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FY22 Development of Improved Grout Waste Forms for Supplemental Low Activity Waste Treatment

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

H. Xu
Vitreous State Laboratory of The Catholic University of America

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

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Final Report

FY22 Development of Improved Grout Waste Forms for Supplemental Low Activity Waste Treatment

prepared by

Weiliang Gong, Hui Xu, and Ian L. Pegg

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

for

Atkins Energy Federal EPC, Inc.
Columbia, MD 21046

and

Washington River Protection *Solutions*, LLC
Richland, WA

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Rev. 2, 4/14/25

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:** 4/14/25
VSL Program Director/Principal Investigator

I. Joseph: Innocent Joseph **Date:** 04/14/2025
Atkins Sub-Contract Manager

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List of Abbreviations

AgZ	Silver Zeolite
ASAS	Alkali Silicate Activated Slag
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
BWOB	By Weight of Binder
CA	Monocalcium Aluminate
CAC	Calcium Aluminate Cement
CASH	Calcium Aluminosilicate Hydrate
Cc	Calcium Carbonate
CHT	Calcined Hydrotacite
COCs	Constituents of Concern
CŜ	Calcium Sulfate
Cst	Calcium Stearate
CSA	Calcium Sulfoaluminate Cement
CUA	Catholic University of America
DFLAW	Direct Feed LAW
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
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
LI	Leachability Index
MC	Microfine Cement
MK	Metakaolin
MPC	Microfine Portland Cement
NQA	Nuclear Quality Assurance
NSAS	Neutral Salt Activated Slag
OPC	Ordinary Portland Cement
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	Quartz
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

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.

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 Supplemental Low-Activity Waste (SLAW) 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 (PA). The results indicated that the estimated inventory of grouted SLAW 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. In that work, a range of alternative formulations were developed and characterized, and the results confirmed that there is considerable scope for improvement of SLAW waste form performance through novel formulation approaches [8].

Accordingly, in FY22, WRPS tasked Atkins-VSL with further investigation and development of these formulations [9], which is the subject of the present testing.

The present work was conducted according to a Test Plan [10] that is responsive to the WRPS Scope of Work (SOW) [9]. The SOW noted that, for the purposes of this work, it could be assumed that technetium is present in the waste as pertechnetate.

1.2 Objectives

The objective of this work is to build on the results of the FY21 work and perform laboratory-scale testing to further develop and demonstrate methods to reduce the release rates of nitrate, iodine, and technetium from grouted LAW waste forms. The primary focus was on further development of the three most promising grout formulation systems investigated in the FY21 work [8]. In addition to efforts to further reduce release rates of the COCs, the work also investigated methods to increase waste loadings. As in the previous work, the technical approaches include:

- Assessment of geopolymer formulations with different activator types, e.g., neutral salt and alkali silicate;
- Assessment of alternative Portland Cement (PC)-based formulations;
- Assessment of Cement Free formulations;
- Promotion of grout getter phases, pore plugs, admixtures, and reformulation to reduce permeability and porosity;
- Application of maximum packing density to formulate both geopolymer based formulations;
- Assessment of geopolymer formulations with removal of fillers to further increase waste loading.

Per a previous assessment [6], there is a need for new grout formulations that reduce the release rate of nitrate, technetium, and iodine from SLAW grout by factors of approximately 3.2 (nitrate), 10 (technetium), and 32 (iodine) based on the parameter values evaluated in the simulations (e.g., inventory, waste form properties including waste loading, which determines total waste orm volume and surface area). The testing included evaluation of fresh and cured properties with the primary focus being on leaching of the COCs in the Environmental Protection Agency (EPA) Method 1315 test.

1.3 Testing Approach

In the FY21 work [8] the effects of waste solids on grout performance were assessed by conducting tests at two different waste simulant concentrations (5.6 M and 1 M). Obviously, higher concentrations are preferred in practice since they lead to lower volumes of grout waste form for disposal. Therefore, an important objective of the present phase of testing was to improve waste loadings while maintaining or improving retention of the COCs. Thus, the present work focused on testing using a waste simulant concentration of 5.6 M Na.

The results from the FY21 work showed that, of the formulations tested, those based on neutral salt activated slag (NSAS) and Portland cement ultrahigh performance concrete (PUHPC) showed the best performance in terms of COC retention. Though PUHPC exhibited excellent retention of COCs, the waste loading was low and thus economically not viable. The present work therefore tested further refinements of NSAS-based formulations to improve retention of COCs. The FY21 results for formulations based on alkali silicate activated slag (ASAS) were less promising but in view of the natural alkaline nature of the waste, which could be leveraged for alkali activation of constituents such as blast furnace slag, these were investigated further in the present work. A variety of additives were included in both NSAS- and ASAS-based formulations including calcined hydrotalcite and Ag-zeolite as getters for iodine and hydrophobic admixtures for reducing capillary porosity and, thereby, permeability. In addition, superfine blast furnace slag was included to enhance the alkali activation process. Finally paste-only formulations were developed as a potential method to increase waste loadings.

As noted above, in FY12, WRPS began a program of 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 for supplemental treatment of LAW [3-6]. In the present work, the reference Cast Stone formulation was modified and optimized by including superfine counterparts of Portland cement and blast furnace slag to enhance hydration and reaction progress as well as the use of a plug admixture to reduce the porosity of the cured waste form. In addition, the formulation principles employed in the “Cement-Free” modifications of Savannah River Site (SRS) Saltstone developed by VSL for Savannah River Remediation LLC (SRR) [11] were investigated for Cast Stone as a potential approach for improving its performance with respect to retention of COCs.

In view of the exploratory nature of this work and the relatively limited time available for iteration, a phased approach was used. In particular, the time required for sample curing (28 days) and EPA Method 1315 testing (63 days) are a substantial fraction of the project duration. Therefore, the formulation development and testing was performed in four phases, as follows:

- In the first phase of testing, the primary focus was on developing improved formulations based on Cast Stone and Cement-Free compositions by including Microfine Blast Furnace Slag (BFS) and Portland cement; optimizing FY21 NSAS formulations to favor Aluminate Ferrite Monosulfate (AFm) formation; and optimizing ASAS formulations to extend the set time. These formulations were screened by testing set time, compressive strength, and leachability on the EPA Method 1315 procedure up to 14 days (versus 63 days for the full test).

- In the second phase of testing, the formulations based on Cast Stone, Cement-Free, NSAS, and ASAS were further modified by including Microfine BFS, Microfine Portland cement, hydrophobic admixtures, calcined hydrotalcite, and ground Ionex Ag-900. Most of these waste forms 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.

- In the third testing phase, attempts were made to develop filler-free, paste-only NSAS waste forms to improve waste loading.

- In the fourth phase of testing, three of the better-performing formulations were selected for additional characterization with respect to rheology, isothermal calorimetry, and the Toxicity Characteristic Leaching Procedure (TCLP, EPA Method 1311).

SECTION 2.0
ALTERNATIVE GROUT FORMULATIONS

In the FY21 work [8], several alternative grout formulation approaches were investigated to assess their potential to achieve the desired improvements in retentions. The present work focused primarily on a few promising formulation systems that were identified in the FY21 work, specifically, the neutral salt activated slag formulations and alkali silicate activated slag formulations. The primary objectives were to further reduce release rates of the COCs and to increase waste loadings. In addition, Cement-Free and modified Cast Stone formulations were also included in this testing phase. The sections below provide a brief summary of the alternative grout formulation technology and approaches for improving performance that were considered for application to supplemental LAW immobilization.

2.1 Geopolymers

This approach builds on the FY21 work to further investigate the application of geopolymer technology for improved SLAW waste forms. Geopolymers are cementitious materials that are 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 BFS, metakaolin (MK), and fly ash (FA). The activator is typically an aqueous solution of alkali hydroxide, alkali silicate, alkali carbonate or sulfate. Alkali activation of calcium-free or low-calcium aluminosilicate materials such as Class F fly ash (FFA) or metakaolin yield 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. Alkali activation of blast furnace slag yields calcium aluminosilicate hydrate (CASH). The high-sodium, high-pH nature of Hanford LAW streams make them a natural activator solution for the formation of geopolymers. Research and development programs in geopolymers have been ongoing at VSL for over 15 years. That work has addressed low-carbon-footprint alternatives to Ordinary Portland Cement (OPC)-based construction materials as well as geopolymer technology specifically tailored to address certain radioactive waste immobilization problems.

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 insoluble oxyhdroxide or sulfide, as in the OPC-based SRS Saltstone. Alkali activation of blast furnace slag enhances formation of calcium aluminosilicate hydrate phases and AFm type phases [12]. Alkali sulfate activated slag yields AFt (ettringite, $Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$) as the primary secondary phase. 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 $[Ca_2(Al,Fe)(OH)_6]\cdot X\cdot xH_2O$ where X is an exchangeable singly-charged (e.g., chloride) or half of a doubly-charged anion (e.g., sulfate, carbonate). Alkali carbonate activated slag yields layered double hydroxide (LDH) type AFm as the primary secondary phase. Alkali silicate activated metakaolin is favored for iodine, Cs, and Sr due to its similarity to the zeolitic structure [13].

Geopolymers have also been investigated for grouting of Hanford secondary wastes, LAW, and Idaho sodium bearing waste [14-19]. These waste forms are based on alkali-activated binders that do not include OPC and typically include significant amounts of BFS.

Sulfate-activated slag (SAS) based waste forms have been developed for the immobilization of liquid secondary wastes from the WTP, which are high in ammonia [20-23]. The high pH of conventional grouts leads to release of ammonia gas. This is prevented in the SAS formulations by a pretreatment step in which the ammonium ion is precipitated as the mineral struvite immediately prior to adding the dry mix for grout formation. The process has been demonstrated successfully at multiple scales, up to 110-gallon drum scale [23]. Subsequent small-scale testing showed that under some conditions and with some source materials, volumetric expansion was observed during curing [24, 25]. Testing is ongoing to identify the origin of that behavior and to develop potential mitigation approaches.

Based on the results from the FY21 work [8], two geopolymer systems were included in the present work for further development, as described below.

2.1.1 Neutral Salt Activated Slag (NSAS)

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) [26]. However, neutral salt activated slag grouts usually take longer to harden and show delayed compressive strength development as compared to alkali silicate activated slags. This delayed strength development can be mitigated by using blended activating solutions of sodium carbonate or sulfates with sodium hydroxide or silicate solutions. In the present application, these species can be provided by the LAW material which is to be stabilized.

In the early stages of sodium carbonate activation of slag, calcium and mixed sodium-calcium carbonates are the predominant crystalline reaction products, rather than strength-giving phases such as calcium silicate hydrates, which is the main cause of delayed strength development. At later stages, highly cross-linked CASH type phases with sodium incorporated form, as also do LDH phases including hydrotalcite and AFm-type phases.

Sodium sulfate activation of slags typically leads to the formation of CASH-type phases with a low Ca/Si ratio, and ettringite as the main secondary reaction product. Since the setting of Na_2SO_4-activated slag cements is much faster than that of Na_2CO_3-activated slags, sodium sulfate can be used to accelerate setting.

Thus, in the FY21 work [8], which formed the starting point for the present work, the approach employed to design the neutral salt activated slag (NSAS) formulations for SLAW was to promote AFm and/or AFt formation in cured grout waste forms. Both AFm and AFt phases are well known for being potential hosts for anionic species including iodine, in particularly. Increased formation of LDH/AFm and/or AFt phase may improve leaching resistance of anion species such as iodine. While AFm or AFt formation is primarily determined by the activator composition, slag composition, silica fume, light-burned MgO, calcined hydrotalcite, and reaction progress play important roles in determining gel composition and type of secondary phases. Some of the potential test variations considered include:

- Activator compositions: Different ratios of Na_2CO_3 (NC) to Na_2SO_4 ($N\dot{S}$) can be included to control the proportions of LDH/AFm and AFt phases in the cured grout waste forms.
- Including silica fume in neutral salt activated slag may reduce the yield of AFm and/or AFt phases and increase yield of stratlingite and CASH gel. Stratlingite may help in forming a dense matrix. Although stratlingite belongs to the AFm-type phases, its anion specie silicate is not exchangeable and thus it may have less utility for hosting iodide.
- Light-burned MgO may promote formation of LDH phases and it also functions as a shrinkage-reducing admixture to reduce dry shrinkage at early curing times of grout waste forms.
- Including microfine blast furnace slag can enhance reaction progress and to improve performance during early curing times.
- Calcined hydrotalcite may act as an accelerator to enhance strength development and nucleate centers for LDH formation.

Slag composition is an important factor in the formation of secondary phases in the waste form. An increase in MgO content can promote LDH formation and an increase in Al_2O_3 content enhances stratlingite formation. While testing with a range of slag compositions was not part of the present work, inclusion of light-burned MgO and/or calcined hydrotalcite was assessed.

2.1.2 Alkali Silicate Activated Slag (ASAS)

Alkali-activation of blast furnace slag typically employs a highly alkaline solution containing alkali silicate. Sodium silicate activated slag yields alkali (Na, K) substituted CASH gel together with secondary phases such as LDH type hydrotalcite and stratlingite when the MgO content of slag is high, or zeolite/AFm phases when the MgO content is low [12, 27]. The alkaline SLAW solution can form the basis for such an activator. Again, light-burned MgO can be included to promote LDH formation and to control shrinkage. Introducing silica fume in the ASAS formulations tends to promote stratlingite formation at the expense of hydrotalcite. Therefore, less silica fume was included in the present formulations.

ASAS formulations investigated in the FY21 work formed the starting point for the present work. Previous testing showed ASAS-based grouts exhibited fast setting. An objective of the present work was therefore to modify the formulations to obtain an adequate set time.

2.2 Application of Ultrahigh Performance Concrete Principals

Advances in the science of concrete materials have led to the development of a next generation of cementitious composites called ultrahigh performance concrete (UHPC), which exhibits very high compressive strength and durability. Several authors have identified some of the basic principles used in UHPC [28-30].

A key aspect of the design of UHPC mixes is the packing density optimization principle. The mix is proportioned such that the fine aggregates have a wide particle size distribution in granular class sizes to achieve maximum packing density, yielding a highly dense, low-porosity mixture. The matrix properties are improved by the addition of pozzolanic nanoparticles such as silica fume. In addition, extremely low water to dry mix (w/dm) ratios (e.g., 0.15 to 0.25) can be achieved by large dosages of superplasticizer, which decreases the porosity in the cured material. In general, the mechanical and chemical durability of cementitious and geopolymer materials are inversely related to the porosity. Therefore, reducing porosity provides one route for improving the durability of grout waste forms.

In the FY21 work [8], a conventional Portland cement based UHPC (PUHPC) formulation was tailored to include blast furnace slag for solidifying SLAW. Blast furnace slag (20% replacement) was included in the formulation to provide sulfide species and a reducing environment in the waste form to enhance the immobilization of pertechnetate (simulated in the present work by the surrogate perrhenate). Although the UHPC formulation yielded exceptional leaching resistances for all the COCs tested including iodine in the FY21 work, the waste loading was low. It is challenging to increase waste loading significantly because one of the key design principles of UHPC formulations requires a low w/dm ratio (as low as 0.15 to 0.25) for the reasons described above. Therefore, the PUHPC formulations were not further explored in the present work. However, some of the key UHPC principles listed above were employed to formulate waste forms, such as including sand and ground quartz in a 5:1 proportion in neutral salt and alkali silicate activated slags to improve the packing density. This sand to grout quartz ratio is commonly applied in the literature in UHPC formulations to increase packing density.

2.3 Improved Cast Stone and Cement-Free Waste Forms

As noted above, in FY12, WRPS began a program of 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 for supplemental treatment of LAW [2-5]. The nominal Cast Stone formulation employs a dry mix of 8 wt% Portland cement Type I/II (OPC), 45 wt% Class F fly ash (FFA), and 47 wt% ground granulated blast furnace slag (BFS) (grade 100) [2]. That formulation is a modification of the nominal Savannah River Site (SRS) Saltstone formulation: 10 wt% OPC, 45 wt% FFA, and 45 wt% BFS [31]. The down-selection of the nominal Cast Stone formulation as a baseline for use with Hanford wastes was performed by CH2M Hill at the 222-S Laboratory [31].

In this work, the Cast Stone formulation was modified and improved by including ultrafine Portland Cement and blast furnace slag, a pore plug admixture, and calcined hydrotalcite. The finer particle size and higher surface area makes the Portland cement and blast furnace slag much more reactive.

While the roles of BFS and FFA in the Saltstone formulation are well-defined, the driver for the inclusion of OPC as a minor component is somewhat unclear and may well be a historical artifact of the formulation development process. At the SRS Saltstone Facility, removal of that minor component, if viable, could have significant advantages in terms of material handling logistics, storage silo utilization, process control, and overall process simplicity. Consequently, Savannah River Remediation, LLC (SRR) tasked VSL with the investigation and development of "cement-free" saltstone formulations to determine whether they could have the potential for equivalent or better performance than the present 45-45-10 blend. Results from that work have demonstrated that equal and even better performance can indeed be achieved in such "cement-free' formulations [11, 32]. The reference "Cement Free" formulation employs a dry mix of 60% BFS and 40% FFA with a w/dm = 0.60. A grade 100 blast furnace slag was included in this reference formulation.

In this study, the reference "Cement-Free" formulation was modified by including microfine blast furnace slag and a reduced w/dm ratio to enhance reaction progress during the alkali activation in the presence of the relatively low alkalinity SLAW simulant (1.7 moles of free hydroxyl). In addition, the SLAW simulant may be amended with alkali hydroxide to increase its hydroxyl concentration and thus further enhance the alkali activation process. Alkali hydroxide activated slag typically favors formation of hydrotalcite [33]. Hydrotalcite is a well-known host phase for a variety of anionic species [34-36]. In addition, calcined hydrotalcite was included as an ingredient in some of the dry mixes. Calcined hydrotalcite regenerates its original layered structure during hydration and can potentially sequester anionic species such as iodide, iodate, and pertechnetate in the SLAW.

2.4 Alternative CAC–BFS based Formulations

The objective of this formulation approach was to test the feasibility of Calcium Aluminate Cement (CAC)–BFS waste forms for SLAW with AFm and AFt as the main secondary phases to improve the retention of iodine, technetium, and nitrate. This approach employs a ternary binder system (BFS-CAC-X), where CAC stands for calcium aluminate cement and X is hydrated lime ($Ca(OH)_2$), calcium sulfate ($C\hat{S}$), or calcium carbonate (Cc). CAC–BFS blends, particularly where the BFS ratio is higher than about 40%, lead to the formation of the stable AFm phase stratlingite (C_2ASH_8), instead of calcium aluminate hydrates [37]. When the CAC content is high and $C\hat{S}$ is low, the AFt forms first, followed by monosulfate (AFm) formatiom. When the $C\hat{S}$ content is high, it may also react directly with CAC to form AFt ettringite and AFm monosulfate. When calcium carbonate (e.g., limestone powder) is added to the system instead, calcium carbonate or calcium hydroxide will react with calcium aluminate cement to form the AFm hemicarboaluminate or moncarboaluminate. Consequently, these quaternary binder systems should provide considerable scope for tuning the content of getter phases such as AFm and AFt.

2.5 Promotion of Grout Getter Phases

This approach employed cementitious or geopolymer formulations tailored to incorporate LDH phases that are capable of sequestering and immobilizing iodine, nitrate, and nitrite [34 -36]; these phases are thermodynamically stable and compatible with other phases in these waste forms. AFm belongs to the general LDH structure type; AFt phases are related to AFm and are well known as major secondary phases present in calcium sulfoaluminate cement (CSA), sodium sulfate activated slag, and systems involving Portland cement blended with CSA, calcium aluminate cement (CAC), and gypsum. The present work further investigated LDH/AFm and/or AFt phases, either by including them in the dry mix as additives, e.g., calcined hydrotalcite and/or by modifying the grout formulations to promote *in situ* formation of these phases during hydration or activation and curing, such as by controlling the ratios of Na_2CO_3 to Na_2SO_4 in neutral salt activated slag formulations and including light-burned MgO (see descriptions in Sections 2.1 and 2.2).

2.6 Pore Plugs to Reduce Permeability

This approach employs inorganic admixtures to reduce porosity by occluding pores in the cured grout structure (“pore plugs”). Effective plugging of the capillary pores may significantly decrease the permeability and provide slower diffusion of species such as iodine, nitrate, and nitrite, in particular; in addition, however, the retention of all species is likely to be improved by this process. One approach in this regard involves the use of integral crystalline waterproofing admixtures. The mechanism of action involves the release of silicate or carbonate during curing of the grouts and the released species react with free lime as a result of cement hydration to form crystals that block capillary pores; this decreases the available migration pathways of target species such as nitrate, technetium, and iodine. Examples of such admixtures include Hycrete System M1000, BASF Masterlife 300D and XYPEX ADMIX C500. In the present work, Xypex ADMIX C500 was employed in the improved Cast Stone and Cement-Free formulations since it is likely these pore plug admixtures would not work well in alkali activated materials. Pore plugs are usually used in Portland cement-based concrete where calcium silicate hydrate (CSH) is the main hydration product. Pore plugs also react with free hydrated lime that is present as a hydration product of Portland cement to form additional CSH gel to precipitate in the pores. In alkali activated materials, free hydrated lime is typically not present and, even if it is present, aluminosilicate species released from alkali activation of BFS will combine with hydrated lime to precipitate CASH gel.

In addition, the use of nanoparticles such as silica fume to improve the packing density of the mixture and to fill in the pores can also reduce the permeability of the waste form.

2.7 Admixtures and Reformulation to Reduce Porosity

The objective of this approach is similar to that described in Section 2.6 (i.e., to reduce the permeability of the waste form and hence the mobility of the COCs) but the methods are different. The general approach is to reduce the water to dry mix ratio (w/dm) since high w/dm values are known to correlate with increased porosity and permeability of the resulting cured grouts. Decreasing the w/dm ratio with no other change results in poor workability and difficulty in mixing and pumping. These effects may be mitigated through the use of admixtures and formulation modifications such that a waste form grout may be formulated with adequate workability at the minimum w/dm.

Superplasticizing water reducers generally are not efficient in reducing w/dm ratio and improving rheological properties in alkali activated materials. As an alternative, certain hydrophobic admixtures may be included in a waste form grout mix as an integral waterproofing modification. Hydrophobic admixtures such as calcium stearate (Cst, $C_{17}H_{35}COO)_2Ca$), oleates, silanes, and powdered silicone are known to reduce capillary water absorption or permeability in both cementitious and geopolymer materials, and to improve their long-term durability [38-41].

