E-13	0.94	0.96	3067
CSMP3S1R1*	#	0.14	2.01E-09	2.06E-09	8.95E-10	8.74E-14	0.63	0.62	15736
CSMA8S2R10[$]	AgZ	0.14	1.19E-09	1.31E-09	5.10E-10	3.27E-13	0.61	0.56	2402
CAMP8S2R2*[$]	AgZ	0.14	2.13E-09	2.03E-09	8.42E-10	9.64E-14	0.57	0.60	13431
CSMP3S1R2[$]	AgZ	0.14	1.30E-09	1.40E-09	5.22E-10	1.63E-13	0.57	0.54	4911

* Formulations selected for further considerations

AgZ removed before grouting

[$] Grout samples prepared with 3.5 M Na; all other samples were prepared with 5.6 M Na AltLAW

Table A3. Data Summary of Observed Diffusivity and Retardation Factors (Prior to FY24).

Grout ID	Ref.	Additive	SF (BWOS)	D_{obs}, cm^2/s			Retardation Factor	
				NO_3^-	NO_2^-	Na	NO_3^-	NO_2^-
CSM0.40A3S	FY21	CTH	0.06	8.82E-10	1.00E-09	9.13E-10	1.48	1.31
CSM0.40A4S*	FY21	CTH	0.06	5.50E-11	8.25E-11	1.58E-10	4.11	2.75
CSM0.40A8S*	FY21	AgZ	0.06	4.05E-11	5.81E-11	1.70E-10	5.99	4.20
CSMA3S1	FY22	CTH	0.06	2.01E-09	2.28E-09	1.94E-09	1.38	1.22
CSMA8S1	FY22	AgZ	0.06	1.55E-09	1.56E-09	1.35E-09	1.24	1.24
CSMA1S3	FY22	CTH	0.00	1.72E-09	2.02E-09	2.47E-09	2.05	1.75
CSMA3S1R1	FY23	CTH$	0.06	1.87E-09	1.75E-09	1.49E-09	1.14	1.22
CSMA8S2	FY23	AgZ	0.06	1.64E-09	2.04E-09	2.14E-09	1.87	1.51
CSMA8S3	FY23	AgZ	0.06	1.82E-09	2.23E-09	2.66E-09	2.09	1.72
CSMA8S4	FY23	AgZ	0.00	3.87E-09	7.37E-09	4.71E-09	1.74	0.92
CSMA8S5cp	FY23	AgZ	0.00	8.38E-10	1.73E-09	1.67E-09	2.84	1.38
CSMA8S2R1	FY23	AgZ	0.06	1.34E-09	9.74E-10	1.10E-09	1.17	1.62
CSMA8S7	FY23	AgZ	0.00	1.89E-09	3.43E-09	2.39E-09	1.80	1.00
CSMA8S8	FY23	AgZ	0.00	2.01E-09	1.56E-09	2.68E-09	1.91	2.46
CSMA8S2R3	FY23	AgZ	0.06	1.49E-09	1.06E-09	9.93E-10	0.95	1.35
CSMA3S4	FY23	AgZ/CTH	0.00	9.18E-10	7.71E-10	2.11E-09	3.29	3.93
CSMA3S5	FY23	C_3A/CH	0.00	1.43E-09	1.24E-09	2.48E-09	2.48	2.88
CSMA3S3	FY23	AgZ/CTH	0.08	2.60E-09	1.88E-09	2.13E-09	1.17	1.62
CSMA1S4	FY23	AgZ/CTH	0.00	1.63E-09	1.30E-09	2.33E-09	2.04	2.57
CSMA3S3.5M1	FY23	AgZ/CTH	0.00	4.86E-10	3.10E-10	1.58E-09	4.64	7.32

* 1 M Na AltLAW; $ AgZ removed before grouting; AgZ = Ionex Ag-400; C_3A = tricalcium aluminate; CH = calcium hydroxide; References: FY21 [8]; FY22 [9]; FY23 [10].

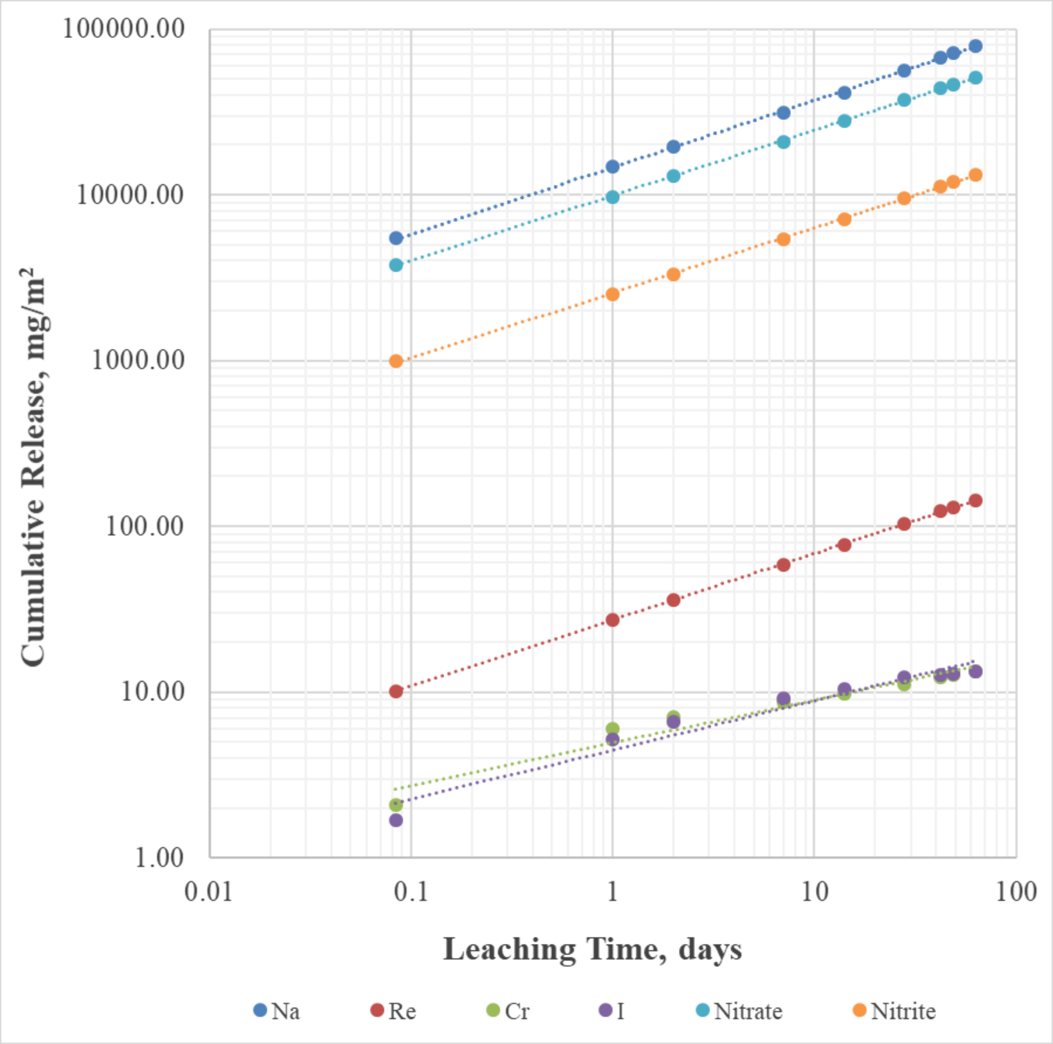

Figure A1. Cumulative release vs. leaching time on log-log scale (CSMA8S2R5).

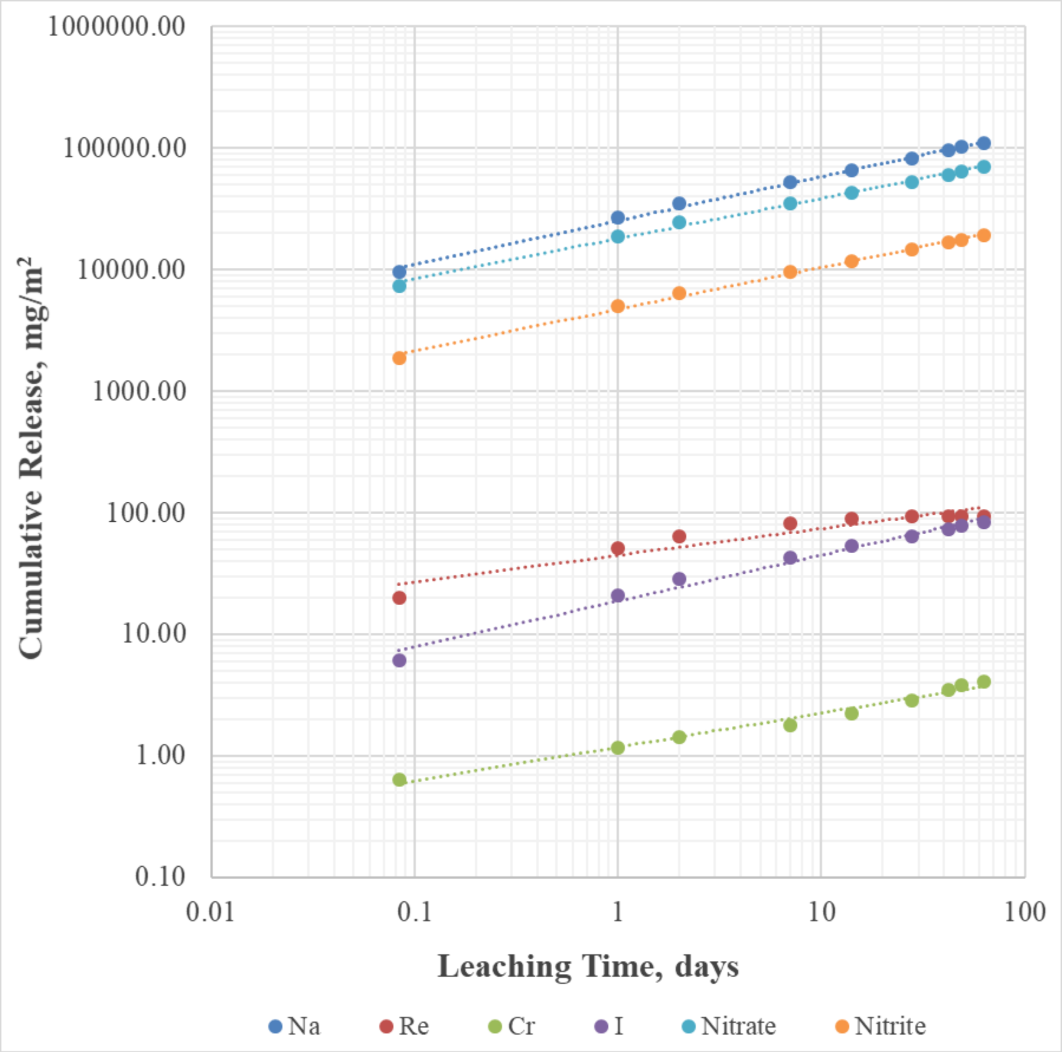

Figure A2. Cumulative release vs. leaching time on log-log scale (CSMA8S2R6).