A further possible modification is to add redispersible, vinyl acetate-ethylene copolymer powder in the waste form grout formulations. It is well known that polymers can enhance rupture strength, bonding forces, freeze-thaw properties, weathering resistance, wear resistance, and also durability of cementitious and geopolymer materials. They can also enhance the hydrophobic properties to reduce absorption of water and can also prevent cracking [42].

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

3.1 Waste Simulant

The SLAW simulant composition that was used in the present work, which is the same as that used in FY21 [8], is shown in Table 3.1. This 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.

Simulants with 5.6 M Na were spiked with I (as iodide) and Re (as a non-radioactive surrogate for Tc, added as hydrogen perrhenate), all at levels of 350 mg/L or ~0.28 g/kg simulant to ensure that detectable levels were present in the leachates from the EPA Method 1315 tests[1]. Previously, the simulant was spiked with I and Re at 1 g/kg simulant, respectively. It is noted that rhenium is less easily reduced than technetium and may therefore overestimate the release of technetium from reducing grouts [45]. Chromium was added as $Na_2Cr_2O_7 \cdot 2H_2O$ using a molar ratio of 0.0043 Cr/Na which is the Best Basis Inventory (BBI) value in Table 3-3 in reference [2]. The resulting simulant contained 1.25 g/L Cr. 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. 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 simulant is shown in Table 3.2. The measured density was about 1.25 g/mL for the 5.6 M Na SLAW simulant.

3.2 Raw Materials for Preparing SLAW Waste Forms

A range of raw materials, aggregates/fillers, and additives were used for formulating grout waste forms for SLAW, as described in the following sections. XRF analyzed compositions of raw materials are listed in Table 3.3.

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 C989. The slag was chosen due to the geographical proximity of the source to the Hanford Site and the fact that it was

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[1] For comparison, the mean concentration of ^{129}I in the Hanford LAW inventory at a Na concentration of 5.6 M is about 0.65 mg/L [43]; the mean concentration of ^{99}Tc in the Hanford LAW inventory at a Na concentration of 5.6 M is about 6 mg/L [44].

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) [20-23].

DE NEEF MC 500 Microfine cement (MC) is a blast furnace slag, called Microfine BFS, composed of ultrafine particles and was provided by GCP Applied Technologies. DE NEEF MC 500 has a grain size of d_{95} equal to 9.5 microns and d_{50} of 3.5 microns. The composition is comparable to that of high sulfate-resistant cements. Microfine cement is much more reactive than conventional blast furnace slag grade 100 and 120 simply due to its smaller particle size. In this work, microfine slag was used to replace NewCem BFS grade 100 from Lafarge-Holcim's Seattle Plant (BFS SE). Microfine slag was primarily included in improved Cast Stone and Cement-Free formulations to enhance setting and early strength. It was also included in paste-only NSAS formulations. XRD analysis indicated distinct phase compositions between the two blast furnace slags (Figures 3.1 and 3.2). Abundant crystalline phases such as dicalcium (C_2S) and tricalcium (C_3S) silicates were present in the Microfine BFS while calcium sulfate phases, mainly the dihydrate, were present in BFS SE. In addition, Microfine BFS (Figure 3.1) had a significantly lower glass content than BFS SE (Figure 3.2) based on the area of the wide, amorphous peak around two-theta between 25 and 35°.

Class F fly ash (FFA) is one of the raw materials in the Cast Stone waste forms developed for Hanford Low Activity Waste [3-6]. Cast Stone formulations previously tested at PNNL [3-6] used a high-Ca fly ash produced from the combustion of coal at the Centralia Power Plant in western Washington. However, that power plant is now closed, and the fly ash is no longer available. Therefore, for the present work, that fly ash was replaced by Class F fly ash from the Jewett Plant in Texas, which was provided by Headwaters, Inc. The Jewett fly ash (JW FFA) contains about 13 wt% calcium oxide, which is close to that in the Centralia fly ash [8].

Portland Cement (PC) Type I/ II from Holcim US was used as an ingredient in the Cast Stone waste forms. The Portland cement conformed to the specification defined by ASTM C150. It contained 51 wt% C_3S, 18 wt% C_2S, 7 wt% C_3A, and 9 wt% C_4AF. Note that in standard cement chemistry notation, $C = CaO$, $S = SiO_2$, $A = Al_2O_3$, $F = Fe_2O_3$.

Microfine Portland cement (MPC) called MasterRoc® MP 650 from Master Builders Solutions was used as an ingredient in improved Cast Stone waste forms. MasterRoc® MP 650 has a grain size of d_{93} <15 microns and a d_{50} < 5 microns. The Blaine fineness is >625 m^2/kg, compared to 396 m^2/kg for Type I/ II Portland Cement from Holcim US.

Light-burned MgO marketed under the brand name Sika Control® SC was used as an ingredient in several formulations for SLAW. Light burned MgO is a shrinkage compensating and reduction admixture used to produce Portland cement and geopolymeric materials with reduced potential for drying shrinkage, cracking, and curling, 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 [46].

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. Silica fume was also used to prepare the alkali silicate activator by dissolving it in a SLAW simulant solution that was previously amended with potassium hydroxide. In this testing, silica fume that was allocated to the activator was added as the solid. In this way, the lower soluble silicate concentration during early curing time should extend the set time of the resulting geopolymer grouts.

3.2.2 Sand/Fillers

As described in Section 2.3, fine sand, ground quartz, and silica fume were included in waste form mixes to optimize the packing density of the resulting SLAW 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 A25 from Agsco Corporation, with a mean particle size of 5 microns.
- Silica fume may be added as a reactive nano filler to improve rheology and particulate packing, particularly in the case of NSAS-based waste forms. During the late curing stages, silica fume may participate in gel formation by enhancing formation of calcium aluminosilicate hydrate and stratlingite.

3.2.3 Additives

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

- XYPEX ADMIX C500 was provided by Xypex Chemical Corporation. This admixture functions as a pore plug to reduce water permeability. This was tested only in the waste form based on Portland cement ultrahigh performance concrete. Typically, the dosage rate is about 3% by weight of cement. It was added to the mixture at the time of batching.
- EUCON Hydrapel 2.5 (Hdp) is a silicon polymer-based, plasticizing/efflorescence controlling/water-repellent admixture, provided by Euclid Chemical. It was added to some grout mixes at a dosage of 0.575% to 1.0% by weight of dry mix (BWODM) or by weight of slag (BWOS).
- GP SHP 50 silicone hydrophobic powder was provided by Dow Corning. It is a free-flowing powder designed for cementitious dry mix application. The admixture is usually applied as a barrier to the capillary movement of liquid water in cementitious materials. GP SHP 50 is a three-component granule (200-300 microns), consisting of a

powder carrier, an encapsulant and finely dispersed silicone. The encapsulant provides storage stability in the powdered composition and the active ingredient is released upon addition of water. This hydrophobic admixture has been tested at VSL in geopolymer concretes and proved efficient in improving hydrophobicity. GP SHP 50 was added at 1% by weight of slag in alkali silicate activated slag formulations.

- Calcium stearate is known for efficiently reducing water absorption in alkali activated materials through optimizing microstructure and introducing a hydrophobic film [38]. However, the potential negative impact of the high salt concentrations in SLAW on such performance improvement was a primary concern of this study. Calcium stearate was added at a dose of 5% by weight of slag in alkali silicate activated slag formulations.

- Commercially available hydrotalcite ($Mg_6Al_2(OH)_{16}(CO_3)\cdot 4H_2O$) was calcined at 475 °C for 5 hours. The calcined hydrotalcite (CHT) powders were then hydrated in 1 M Na SLAW for 24 hours; X-ray diffraction (XRD) analysis showed that its hydrotalcite structure was fully recovered. The objective was for the calcined hydrotalcite to restructure around the available anion species in the waste to enhance their retention in the waste form. The amount added was typically around 5 – 10 wt% based on the Phase 1 work [8].
- Ionex Ag-900 (AgZ) manufactured by Molecular Products Limited is a silver-exchanged zeolite with a mordenite crystalline structure. It contained a minimum of 9 wt% silver and had a nominal pore size of 0.4 nm. Ground Ionex Ag-900 was used as a getter for iodine in some waste forms. The amount added was typically around 5 wt% based on the Phase 1 work [8].

XRF analyzed chemical compositions for selected raw materials used for preparing SLAW waste forms are shown in Table 3.3. Note that loss-on-ignition is not included in the chemical compositions.

3.3 Testing Approach

The primary objective of this work was to further develop and demonstrate methods to reduce the release rates of the COCs from grouted SLAW waste forms. The formulations and recipes for the SLAW waste form samples that were prepared and tested in this work included following types of waste form formulations:

- ICS – Improved Cast Stone waste form
- ICF – Improved Cement Free waste form
- CSM – Mortar of neutral salt activated slag
- CSMP – Paste of neutral salt activated slag
- SFM – Mortar of alkali silicate activated slag
- SFMP – Paste of alkali silicate activated slag

Fine sand and ground quartz powder were included typically at 35% :7% in a mortar mix composition and they were removed completely in the paste mix compositions.

As noted in Section 1.3, to address this objective, a four-stage phased testing approach was employed.

- In the first testing phase, the primary focus was on developing improved formulations based on Cast Stone and Cement free materials. Microfine BFS, Portland cement and XYPEX ADMIX C500 were included in the Cast Stone formulation to improve its performance. Portland cement was removed in the reference Cast Stone formulation to yield Cement Free formulations but with Microfine BFS. In addition, a NSAS formulation from the FY21 work [8] was modified to favor AFm formation and an ASAS formulation was optimized to extend set time. An attempt was also made to develop a waste form based on the ternary binder BFS-CAC-$Ca(OH)_2$). These formulations were screened by testing set time and compressive strength. Selected waste forms were subject to an abbreviated EPA Method 1315 test (14 days) to expedite testing progress.

- The second stage was the primary testing phase of the present work. Formulations based on Cast Stone, Cement-Free, alkali silicate and neutral salt activated slags were further modified and optimized by including one or more raw materials such as Microfine BFS, Microfine PC, hydrophobic admixture, calcined hydrotalcite, and ground Ionex Ag-900. Most waste forms 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.

- In the third phase of testing, attempts were made to develop filler-free, paste-only formulations, primarily based on neutral salt activated slag waste forms, to improve waste loading.

- In the fourth phase of testing, three of the better-performing formulations were selected for additional characterization with respect to rheology, isothermal calorimetry, and the Toxicity Characteristic Leaching Procedure (EPA Method 1311).

Waste form formulations developed during each of these testing phases are summarized in Table 3.4. Those formulations are described in the following section. The sample nomenclature is as follows: After the letters designating the formulation type (e.g., ICS) the decimal number (e.g, “0.50”), if present, designates the w/dm ratio. The next character is a W for Cast Stone and Cement-Free formulations, which are all pastes or, for other formulations, a P or an A for paste and mortar samples, respectively. The next number (following W, A, or P) is the series number (1, 2, 3…) for formulation modifications. S indicates that the grout samples are prepared with the simulant spiked with I, Cr, and Re. The number after the S indicates a different batch with the same composition or with a minor modification.

3.4 Formulations and Recipes

The formulations and recipes for the SLAW waste form samples that were prepared and tested in this work in each testing phase are described in the following sections.

3.4.1 Improved Cast Stone Formulations

The nominal Cast Stone dry blend consists of 47 wt% BFS, 45 wt% FFA, and 8 wt% OPC with a w/dm of 0.60. The fly ash used in this study was from Jewett Power Plant, TX. The Jewett fly ash has a similar CaO content to the one from the Centralia Power Plant, WA used in other Cast Stone work [3-6]. The blast furnace slag grade 100 was from the Lafarge-Holcim Seattle Plant. The nominal Portland cement was Type I/II. In this work, the nominal Cast Stone formulation was modified by varying the w/dm ratio and including one or more raw materials such as Microfine PC, Microfine BFS, XYPEX ADMIX C500, calcined hydrotalcite, and Eucon Hydrapel 2.5.

The parameters for formulating improved Cast Stone waste forms are listed in Table 3.5 and the grout mix compositions are listed in Table 3.6. The recipes are shown in Table 3.7. The dry mix consists of Portland cement, fly ash, blast furnace slag, and a pore plug admixture. The PC:FFA:BFS proportion was 1:5.6:5.9, which is typical for the reference Cast Stone formulation. These ratios were kept the same for formulations ICS0.6W1S; ICS0.5W1S and ICS0.45W1S with 4-6% XYPEX ADMIX C500 in the dry mix and w/dm from 0.45 to 0.60. The PC:FFA:BFS was changed to 1:1.7:3.7 in ICS0.5W3S by increasing proportions of Microfine PC and Microfine slag at the expense of FFA. In addition, the formulation was further modified by adding 1% by weight of the dry mix of hydrophobic admixture Eucon Hydrapel 2.5 in ICS0.5W3S.

3.4.2 Improved Cement-Free Formulations

The reference "Cement-Free" formulation employs a dry mix of 60% BFS and 40% FFA with a w/dm = 0.60 [11]. The dry mixes for the modified formulations employed blast furnace slag, fly ash, a pore plug admixture, and calcined hydrotalcite. A grade 100 blast furnace slag and Class F fly ash were employed. The reference Cement Free formulation was modified by including 4.27% XYPEX ADMIX C500 in the dry mix while the w/dm was reduced to 0.50 (ICF0.50W1S). The BFS/FFA ratio was maintained at about 1.5. The reference Cement Free formulation was further modified by reducing the w/dm to 0.45 and including 5% calcined hydrotalcite in the dry mix and 9% KOH (assay 90.84%) by weight of the dry mix to increase the concentration of (K, Na)OH to 5 M in the SLAW simulant (ICF0.45W1S). The higher molar alkali hydroxide concentration was intended to accelerate the alkali activation process. Formulation parameters, waste form compositions, and recipes are shown in Tables 3.5 to 3.7, respectively.

3.4.3 Alternative CAC-BFS Based Formulations

In this study, only one formulation based on ternary BFS-CAC-X was tested. The formulation contains 24% BFS (SE), 73.5% CAC, and 2.5% $Ca(OH)_2$, with a w/dm = 0.45. Trial testing with this formulation yielded a pourable grout with low compressive strength even after curing at RT for 28 days. This trial test employed a grade 100 BFS from Lafarge-Holcim Seattle Plant and Ciment Fondu calcium aluminate cement (~40% Al_2O_3) from Kerneos. Based on the low compressive strength, this formulation was not pursued further in the present work. However, further work to include use of more reactive raw materials such as amorphous calcium aluminate cement and Microfine BFS to increase rate of hydration may be useful.

3.4.4 Formulations Based on Neutral Salt Activated Slag

The formulation parameters for the waste forms based on neutral salt activated slag are listed in Table 3.8. Mortar and paste mix compositions developed according to the formulating parameters summarized in Table 3.8 are shown in Tables 3.9 and 3.10, respectively. The corresponding recipes are shown in Tables 3.11, 3.12, and 3.13.

Variables for formulating mortar and paste waste form mix compositions included:

- w/dm from 0.40 to 0.45. The dry mix contained mainly BFS and certain formulations included CHT or AgZ. Light-burned MgO was used in all the NSAS formulations.
- Sodium carbonate and sodium sulfate were included as activators with proportions specified in terms of Na_2O by mass fraction of slag (BMFOS). The sodium carbonate contribution from the SLAW simulant was calculated as a part of the activator. The total Na_2O for sodium carbonate (NC) and sodium sulfate (NŚ) was set to 0.05. The following ratios of NC : NŚ in terms of Na_2O BMFOS were employed in an effort to chemically control the ratios of AFm and/ AFt phases: 0.025 : 0.025; 0.05: 0; 0.01 : 0.04; 0.03 : 0.02.
- Sodium carbonate and/or sodium sulfate were added as the solids together with other dry ingredients (see mortar formulations in Table 3.9) or dissolved in the SLAW simulant before mixing with the dry ingredients (see paste formulations in Table 3.10).
- Light-burned MgO was generally fixed at 0.05 BMFOS. In formulation CSMP1S5, light-burned MgO was increased to 0.07 BMFOS to mitigate increased shrinkage due to removal of sand/fillers.
- 32.5% fine sand and 6.5% ground quartz were included in mortar mix compositions. Sand and ground quartz were removed in the paste formulations.

- Additives to enhance leaching resistance including calcined hydrotalcite and ground Ionex Ag-900. Calcined hydrotalcite was added at 0.05 BMFOS in paste formulations CSMP3S2, CSMP3S3, and CSMP1S3, and at 0.10 BMFOS in mortar formulations CSMA3S1 and CSMA1S3. Ground Ionex Ag-900 was added at 0.05 BMFOS in both mortar and paste formulations CSMA8S1, CSMP8S2, and CSMP8S3.

- EUCON Hydrapel 2.5 was included as the hydrophobic admixture at 0.005 to 0.01 BMFOS. Calcium stearate was included at 0.05 BMFOS.

- Two types of BFS were included in formulations: Grade 100 BFS from Lafarge-Holcim Seattle Plant (BFS SE) and ultrafine blast furnace slag (Microfine BFS).

3.4.5 Alkali Silicate Activated Slag

The formulation parameters for the waste forms based on alkali activated slag are listed in Table 3.14. The mix compositions derived from the formulation parameters are shown in Table 3.15 and the respective recipes are shown in Table 3.16.

A w/BFS ratio of about 0.425 was typically used. In the FY21 work, a molar alkali hydroxide concentration of about 7 was employed, yielding a fresh grout that showed fast setting [8]. In this study, the molar alkali hydroxide concentration was lowered to 5 to slow setting. The molar ratio SiO_2/M_2O is an important parameter for an alkali activator composition; for these formulations, it was defined by the amount of silica fume allocated to the activator and all of the alkali oxides (from NaOH in the SLAW plus the KOH amendment). When silica fume was dissolved in the KOH-amended SLAW simulant solution before grouting, fast setting was observed. Therefore, the silica fume was instead added with the other dry ingredients to achieve a reasonably long workable time.

5% BWOS of light-burned MgO was included in all of the ASAS formulations to reduce dry shrinkage and to promote LDH phase formation. In addition, two types of hydrophobic admixtures, calcium stearate and GP SHP 50 silicone powder, were included in the ASAS-based formulations in an effort to reduce water absorption and permeability of the cured waste forms.

35% fine sand and 7% ground quartz powder were included in all of the ASAS-based mortar mix compositions (SFMA9S2, SFMA9S3, and SFMA9S4). Fine sand and ground quartz were removed to yield a paste mix composition (SFMP9S4) in an effort to increase waste loading.

SECTION 4.0
TEST METHODS

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

4.1 Sample Preparation

The recipes presented in Section 3.4 were used to prepare the waste form samples for testing. The dry ingredients were blended in a 7-quart planetary mixer, then an appropriate quantity of SLAW simulant was poured into the dry mixture and mixed at an intermediate speed (about 100 rpm) for about 6 minutes. The 7-quart mixer allowed for preparation of small batches of grout samples (maximum 5 kg of grout). For larger batches (7 to 8 kg), a K-Lab Intensive Mixer (20 L) was used to prepare grout samples. The mixing time was about 3 to 6 min at an intermediate speed (about 250 rpm for both the mixing blade and the container). The majority of the samples in this work were prepared with the 7-quart planetary mixer.

For all of the ASAS formulations and Cement-Free ICF0.45W1S, solid KOH was first dissolved in the SLAW simulant prior to mixing with the dry ingredients. Dissolution of alkali hydroxide is a strongly exothermic process and therefore the solid NaOH and KOH were added slowly (typically, over the course of about an hour) to avoid overheating of the solution. The solution was typically prepared in advance and allowed to cool to ambient temperature (for several hours or overnight) before mixing with the dry ingredients.

For the mortar waste forms based on neutral salt activated slag, solid sodium carbonate and/or sodium sulfate were added together with dry ingredients before mixing with the SLAW simulant. For the paste waste forms based on neutral salt activated slag, solid sodium carbonate and/or sodium sulfate were mixed with the SLAW simulant before mixing with dry ingredients.

EUCON Hydrapel 2.5, a liquid hydrophobic admixture, was added while mixing the SLAW simulant with dry ingredients for better distribution. Solid hydrophobic admixtures, calcium stearate and GP SHP 50 silicone powder were added together with other dry ingredients before mixing with the SLAW simulant.

A vibrating table was used to compact fresh grouts and remove air bubbles. A vibrating table (3600 vpm) manufactured by Humboldt Mfg Co. was used in the early part of the work but a more powerful vibrating table manufactured by Vibco equipped with a high frequency vibrator (9000 vpm, 8500 N force) was used for the balance of the work. The typical frequency used to compact and remove air bubbles from a fresh grout was between 4500 to 6300 vpm. Tests demonstrated that the Vibco table was much more efficient in compacting fresh grouts than the

Humboldt table. An extremely viscous, dry grout or paste sample became fluid after a few seconds under influence of vibration.

The fresh paste was poured into 2”x4” cylindrical molds. All of the cylindrical samples sealed with lids to prevent moisture loss were cured at room temperature. The fresh grout or paste was sampled as needed for testing for properties such as set time and bleed water monitoring.

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 one centimeter from the top, and cured in a sealed configuration at room temperature for 24 hrs. The sealed molds are then weighed, any liquid is absorbed using tissue paper, and the samples are then weighed again. The mass loss is 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, the surface shows superhydrophobicity. When water droplets immediately spread over the grout surface, the surface shows little hydrophobicity.

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 is thus calculated from the following formula:

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

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 [11]. 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 [47]. All measurements were performed at 25 °C. The heat flow produced by the samples was monitored continuously during 14 days of curing.

Compressive strength: Compressive strength was measured by applying a compressive axial load to unmolded cylinders until failure occurs. 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 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.

An abbreviated version of this method was employed for leach testing during the first testing phase, as described in Section 3.3.

Toxicity Characteristic Leaching Procedure (TCLP): The TCLP leach test was performed in duplicate on selected cured samples per EPA SW-846 Method 1311. 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 [48], 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 quantity is termed the "dry bulk density" in [48].

Porosity was calculated as the ratio of the simulant volume present in the cured sample to the measured saturated sample volume [49]. 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:

$$\rho_s = \rho_m/(1-\eta), \tag{4.2}$$

where ρ_s is the particle density, ρ_m is the matrix skeleton density, and η is the porosity [48].

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 Phase 1 Results

As described in Section 3, a range of alternative grout compositions were considered as the waste forms for SLAW including improved Cast Stone, Cement-Free, alkali silicate activated slag, and neutral salt activated slag. Graded aggregate/filler blends typical for ultrahigh performance concrete formulations were included in ASAS and NASA based waste forms. Table 5.1 summarizes the measured set times, compressive strengths, and leachability indices of all of the alternative grout compositions.

No bleed was observed in any of the paste and grout samples after curing at room temperature for 24 hrs. While the fresh paste samples for improved Cast Stone and Cement Free mix compositions were pourable, the fresh grout samples for ASAS and NSAS based mix compositions were typically more viscous as a consequence of the low w/dm values that were used to reduce the porosity.

5.1.1 Improved Cast Stone and Cement-Free Formulations

Formulating parameters, mix compositions, and recipes for improved Cast Stone and Cement-Free waste forms are shown in Tables 3.5, 3.6, and 3.7. The testing results are summarized in Table 5.1.

The nominal Cast Stone dry blend consists of 47 wt% BFS, 45 wt% FFA, and 8 wt% OPC with a w/dm of 0.60. In this work, the nominal Cast Stone formulation was modified by including one or more raw materials such as Jewett fly ash, Microfine PC, Microfine BFS, XYPEX ADMIX C500, calcined hydrotalcite, and Eucon Hydrapel 2.5. The w/dm ratio varied from 0.45 to 0.60.

All of the improved Cast Stone formulations yielded pourable pastes with slow setting characteristics (Table 5.1). In the FY21 work, CS-5.6M1S represented a nominal Cast Stone formulation with Jewett fly ash replacing the FFA from the Centralia Power Plant, WA [8], which is no longer available. Formulation CS-5.6M1S was modified by introducing 5.96% XYPEX ADMIX C500 and Microfine BFS, yielding ICS0.6W1S. The set time was longer than 24 hrs. The compressive strength was 1524 psi after curing at room temperature for 7 days, as compared to 1025 psi for CS-5.6M1S. Compressive strength increased to 2404 psi, as compared to 2850 psi for CS-5.6M1S, after curing for 28 days. It is likely that the Microfine BFS enhanced the early strength but caused a lower strength gain in the late curing stages. When w/dm was reduced to 0.50 (ICS0.5W1S), the initial set time was 34.38 hrs while the compressive strength increased to 1861 psi after curing for 7 days and 2533 psi after 28 days. When w/dm was further lowered to 0.45 and PC Type I /II was replaced with Microfine PC (ICS0.45W1S), the fresh grout set between 12 and 48 hrs. The compressive strength was 2351 psi after 7 days and increased to 2846 psi after 28 days.

It should be noted that when an ingredient is replaced by a microfine counterpart, the *chemical composition also changes* since only a limited range of products are commercially available. XRF analysis shows that the chemical composition of the Microfine BFS is between that of the BFS SE and PC Type I/II (Table 3.3). In particular, the CaO content is ~51% in Microfine BFS and ~60% in both PC I/II and Microfine PC, whereas the CaO content is about 40% in BFS SE (Table 3.3). Microfine BFS contains elevated concentrations of calcium silicate phases (Figure 3.1). which are the primary phases of Portland cement in terms of equilibrium phases. From a chemical perspective, as distinct from a surface area perspective, it is likely that Microfine BFS would not be as easily activated by the SLAW simulant.

The reference "Cement-Free" formulation employed a dry mix of 60% BFS and 40% FFA with a w/dm = 0.60. In this study, the reference Cement-Free formulation was modified by including 4.27% XYPEX ADMIX C500 in the dry mix while the w/dm was reduced to 0.50 (ICF0.5W1S). The grade 100 slag was replaced with Microfine BFS. The fresh grout set between 10 and 44 hrs. Compressive strength was 1826 psi after curing for 7 days and increased to 2957 psi after 28 days.

5.1.2 Neutral Salt Activated Slag

Formulating parameters, mix compositions, and recipes for NSAS mortar formulations are shown in Tables 3.8, 3.9, 3.11, and 3.12, respectively. The testing results are summarized in Table 5.1.

Alkali-activation of slag can be induced by neutral salts such as sodium carbonate and/or sodium sulfate. Formulation CSM0.40A3S was developed for SLAW simulant with 5.6 moles of Na in the FY21 work [8]. The formulation used a dosage of Na_2CO_3 and Na_2SO_4 in equal amounts, e.g., 0.025 Na_2O BMFOS with calcined hydrotalcite at 0.1 BMFOS and EUCON Hydropapel 2.5 at 0.0058 BMFOS (Table 3.11). The w/dm ratio was 0.40. Light-burned MgO was included to enhance alkali activation. The formulation was redesigned by removing silica fume and using Na_2CO_3 only to promote LDH and AFm formation in the curing grout (CSM0.40A1S1 and CSM0.40A1S2). CSM0.40A1S1 was prepared in an 8-kg batch with K-lab intensive mixer, yielding a viscous grout. The initial set time was 293 min. The compressive strength was 4917 psi after 7 days and 7035 psi after curing for 28 days. The w/dm ratio was increased to 0.425 in CSM0.40A1S2. The initial set time increased to 583 min. The compressive strength was 4977 psi after 7 days and 6390 psi after curing for 28 days.

5.1.3 Alkali Silicate Activated Slag

Formulating parameters, mix compositions, and recipes for ASAS based waste forms are shown in Tables 3.14, 3.15, and 3.16. The testing results are summarized in Table 5.1.

In the FY21 work [8], mortar formulation SFM0.40A9S1 was extensively tested. The formulation used w/dm = 0.44 and the molar alkali calculated as hydroxide was about 7. In addition, calcium hydrotalcite at 10% BMFOS was included for enhancing sequestration of anion species and COCs and EUCON Hydrapel 2.5 was added at 0.0058 BMFOS for hydrophobicity. The set time was short, about 65 min, and leaching indices were not improved. To extend the set time the molar MOH was lowered to 5 in SFMA9S1 without amending hydrophobic admixture. The w/dm was lowered to 0.425 as the grout mix did not contain calcined hydrotalcite, which demands a significant amount of water for structural regeneration. KOH solid was dissolved in the 5.6 M Na SLAW simulant solution and then mixed with the dry ingredients. SFMA9S1 was prepared per the recipe in Table 3.16. The mix yielded a workable but viscous grout with an initial set time of 125 min. The compressive strength was 5154 psi after 7 days and 6361 psi after curing for 28 days, comparable to the strength values for SFM0.40A9S1 tested in the FY21 work [8]. Calcium stearate was included as the hydrophobic admixture at 0.05 BMFOS in mortar formulation SFMA9S2 while other formulating parameters were maintained unchanged. The initial set time was 120 min. Compressive strength was 4967 psi after 7 days and increased to 5728 psi after 28 days. Calcium stearate has been recognized as an efficient hydrophobic admixture in geopolymers [39]. However, little hydrophobicity was observed on the grout surface, which instead showed easy wettability (Table 5.2). It is possible that strong interactions between calcium stearate and salts present in the SLAW simulant impact the hydrophobic performance of the cured grout. In addition, the presence of calcium stearate had a negative impact on compressive strength.

5.1.4 EPA Method 1315 14-Day Leaching Results

The NRC Technical Position on Waste Form [50] 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 assess long-term performance, take precedence for the IDF. The present work, per the WRPS SOW [9], used the EPA Method 1315 test, which is derived from and is similar to the ANSI/ANS 16.1 test. In the first testing period, an abbreviated 14-day version of the EPA Method 1315 test was used. Solutions were sampled for analysis only at 7 and 14 days to expedite testing progress. 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.

Six formulations were selected for abbreviated leach testing, representing improved Cast Stone, Cement-Free, NSAS and ASAS formulations (Table 3.4). The measured LIs for Na, Re, Cr, I, NO_3^-, NO_2^- at 14 days are reported in Table 5.1 and shown in Figures 5.1 to 5.6. 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.

LI values for Na: Mixes based on Cast Stone, Cement-Free, and neutral salt activated slag (ICS0.5W1S, ICS0.45W1S, ICF0.5W1S, and CSM0.40A1S2) yielded comparable LI values for sodium, at around 8.3 (Figure 5.1). The LI Na value for alkali silicate activated slag (SFMA9S1 (5M MOH) was 8.18. With addition of a hydrophobic admixture (calcium stearate, SFMA9S2), the LI Na value dropped to 8.01, indicating that calcium stearate negatively impacted leaching resistance.

LI values for Re: Three Cast Stone and Cement-Free mixes yielded comparable LI values for Re, at around 8.7 (Figure 5.2). The LI Re value for neutral salt activated slag (CSM0.40A1S2) was the highest (9.44). The LI Re value for alkali silicate activated slag was 8.95 (SFMA9S1). When calcium stearate was included in the mix, the LI Re value was lowered to 8.30 (SFMA9S2).

LI values for Cr: All mix compositions tested, except for SFMA9S2 yielded LI values for Cr of 13-14 (Figure 5.3). The LI Cr value for alkali silicate activated slag was 13.79 (SFMA9S1). With the inclusion of calcium stearate, the LI Cr value dropped to 12.09. Nevertheless, all the formulations tested show excellent Cr leach resistance as compared to the metric. It is likely that Cr^{6+} is susceptible to the reducing environment and it is reduced to Cr^{3+}, which then hydrolyzes to insoluble $Cr(OH)_3$ in the alkaline environment present in the curing grout.

LI values for I: Three Cast Stone and Cement-Free mixes yielded comparable LI values for I, at 8.6-8.7 (Figure 5.4). The LI I value for neutral salt activated slag (CSM0.40A1S2) was 8.50. The LI I values for the two ASAS mixes were lower at around 8.3.

LI values for NO_3^-, NO_2^-: The LI values for nitrate and nitrite were generally very close to each other for most of the mixes tested, suggesting that they are retained and released by similar mechanisms (Table 5.1, Figures 5.5 and 5.6). The LI values for nitrate were 8.5-8.8 for most of the mixes. LI values for nitrate and nitrite were 8.31 and 8.25, respectively, for the ASAS mix (SFMA9S1). With amendment of calcium stearate in the mix, LI values for nitrate and nitrite dropped slightly in SFMA9S2. Addition of calcium stearate failed to yield a hydrophobic waste form and decreased the mechanical strength and chemical durability of the tested waste forms.

The results from the first testing period can be summarized as follows:

- Four types of waste forms were developed for 5.6M Na SLAW including Cast Stone, Cement-Free, NSAS, and ASAS
- Geopolymer formulations yielded thicker pastes while the Cast Stone and Cement-Free formulations yielded easily pourable grouts.
- Set time was successfully extended to 2 hrs for NSAS-based waste forms
- All of the formulations yielded cured waste forms with high compressive strengths.
- The results from EPA 1315 14-day leach testing showed that all of the waste forms exhibit excellent leaching resistance for Cr with LI values far exceeding the estimated performance metric requirement for Cr of 10.4. Based on the results from these abbreviated tests, the steady state LI nitrate values for Cast Stone, Cement-Free, and neutral salt activated slag formulations would be expected to exceed the estimated performance metric requirement for nitrate of 8.70. However, improvements in leach resistance for iodine and rhenium are likely required.

5.2 Phase 2 Results

The primary focus of this testing phase was on modifications of Cast Stone, Cement-Free, NSAS, and ASAS formulations to further improve the leaching performance by introducing methods and approaches described in Sections 2 and 3. However, the scope and schedule did not permit testing of all such possible modifications. The Cast Stone formulation was modified by incorporating hydrophobic admixture and Microfine Portland cement. The Cement-Free formulation was optimized by increasing the molar MOH in the SLAW simulant. The formulation based on alkali activated slag was modified by incorporating an efficient hydrophobic admixture and use of a higher molar MOH to enhance the alkali activation process. The ASAS formulations used BFS SE from Lafarge-Holcim Seattle Plant to increase the set time. The formulation based on neutral salt activated slag was further optimized by including an efficient hydrophobic admixture, a getter, and Microfine BFS. Calcined hydrotalcite was added to improve fixation of anionic species in the SLAW. Calcined hydrotalcite rehydrates and restructures in the SLAW simulant solution and, in the process, absorbs available anion species. In addition, a silver-zeolite getter was included in a formulation based on neutral salt activated slag for comparison.

Formulations tested during this testing period are listed in Table 3.4. All of these mixes were prepared with 5.6 M Na SLAW simulants spiked with I, Re, and Cr. Measured fresh and cured properties are summarized in Table 5.3. All of the grout samples were cured at room temperature for 28 days except for ICS0.5W1S. ICS0.5W1S, which was cured for over five months, allowing assessment of curing time on leaching resistance. Waste forms with slow reaction kinetics such as Cast Stone and Cement-Free grout may require an extended curing time to reach their maturity conditions as described in concrete maturity literature [51]. The grout samples were then subjected to 63-day leach testing via EPA Method 1315.

5.2.1 Set Time and Compressive Strength

No bleed was observed in any of the paste and grout samples after curing at room temperature for 24 hrs. Again, while the fresh pastes for improved Cast Stone and Cement-Free mixes were pourable even at a w/dm as low as 0.45, the fresh grouts for ASAS- and NSAS-based mixes were typically more viscous, and not pourable at w/dm ratio = 0.425. However, these fresh grouts became immediately fluid under the influence of vibration on a Vibco vibration table at vibration frequencies between 4500 and 6300 vpm. Commercially available vibrators used in the construction and building industries typically employ vibration frequencies up to 15,000 vpm.

5.2.1.1 Improved Cast Stone and Cement-Free Formulations

Formulating parameters, mix compositions, and recipes for improved Cast Stone and Cement-Free waste forms are shown in Tables 3.5, 3.6, and 3.7. The test results are summarized in Table 5.3.

The Cast Stone formulation was further modified by introducing EUCON Hydrapel 2.5 to induce internal hydrophobicity and by using a large proportion of Microfine BFS in ICS0.5W3S

(Table 3.5). The set time was reduced from over 10 hrs for other Cast Stone mixes to 430 min. A Microfine BFS to FFA ratio of 2.2 was used, as compared to the reference value of about 1 in Cast Stone formulations. Compressive strength increased to 2893 psi after curing for 7 days and increased to 3607 psi after 28 days. Apparently, inclusion of higher proportion of Microfine BFS accelerated both setting and strength development.

The Cement-Free formulation was modified by lowering w/dm from 0.50 in ICF0.50W1S to 0.45 in ICF0.45W1S, increasing molar MOH (M = K and Na) to 5, and incorporating calcined hydrotalcite at the expense of XYPEX ADMIX C500. The initial set time was 165 min. Compressive strength was 3202 psi after curing for 7 days and increased to 4541 psi after 28 days. Inclusion of a higher molar MOH greatly enhanced the alkali activation process. Rehydration of calcined hydrotalcite removed water and anion species in the SLAW simulant, which likely also contributed to faster setting and strength improvement.

5.2.1.2 Neutral Salt Activated Slag

Formulating parameters, mix compositions, and recipes for NSAS based waste forms are shown in Tables 3.8, 3.9, 3.11, and 3.12. The test results are summarized in Table 5.3.

Formulation CSM0.40A3S was developed for SLAW simulant with 5.6 M Na in the FY21 work with dosage of Na_2CO_3 and Na_2SO_4 in equal amounts [8]. The w/dm ratio was 0.40. This formulation was modified by slightly increasing w/dm from 0.40 to 0.425 to improve workability of the fresh grout, yielding CSMA3S1 (Table 3.11). The dry mix contained BFS SE and calcined hydrotalcite. EUCON Hydrapel 2.5 was included in CSMA3S1 as in the formulation CSM0.40A3S. The fresh grout was pourable. Initial set time was 872 min. The as cured grout surface showed good hydrophobicity, indicating that EUCON Hydrapel 2.5 was an effective hydrophobic agent. Compressive strength was 6418 psi after curing for 7 days and increased to 6936 psi after 28 days. As a comparison, the initial set time was 165 min and 28 day compressive strength was as high has 10,287 psi for CSM0.40A3S tested in the FY21 work [8].

Formulation CSM0.40A3S was modified by slightly increasing w/dm from 0.40 to 0.425 and incorporating Ag-900 and calcium stearate, yielding CSMA8S1 (Table 3.12). The resulting grout was viscous and not pourable, although the fresh grout became fluid after vibration on the Vibco table. The set time was about 24 h. The cured grout surface did not show any degree of hydrophobicity. Compressive strength was 4643 psi after curing for 7 days and increased to 7539 psi after 28 days.

Formulation CSM0.40A1S2 was modified by incorporating calcined hydrotalcite and replacing BFS SE with more reactive Microfine BFS, yielding CSMA1S3. This formulation used 100% Na_2CO_3 without silica fume to promote LDH and/or AFm phase formation in the curing grout. The initial set time was greatly reduced to 40 min. The compressive strength was 5186 psi after 7 days and 6204 psi after curing for 28 days. Though Microfine BFS was very reactive in terms of setting acceleration, compressive strength was not improved during the later curing stages. The Microfine BFS contained significantly higher CaO content than BFS SE causing it to behave more like Portland cement.

5.2.1.3 Alkali Silicate Activated Slag

Formulating parameters, mix compositions, and recipes for ASAS based waste forms are shown in Tables 3.14, 3.15 and 3.16. The test results are summarized in Table 5.3.

5 M MOH and calcium stearate were employed for formulating SFMA9S2 during the first testing phase. Calcium stearate was replaced by an alternative hydrophobic admixture SH GP SHP 50 silicone, yielding SFMA9S3. Initial set time was 129 min. The grout surface showed great hydrophobicity. Compressive strength was 4392 psi after 7 days and increased to 5400 psi after 28 days. Molar MOH was increased slightly to 5.6 with calcium stearate as the hydrophobic admixture, yielding SFMA9S4. A slightly longer set time was measured at about 150 min. The grout surface showed high wettability without any trace of hydrophobicity, which again indicated inefficiency of this hydrophobic admixture in the alkali silicate activated slag (Table 5.2). Compressive strength was 5157 psi after 7 days and increased to 7008 psi after 28 days. A slight increase in molar MOH in the SLAW simulant tailored with amendment of KOH greatly enhanced strength development without shortening setting. To increase waste loading, mortar mix SFMA9S4 was modified by removing sand and ground quartz and replacing calcium stearate with SH GP SHP 50 silicone, yielding SFMP9S4. The waste loading of SLAW increased from 18.60 wt% to 31.87 wt%. Initial set time was 157 min, comparable to its mortar counterpart. The grout surface showed great hydrophobicity, indicating efficiency of the silicone based hydrophobic admixture. Compressive strength was 5221 psi after 7 days but, surprisingly, the 28-day compressive strength was only 5042 psi, significantly lower than the value for its mortar counterpart (SFMA9S4). The samples showed a premature failure pattern during compression. Although the same dosage of SH GP SHP 50 silicone was used in both the paste and mortar mixes, the actual amount of silicone powder almost doubled (Table 3.14). Thus, it is possible that the silicone based hydrophobic admixture was overdosed, which may have caused the reduction in the 28-day compressive strength.

5.2.2 EPA Method 1315 63-Day Leaching Results

The Phase 2 samples were subjected to leach testing with EPA Method 1315 for 63 days after curing the grout samples at room temperature for 28 days. The measured LI values for Na, Re, Cr, I, NO_3^-, NO_2^- at 63 days are summarized in Table 5.3. The LI values at each sampling time are reported in Tables 5.4 to 5.9. These values are also plotted as functions of time and formulation type in Figures 5.7 to 5.12 and as functions of time and leached species in Figures 5.13 to 5.20. At the time of writing, some of these tests are still ongoing; the new data will be added to the respective tables and figures in a revision of this report.

Also shown in Figures 5.8 to 5.11 (black lines) are 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.

As for the Phase 1 testing, sodium and nitrite were measured, in addition to rhenium, chromium, iodine, and nitrate, in order to provide additional measures of the leaching behavior of soluble species to better characterize the overall retention properties of the waste form.

LI values for Na: LI values at 63 days for Na varied from formulation to formulation in a fairly narrow range of about 8.4 to 8.9 (Table 5.3). In comparison, the Na LI value for the reference Cast Stone formulation (e.g., Mix# 51) was 8.1 [2]. In the FY 21 work, mixes based on neutral salt activated slag and Portland cement ultrahigh performance concrete yielded higher LI values for sodium, in the range of about 9 - 11 [8]. However, these grout samples were made with 1 M Na SLAW and therefore the waste loading was lower. In contrast, the present work tested a range of formulations with 5.6 M SLAW simulant. Obviously, higher concentrations are preferred in practice since they lead to lower volumes of grout waste form for disposal. However, the results at lower waste loadings, which often showed improved waste form leaching performance, are useful in providing a basis for assessment of the effects of waste feed concentration as an optimization variable.

LI values for Re: Formulations based on neutral salt activated slag yielded waste forms that showed very good resistance to Re leaching. The 63-day LI values for Re were between 11 and 12.3. The LI values for the mixes based on Cast Stone and Cement-Free formulations were between 8.8 and 8.9. This may be due to the slower reaction progress than in neutral salt activated slag causing less slag to react, resulting in a less reduced environment in the curing grout. In particular, the Microfine BFS contains less sulfide, 3.90 wt% as SO_3 as compared to 5.03% SO_3 in BFS SE (Table 3.3), likely resulting in a lower reduction capacity in the cured grout sample. In this sense, this particular superfine slag provided by GCP Applied Technologies may be not be the optimum material for use in improved Cast Stone and Cement-Free formulations. Alternative slags such as superfine and grade 120 with desirable chemical compositions and reduction capacity could be investigated for future formulations.

Two mixes based on alkali silicate activated slag yielded LI values of 9.34 for SFMA9S3 and 10.57 for SFMP9S4. The molar MOH in the SLAW simulant was increased to 5.6 in SFMP9S4 and thus more slag reacted, resulting in a more reducing environment. It is noted that rhenium is less easily reduced than technetium [45] and therefore, the actual LI values for Tc are expected to be even higher for the mixes developed in this study.

As can be seen in Figure 5.8 and Table 5.3, three mixes based on neutral salt activated slag 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]. Formulations based on neutral salt activated slag showed a rapid increase in LI value for Re with increasing leach time and the steady state was not reached even after 49 days (Figure 5.8). In contrast, for formulations based on Cast Stone and Cement-Free, the LI value rapidly reached its steady state after leaching for 14 days (Figure 5.8).

LI values for Cr: All of the formulations tested during this second testing period showed excellent resistance to Cr leaching. The 63-day LI values for Cr were between 12 and 14 and the steady state was reached rapidly, within about 7 days, indicating that Cr^{6+} was fully reduced and likely hydrolyzed to precipitate highly insoluble $Cr(OH)_3$ apparently not susceptible to the oxidative environment. As can be seen in Figure 5.9 and Table 5.3, all of the mixes have Cr LI values better than the estimated performance metric requirement for chromium.