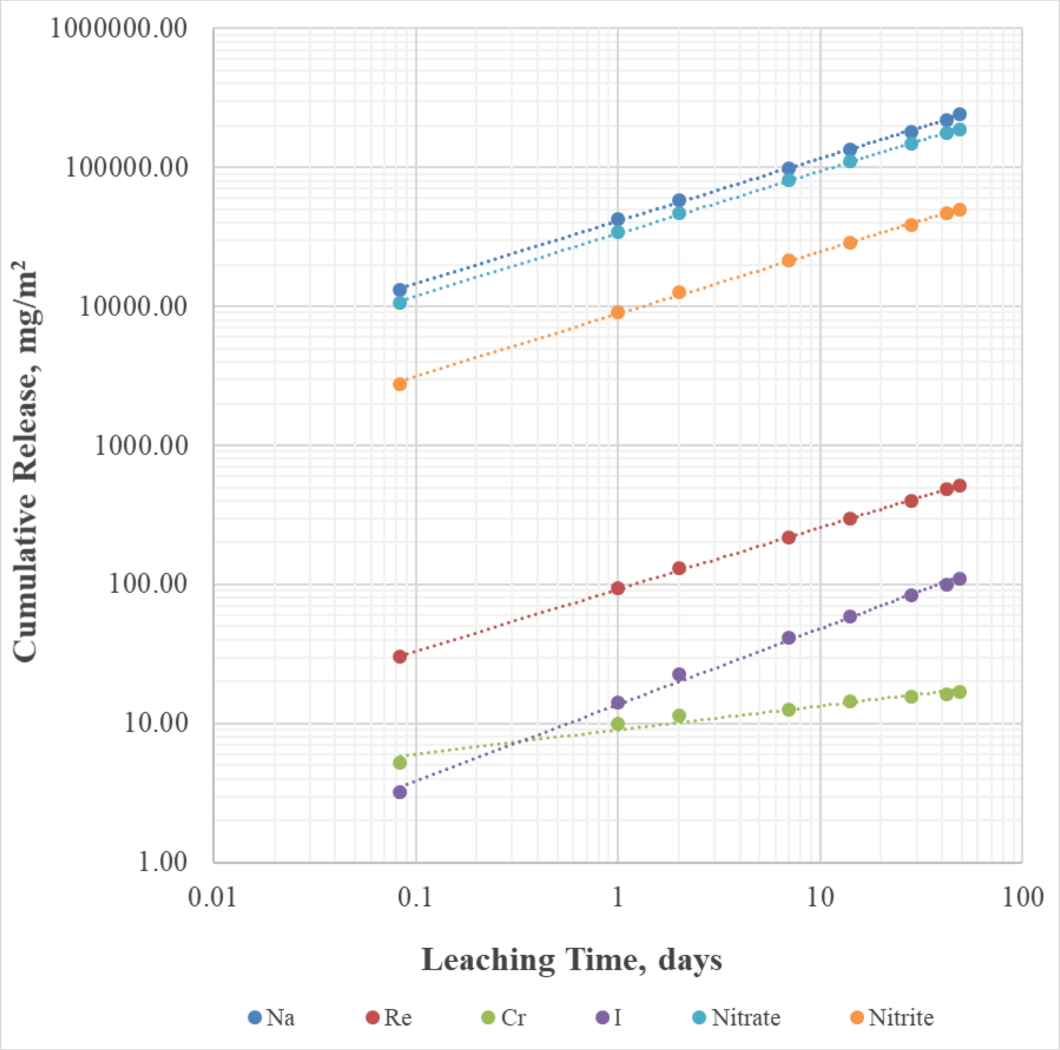

Figure A3. Cumulative release vs. leaching time on log-log scale (CSMA8S2R13).

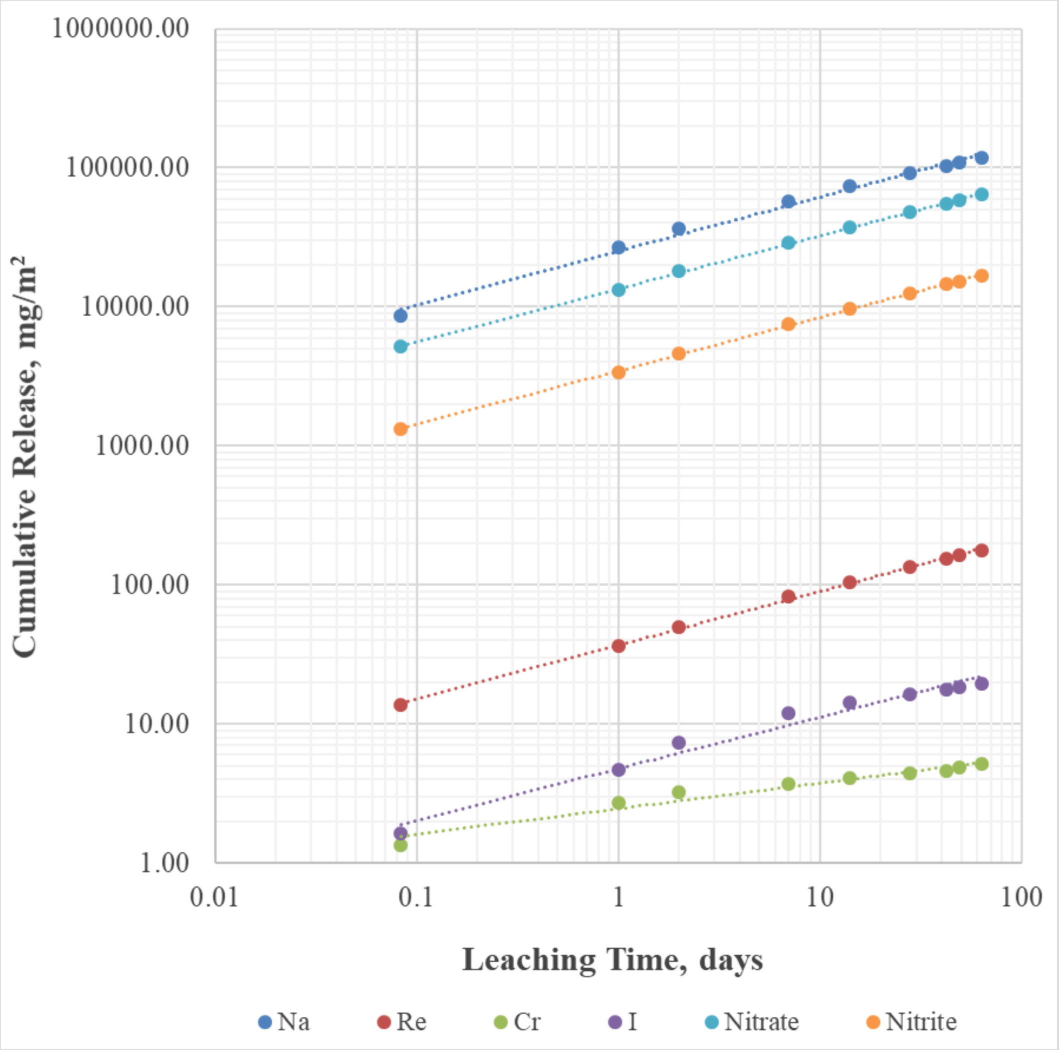

Figure A4. Cumulative release vs. leaching time on log-log scale (CSMA8S2R4).

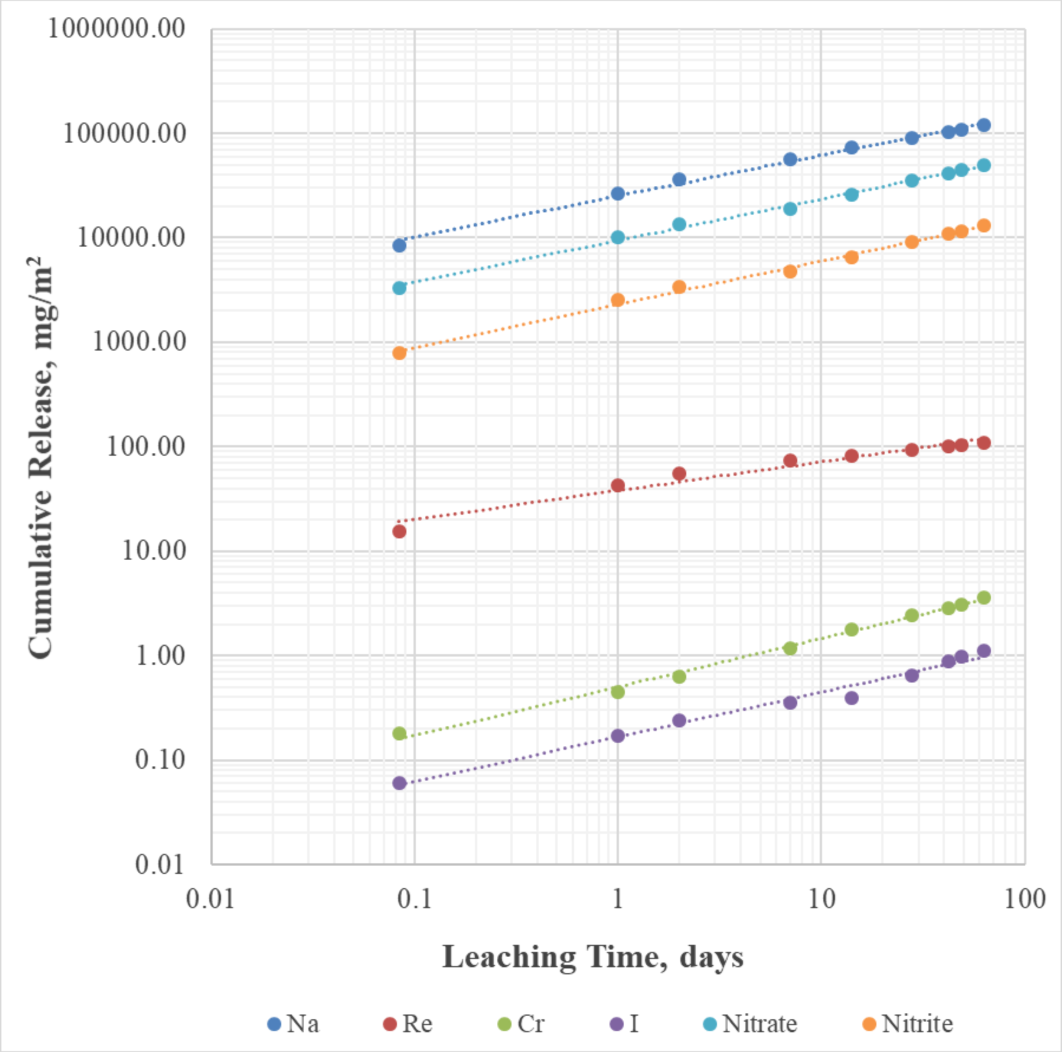

Figure A5. Cumulative release vs. leaching time on log-log scale (CSMA8S2R3s).

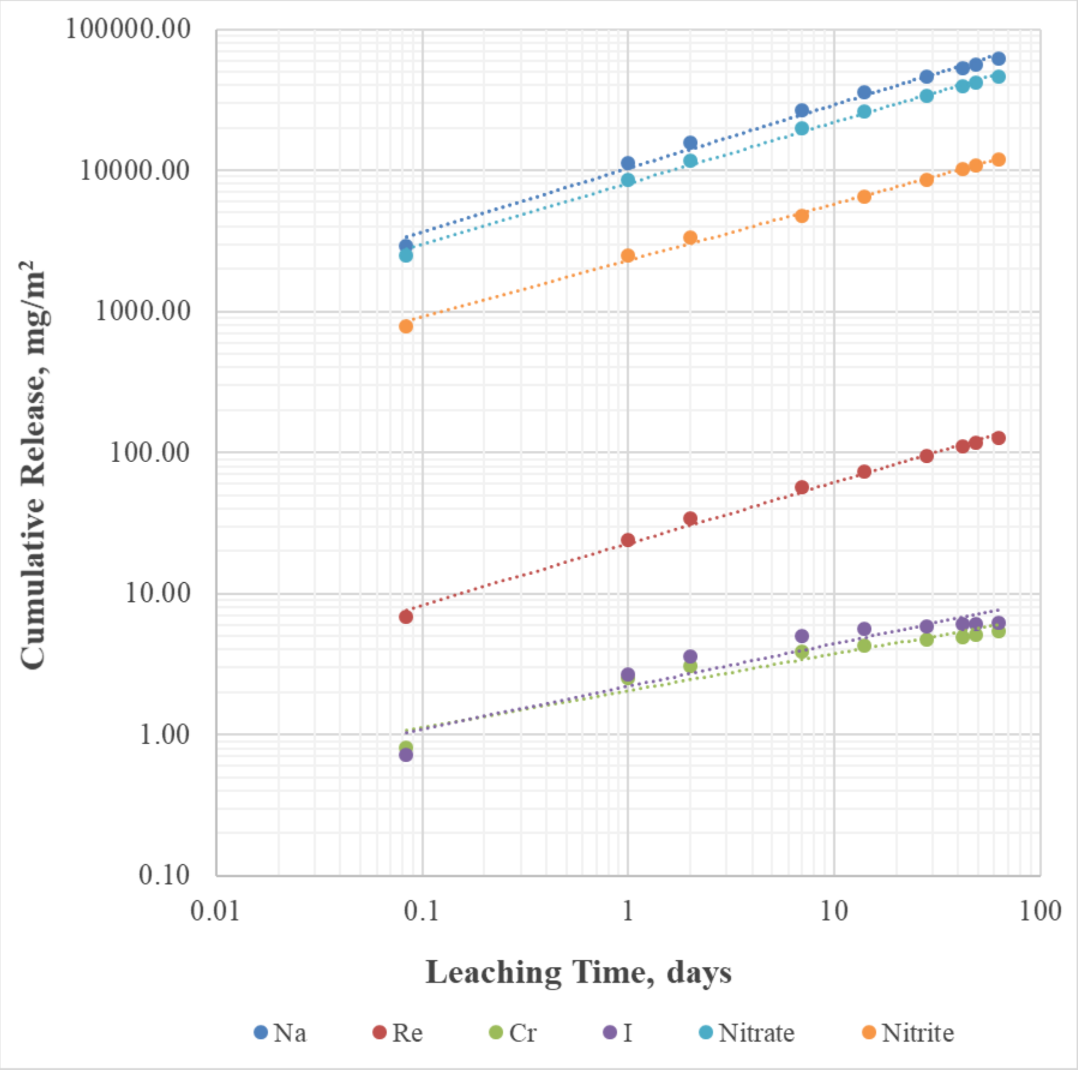

Figure A6. Cumulative release vs. leaching time on log-log scale (CSMA8S2R3c).