LI values for I: The 63-day LI values for I ranged from about 8.7 to 8.9 for the mixes based on Cast Stone, Cement-Free, and neutral salt activated slag; the LI values were slightly lower (about 8.5) for two mixes based on alkali silicate activated slag (Table 5.3). As a comparison, for a range of Cast Stone formulations enhanced with various additives, the steady state LI values for I ranged from 7.6 to 9.2 [2]. Formulation CSMA8S1 included 5 wt% AgZ as a getter with Microfine BFS to replace BFS SE. The LI value for I was 8.9. Although Ionex Ag-900 is known to be an efficient getter for iodine in the alkaline SLAW simulant by precipitating AgI in the nanopores of the zeolitic structure, this process can be disrupted by the release of sulfide during grout reactions. In particular, activation of BFS will create a reducing environment and release of sulfide will destabilize 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 [52]. In addition, the zeolite matrix as the protective barrier for nano-AgI may be lost due to significant involvement in geopolymerization. Calcined hydrotalcite was included in two neutral salt activated slag formulations (CSMA3S1 and CSMA1S3) to promote the formation of AFm and/or AFt phases in the curing grout samples. While hydrotalcite, AFm, and AFt phases are well known for sequestrating iodine, the LI values for I were still below the estimated performance metric requirement. This may be due to iodide having to compete for anion exchange sites with the large excess of other anions (nitrate, nitrite, carbonate, sulfate) that are present in the SLAW simulant and the pore solution in the curing grout. Overall, therefore, improvement of leach resistance for iodine remains a high priority for future formulation work.

As can be seen in Figure 5.10 and Table 5.3, all of the formulations have iodine LI values below the estimated performance metric requirement for iodine of 10.52 (diffusivity = 3×10^{-11} cm^2/s) [6]. In the FY21 work, two mixes based on neutral activated slag and one mix based on Portland cement ultrahigh performance concrete had iodine LI values better than the estimated performance metric requirement for iodine of 10.52. However, these waste forms were prepared with 1 M Na SLAW and therefore had lower waste loadings. Among other effects, the lower Na concentration will result in lower concentrations of anions that compete with iodide for competitive absorption and thus should improve iodine immobilization in hydrotalcite, AFm, and AFt phases in the curing grout. It is possible that retention could be improved by addition of tricalcium aluminate, which may hydrate in the SLAW simulant to form AFm phases for removal of most anion species including iodine before grouting through neutral salt activation of slag. In addition, Ag-zeolite getter with a higher Ag loading may improve getter performance for iodine. For example, a silver loaded zeolite synthesized at VSL contains about 62% Ag_2O and may be worth testing.

LI values for NO_3^-, NO_2^-: The 63-day LI values for nitrate and nitrite were very close to each other for each formulation (Table 5.3, Figures 5.11 and 5.12). The 63-day LI values for nitrate and nitrite varied from formulation to formulation in the range of 8.4 and 8.8. As can be seen in Figure 5.11 and Table 5.3, five of the eight grout formulations tested 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]. These formulations include ICS0.5W3S, ICF0.45W1S, CSMA3S1, CSMA1S3, and CSMA8S1. The exceptions are an improved Cast Stone mix ICS0.5W1S with LI value for nitrate at around 8.66, and two formulations based on alkali silicate activated slag with a LI value for nitrate at around 8.45, which is slightly better than the value (about 8.0) for an alkali silicate slag mix tested in the FY21 work [8]. In fact, the present ASAS formulations with an extended set time showed considerable improvement in overall leaching performance over the formulations developed in the FY 21 work. The LI values for nitrate and nitrite slightly over 10 were observed for the mixes with 1 M Na SLAW in the previous work [8].

5.3 Phase 3 Results

The primary focus of this exploratory testing phase was on developing sand/filler free, paste-only formulations based on neutral salt activated slag. Methods and approaches described in Sections 3.3.4 were applied such as including an efficient hydrophobic admixture, a getter, and Microfine BFS. Calcined hydrotalcite was added to improve fixation of anionic species in the SLAW. In addition, a silver-zeolite getter was included in a formulation based on neutral salt activated slag for comparison.

Formulating parameters, mix compositions, and recipes for paste formulations based on neutral salt activated slag are shown in Tables 3.8, 3.10, and 3.13, respectively. The paste formulations developed during this testing period are shown in Table 3.4 and the test results are summarized in Table 5.10. Information on grout surface hydrophobicity is provided in Table 5.2.

Mortar formulation CSMA3S1 was modified by removing sand and ground quartz, replacing BFS SE with Microfine BFS, and including 5% calcined hydrotalcite to yield CSMP3S2 and CSMP3S3. CSMP3S2 was prepared by mixing solid sodium carbonate and sodium sulfate together with other dry ingredients before mixing with the SLAW simulant, resulting in a thick paste. The as-cured grout surface showed good hydrophobicity when EUCON Hydrapel 2.5 was used as the hydrophobic admixture. Compressive strength was 6605 psi after curing for 7 days and increased to 6990 psi after 28 days. CSMP3S3 was prepared by first dissolving sodium carbonate and sodium sulfate in the SLAW simulant before adding the dry mix, which also resulted in a thick paste. The initial set time was 120 min, significantly shorter than 872 min for its mortar counterpart, CSMA3S1. The as-cured grout surface showed good hydrophobicity. Compressive strength was 6310 psi after curing for 7 days and increased to 7234 psi after 28 days.

Mortar formulation CSMA1S3 was modified by removing sand and ground quartz, and including 5% BWOS calcined hydrotalcite and 0.75% BWOS EUCON Hydrapel 2.5 to yield CSMP1S3. Both formulations used Microfine BFS and sodium carbonate was the only activator. CSMP1S3 was prepared by first dissolving sodium carbonate in the SLAW simulant before mixing, resulting in a very thick paste. However, vibration on the Vibco table caused the fresh paste to flow. The initial set time was 128 min, much longer than 40 min for its mortar counterpart. The as-cured grout surface showed little hydrophobicity. Compressive strength was 6128 psi after curing for 7 days and increased to 7165 psi after 28 days.

CSMP3S2, CSMP3S3, and CSMP1S3 were subjected to EPA Method 1315 leach testing. However, surprisingly, all of the cylindrical samples cracked after leaching for 1 or 2 days.

To test which ingredient was responsible for cracking, CSMP3S3 was modified by removing calcined hydrotalcite and the hydrophobic admixture and increasing light-burned MgO from 4% to 7% BWOS to mitigate shrinkage, yielding CSMP1S5. CSMP1S5 was prepared by first dissolving sodium carbonate and sodium sulfate in the SLAW simulant. The initial set time was 89 min. Compressive strength was 4806 psi after curing for 7 days and increased to 6383 psi after 28 days. However, one of the 2” cylindrical grout samples cracked during demolding.

Formulation CSMP1S3 was modified by replacing calcined hydrotalcite with Ionex Ag-900 and increasing the w/dm to 0.45 for improved workability, yielding CSMP8S2. The initial set time was as 197 min. Compressive strength was 4609 psi after curing for 7 days and increased to 5813 psi after 28 days. The grout sample cracked after leaching for 14 days.

CSMP3S5 used an activator containing mostly sodium sulfate and a w/dm of 0.45 and included light-burned MgO and EUCON Hydrapel 2.5. The initial set time was 365 min. The as-cured grout surface showed good hydrophobicity. Compressive strength was 6561 psi after curing for 7 days and increased only slightly to 6786 psi after 28 days. This sample cracked after leaching for 2 days.

All of the formulations described above used Microfine BFS and most of them cracked after leaching for 1 or 2 days. The cracking appeared to be independent of the use of calcined hydrotalcite, Ionex Ag-900, and hydrophobic admixture, suggesting that the Microfine BFS could be responsible for causing cracking. To test this hypothesis, formulation CSMP3S4 was developed with BFS SE. CSMP3S4 used an activator containing mostly sodium carbonate and a w/dm of 0.45 and included EUCON Hydrapel 2.5. Sodium carbonate was dissolved in the SLAW simulant before mixing with the dry ingredients. The fresh paste was pourable with an initial set time of 9-24 hrs. A longer set time is expected because BFS SE is much less reactive as compared to Microfine BFS. The as-cured grout surface showed good hydrophobicity. Compressive strength was 5607 psi after curing for 7 days and increased to 7766 psi after 28 days. Cracking has not yet been observed after 63 days of leaching.

In summary, the paste samples prepared with Microfine BFS often experienced cracking during demolding and leaching, which most likely was associated with large shrinkage. Cracking was not observed in samples in which the Microfine BFS was replaced with BFS SE. However, no cracking was observed with the mortar version of the formulation (CSMA1S3), which also used Microfine BFS. This suggests that including sand and ground quartz in the mix yields a more rigid matrix that resists shrinkage and cracking. The BFS SE slag was used in a range of alternative grout formulations in the FY21 work and yielded mechanically and chemically durable waste forms for SLAW, with no sign of cracking. As noted previously, in addition to particle size, there are also chemical composition differences between the Microfine BFS and BFS SE. For example, the Microfine BFS has a higher CaO content (~51 wt%) as compared to ~43 wt% CaO in BFS SE, more closely resembling Portland cement (Figure 3.1). However, it is not clear why this, in and of itself, would cause cracking.

5.4 Phase 4 Results

Based Phase 1 and 2 test results and discussion with WRPS, three formulations (ICS0.5W1S, CSMA3S1 and CSMA8S1) were selected for additional characterization with respect to rheology, isothermal calorimetry, and TCLP testing.

Table 5.11 provides a summary of the set time, bleed, compressive strength, and rheological properties of the selected formulations. Figures 5.21 and 5.22 show the shear stress and viscosity versus shear rate, respectively. Rheological data are not available for CSMA8S1, which was very viscous and outside the range of the rheometer.

Isothermal calorimetry measurements were made on the three selected formulations using paste samples in which the sand and ground quartz (inert ingredients) were removed. The normalized heat flow results are shown in Figure 5.23 and the normalized heat release results are shown in Figure 5.24. The results are summarized in Tables 5.12 and 5.13. Normalization is with respect to the mass of wet grout.

ICS0.50W1S showed the highest heat flow (main hydration peak) at the earliest curing time (19.83 hrs) because of the inclusion of Microfine BFS but this occurs earlier than the measured set time of 34.4 hrs. This is likely because the set time is determined not only by reaction progress but also the type of gel that is formed. It is possible that CSH gel formation dominated in ICS0.50W1S due to the high CaO in the Microfine BFS and the presence of Portland cement. The CSH gel is susceptible to interference from the waste solids. In contrast, CASH formation dominated in the two CSM grout samples and sodium can be incorporated in the CASH structure to replace calcium.

Significantly higher heat releases were observed, particularly during early curing, for ICS0.5W1S than for the two neutral salt activated slag samples. However, the compressive strength was the lowest for ICS0.5W1S. This is also likely a consequence of CSH versus CASH gel formation and the better compatibility of the latter with the salts in the waste.

TCLP testing was conducted on the three selected formulations; the results are summarized in Table 5.14. Chromium concentrations are less than the instrumental detection limit of 0.02 mg/l, far below its EPA UTS value of 0.60 mg/l. There is no EPA UTS limit for Re. Two formulations based on neutral salt activated slag yielded a lower TCLP concentration for Re than the improved Cast Stone, consistent with EPA 1315 testing results. The TCLP concentrations for other heavy metals such as Ag, As, Ba, Ni, Pb, and Zn were below their respective EPA UTS limits likely due to precipitation of insoluble hydroxides or sulfide compounds. Among these heavy metals, As, Ba, Ni, and Pb are typically present as impurities in the blast furnace slag and fly ash.

Selected grout samples including three final formulations were characterized with respect to density, porosity, and saturated hydraulic conductivity. Table 5.15 summarizes the measured values of the apparent density, matrix skeleton density, particle density, and porosity.

The apparent densities of the cured grouts range from 1.77 to 2.17 g/cm^3. Three mortars based on neutral salt activated slag (CSMA3S1, CSMA8S1, and CSMA1S3) show the highest apparent density, ranging from 2.03 to 2.16 g/cm^3, owing to included sand and ground quartz in the mixes. Improved Cast Stone samples were much less dense, about 1.77 g/cm^3, which can be compared to the range of about 1.7 to 2.0 g/cm^3 for Cast Stone [2]. Two paste samples based on neutral salt activated slag (CSMP8S2 and CSMP3S3) had intermediate apparent density.

Matrix skeleton densities ranged from 1.13 to 1.79 g/cm^3, with the lowest density for improved Cast Stone samples (about 1.13 g/cm^3) and the highest density for mortars (1.65 to 1.79 g/cm^3. Matrix skeleton densities for two paste samples based on neutral salt activated slag were around ~1.35 g/cm^3.

The porosity for improved Cast Stone samples was about 0.51, compared to the range of about 0.47 - 0.62 for Hanford Cast Stone [2]. The porosity was as low as 0.29 for the mortars based on neutral salt activated slag. The porosity was about 0.45 for two paste samples based on neutral salt activated slag.

The particle densities ranged from 2.29 to 2.53 g/cm^3 with lower value for improved Cast Stone samples.

5.5 Appendices

Calculated waste loadings of various grout mix compositions are summarized in Table A1 of Appendix A. Initial concentrations in kg/m^3 for calculating leaching indices are reported in Table B1 of Appendix B. Concentration data of contaminants are shown in Tables B2 to B7 of Appendix B and cumulative percent release data are shown in Tables B8 to B13 of Appendix B.

SECTION 6.0
SUMMARY AND CONCLUSIONS

The objective of this work was to build on the results of the FY21 work to perform laboratory-scale testing to develop and demonstrate methods to reduce the release rates of iodine, technetium, nitrate, and chromium from grouted LAW waste forms. In the FY21 work, formulations based on neutral salt activated slag and PUHPC showed the best performance. However, due to its lower waste loading, formulations based on PUHPC were not pursued in the present work. The primary focus of the present work was on further refinement of the neutral salt activated slag formulations as well as those based on Cast Stone, Cement-Free, and alkali silicate activated slag formulations. All of the testing employed an SLAW simulant with 5.6 M sodium.

A four-phase testing approach was employed. In the first testing phase, the primary focus was on developing improved formulations based on Cast Stone and Cement-Free compositions by including superfine BFS and Portland cement. In addition, an FY21 formulation based on neutral salts activated slag was optimized in favor of AFm formation and a formulation based on alkali activated slag was optimized to extend set time. These formulations were screened by measuring set time, compressive strength, and performing an abbreviated EPA Method 1315 test (14 days). In Phase 2 testing, down-selected formulations were subjected to the full 63-day EPA Method 1315 test along with the measurement of other properties. Formulations based on Cast Stone, Cement Free, alkali silicate and neutral salt activated slags were further modified and optimized by including Microfine BFS, Microfine Portland cement, hydrophobic admixture, calcined hydrotalcite, and ground Ionex Ag-900. Most of the waste forms 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. Phase 3 testing was an exploratory study intended to develop sand/filler-free, paste-only formulations to improve waste loading, with a focus on neutral salt activated slag systems. In Phase 4, three formulations were selected for additional testing with respect to rheology, isothermal calorimetry, and TCLP leaching.

The results from the present work show that many of the alternative formulations that were developed exhibit superior retention of the target COCs as compared to the reference Cast Stone waste form. 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 SLAW waste form performance through these novel formulation approaches.

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

- Three NSAS-based 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 12.28 corresponds to a diffusivity of 5.24×10^{-13} cm^2/s, which is a factor of 39 lower than the performance metric for technetium.

- None of the nine new grout formulations tested has 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].

- Five of the nine new grout 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 exceptions include the ASAS formulations and one improved Cast Stone formulation. The highest measured LI value for nitrate of 8.81 corresponds to a diffusivity of 1.55×10^{-9} cm^2/s.

- All of the nine new grout 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 13.85 corresponds to a diffusivity of $>1.4 \times 10^{-14}$ cm^2/s.

Future work should continue these efforts to improve the leaching performance of these prospective waste forms, with particular emphasis on iodine. Approaches to improve iodine retention include direct formation of AFm phases in the SLAW before grouting, and the use of Ag-zeolite getters with higher silver loadings. Formulations based on neutral salt activated slag should be further optimized, including testing of a range of slag sources and compositions. It is noted that the leaching results from the present work are compared to the estimated performance metrics for disposal at the IDF. However, off-site disposal paths are also under consideration, some of which could have less restrictive waste form performance requirements, which could broaden the range of acceptable formulations and formulation types. In particular, for example, the various cement-free waste forms have the additional benefit of a lower carbon footprint since OPC is one of the largest contributors in that regard.

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 are implemented through a Quality Assurance Project Plan (QAPP) for WRPS work that is conducted at VSL [53]. Test and procedure requirements by which the testing activities are planned and controlled are also defined in that plan. The program is supported by VSL standard operating procedures that will be used for this work [54].

This work does 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), are not applicable.

SECTION 8.0
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Table 3.1. Composition of LAW Simulant; "HTWOS Overall Average" from [2].

Constituent	Moles per Mole of Na	Mol/L at 5.6 M Na
Na	1.000	5.600
K	0.007	0.039
Al	0.061	0.342
Cl	0.008	0.045
F	0.006	0.034
SO_4	0.017	0.095
PO_4	0.01	0.056
NO_2	0.113	0.633
NO_3	0.324	1.814
CO_3	0.055	0.308
TOC	0.015	0.084

Note: The simulant is spiked with I and Re each at concentrations of 350 mg/L and Cr at a concentration of 1.25 g/L.

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

Analyte	Target (Moles)	Reagent	Molecular Weight	Assay	Target Masses (g)
Al	0.3416	$NaAlO_2$	81.970108	1.000	28.00
OH^-	1.7136	NaOH	40.01	0.992	69.11
SO_4^{2-}	0.0952	Na_2SO_4	142.04	0.998	13.55
Cl^-	0.0448	NaCl	58.443	1.000	2.618
NO_3^-	1.8144	$NaNO_3$	84.995	0.992	152.10
NO_2^-	0.6328	$NaNO_2$	68.995	0.997	43.79
CO_3^{2-}	0.3080	Na_2CO_3	105.98844	0.998	32.71
K	0.0392	KNO_3	101.1052	0.997	3.975
PO_4^{3-}	0.0560	Na_3PO_4	163.94	0.992	9.255
TOC	0.0840	CH_3COONa	82.034	0.993	6.939
F	0.0336	NaF	41.988	0.990	1.425
Re	350 mg/L	$HReO_4$ (Re)	186.207	0.500*	0.700
I	350 mg/L	NaI	149.894	0.990	0.418
Cr	0.0241	$Na_2Cr_2O_7 \cdot 2H_2O$	297.9981	1.000	3.588
H_2O	-	DI H_2O	18.02	1.000	886.04
Total, g/L					1254.22

* 50% metal contained in $HReO_4$ solution

Table. 3.3. XRF Analyzed Compositions (wt%) of Raw Materials Used to Prepare SLAW Waste Forms.

Oxide	**JW FFA**	**BFS SE**	**Microfine BFS**	**Microfine PC**	**OPC I/II**	**Light-Burned MgO**	**Ionex Ag-900**
Ag_2O	-	-	-	-	-	-	25.04
Al_2O_3	19.60	12.19	8.53	5.26	4.18	0.36	9.62
BaO	0.32	<0.01	0.05	<0.01	0.05	<0.01	<0.01
CaO	12.53	43.11	50.53	61.95	60.23	4.20	0.92
Fe_2O_3	4.34	0.78	0.58	3.01	2.97	0.65	1.32
K_2O	1.46	0.53	0.52	0.56	1.35	0.01	0.58
MgO	2.72	4.85	4.67	1.47	3.86	92.24	1.88
MnO	0.06	0.15	0.10	0.06	0.14	0.02	0.09
Na_2O	0.77	0.24	0.25	0.80	0.39	<0.01	0.33
P_2O_5	0.19	0.01	0.05	0.05	0.06	0.06	0.17
SiO_2	55.54	32.38	29.91	21.99	19.87	1.89	59.74
SO_3	0.87	5.03	3.90	4.33	6.43	0.15	<0.01
SrO	0.26	0.06	0.09	0.04	0.11	0.00	<0.01
TiO_2	1.22	0.51	0.78	0.29	0.21	0.02	0.17
ZnO	0.01	<0.01	0.01	0.06	0.07	0.37	0.01
ZrO_2	0.04	0.04	0.03	0.01	<0.01	<0.01	0.03
Sum	99.93	99.89	99.98	99.88	99.90	99.96	99.91

Table 3.4. Waste Form Formulations Developed during Respective Testing Phases.

Testing Phase	Grout ID	Type of Materials	EPA 1315
Phase 1	ICS0.6W1S	ICS, Paste	-
	ICS0.5W1S	ICS, Paste	Abbreviated
	ICS0.45W1S	ICS, Paste	Abbreviated
	ICF0.5W1S	ICF, Paste	Abbreviated
	SFMA9S1	ASAS, Mortar	Abbreviated
	SFMA9S2	ASAS, Mortar	Abbreviated
	CSM0.40A1S1	NSAS, Mortar	-
	CSM0.40A1S2	NSAS, Mortar	Abbreviated
Phase 2 (Primary Testing Phase)	ICS0.5W1S	ICS, Paste	Full
	ICF0.45W1S	ICF, Paste	Full
	ICS0.5W3S	ICS, Paste	Full
	SFMA9S3	ASAS, Mortar	Full
	SFMP9S4	ASAS, Paste	Full
	CSMA8S1	NSAS, Mortar	Full
	CSMA3S1	NSAS, Mortar	Full
	CSMA1S3	NSAS, Mortar	Full
Phase 3 (Exploratory)	CSMP8S2	NSAS, Paste	-
	CSMP1S3	NSAS, Paste	-
	CSMP3S2	NSAS, Paste	-
	CSMP3S3	NSAS, Paste	-
	CSMP3S4	NSAS, Paste	Full
	CSMP3S5	NSAS, Paste	-
	CSMP1S5	NSAS, Paste	-

Table 3.5. Formulating Parameters for Waste Forms Based on Cast Stone and Cement-Free Formulations.

Grout ID	**w/dm**	**Dry Mix (100%)**						**Add BWODM**	
		MPC	**PC I/II**	**FFA**	**MC**	**XYPEX**	**CTH**	**KOH**	**Hdp**
ICS0.6W1S	0.60	-	7.52	42.32	44.20	5.96	-	-	-
ICS0.5W1S	0.50	-	7.66	43.08	44.99	4.27	-	-	-
ICS0.45W1S	0.45	7.60	-	42.75	44.65	5.00	-	-	-
ICS0.5W3S	0.50	15.00	-	25.00	55.00	5.00	-	-	1%
ICF0.5W1S	0.50	-	-	37.79	57.94	4.27	-	-	-
ICF0.45W1S	0.45	-	-	38.00	57.00		5.00	9%	-

Add = Additive to improve leaching resistance; CTH = Calcined hydrotalcite; MC = Microfine BFS (cement) MC500; MPC = Microfine Portland cement; Hdp = Eucon Hydrapel 2.5; XYPEX = XYPEX ADMIX C500

Table 3.6. Formulations for Improved Cast Stone Waste Forms for SLAW (in wt%).

Formulation	**Add/PC**	**PC**	**MC**	**FFA**	**KOH**	**Add**	**SLAW**	**Hdp**	**Sum**
ICS0.6W1S	XYPEX/PC I/II	4.06	23.83	22.82	-	3.21	46.08	-	100.00
ICS0.5W1S	XYPEX/PC I/II	4.49	26.36	25.23	-	2.50	41.42	-	100.00
ICS0.45W1S	XYPEX/MPC	4.64	27.29	26.12	-	3.06	38.89	-	100.00
ICS0.5W3S	XYPEX/MPC	8.73	32.00	14.54	-	2.91	41.24	0.58	100.00
ICF0.5W1S	XYPEX/-	-	33.94	22.14	-	2.50	41.42	-	100.00
ICF0.45W1S	CTH/-	-	33.23	22.15	5.29	2.92	36.42	-	100.00

MPC = Microfine Portland cement
MC = Microfine slag (DE Need MC500)
FFA = Jewett fly ash (Class F)
XYPEX = XYPEX C500 ADMIX
CTH = Calcined hydrotalcite
Hdp = Eucon Hydrapel 2.5

Table 3.7. Recipes for Improved Cast Stone and Cement-Free Formulations.

Type of Waste Form		**Improved Cast Stone**				**Cement-Free**	
Formulation ID		**ICS0.6W1S**	**ICS0.5W1S**	**ICS0.45W1S**	**ICS0.5W3S**	**ICF0.5W1S**	**ICF0.45W1S**
Order	**Chemical**	**Target Weight (g)**					
4	Microfine BFS	935.65	1027.89	1036.83	1287.37	1323.71	1262.69
4	Portland Cement	159.26	174.96	-	-	-	-
4	Microfine PC	-	-	176.48	351.10	-	-
4	Class F fly ash	895.83	984.15	992.71	585.17	863.29	841.79
4	CHT	-	-	-	-	-	110.76
4	XYPEX C500	126.15	97.50	116.11	117.03	97.50	-
3	HYDRAPEL 2.5	-	-	-	23.41	-	-
2	KOH (90.84%)	-	-	-	-	-	200.83
1	SLAW 5.6M Na	1809.26	1615.50	1477.88	1659.33	1615.50	1383.92
Total batch, g		3926.15	3900.00	3800.00	4023.41	3900.00	3800.00

Table 3.8. Formulating Parameters for NSAS-Based Waste Forms.

Grout ID	Mortar or Paste	w/dm	Na_2O as in NC	Na_2O as in NŚ	MgO	Add	Hyp	Type BFS	Type Hyp
			Mass Fraction of BFS						
CSM0.40A3S	Mortar	0.400	0.025	0.025	0.05	0.1 CHT	0.0058	SE	Hdp
CSM0.40A1S1	Mortar	0.400	~0.05	-	0.05	-	-	SE	-
CSM0.40A1S2	Mortar	0.425	~0.05	-	0.05	-	-	SE	-
CSMA8S1	Mortar	0.425	0.025	0.025	0.05	0.05 AgZ	0.05	SE	Cst
CSMA3S1	Mortar	0.425	0.025	0.025	0.05	0.1 CHT	0.0058	SE	Hdp
CSMA1S3	Mortar	0.425	~0.05	-	0.05	0.1 CHT	0.0075	MC	Hdp
CSMP3S2	Paste	0.425	0.025	0.025	0.05	0.05 CTH	0.0058	MC	Hdp
CSMP3S3	Paste	0.425	0.025	0.025	0.05	0.05 CTH	0.0058	MC	Hdp
CSMP1S3	Paste	0.425	~0.05	-	0.05	0.05 CTH	0.0075	MC	Hdp
CSMP8S2	Paste	0.45	~0.05	-	0.05	0.05 AgZ	0.01	MC	Hdp
CSMP3S4	Paste	0.45	~0.045	-	0.05	-	0.005	SE	Hdp
CSMP3S5	Paste	0.45	0.01	0.04	0.05	-	0.0075	MC	Hdp
CSMP1S5	Paste	0.425	0.025	0.025	0.07	-	-	MC	-

Add = Additive to improve leaching resistance (by weight of the dry mix); CTH = Calcined hydrotalcite; AgZ = ground Ag-zeolite (Ionex Ag-900); SE = BFS from Seattle Plant; MC = Microfine BFS MC500; Hyp = hydrophobic admixture; Cst = Calcium stearate; Hdp = Eucon Hydrapel 2.5; NC = sodium carbonate anhydrous; NŚ = sodium sulfate anhydrous.

Table 3.9. Mortar Formulations for NSAS-Based Waste Forms (in wt%).

Grout ID	Add/Hyp/BFS	BFS	NC	NŚ	MgO	Sand	QZ	SF	Add	Hyp	SLAW
CSM0.40A3S	CTH/Hdp/SE	31.81	0.84	1.80	1.59	32.50	6.50	2.00	3.18	*	19.75
CSM0.40A1S1	SE	36.26	2.40	-	1.81	32.50	6.50	-	-	-	20.52
CSM0.40A1S2	SE	35.55	2.31	-	1.78	32.50	6.50	-	-	-	21.37
CSMA8S1	AgZ/Cst/SE	31.76	0.84	1.60	1.59	32.50	6.50	2.00	1.59	1.59	20.04
CSMA3S1	CTH/Hdp/SE	31.09	0.79	1.78	1.55	32.44	6.49	2.00	3.11	0.18	20.56
CSMA1S3	CTH/MC	32.55	2.05	-	1.63	32.50	6.50	-	3.25	-	21.52

BFS = Blast furnace slag, conventional or superfine; Add = Additive to improve leaching resistance; CTH = Calcined hydrotalcite; AgZ = ground Ionex Ag-900; SE = BFS from Seattle Plant; MC = Microfine BFS MC500; Hyp = hydrophobic admixture; Cst = Calcium stearate; Hdp = Eucon Hydrapel 2.5; NC = sodium carbonate anhydrous; NŚ = sodium sulfate anhydrous.; QZ = Ground quartz powder; SF = Silica fume
* - 0.0058 Eucon Hydrapel 2.5 by weight of solids

Table 3.10. Paste Formulations for NSAS-Based Waste Forms (in wt%).

Grout ID	Add/Hyp/BFS	BFS	NC	NŚ	MgO	SF	Add	Hyd	SLAW
CSMP3S2	CTH /Hdp/sNC/sNŚ/MC	53.10	1.40	3.04	2.65	3.34	2.65	0.30	33.51
CSMP3S3	CTH/Hdp/dNc/dNŚ/MC	53.10	1.40	3.04	2.65	3.34	2.65	0.30	33.51
CSMP1S3	CTH/Hdp/dNC/MC	55.47	3.55	-	2.77	-	2.77	0.41	35.01
CSMP8S2	AgZ/Hdp/dNC/MC	54.32	3.41	-	2.72	-	2.72	0.54	36.30
CSMP3S4	Hdp/dNC/SE	57.25	3.16	-	2.86	-	-	0.29	36.44
CSMP3S5	Hdp/dNŚ/MC	55.98	-	5.17	2.80	-	-	0.42	35.63
CSMP1S5	dNc/dNŚ/MC	57.17	1.55	2.91	4.00	-	-	-	34.37

Add = Additive to improve leaching resistance; CTH = Calcined hydrotalcite; AgZ = ground Ionex Ag-900; SE = BFS from Seattle Plant; MC = Microfine BFS MC500; Hdp= Eucon Hydrapel 2.5; NC = sodium carbonate anhydrous; NŚ = sodium sulfate anhydrous; SF = Silica fume; dNC and dNŚ: Dissolved in SLAW ; sNC and sNŚ: Added as solid; SF = Silica fume

Table 3.11. Recipes for NSAS-Based Waste Forms.

Formulation ID		CSM0.40A1S2	CSMA3S1	CSMA1S3
Order	**Chemical**	**Target Weight (g)**		
4	BFS SE	1416.21	1393.69	-
4	Microfine BFS	-	-	1296.75
4	Light burned MgO	70.81	69.68	64.84
4	Silica fume	-	89.48	-
4	Calcined hydrotalcite	-	139.37	129.67
4	Agsco Silica A-25	258.97	290.82	258.97
4	Yellow sand, air dry	1294.86	1454.11	1294.87
4	Na_2CO_3 (99.7%)	92.36	35.70	81.90
4	Na_2SO_4 (99.8%)	-	80.09	--
3	HYDRAPEL 2.5	-	8.01	-
2	Moisture from sand/Qz	15.54	17.45	15.54
1	SLAW 5.6M Na	851.25	921.58	857.45
Total batch, g		4000.00	4500.00	4000.00

Table 3.12. Recipes for NSAS-Based Waste Forms with Ionex Ag-900.

Formulation ID		**CSMA8S1**	**CSMP8S2**
Order	Component	Mass, grams	Mass, grams
3	BFS SE	1423.37	-
3	Microfine BFS	-	2172.56
3	Sika Control SC (MgO)	71.17	108.63
3	Silica fume	89.65	-
3	Ground Ionex Ag-900	71.17	108.63
3	Agsco Silica A-25	291.35	-
3	Yellow sand, air dry	1456.74	-
3	Eucon Hydrapel 2.5	-	21.73
3	Calcium Stearate	71.17	
3	Na_2CO_3 (99.7%)	37.58	136.70*
3	Na_2SO_4 (99.8%)	72.01	-
2	Moisture from sand and Qz	17.48	-
1	SLAW Simulant 5.6M Na	898.33	1451.76
Total batch, g		4500.00	4000.00

* Na_2CO_3 was dissolved in the SLAW simulant before mixing with other dry components.

Table 3.13. Paste Recipes for NSAS-Based Waste Forms.

Formulation ID		**CSMP1S3**	**CSMP3S3**$^{\$}$	**CSMP3S4**	**CSMP3S5**	**CSMP1S5**
Order	**Component**	**Target Weight (g)**				
4	Microfine BFS	2107.77	2123.55	-	2518.78	2429.58
4	BFS SE		-	2576.04	-	-
4	Light-burned MgO	105.39	106.18	128.80	125.94	170.07
4	Silica fume	-	106.18	-	-	-
4	Calcined hydrotalcite	105.39	133.61	-	-	-
3	HYDRAPEL 2.5	15.81	12.21	12.88	18.89	-
2	Na_2CO_3 (99.7%)*	135.30	56.07	142.80	-	66.05
2	Na_2SO_4 (99.8%)*	-	122.03	-	233.41	123.82
1	SLAW 5.6M Na	1330.35	1340.18	1639.48	1602.98	1460.47
Total batch, g		3800.00	4000.00	4500.00	4500.00	4250.00

$ CSMP3S2 had the same formulation as CSMP3S3 but Na_2CO_3 and Na_2SO_4 were added as the solids

* Na_2CO_3 and Na_2SO_4 were dissolved in SLAW simulant before mixing with dry components.

Table 3.14. Formulation Parameters for ASAS-Based Waste Forms.

Formulation ID	**w/dm**	**Molar MOH***	**Molar SiO_2/M_2O***	**MgO**	**Sand:Qz (wt% in mix)**	**Hydrophobic Admixture**	**Type of Hydrophobic Admixture**
				BMFOS		**BMFOS**	
SFMA9S1	0.425	5.0	~1.0	0.05	35:7	0	-
SFMA9S2	0.425	5.0	~1.0	0.05	35:7	0.05	Calcium stearate
SFMA9S3	0.425	5.0	~1.0	0.05	35:7	0.01	SHP50 Silicone
SFMA9S4	0.435	5.6	~1.0	0.05	35:7	0.05	Calcium stearate
SFMP9S4	0.425	5.6	~1.0	0.05	None	0.01	SHP50 Silicone

* M = K and Na

Table 3.15. Formulations of ASAS-Based Waste Forms (wt%).

Grout ID	**Type Hyp**	**BFS**	**KOH**	**MgO**	**Sand**	**Qz**	**SF**	**Hyp**	**SLAW**	**Sum**
SFMA9S1	-	32.50	2.65	1.32	35.00	7.00	2.34	-	19.19	100.00
SFMA9S2	Calcium stearate	31.98	2.61	1.30	34.44	6.89	2.30	1.60	18.88	100.00
SFMA9S3	SHP50 Silicone	32.38	2.64	1.32	34.87	6.97	2.33	0.36	19.12	100.00
SFMA9S4	Calcium stearate	30.86	3.10	1.19	35.00	7.00	2.71	1.54	18.60	100.00
SFMP9S4	SHP50 Silicone	54.17	5.31	3.67	-	-	4.36	0.62	31.87	100.00

BFS = Blast furnace slag from Seattle Plant
Qz = Ground quartz powder
SF = Silica fume
HYP = Hydrophobic admixture including SHP50 Silicone and Calcium stearate

Table 3.16. Recipes for ASAS-Based Waste Forms.

Order of Addition	**Formulation ID**	**SFMA9S1**	**SFMA9S2**	**SFMA9S3**	**SFMA9S4**	**SFMP9S4**
	Component	**Target Weight (g)**				
4	BFS SE	1455.04	1455.04	1449.81	1381.29	2162.91
4	Sika SC MgO	59.11	59.11	58.90	53.28	146.46
4	Silica fume	109.17	109.17	108.78	126.36	181.34
4	Agsco Silica A-25	1566.89	1566.89	1561.26	1566.65	-
4	Yellow sand	313.38	313.38	312.25	313.33	-
4	Calcium Stearate	-	72.75	-	69.06	-
4	GP SHP 50 Silicone	-	-	16.17	-	24.83
3	Moisture for sand and Qz	18.80	18.80	18.74	18.80	-
2	KOH (90.8%)	118.55	118.55	118.12	138.76	211.94
1	SLAW Simulant, 5.6M Na	859.06	859.06	855.97	832.47	1272.53
	Total batch	4500.00	4572.75	4500.00	4500.00	4000.00

Table 5.1. Summary of Results from Phase 1 Testing.

Grout I.D.	Set time	Compressive Strength (psi)		Leachability Index (14th day)					
		7d	28d	Na	Re	I	Cr	NO_3^-	NO_2^-
ICS0.6W1S	>24 h	1524	2404	-	-	-	-	-	-
ICS0.5W1S	34.38 h	1861	2533	8.39	8.77	8.85	13.26	8.71	8.67
ICS0.45W1S	12-48 h	2351	2846	8.33	8.71	8.79	13.26	8.65	8.61
ICF0.5W1S	10-44 h	1826	2957	8.30	8.62	8.67	13.54	8.56	8.51
SFMA9S1	2.1 h	5154	6361	8.18	8.95	8.35	13.79	8.31	8.25
SFMA9S2	2 h	4967	5728	8.01	8.30	8.21	12.09	8.14	8.24
CSM0.40A1S1	5.9 h	4917	7035	-	-	-	-	-	-
CSM0.40A1S2	5.7 h	4977	6390	8.25	9.44	8.50	13.92	8.46	8.39
Metric	-	-	-	-	>10.7	>10.52	>10.40	>8.70	-

Table 5.2. Qualitative Hydrophilicity of Waste Forms with Different Admixtures.

Grout ID	Materials	Hydrophobic Admixture	Hydrophobicity
SFMA9S1	Mortar/ASAS/SE	None	No
SFMA9S2	Mortar/ASAS/SE	Calcium stearate	Little
SFMA9S3	Mortar/ASAS/SE	SHP50 Silicone	Good
SFMA9S4	Mortar/ASAS/SE	Calcium stearate	Little
SFMP9S4	Paste/ASAS/SE	GP SHP50 Silicone	Good
CSMA8S1	Mortar/NSAS/AgZ/SF/SE	Calcium stearate	Little
CSMA3S1	Mortar/NSAS/CHT/SF/SE	EUCON Hydrapel 2.5	Good
CSMA1S3	Mortar/NSAS/CHT/SF/MC	None	No
CSMP1S3	Paste/NSAS/MC	EUCON Hydrapel 2.5	Little
CSMP3S2	Paste/NSAS/CHT/SF/MC	EUCON Hydrapel 2.5	Good
CSMP3S3	Paste/NSAS/CHT/SF/MC	EUCON Hydrapel 2.5	Good
CSMP8S2	Paste/NSAS/AgZ/MC	EUCON Hydrapel 2.5	Good
ICS0.5W3S	ICS/Plug/MC	EUCON Hydrapel 2.5	Good
CSMP3S5	Paste/NSAS//MC	EUCON Hydrapel 2.5	Good
CSMP3S4	Paste/NSAS//SE	EUCON Hydrapel 2.5	Good

Table 5.3. Summary of Results from the Phase 2 Testing.

Grout I.D.	Materials	Set Time	Compressive Strength (psi)		Leachability Index (63-day Steady-State)					
			7d	28d	Na	Re	Cr	I	NO_3^-	NO_2^-
Mix#51	[2]	-	-	2557	8.10	N/A	>13	8.30	8.30	-
ICS0.5W1S	ICS/Plug/MC	34.4 h	1861	2533	8.61	8.87	13.26	8.91	8.66	8.64
ICS0.5W3S	ICS/Plug/Hdp/MC	7.2 h	2893	3607	8.55	8.92	13.27	8.92	8.71	8.62
ICF0.45W1S	ICF/KOH/MC	2.8 h	3202	4541	8.62	8.90	12.80	8.84	8.72	8.60
SFMA9S3	ASAS/GP/SE	2.2 h	4392	5400	8.39	9.34	12.23	8.47	8.40	8.22
SFMA9S4	ASAS/Cst/SE	2.5 h	5157	7008	-	-	-	-	-	-
SFMP9S4	ASAS/GP/SE	2.6 h	5221	5042	8.38	10.57	12.44	8.54	8.41	8.40
CSMA3S1	NSAS/CHT/Hdp/SE	14.5 h	6418	6936	8.71	12.28	>13.74	8.71	8.70	8.64
CSMA1S3	NSAS/CHT/Hdp/MC	0.7 h	5186	6204	8.61	11.57	12.68	8.83	8.79	8.76
CSMA8S1	NSAS/AgZ/SE	~24 h	4643	7539	8.87	11.02	13.68	8.90	8.81	8.81
Metric	-	-	-	-	-	>10.7	>10.52	>10.40	>8.70	-

Table 5.4. Sodium Leachability Indices for SLAW Waste Forms.

Leach Time, days	**Leach Time, hrs**	**Improved Cast Stone/Cement Free**			**Alkali Activated Slag**		**Neutral Salt Activated Slag**			
		ICF0.45 W1S	ICS0.5W 3S	ICS0.5 W1S	SFMA9 S3	SFMP 9S4	CSMA 3S1	CSMA 1S3	CSMA 8S1	CSMP 8S2
0.08	2	7.86	7.70	7.83	7.58	7.86	7.59	7.64	7.65	7.85
1	24	8.18	7.92	8.36	8.33	7.87	7.94	7.90	8.08	7.91
2	48	8.14	8.03	8.41	7.86	7.94	8.02	8.15	8.21	7.88
7	168	8.23	8.12	8.54	8.01	8.15	8.28	8.25	8.46	7.88
14	336	8.31	8.25	8.64	8.09	8.24	8.50	8.35	8.61	8.07
28	672	8.44	8.40	8.67	8.17	8.31	8.68	8.43	8.77	ND
42	1008	8.61	8.45	8.55	8.34	8.36	8.71	8.49	8.75	ND
49	1176	8.62	8.47	8.52	8.41	8.39	8.74	8.59	8.77	ND
63	1512	8.61	8.54	8.61	8.39	8.38	8.71	8.61	8.87	ND

ND: Not determined due to sample cracking

Table 5.5. Rhenium Leachability Indices for SLAW Waste Forms.

Leach Time, days	**Leach Time, hrs**	**Improved Cast Stone/Cement Free**			**Alkali Activated Slag**		**Neutral Salt Activated Slag**			
		ICF0.45 W1S	ICS0.5W 3S	ICS0.5 W1S	SFMA9 S3	SFMP 9S4	CSMA 3S1	CSMA 1S3	CSMA 8S1	CSMP 8S2
0.08	2	8.39	7.97	7.94	7.58	7.97	7.57	7.79	7.63	8.07
1	24	8.60	8.21	8.77	8.40	7.98	8.07	8.17	8.16	8.18
2	48	8.37	8.34	8.74	7.50	8.05	8.31	8.52	8.43	8.34
7	168	8.45	8.41	8.83	8.15	8.3	8.81	9.11	8.97	8.68
14	336	8.55	8.58	8.92	8.36	8.62	9.49	10.15	9.43	9.33
28	672	8.74	8.68	8.91	8.70	9.05	10.41	10.96	9.93	ND
42	1008	8.85	8.79	8.87	9.00	9.74	11.15	11.58	10.49	ND
49	1176	8.90	8.87	8.83	9.19	10.34	11.77	11.57	10.66	ND
63	1512	8.87	8.92	8.87	9.34	10.57	12.28	11.38	11.02	ND

ND: Not determined due to sample cracking

Table 5.6. Chromium Leachability Indices for SLAW Waste Forms.

Leach Time, days	**Leach Time, hrs**	**Improved Cast Stone/Cement Free**			**Alkali Activated Slag**		**Neutral Salt Activated Slag**			
		ICF0.45 W1S	ICS0.5W 3S	ICS0.5 W1S	SFMA9 S3	SFMP 9S4	CSMA 3S1	CSMA 1S3	CSMA 8S1	CSMP 8S2
0.08	2	10.73	10.69	12.59	10.45	10.54	12.12	12.77	11.45	12.34
1	24	12.47	11.86	13.37	11.99	12.67	12.71	13.20	11.75	13.31
2	48	13.40	12.11	13.50	11.97	12.49	12.43	12.48	12.02	12.84
7	168	12.94	12.77	13.49	12.12	12.43	12.89	12.82	12.96	14.39
14	336	12.68	13.27	13.39	12.08	12.45	12.92	12.72	12.86	>14.29
28	672	12.74	13.57	13.85	12.16	12.48	13.09	12.83	12.91	ND
42	1008	12.69	13.47	13.46	12.15	12.58	13.15	12.91	13.28	ND
49	1176	12.50	13.35	13.10	12.03	12.88	13.23	12.68	12.81	ND
63	1512	12.80	13.27	13.26	12.23	12.44	>13.74	12.48	13.68	ND

ND: Not determined due to sample cracking

Table 5.7. Iodine Leachability Indices for SLAW Waste Forms.