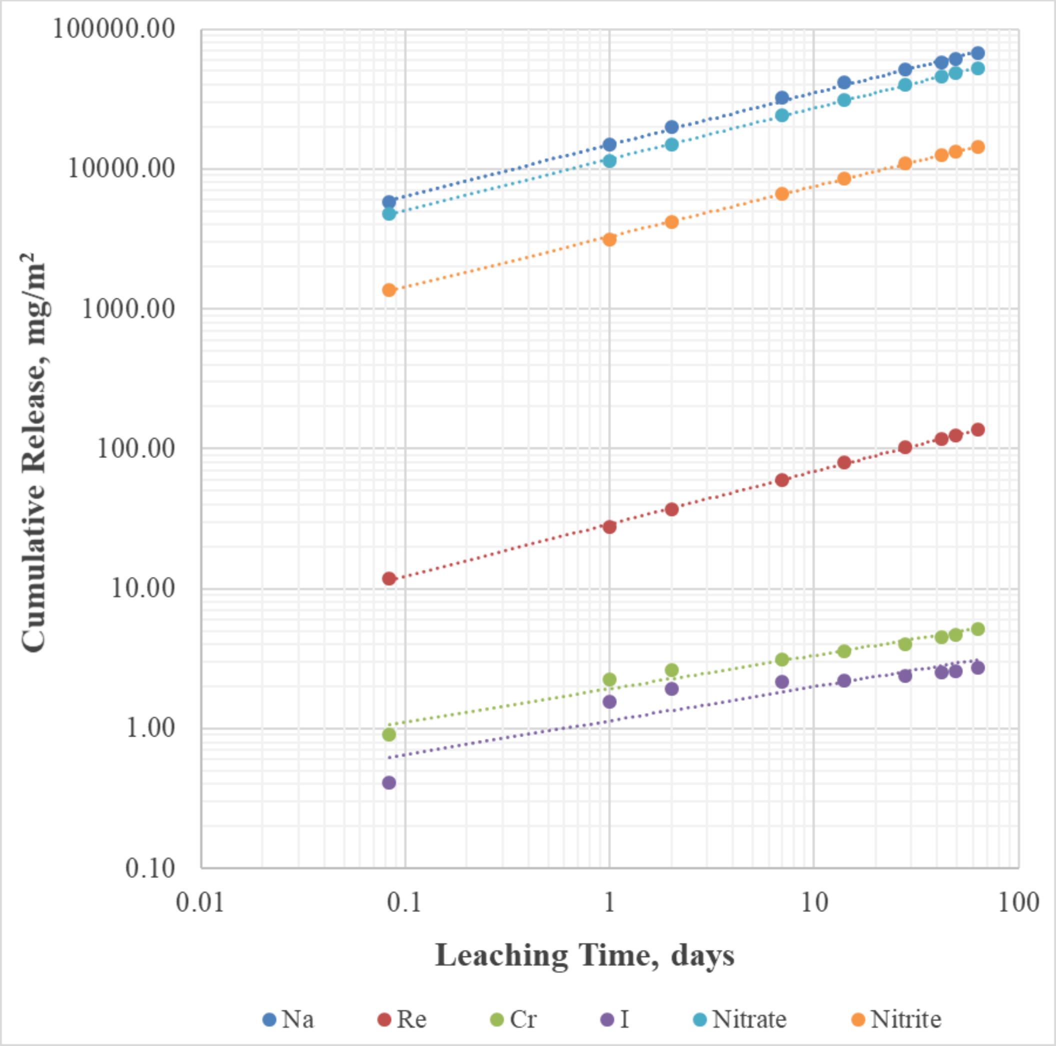

Figure A7. Cumulative release vs. leaching time on log-log scale (CSMA8S2R8).

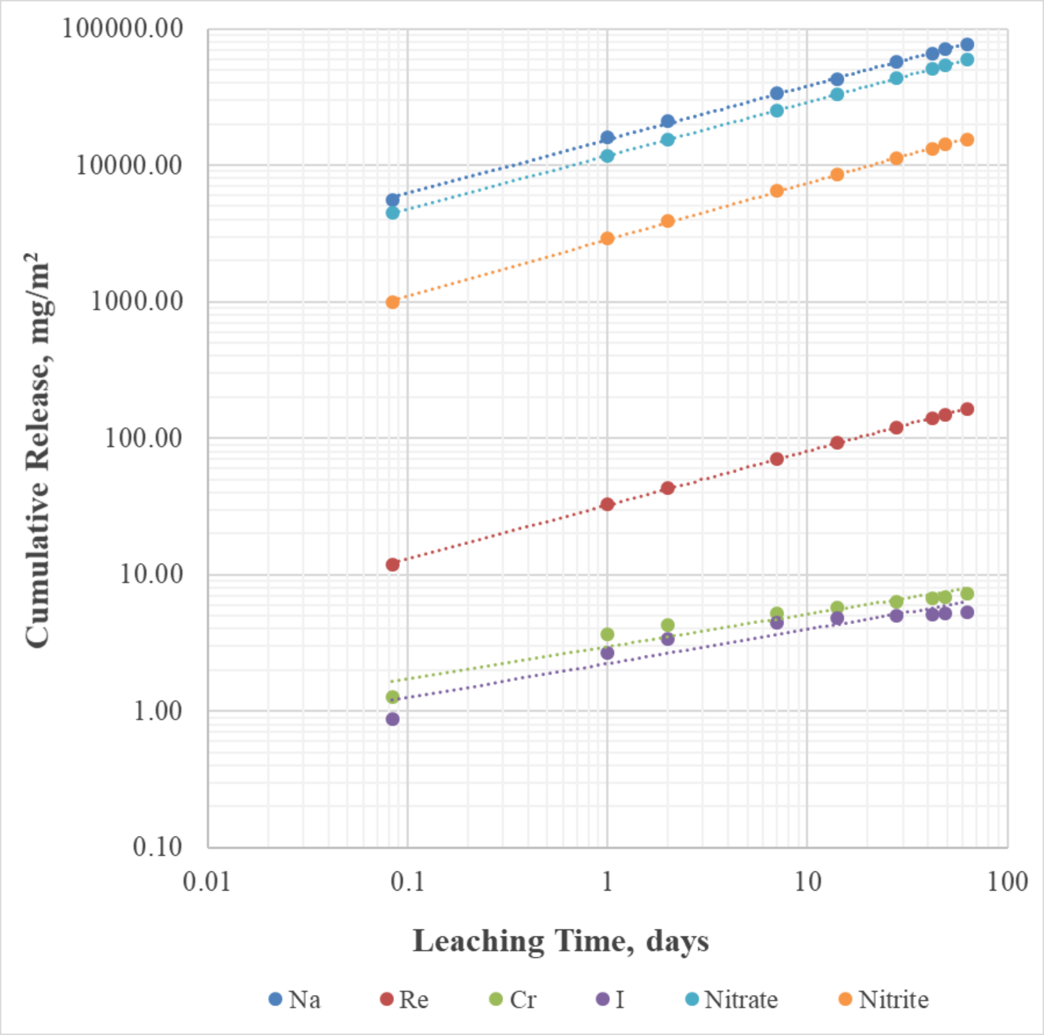

Figure A8. Cumulative release vs. leaching time on log-log scale (CSMA8S2R11a).

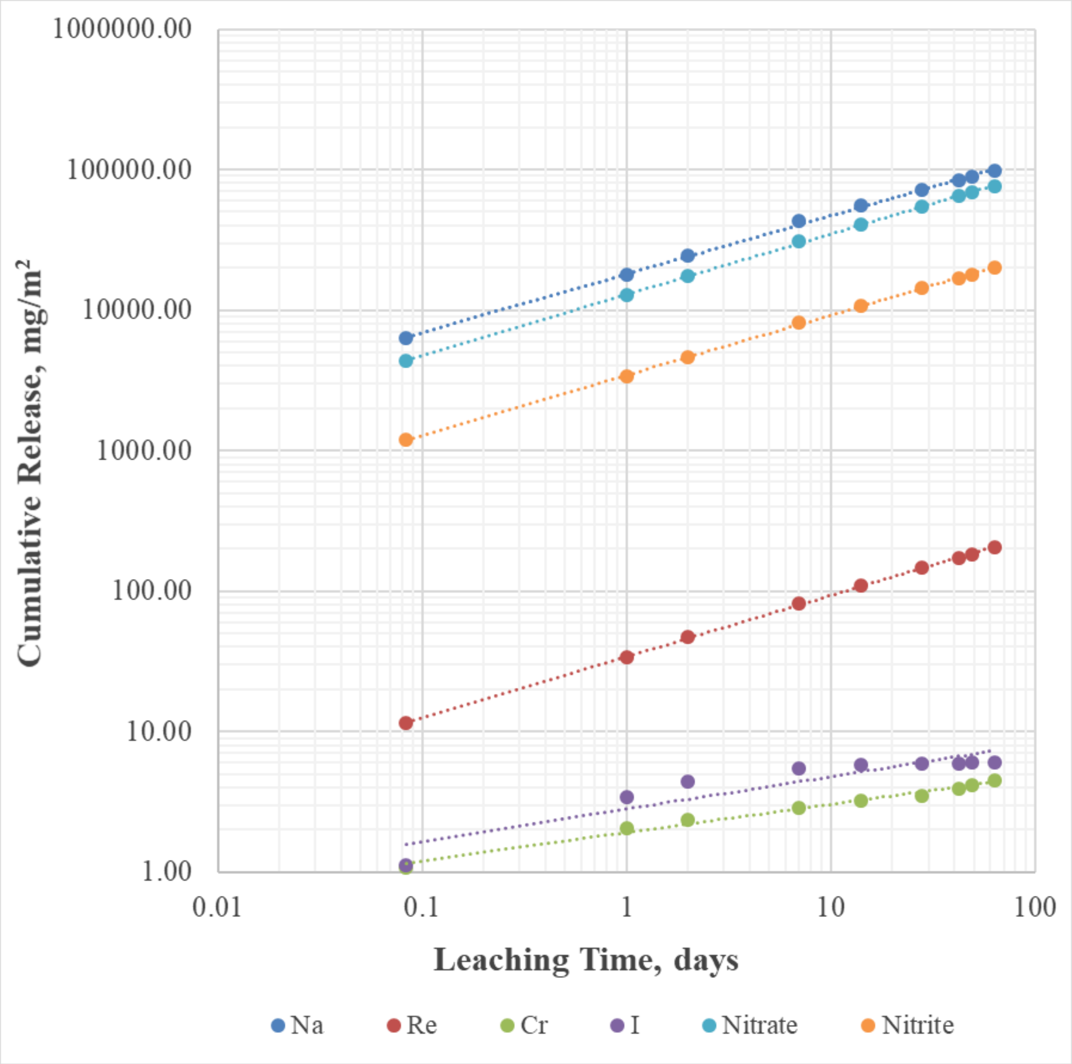

Figure A9. Cumulative release vs. leaching time on log-log scale (CSMA8S2R11b).

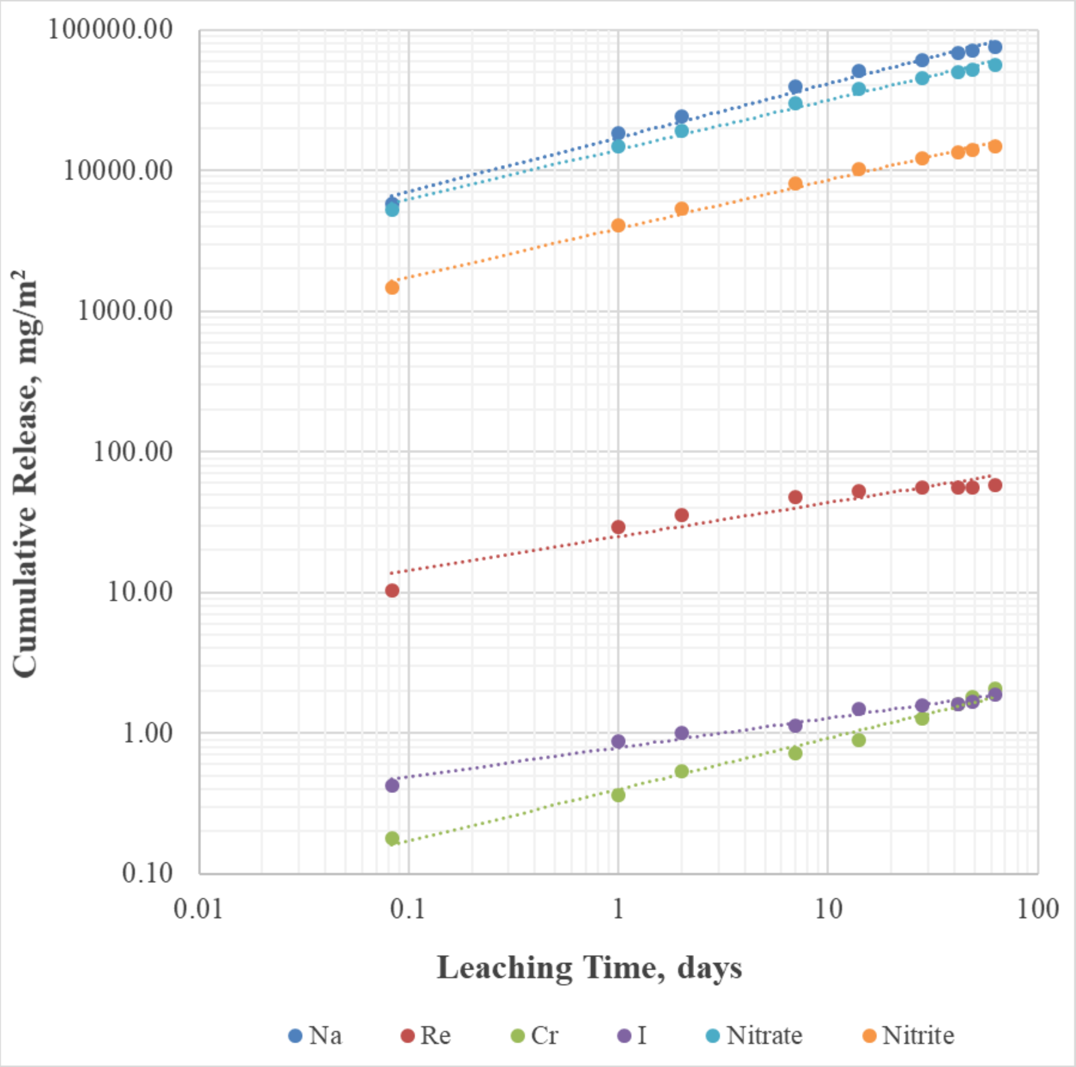

Figure 10. Cumulative release vs. leaching time on log-log scale (CSMA8S2R12a).

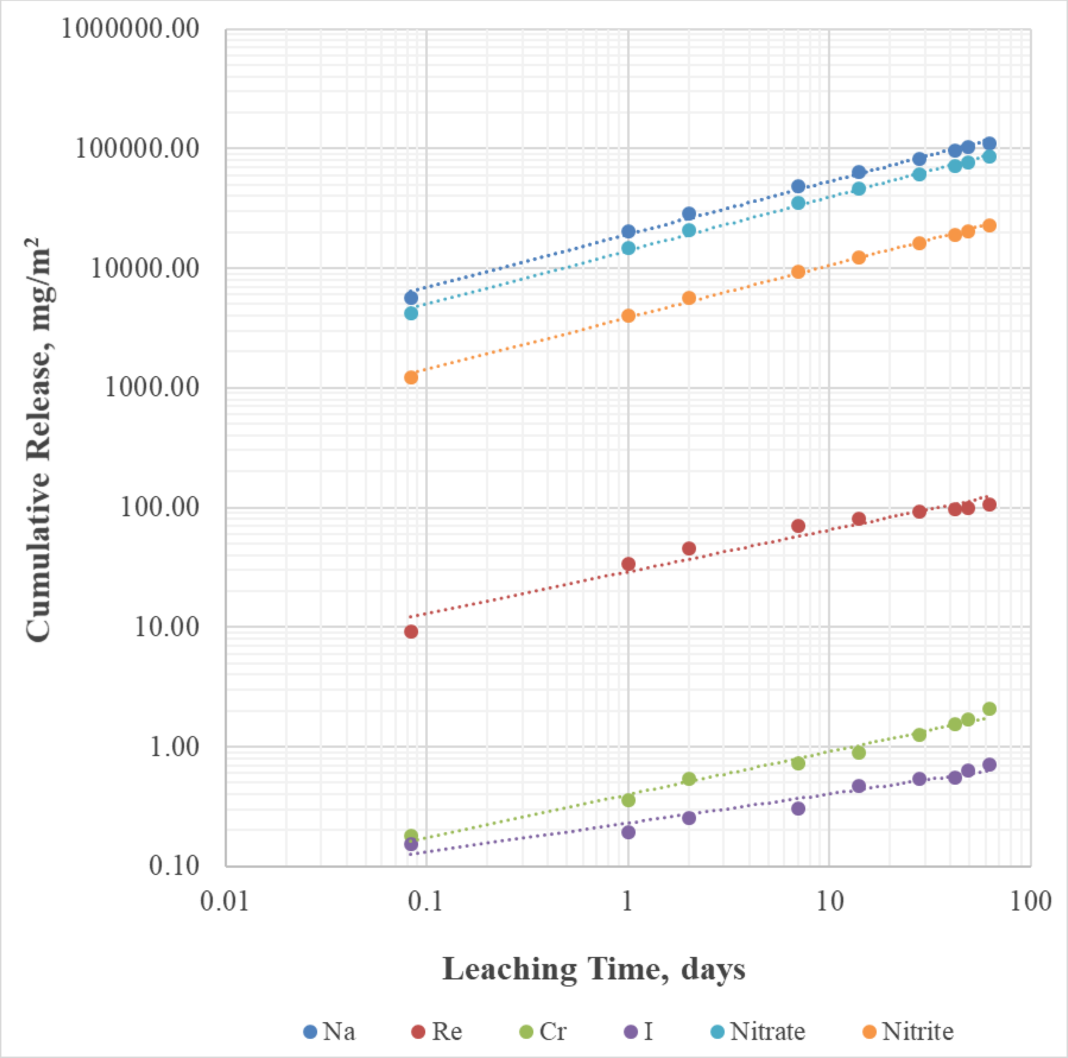

Figure A11. Cumulative release vs. leaching times on log-log scale (CSMA8S2R12c).

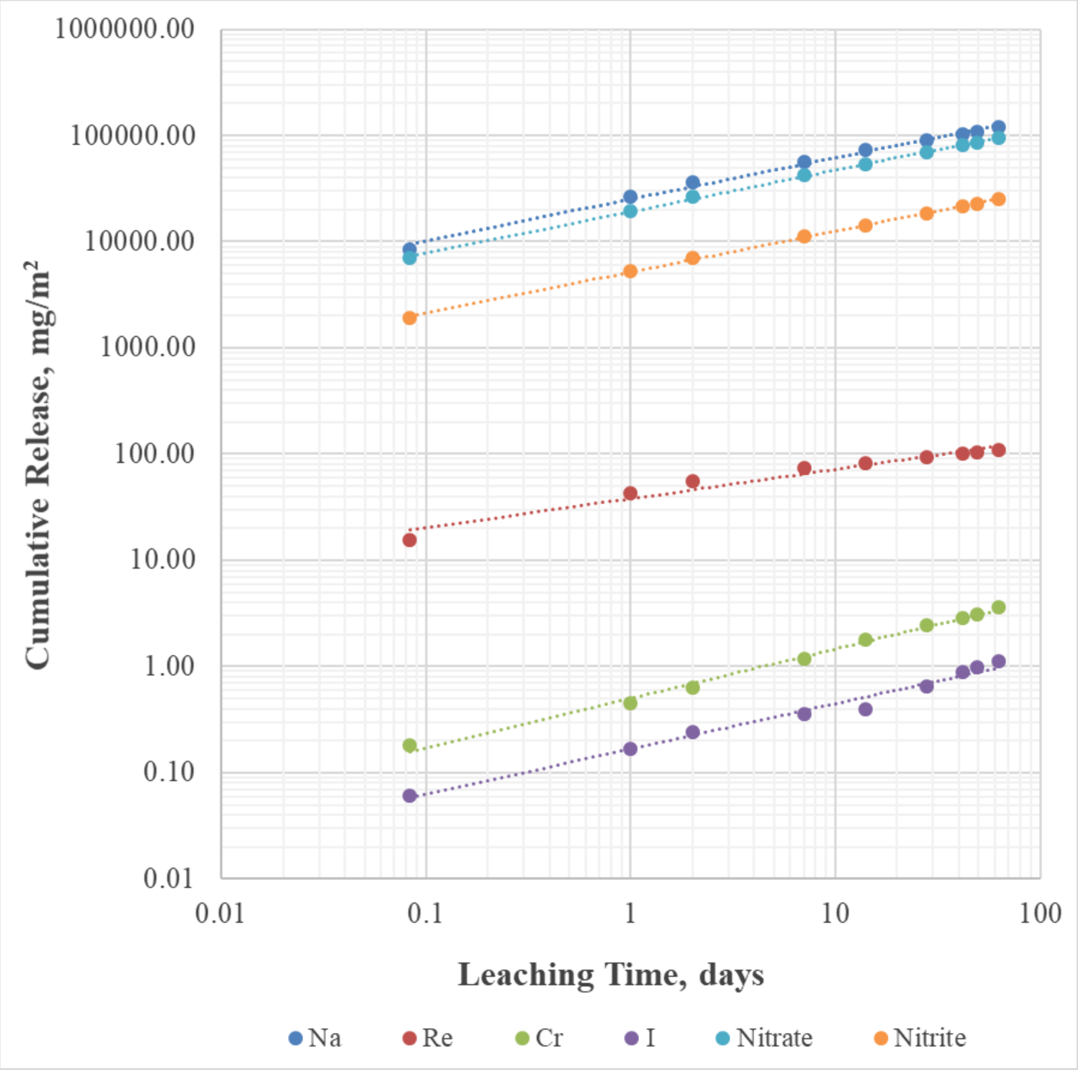

Figure A12. Cumulative release vs. leaching times on log-log scale (CSMA8S2R12d).