Leach Time, days	**Leach Time, hrs**	**Improved Cast Stone/Cement Free**			**Alkali Activated Slag**		**Neutral Salt Activated Slag**			
		ICF0.45 W1S	ICS0.5W 3S	ICS0.5 W1S	SFMA9 S3	SFMP 9S4	CSMA 3S1	CSMA 1S3	CSMA 8S1	CSMP 8S2
0.08	2	8.43	8.10	7.68	7.21	7.49	7.09	7.74	7.48	7.95
1	24	8.47	8.29	8.74	7.86	7.88	7.80	7.93	8.16	8.21
2	48	7.97	8.40	8.73	7.87	7.90	7.94	8.15	8.33	8.08
7	168	8.37	8.12	8.80	7.99	8.12	8.16	8.30	8.58	7.81
14	336	8.50	8.64	8.92	8.12	8.31	8.40	8.46	8.75	8.13
28	672	8.61	8.79	8.91	8.23	8.43	8.54	8.56	8.83	ND
42	1008	8.77	8.74	8.82	8.39	8.54	8.59	8.77	8.86	ND
49	1176	8.84	8.67	8.72	8.48	8.46	8.68	8.89	8.90	ND
63	1512	8.72	8.92	8.74	8.47	8.39	8.71	8.83	8.90	ND

ND: Not determined due to sample cracking

Table 5.8. Nitrate Leachability Indices for SLAW Waste Forms.

Leach Time, days	**Leach Time, hrs**	**Improved Cast Stone/Cement Free**			**Alkali Activated Slag**		**Neutral Salt Activated Slag**			
		ICF0.45 W1S	ICS0.5W 3S	ICS0.5 W1S	SFMA9 S3	SFMP 9S4	CSMA 3S1	CSMA 1S3	CSMA 8S1	CSMP 8S2
0.08	2	8.08	7.87	7.77	7.53	7.78	7.40	7.71	7.50	7.97
1	24	8.34	8.12	8.55	7.89	7.78	7.84	7.95	7.98	7.93
2	48	8.25	8.25	8.56	7.86	7.76	7.98	8.18	8.15	7.85
7	168	8.32	8.23	8.67	8.02	8.10	8.19	8.35	8.41	7.73
14	336	8.44	8.46	8.78	8.14	8.28	8.42	8.47	8.60	8.10
28	672	8.55	8.56	8.77	8.27	8.40	8.45	8.55	8.69	ND
42	1008	8.69	8.61	8.67	8.40	8.49	8.62	8.77	8.76	ND
49	1176	8.72	8.67	8.65	8.45	8.49	8.68	8.79	8.81	ND
63	1512	8.66	8.71	8.66	8.40	8.41	8.70	8.77	8.81	ND

ND: Not determined due to sample cracking

Table 5.9. Nitrite Leachability Indices for SLAW Waste Forms.

Leach Time, days	**Leach Time, hrs**	**Improved Cast Stone/Cement Free**			**Alkali Activated Slag**		**Neutral Salt Activated Slag**			
		ICF0.45 W1S	ICS0.5W 3S	ICS0.5 W1S	SFMA9 S3	SFMP 9S4	CSMA 3S1	CSMA 1S3	CSMA 8S1	CSMP 8S2
0.08	2	8.14	7.65	7.62	7.43	7.63	7.39	7.51	7.46	7.65
1	24	8.30	7.88	8.32	7.79	7.66	7.80	7.76	7.90	7.59
2	48	8.24	7.98	8.40	7.75	7.77	7.94	8.00	8.06	7.55
7	168	8.40	7.95	8.48	7.92	7.97	8.14	8.19	8.32	7.37
14	336	8.53	8.15	8.65	8.04	8.08	8.36	8.21	8.53	8.04
28	672	8.43	8.48	8.74	8.13	8.20	8.29	8.22	8.54	ND
42	1008	8.58	8.56	8.63	8.23	8.41	8.40	8.76	8.55	ND
49	1176	8.60	8.60	8.63	8.30	8.40	8.40	8.76	8.57	ND
63	1512	8.45	8.62	8.64	8.22	8.29	8.64	8.69	8.81	ND

ND: Not determined due to sample cracking

Table 5.10. Summary of Results on Paste-Type NSAS Waste Forms.

Grout I.D.	w/dm	BFS	Materials	Set Time	Consistency	Compressive Strength (psi)		Cracking During Leaching at
						7d	28d	
CSMP3S2	0.425	MC	CTH /Hdp/sNC/sNŚ/MC	-	Thick	6605	6990	1 day
CSMP3S3	0.425	MC	CTH/Hdp/dNc/dNŚ/MC	120m	Thick	6310	7234	0 day*
CSMP1S3	0.425	MC	CTH/Hdp/dNC/MC	128m	Thick	6128	7165	2 days
CSMP8S2	0.45	MC	AgZ/Hdp/dNC/MC	197m	Thick	4609	5813	28 days
CSMP3S4	0.45	SE	Hdp/dNC/SE	9-24h	Slow pour	5607	7766	No
CSMP3S5	0.45	MC	Hdp/dNŚ/MC	365m	Thick	6561	6786	2 days
CSMP1S5	0.45	MC	dNc/dNŚ/MC	89m	Thick	4806	6383	6 days

CTH = Calcined hydrotalcite; AgZ = ground Ionex Ag-900; SE = BFS from Seattle Plant; MC = Microfine BFS MC500; Hdp= Eucon Hydrapel 2.5; NC = sodium carbonate anhydrous; NŚ = sodium sulfate anhydrous; SF = Silica fume; dNC and dNŚ: Dissolved in SLAW ; sNC and sNŚ: Added as solid
* Cracked during demolding

Table 5.11. Data Summary for SLAW Grout Formulations Selected for Phase 4 Testing.

Formulation ID	Set Time	Bleed	Compressive Strength (psi)		Plastic Viscosity (cP)	Yield Stress (Pa)	Yield Stress by Maximum Torque (Pa)
		24 h	7 d	28 d			
ICS0.50W1S	34.4 h	0%	1861	2533	1001	41.53	45.3
CSMA3S1	14.5 h	0%	6418	6936	39000*	218.5*	1562.4
CSMA8S1	~24 h	0%	4643	7539	NM	NM	NM

NM: Not measured, over instrument limit.
* Bingham modeling results are from data in the shear rate range from 0.0005 to 33.59 1/s (R^2 = 0.96) due to significant deviations beyond that range.

Table 5.12. Heat Flow Data for Three SLAW Grout Samples.

Composition	**First Peak**		**Second Peak**		**Main Peaks Indicating Endothermic Reaction**	
	Time, hrs	Heat Flow (mW/g)	Time, hrs	Heat Flow (mW/g)	Time, hrs	Heat Flow (mW/g)
ICS0.50W1S	<0.47	>7.9	-	-	19.83	2.60
CSMA3S1	<0.47	>5.6	-	-	30.56	0.94
CSMA8S1	<0.47	>4.6	6.08	0.17	38.97	0.97

Table 5.13. Heat Release and Compressive Strength Data for Three SLAW Grout Samples.

Composition	**Normalized Heat Release, J/g paste**					**Compressive Strength, psi**	
	6 hrs	24 hrs	48 hrs	7 days (168 hrs)	14 days (336 hrs)	7 days	28 days
ICS0.50W1S	9.96	65.36	98.55	119.98	124.39	1861	2533
CSMA3S1	7.78	16.73	75.39	110.96	121.18	6418	6936
CSMA8S1	6.57	11.90	58.92	100.58	108.77	4643	7539

Table 5.14. TCLP Leachate Concentrations for Selected SLAW Grout Formulations (mg/L).

Formulation	**Sample ID**	**Cr**	**Re**	**Ag**	**As**	**Ba**	**Ni**	**Pb**	**Zn**
CSMA3S1	CSMA3S1-2	<0.002	0.550	0.002	0.006	0.392	0.017	<0.004	0.029
CSMA8S1	CSMA8S1-2	<0.002	0.590	0.007	0.006	0.354	0.023	<0.004	0.033
ICS0.5W1S	ICS0.5W1S	<0.002	1.817	0.001	0.007	0.540	<0.001	<0.004	0.003
Blank	TCLP-1111022	<0.002	<0.001	0.001	<0.002	<0.001	<0.001	<0.004	<0.001
EPA UTS Limit		0.60	-	0.14	5.0	21	11	0.75	4.3

Table 5.15. Apparent Density, Matrix Skeleton Density, Porosity, and Particle Density of Grout Samples.

Sample ID	**Formulation**	**Apparent Density (g/cm^3)**	**Matrix Skeleton Density (g/cm^3)**	**Porosity**	**Particle Density (g/cm^3)**
ICS0.5W1S-2	Improved Cast Stone (w/dm =0.50)	1.77	1.14	0.50	2.28
ICS0.5W1S-3		1.76	1.12	0.51	2.30
ICS0.5W1S-4		1.77	1.13	0.51	2.30
Average		1.77	1.13	0.51	2.29
ICS0.5W3S-2	Improved Cast Stone (w/dm =0.50)	1.81	1.18	0.51	2.39
ICS0.5W3S-3		1.81	1.18	0.50	2.38
ICS0.5W3S-4		1.80	1.18	0.50	2.35
Average		1.81	1.18	0.50	2.37
CSMA1S3-2	NSAS Mortar (w/dm=0.425)	2.16	1.78	0.30	2.54
CSMA1S3-3		2.14	1.77	0.30	2.52
CSMA1S3-4		2.17	1.81	0.28	2.53
Average		2.16	1.79	0.29	2.53
CSMA3S1-2	NSAS Mortar (w/dm=0.425)	2.10	1.70	0.31	2.48
CSMA3S1-4		2.12	1.73	0.32	2.52
CSMA3S1-9		2.13	1.74	0.31	2.53
Average		2.12	1.72	0.31	2.51
CSMA8S1-2	NSAS Mortar (w/dm=0.425)	2.02	1.64	0.30	2.36
CSMA8S1-3		2.06	1.67	0.31	2.42
CSMA8S1-4		2.03	1.64	0.31	2.37
Average		2.03	1.65	0.31	2.38
CSMP8S2-2	NSAS Paste (w/dm = 0.45)	1.91	1.33	0.46	2.47
CSMP8S2-3		1.89	1.32	0.45	2.41
CSMP8S2-4		1.91	1.34	0.46	2.46
Average		1.90	1.33	0.46	2.45
CSMP3S5-2	NSAS Paste (w/dm = 0.45)	1.93	1.37	0.44	2.47
CSMP3S5-3		1.95	1.40	0.44	2.48
CSMP3S5-4		1.96	1.40	0.44	2.51
Average		1.94	1.39	0.44	2.49

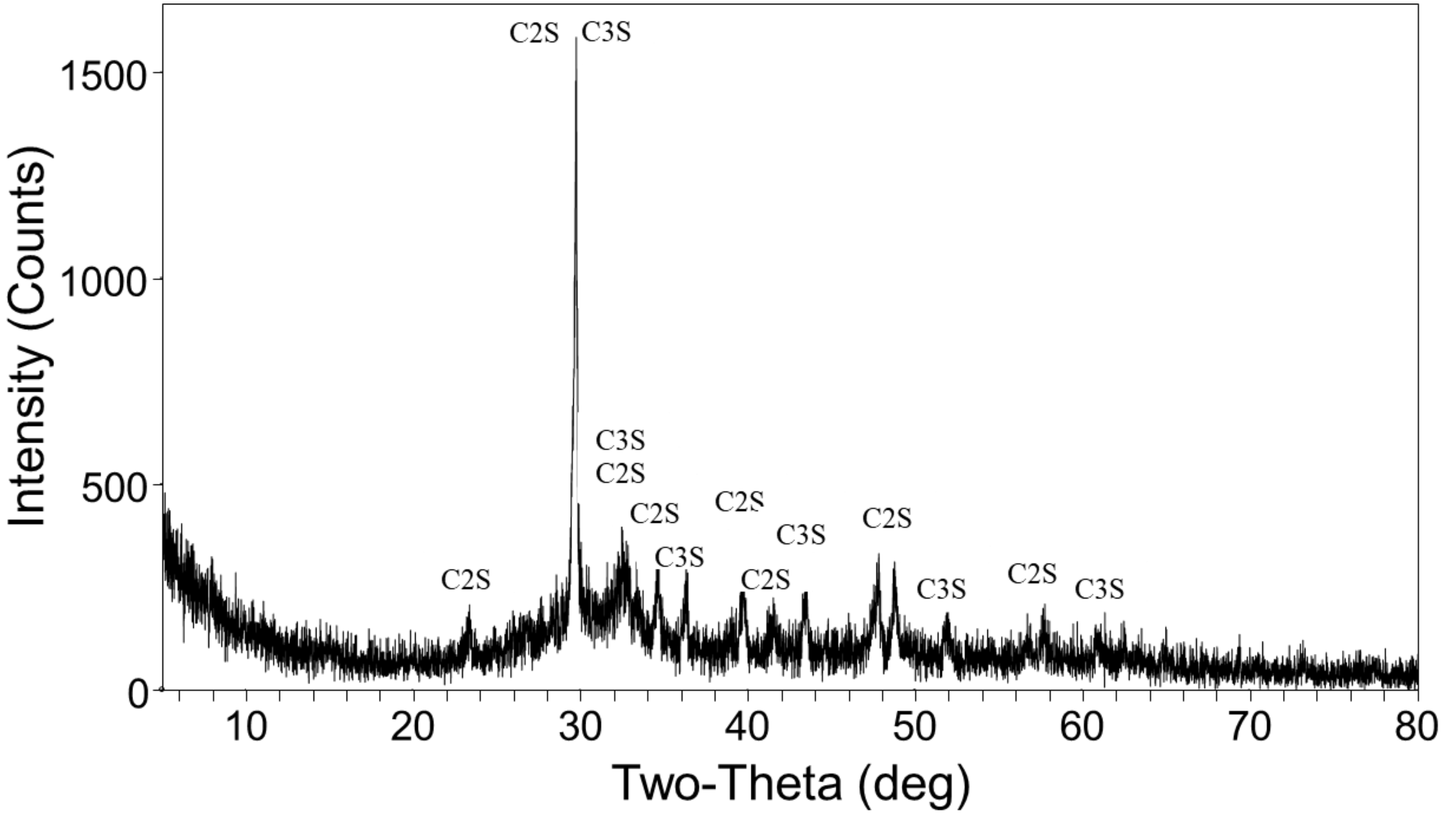

Figure 3.1. XRD pattern for Microfine BFS. Peaks for dicalcium silicate (C2S) and tricalcium silicate (C3S) are indicated.

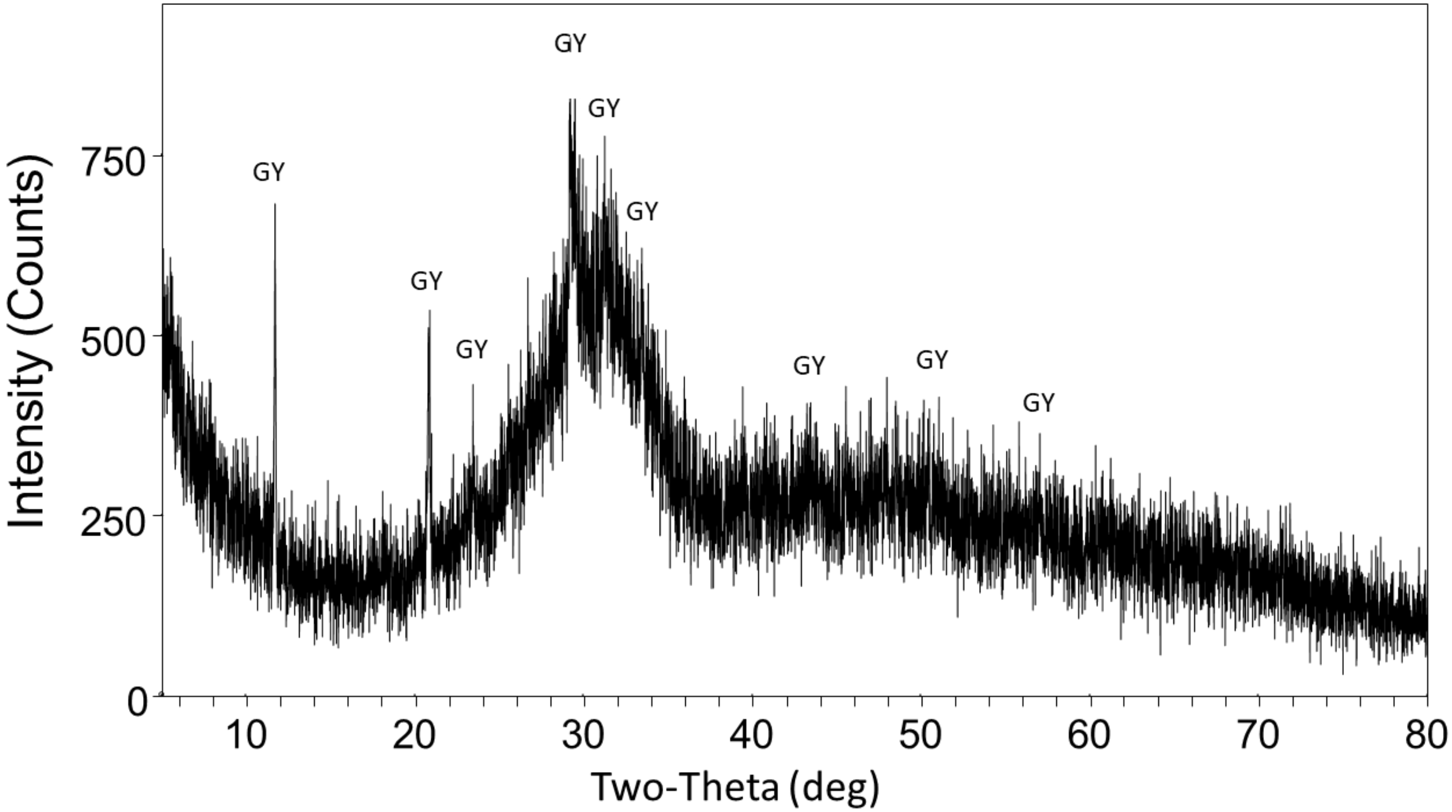

Figure 3.2. XRD pattern for BFS SE showing gypsum (GY) as the main crystalline phase.

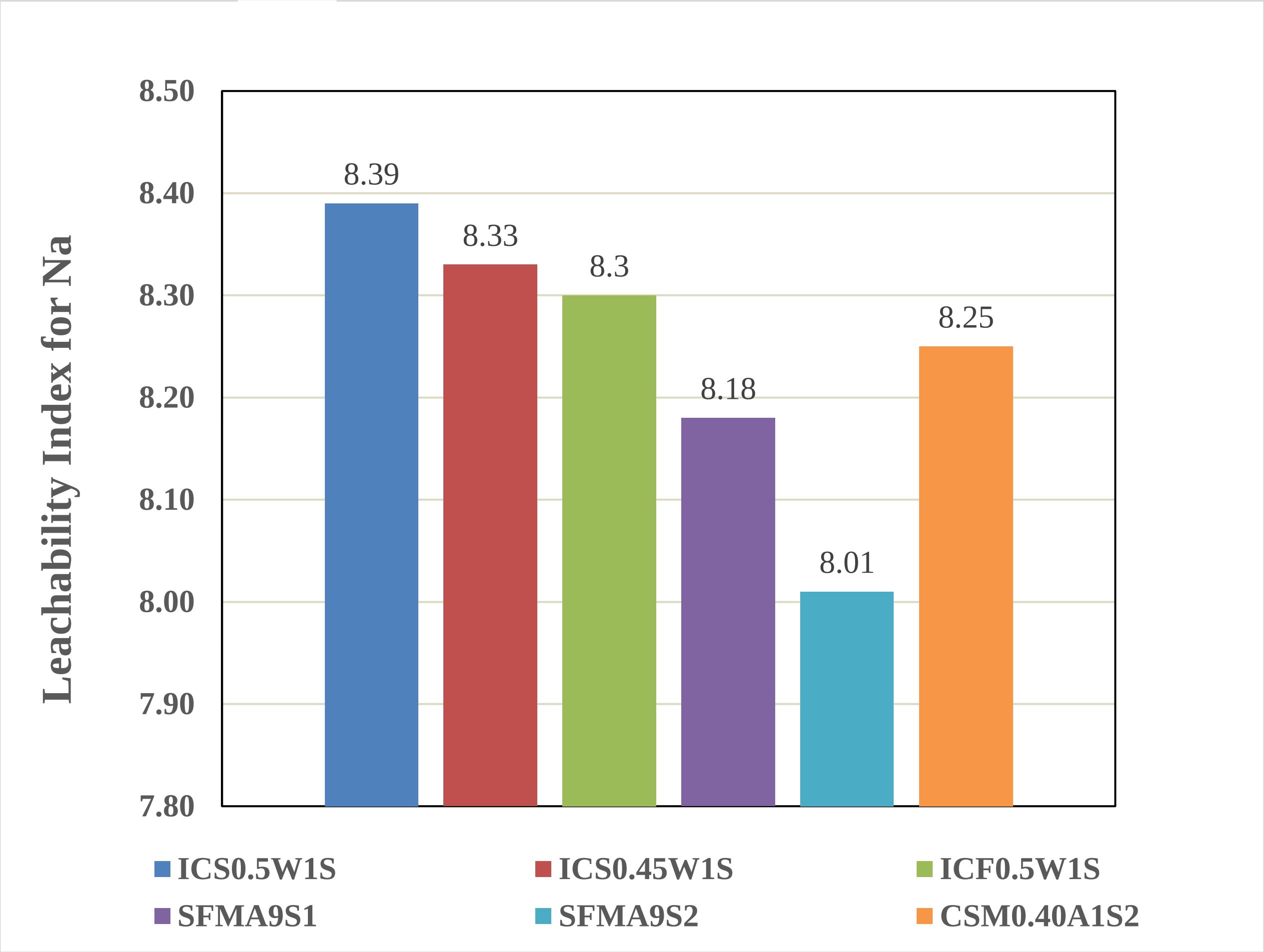

Figure 5.1. 14th-day Leachability Index values for sodium from Phase 1 testing.