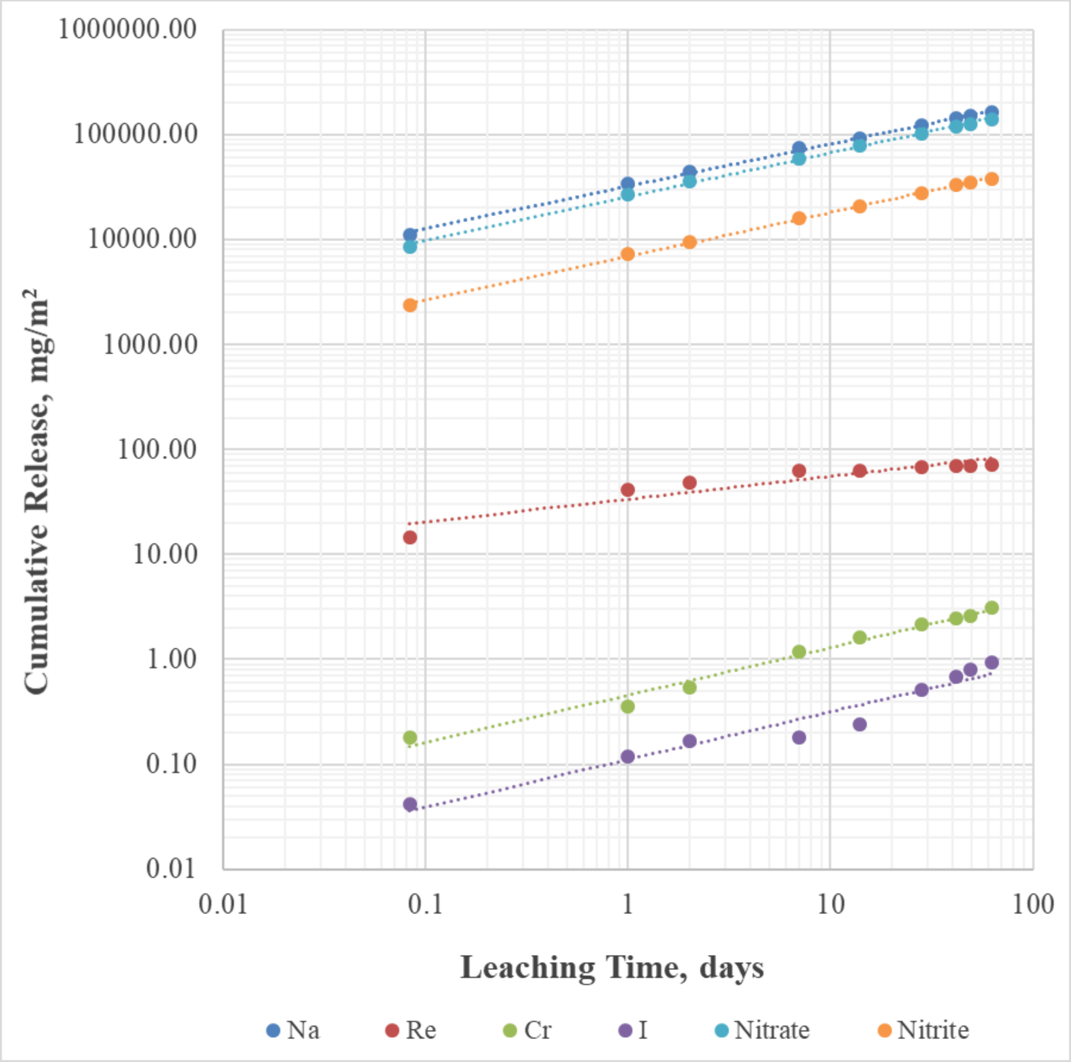

Figure A13. Cumulative releases vs. leaching times on log-log scale (CSMA8S2R12e).

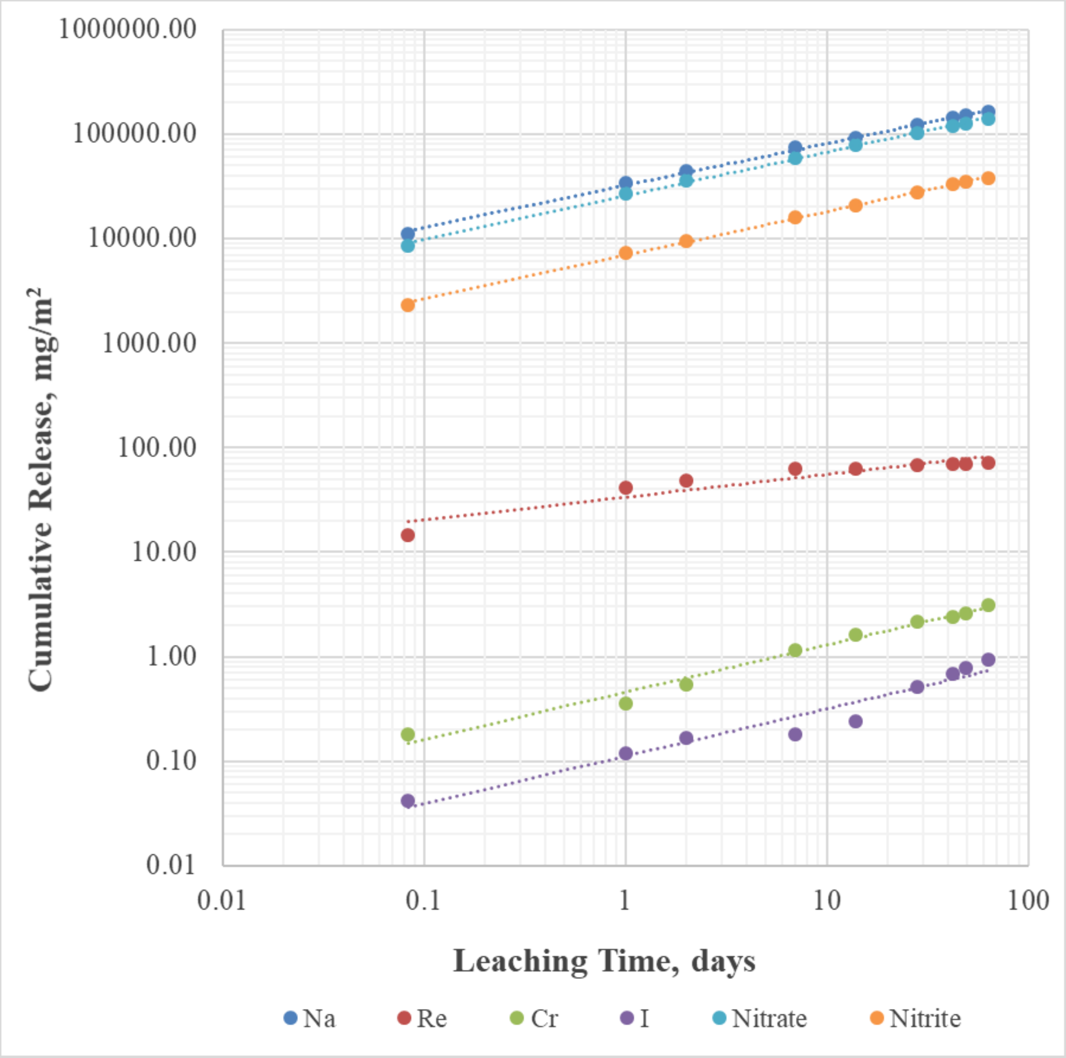

Figure A14. Cumulative release vs. leaching times on log-log scale (CSMA8S2R12f).

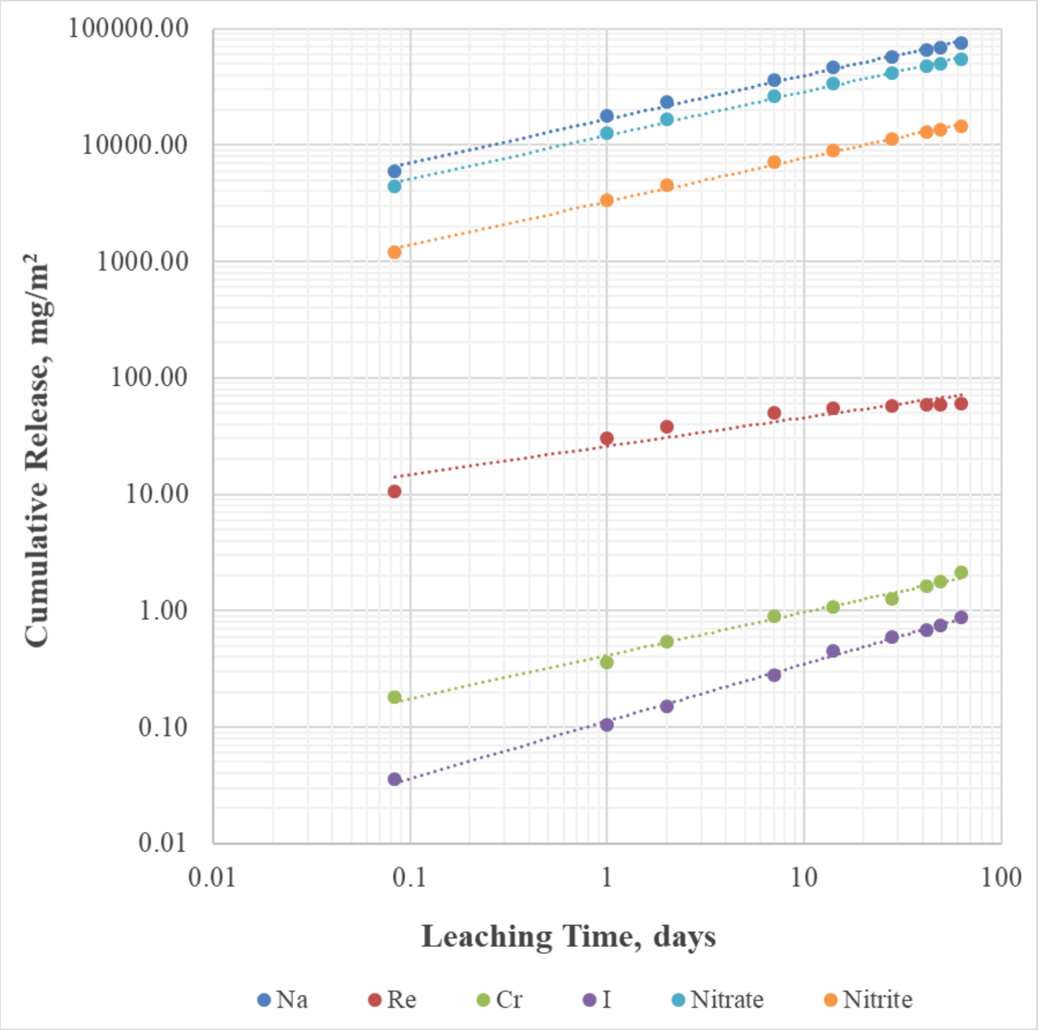

Figure A15. Cumulative release vs. leaching times on log-log scale (CSMA3S1R3).