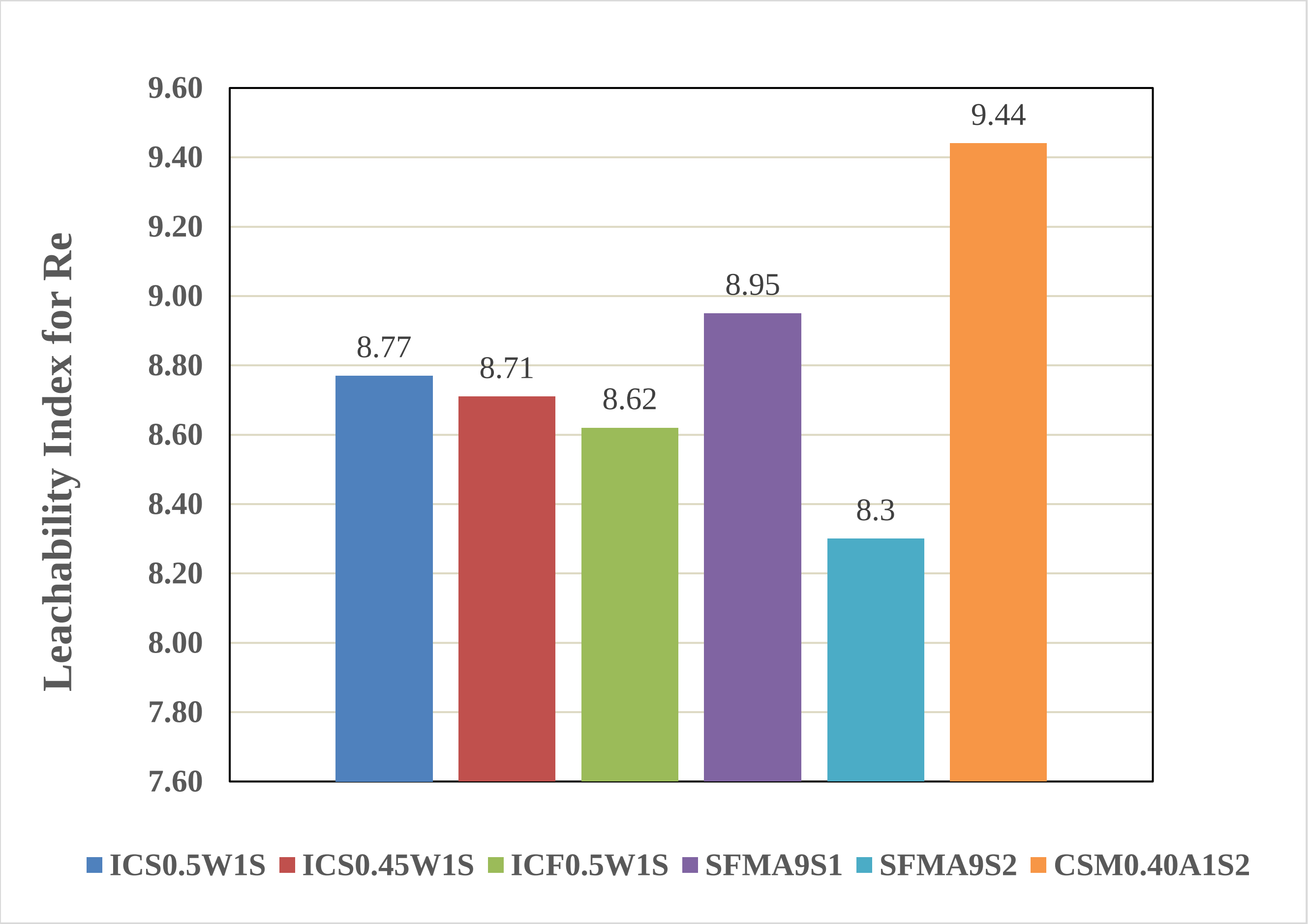

Figure 5.2. 14th-day Leachability Index values for rhenium from Phase 1 testing. The performance metric requirement for technetium is 10.70.

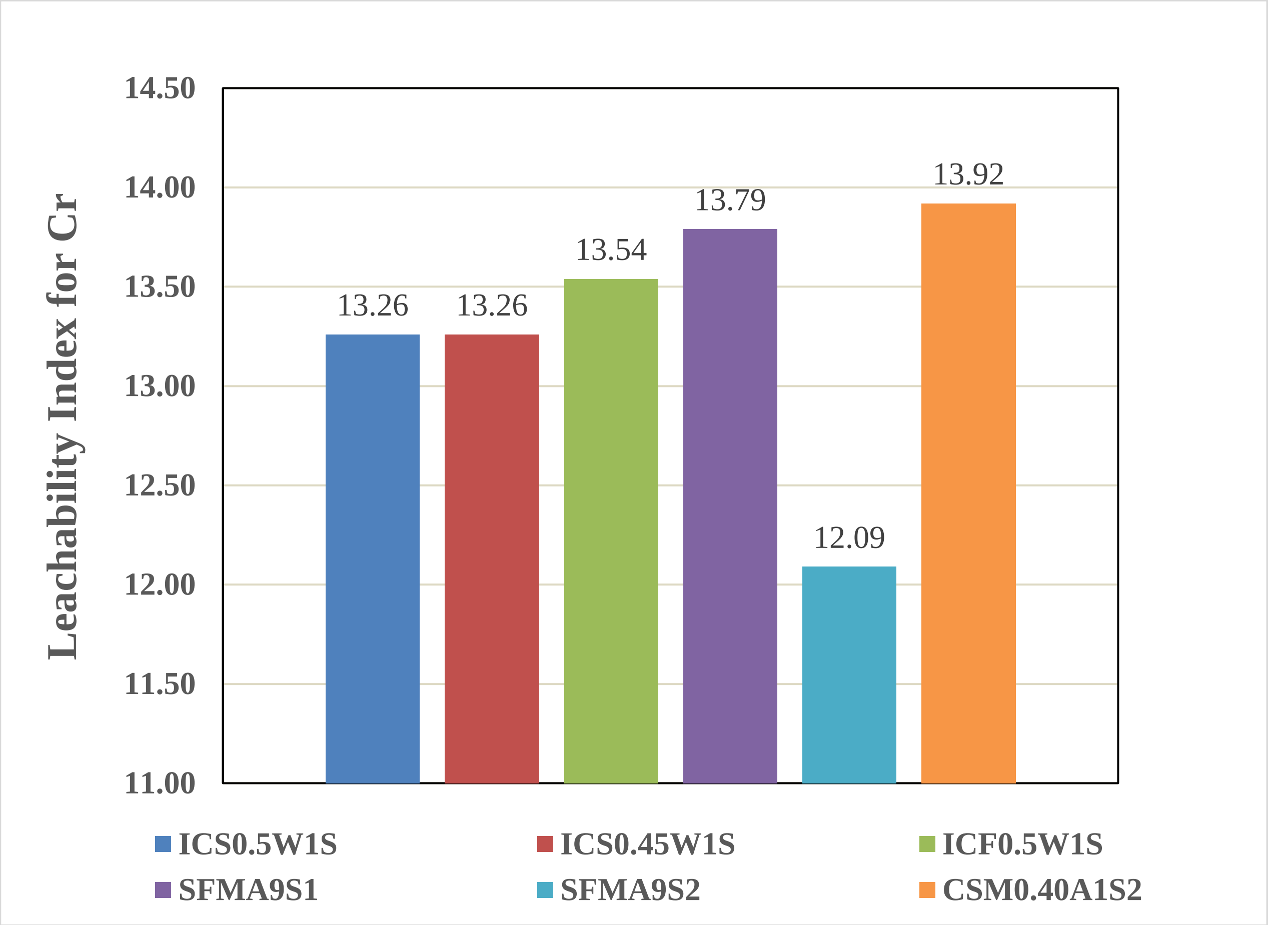

Figure 5.3. 14th-day Leachability Index values for chromium from Phase 1 testing. The performance metric requirement for chromium is 10.40.

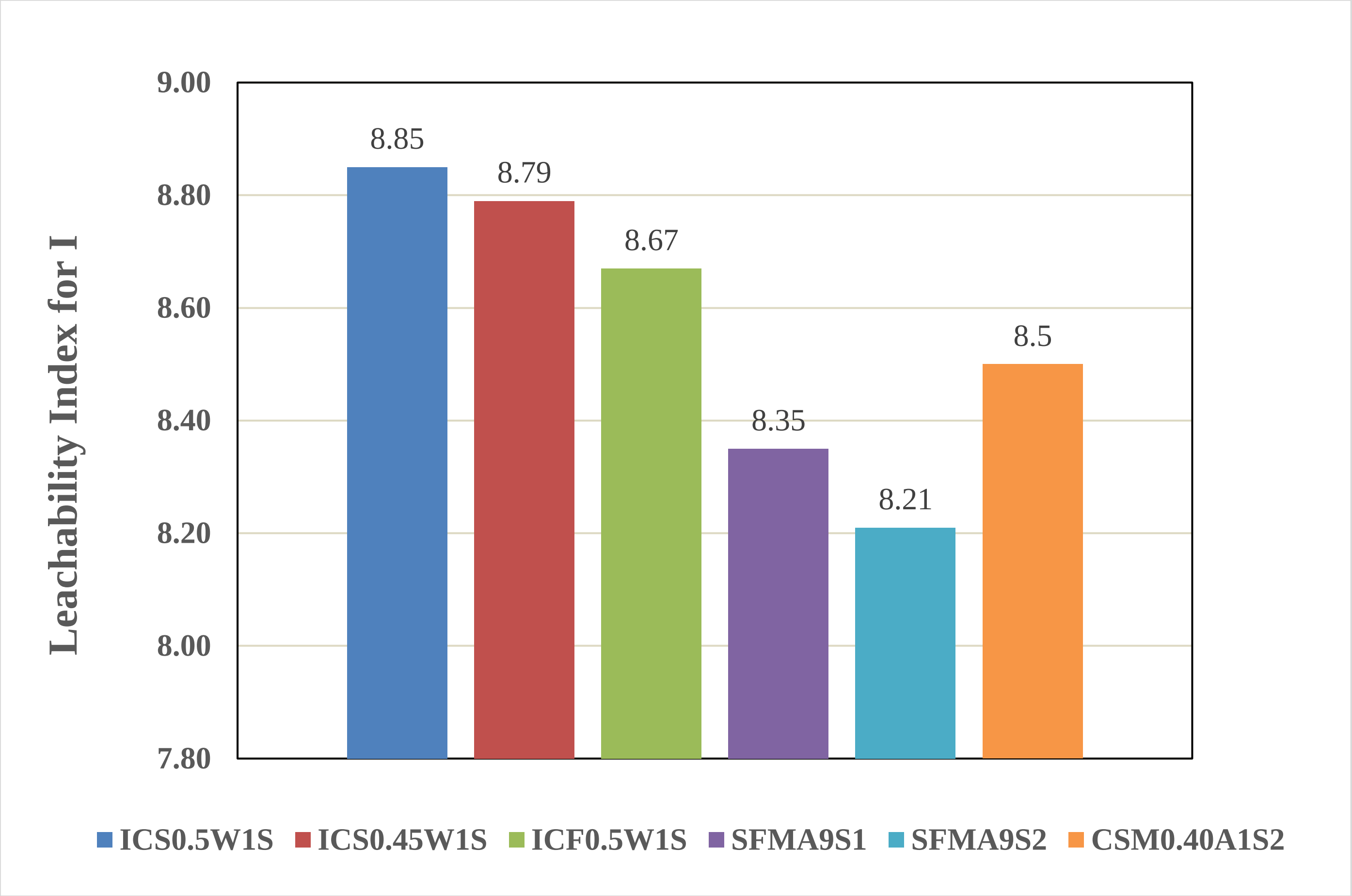

Figure 5.4. 14th-day Leachability Index values for iodine from Phase 1 testing. The performance metric requirement for iodine is 10.52.

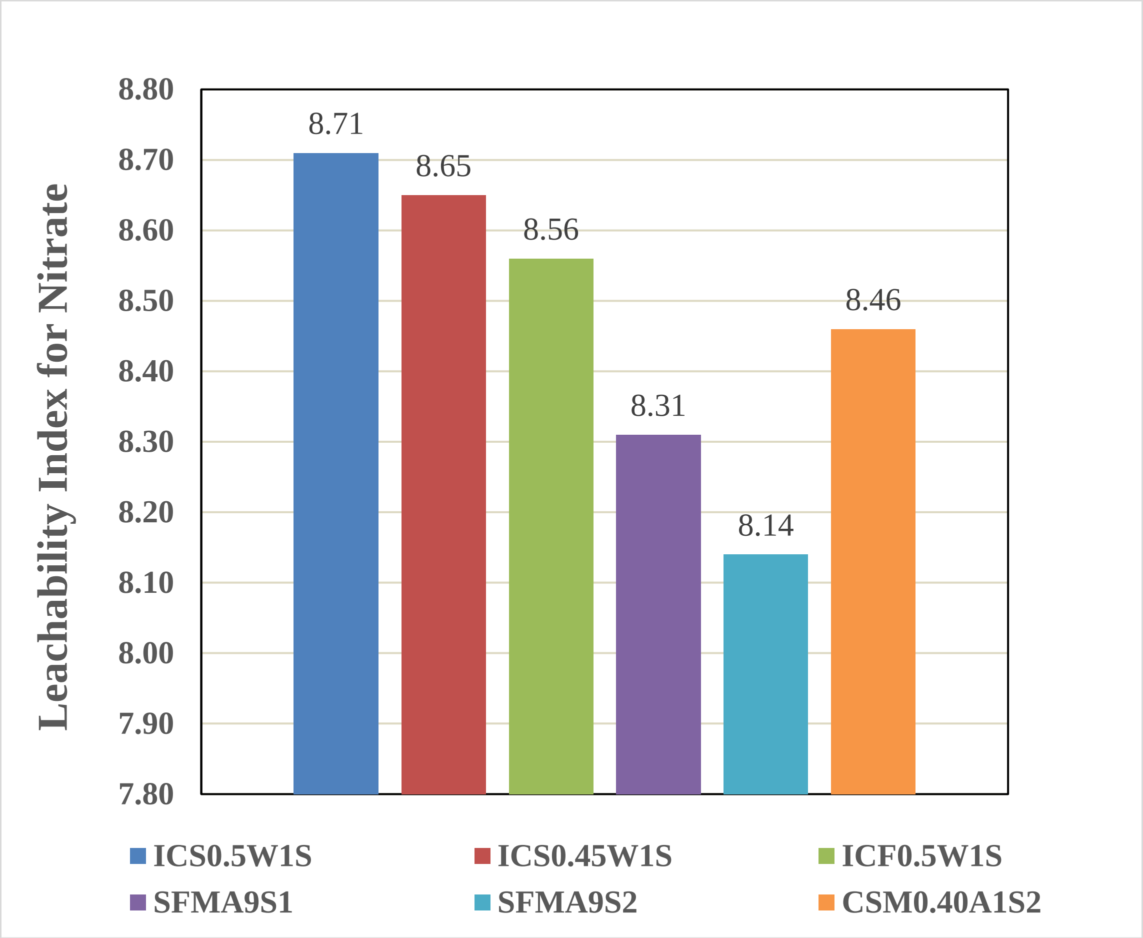

Figure 5.5. 14th-day Leachability Index values for nitrate from Phase 1 testing. The performance metric requirement for nitrate is 8.70.

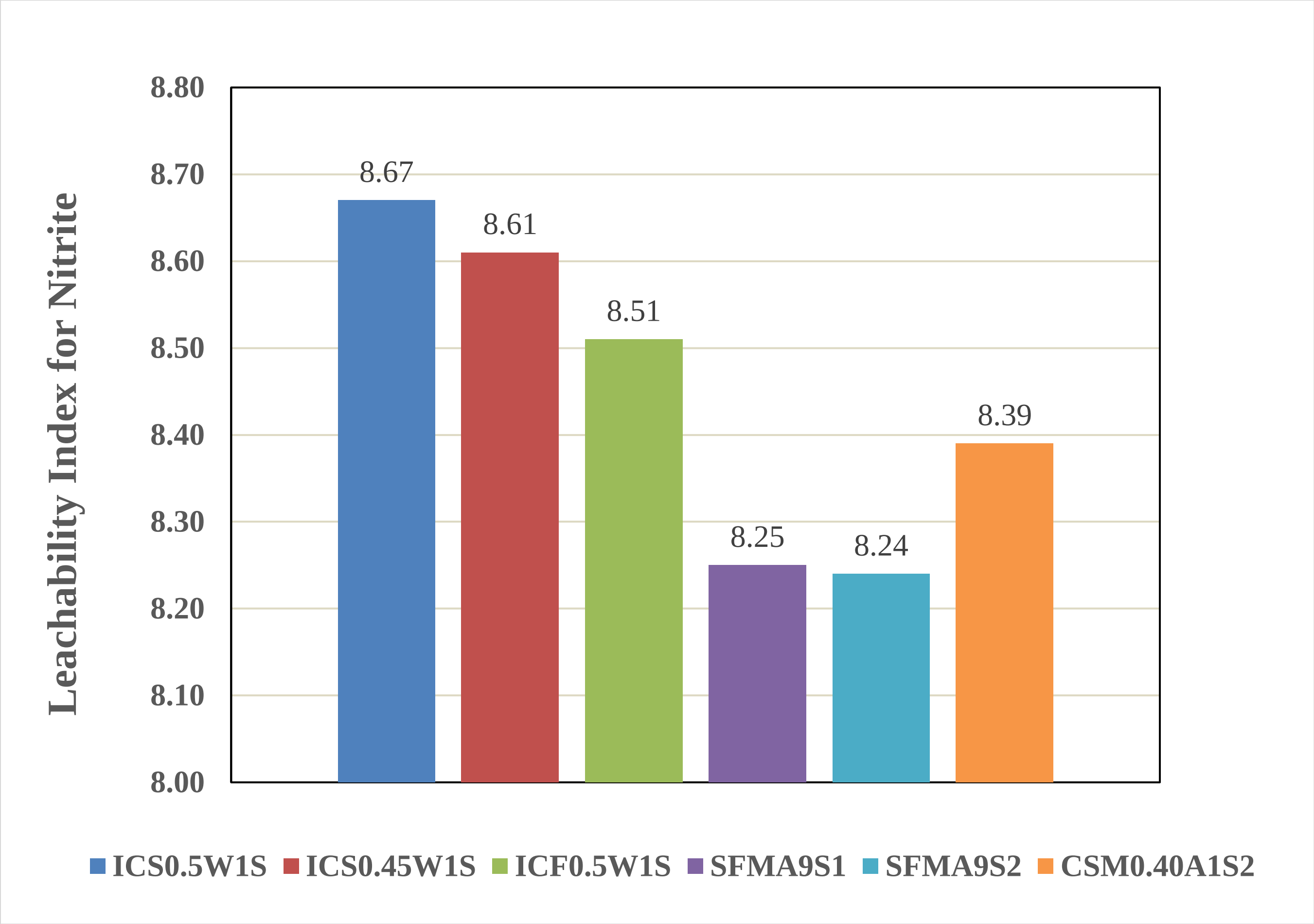

Figure 5.6. 14th-day Leachability Index values for nitrite from Phase 1 testing.

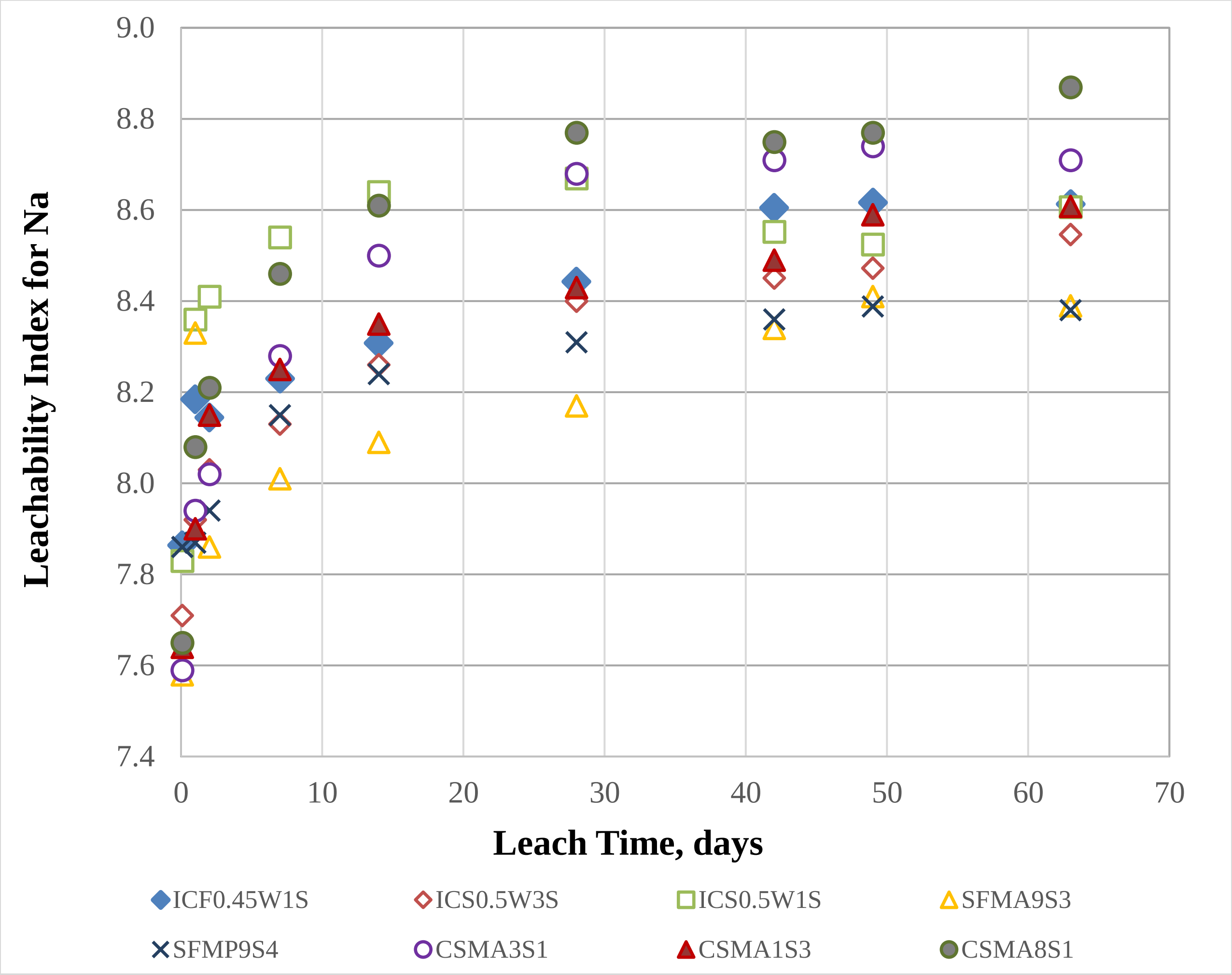

Figure 5.7. Leachability Index values for sodium as functions of time and formulation from Phase 2 testing.