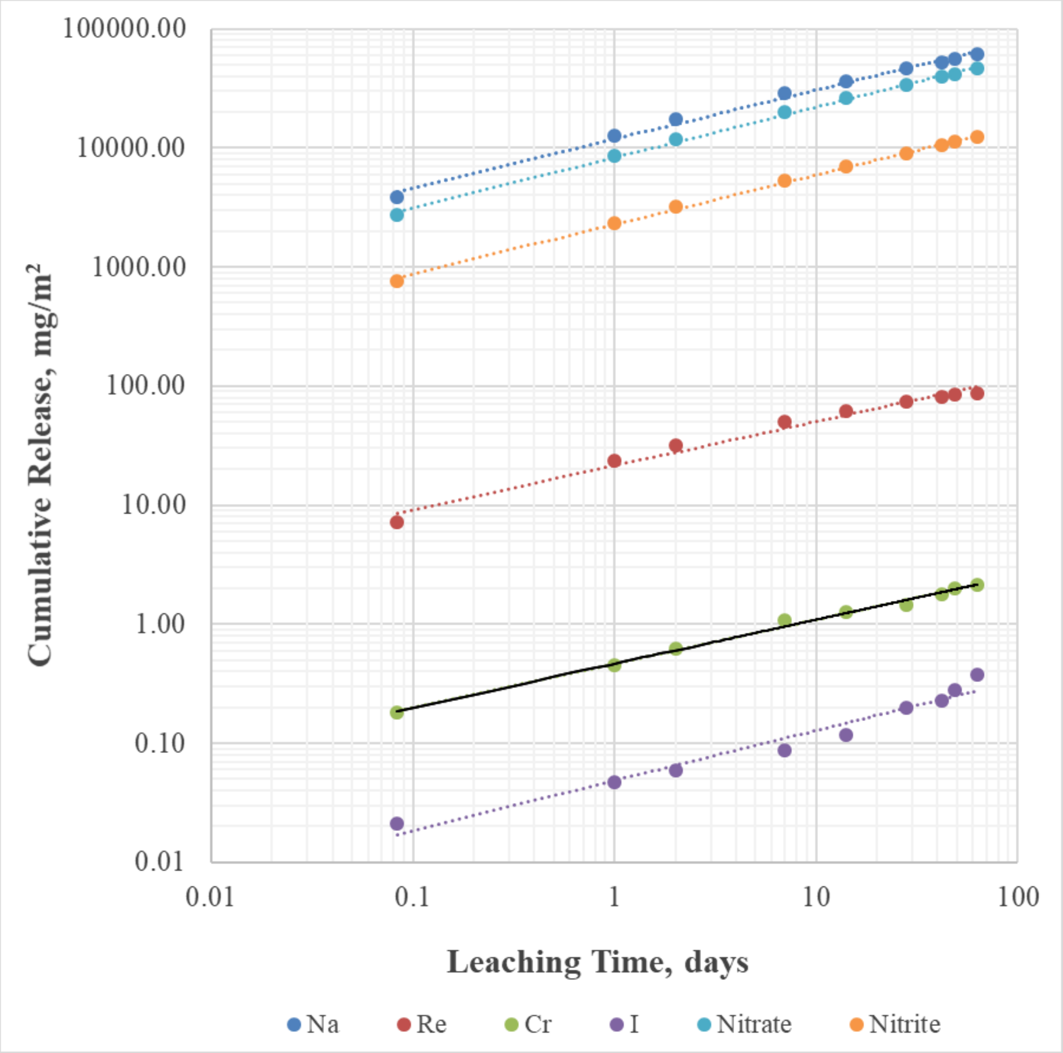

Figure A16. Cumulative release vs. leaching time on log-log scale (CSMA3S1R4).

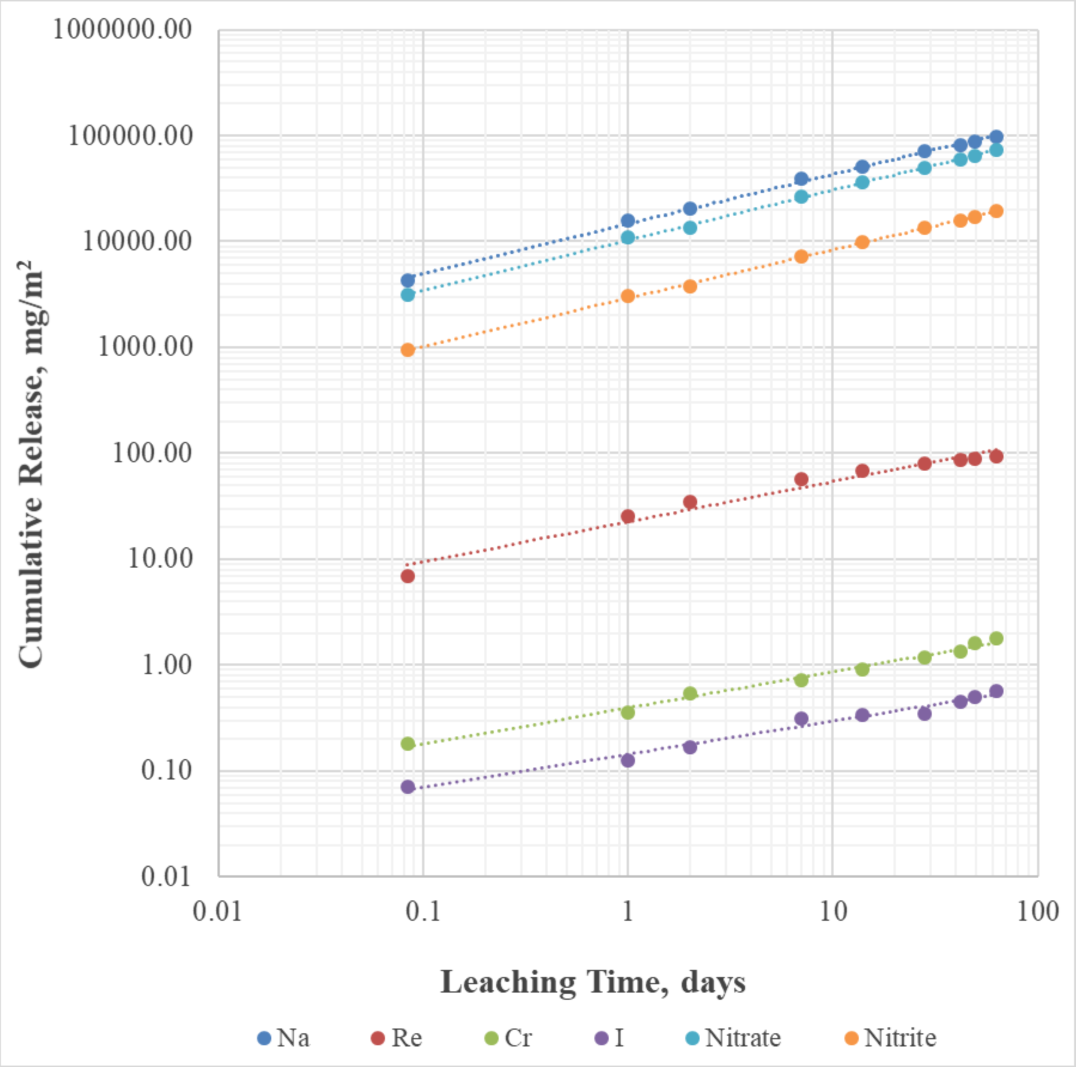

Figure A17. Cumulative release vs. leaching time on log-log scale (CSMP3S1R1).

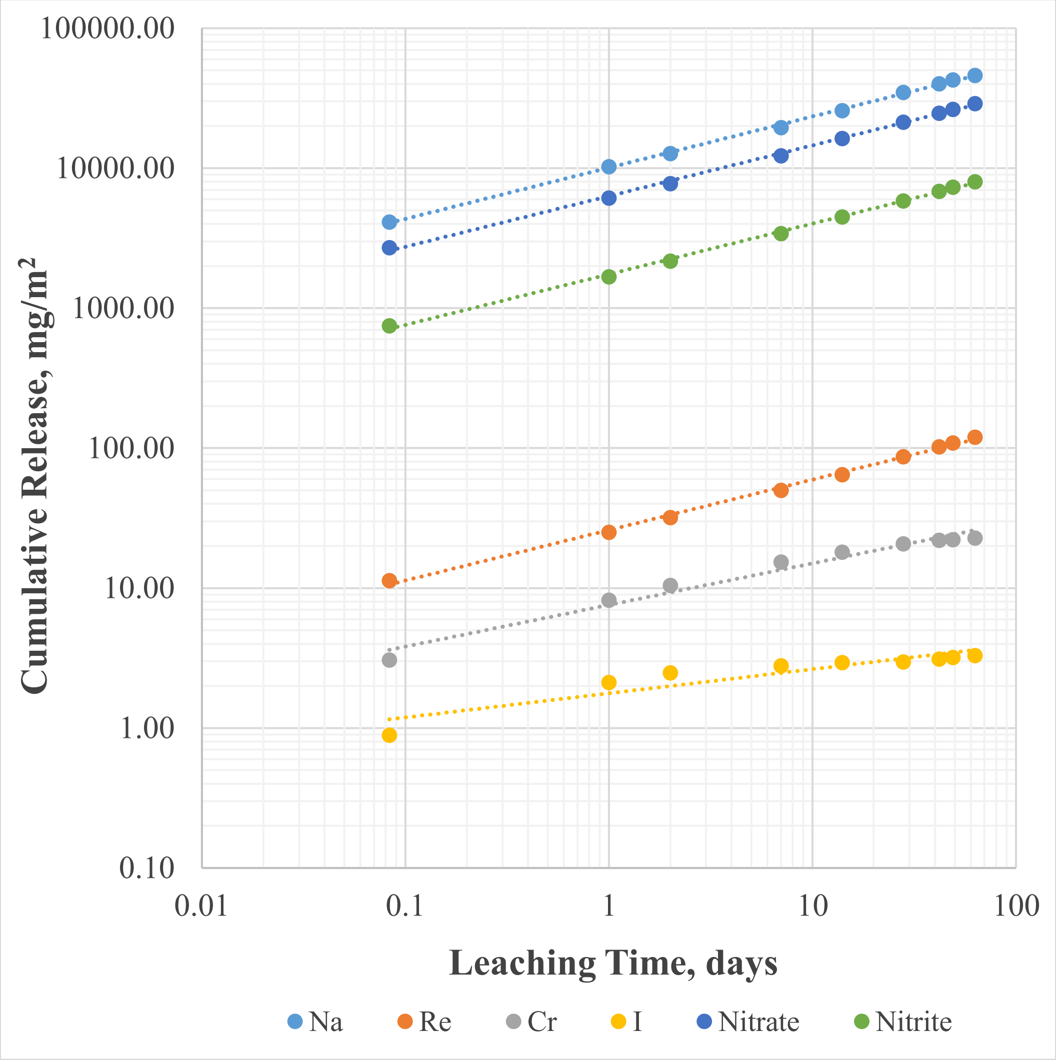

Figure A18. Cumulative release vs. leaching time on log-log scale (CSMA8S2R10).

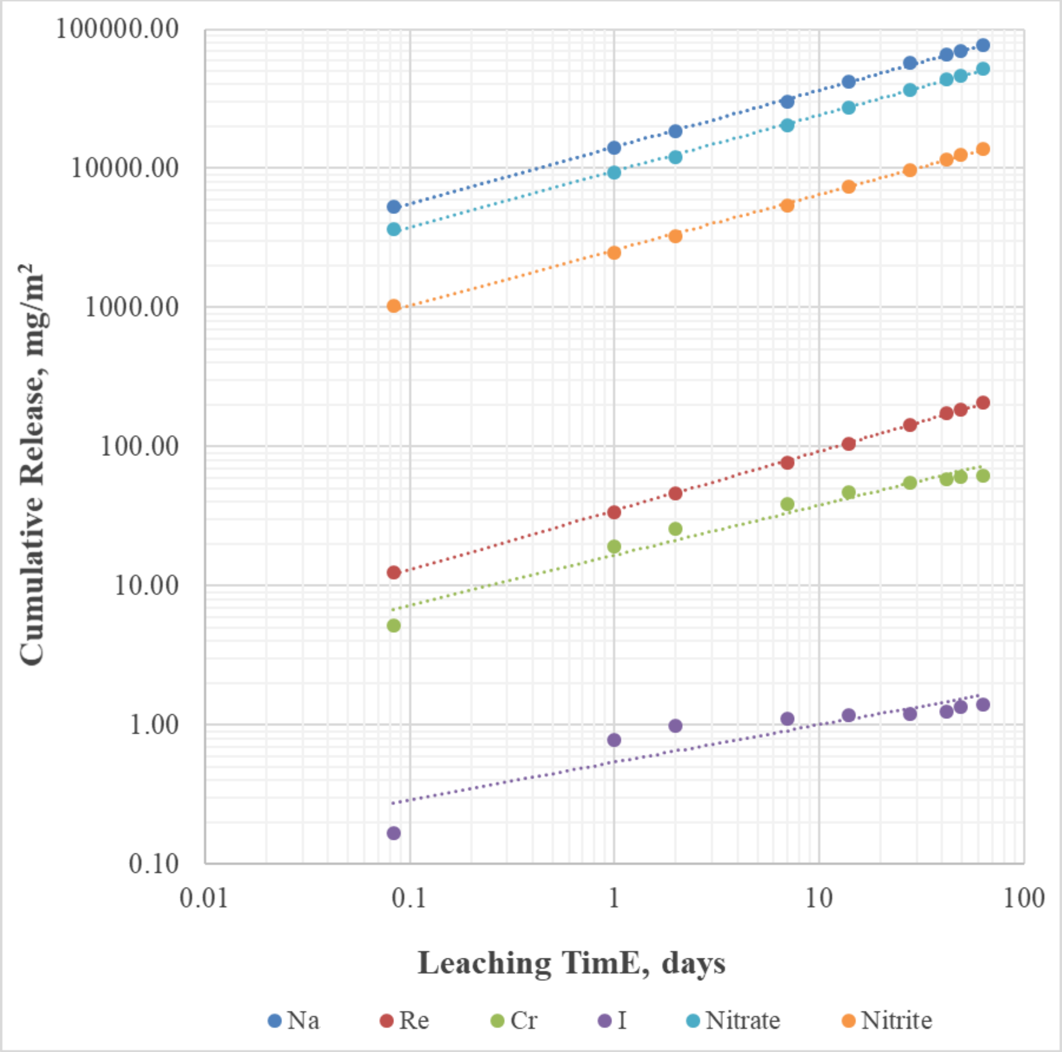

Figure 19. Cumulative release vs. leaching time on log-log scale (CSMP8S2R2).

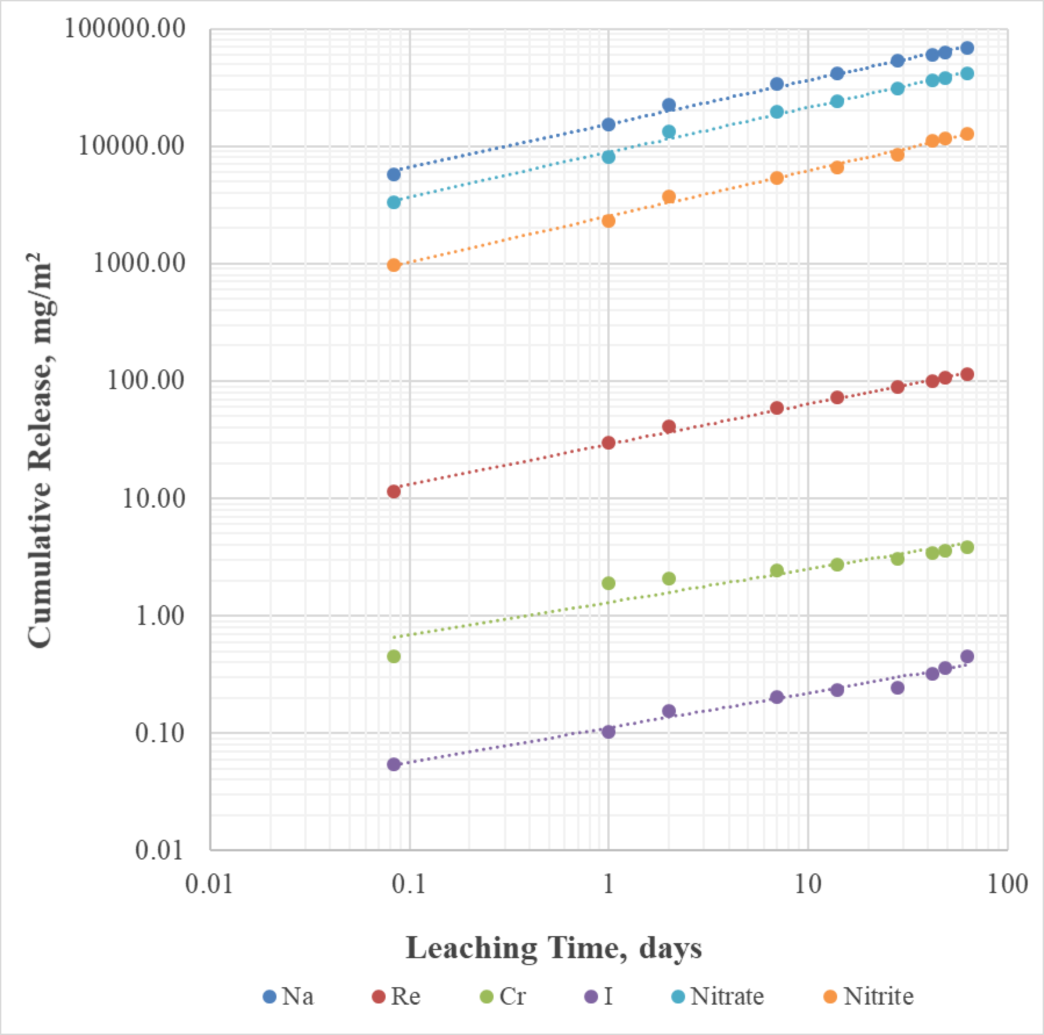

Figure A20. Cumulative release vs. leaching time on log-log scale (CSMP3S1R2).

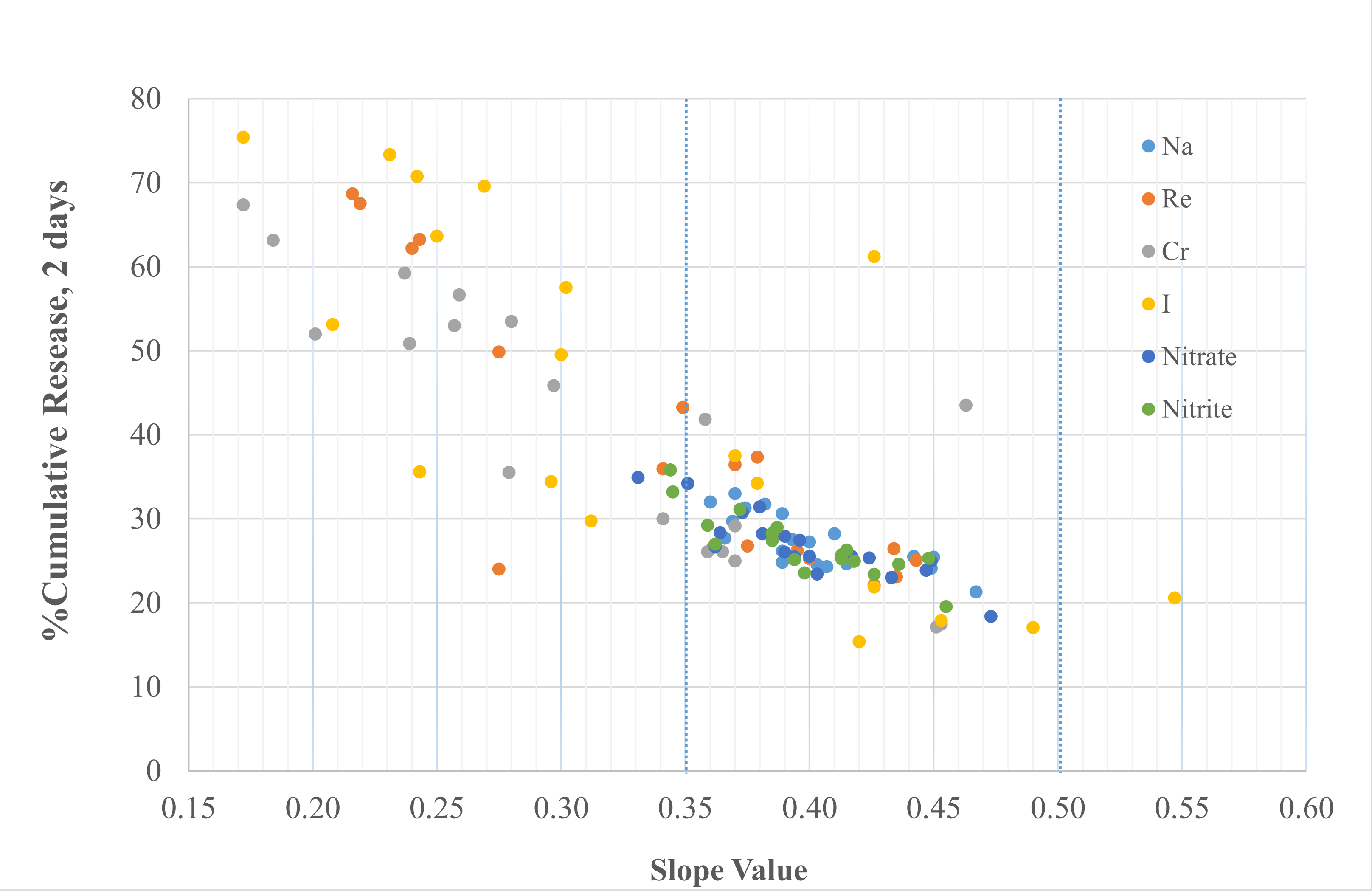

Figure A21. %Cumulative release after leaching for 2 days versus slope value.

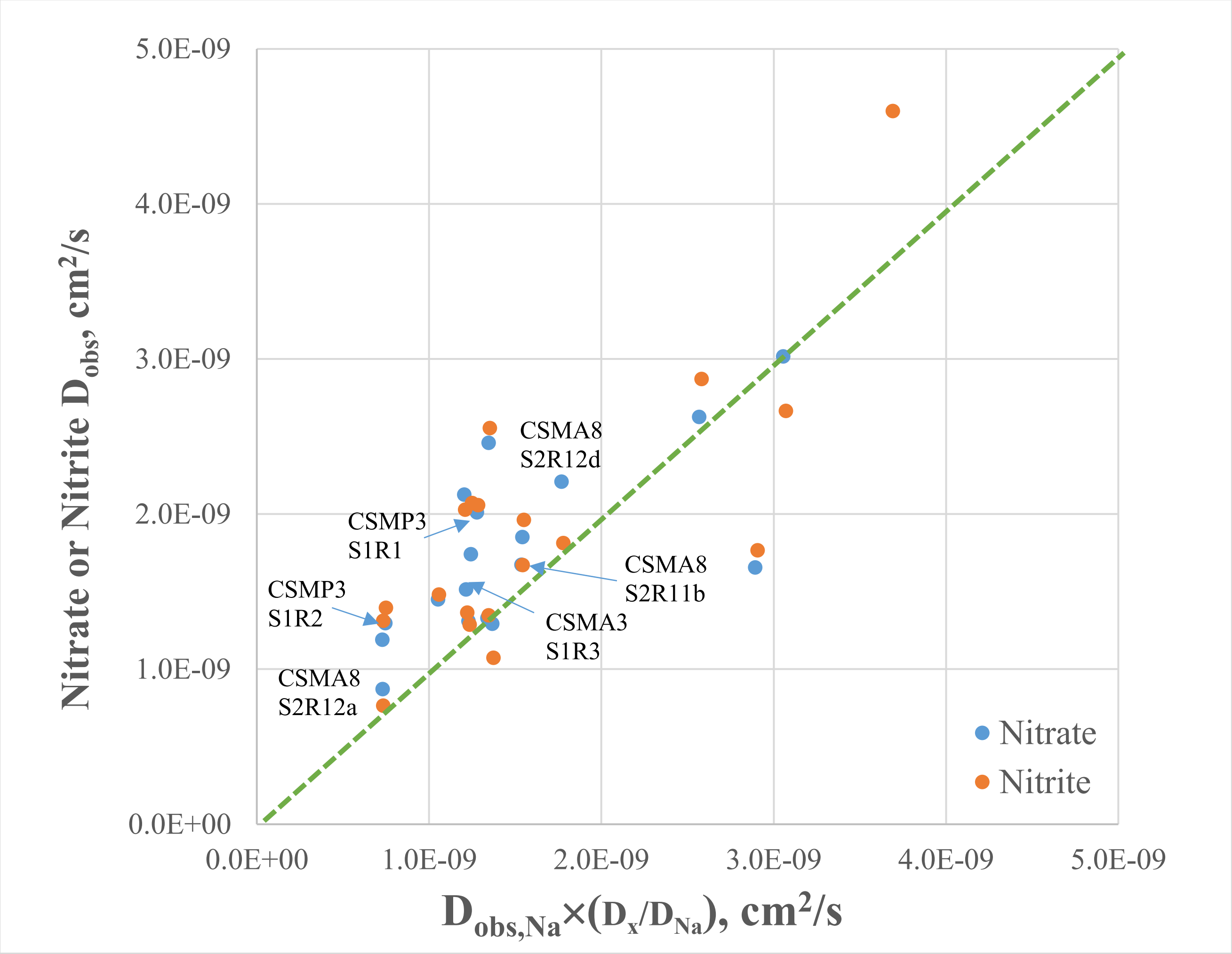

Figure A22. Nitrate and Nitrite D_{obs} values versus $D_{obs,Na}\times(D_x/D_{Na})$ for NSAS waste forms (FY 24).

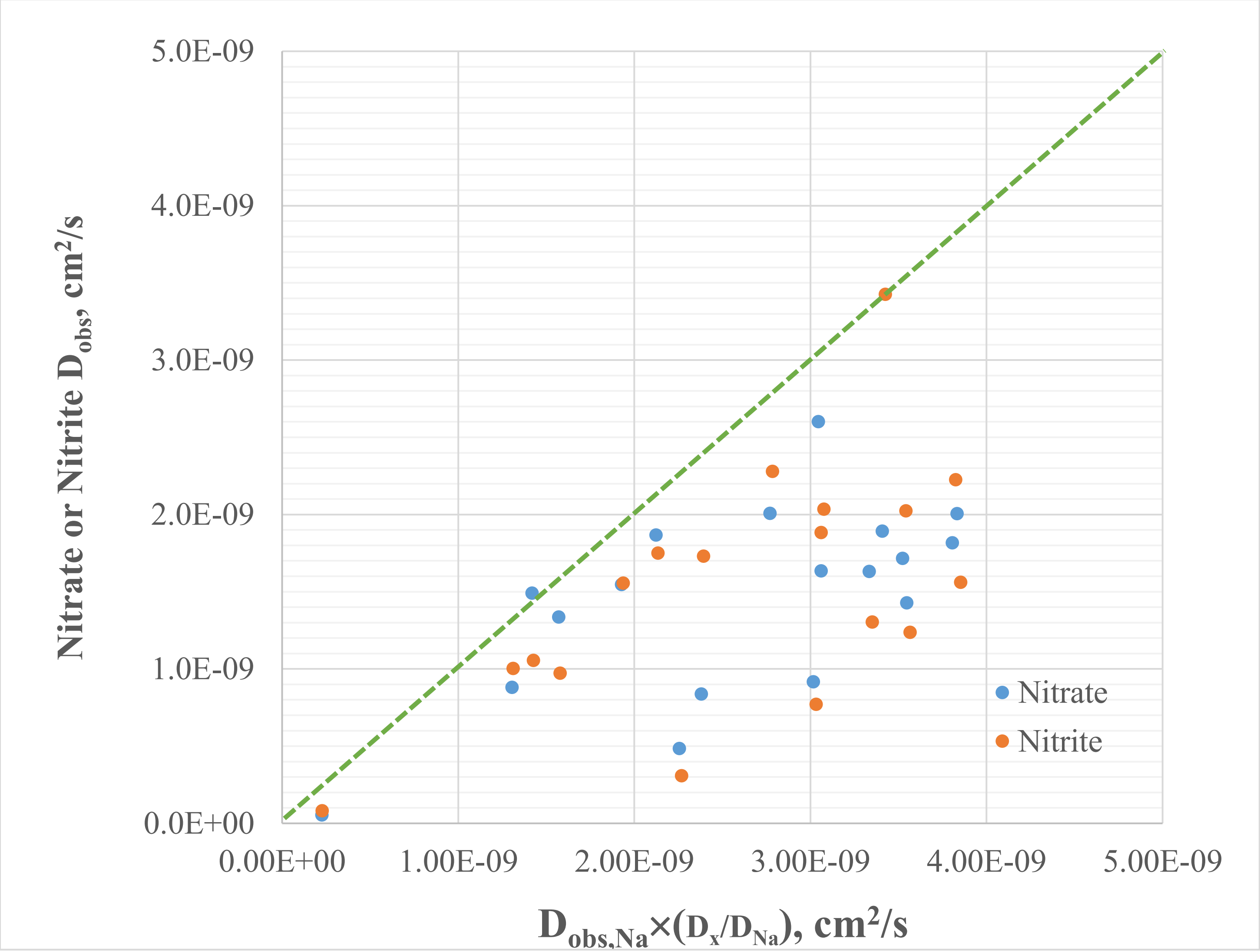

Figure A23. Nitrate and Nitrite D_{obs} values versus $D_{obs,Na}\times(D_x/D_{Na})$ for NSAS waste forms (prior to FY24).

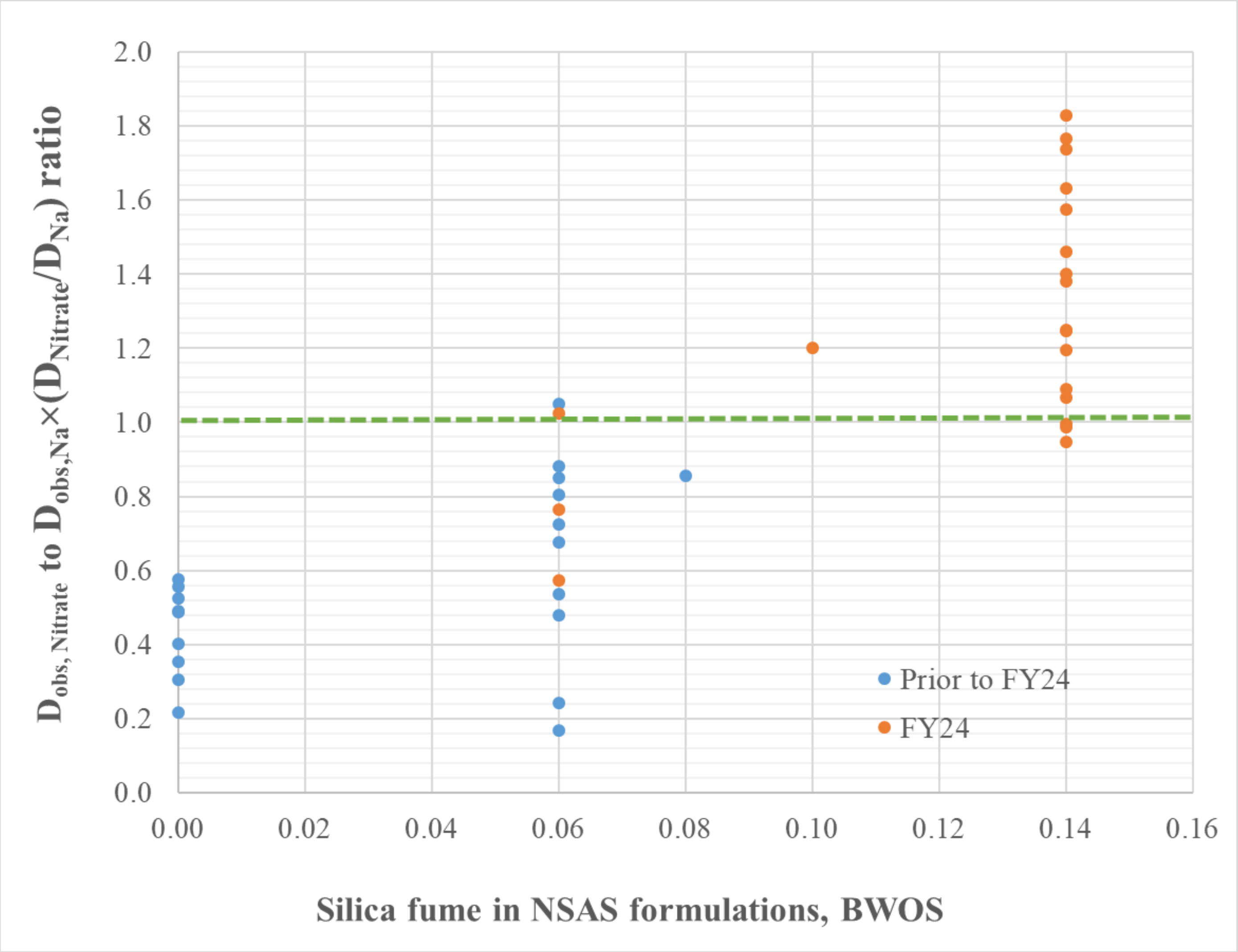

Figure A24. Ratio of Nitrate D_{obs} values to $D_{obs,Na}\times(D_{nitrate}/D_{Na})$ versus silica fume content for NSAS waste forms.

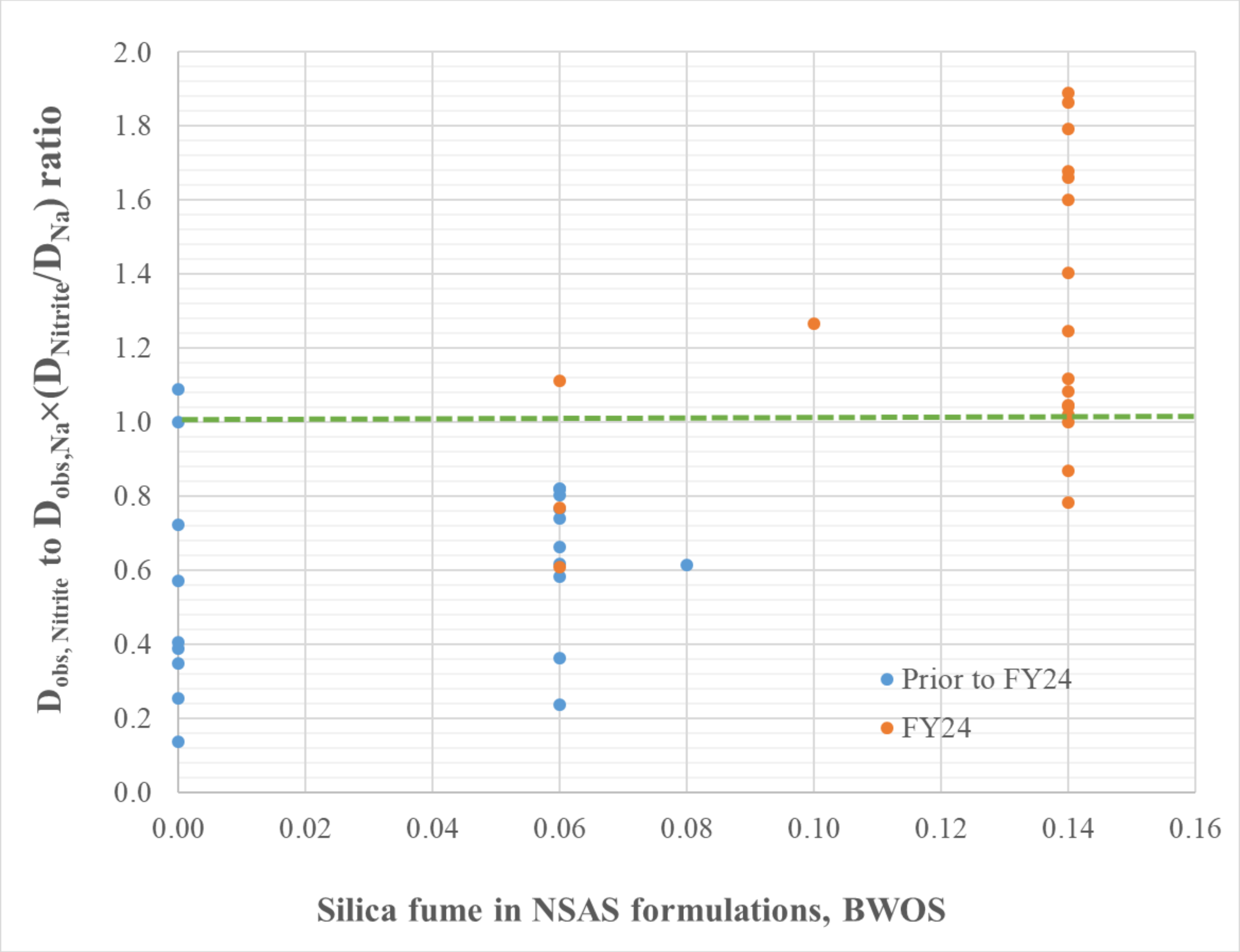

Figure A25. Ratio of Nitrite D_{obs} values to $D_{obs,Na}$×($D_{nitrite}$/D_{Na}) versus silica fume content for NSAS waste forms.