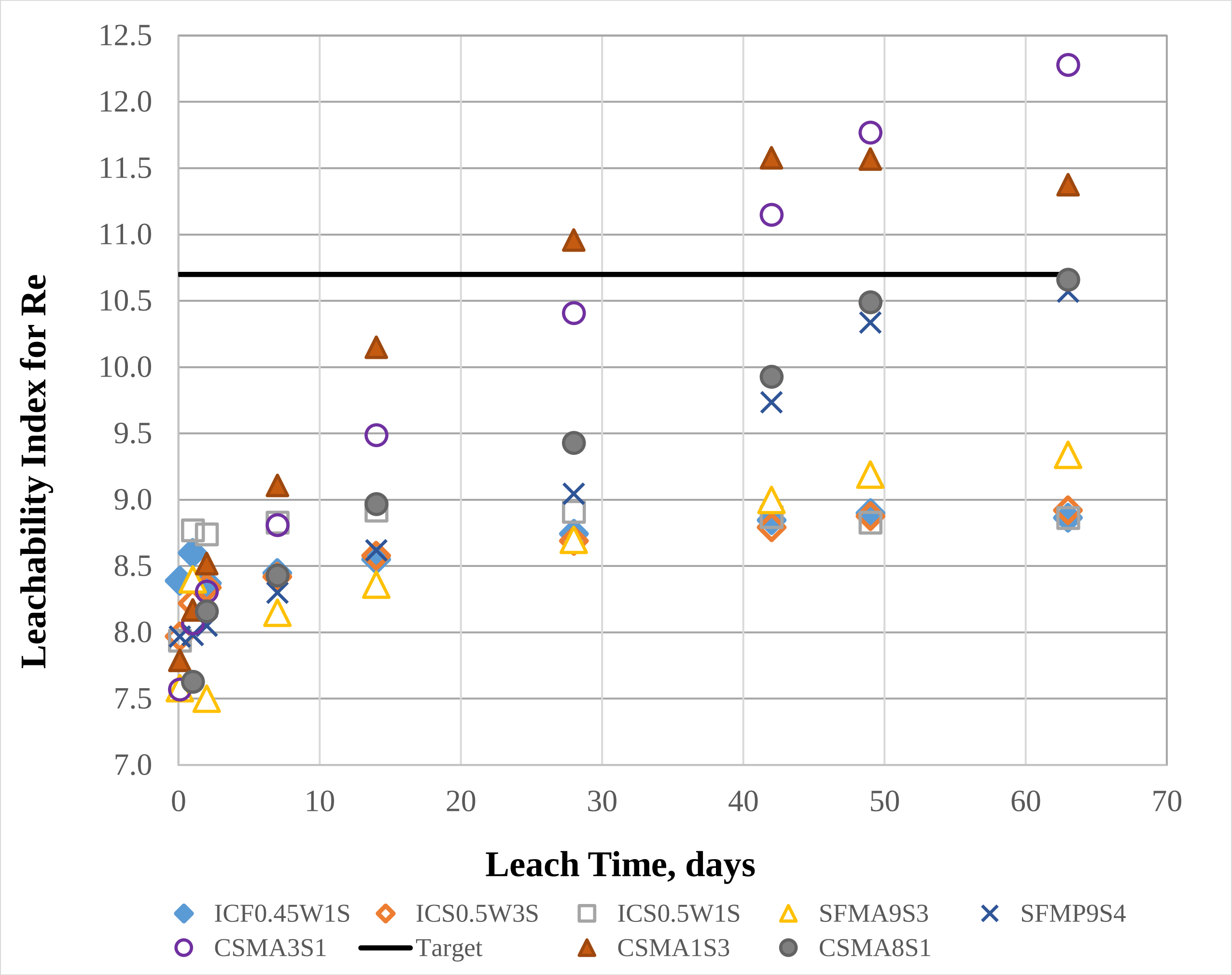

Figure 5.8. Leachability Index values for rhenium as functions of time and formulation from Phase 2 testing.

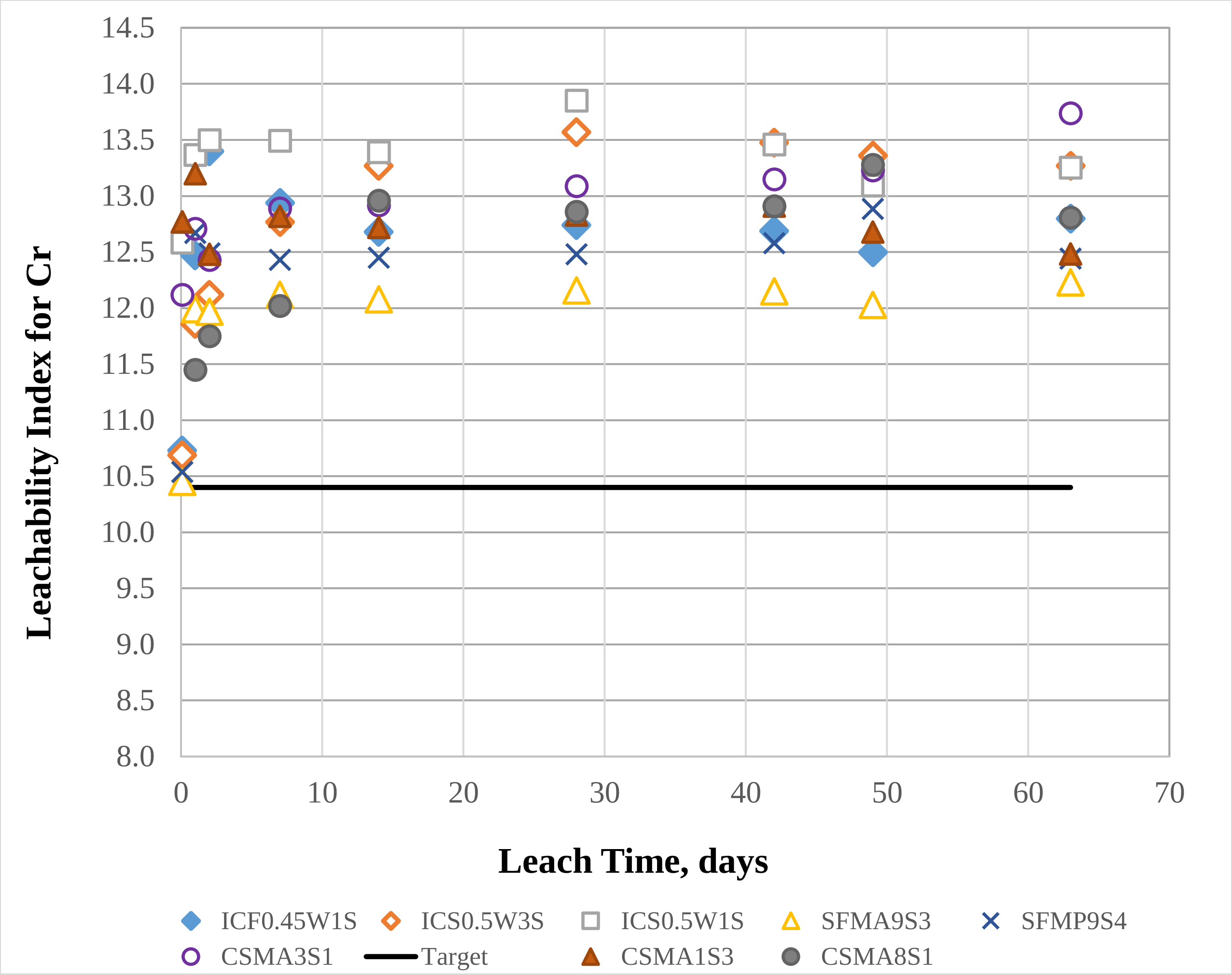

Figure 5.9. Leachability Index values for chromium as functions of time and formulation from Phase 2 testing.

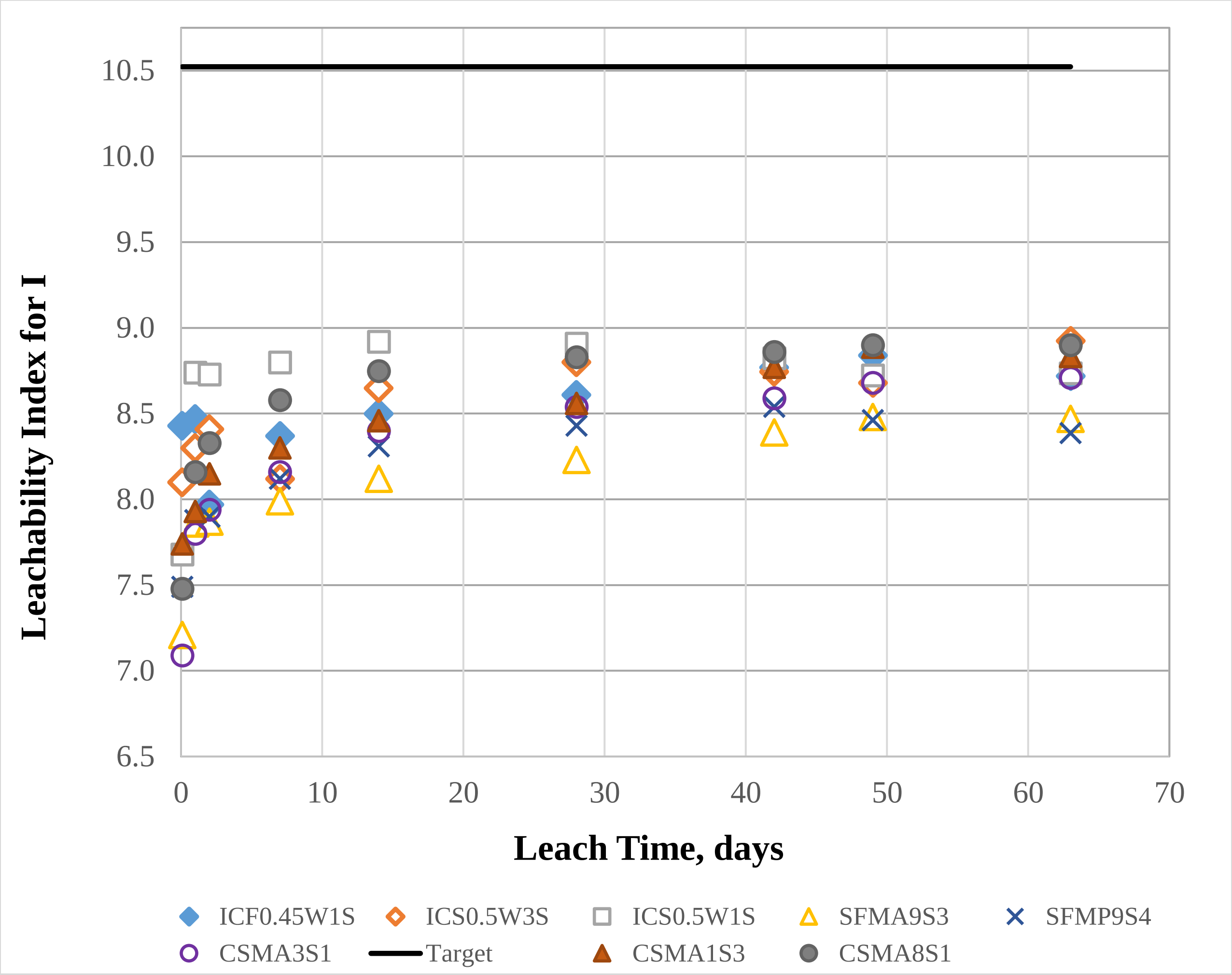

Figure 5.10. Leachability Index values for iodine as functions of time and formulation from Phase 2 testing.

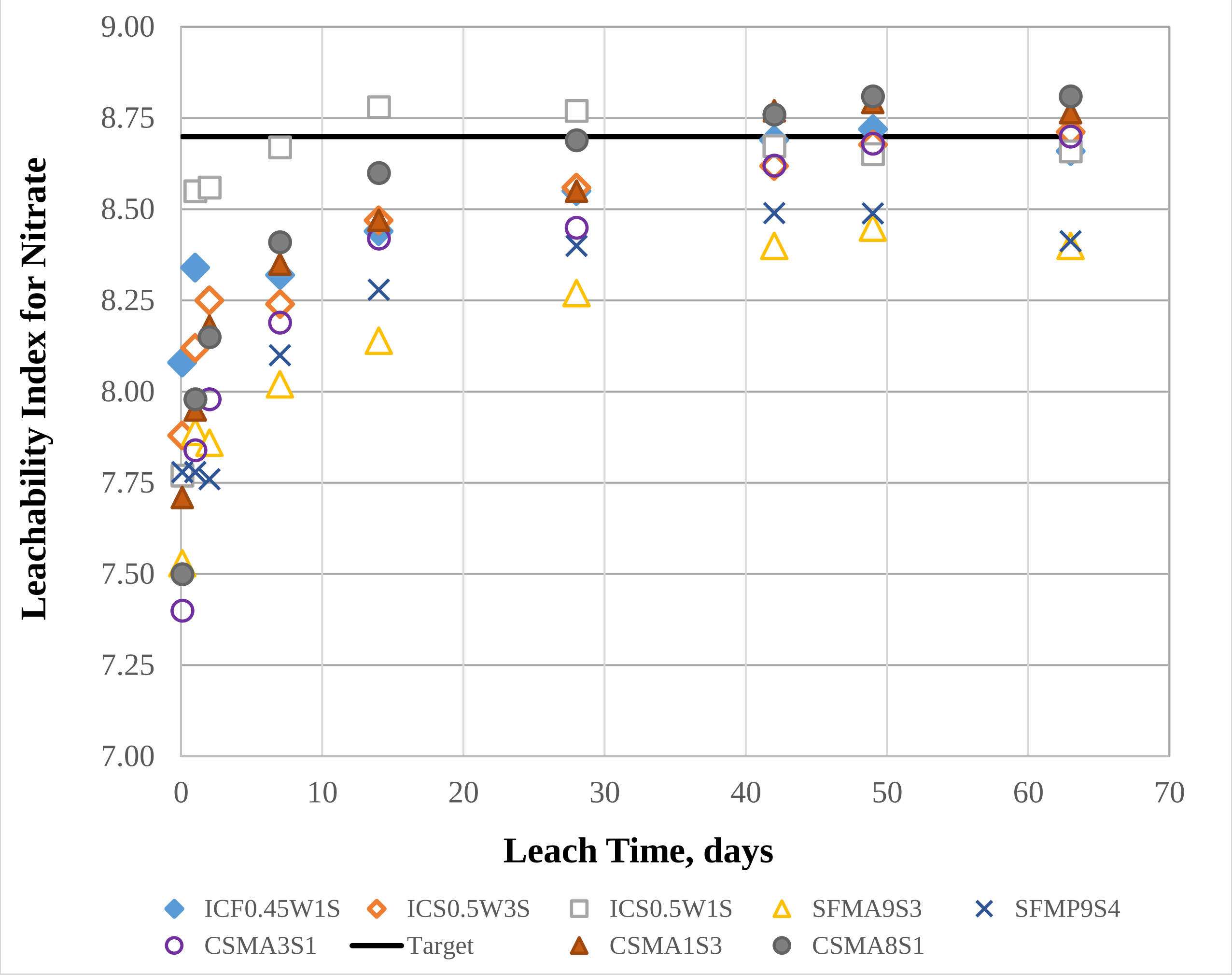

Figure 5.11. Leachability Index values for nitrate as functions of time and formulation from Phase 2 testing.

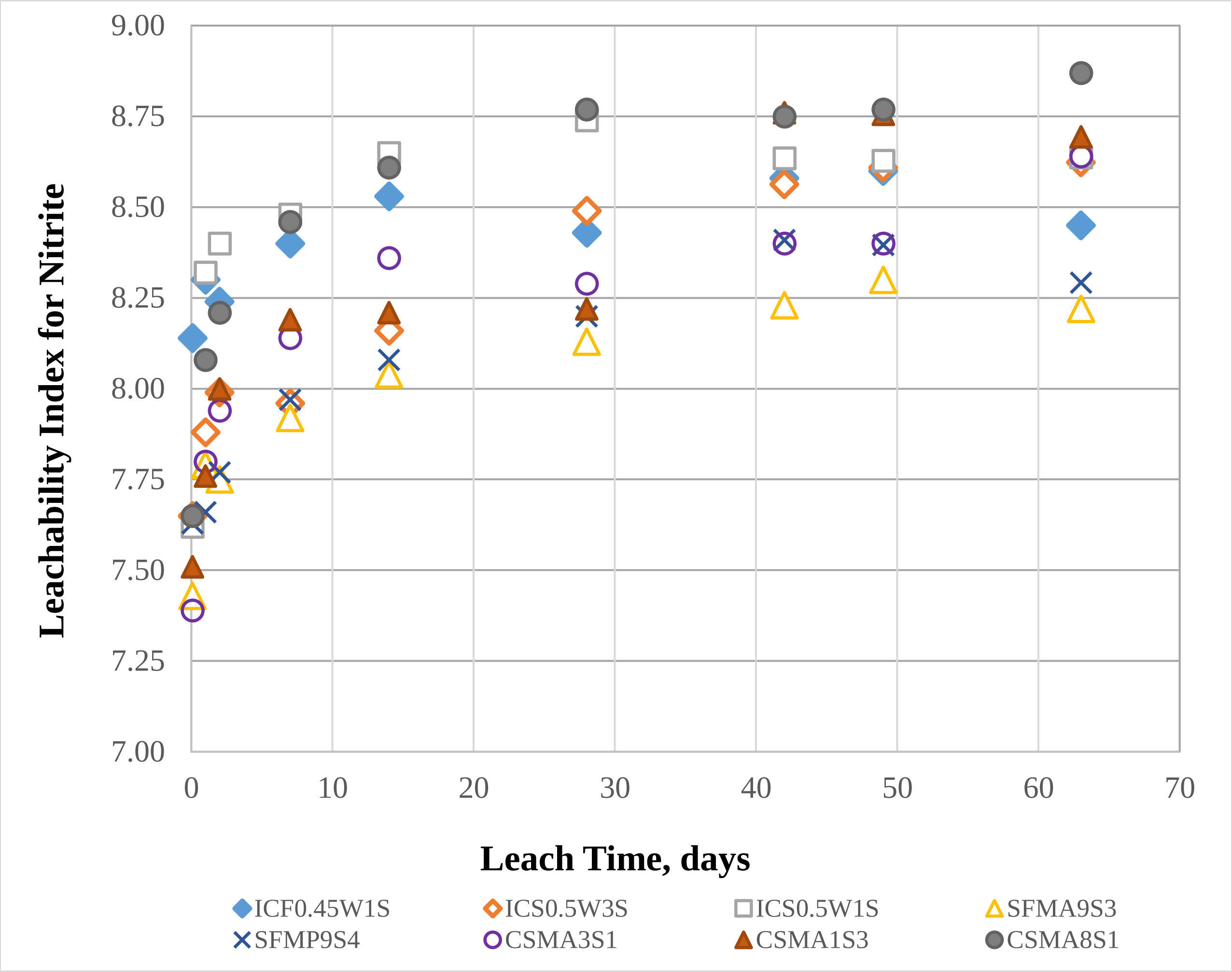

Figure 5.12. Leachability Index values for nitrite as functions of time and formulation from Phase 2 testing.

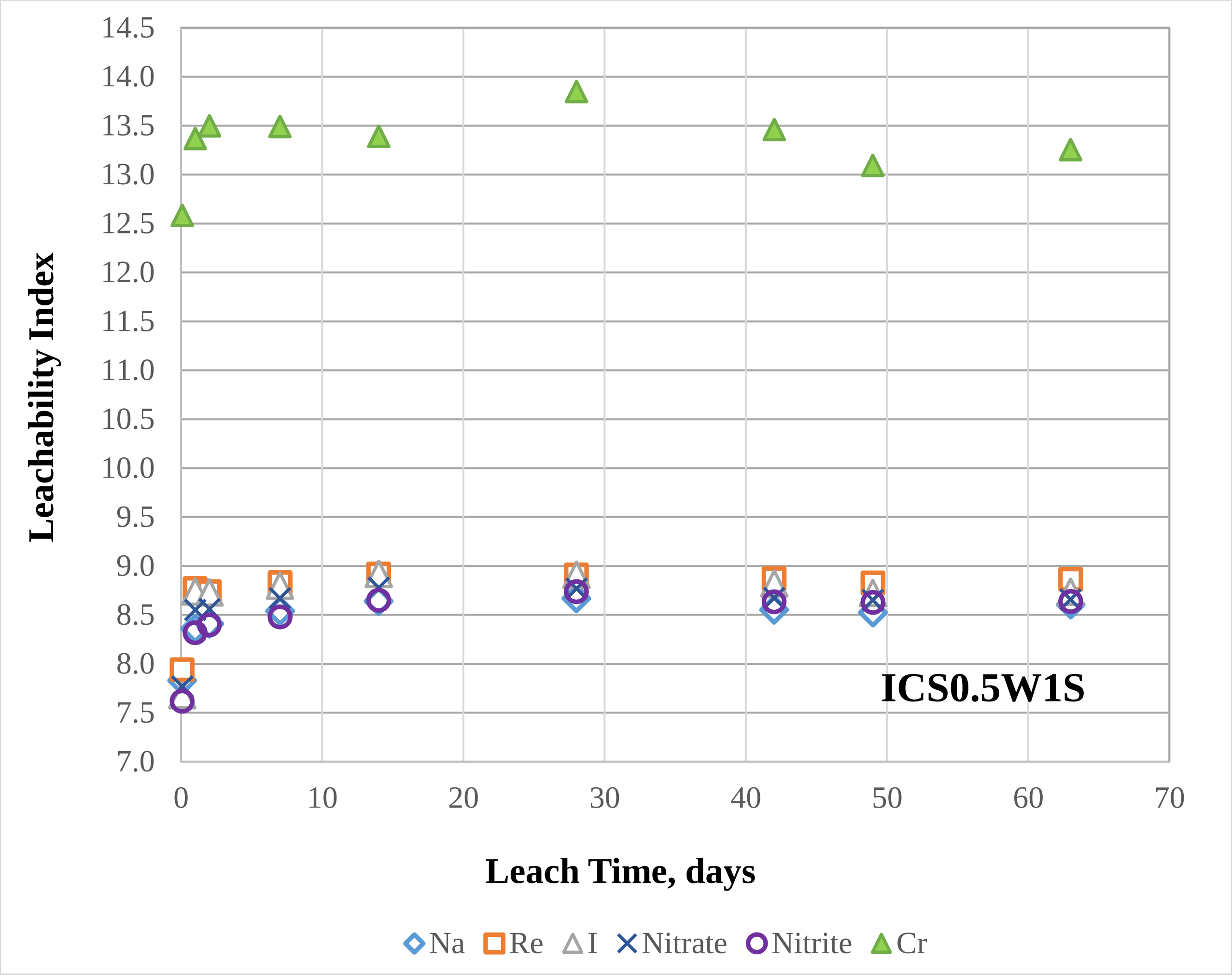

Figure 5.13. Leachability Index values as functions of time and COC for ICS0.5W1S from Phase 2 testing.

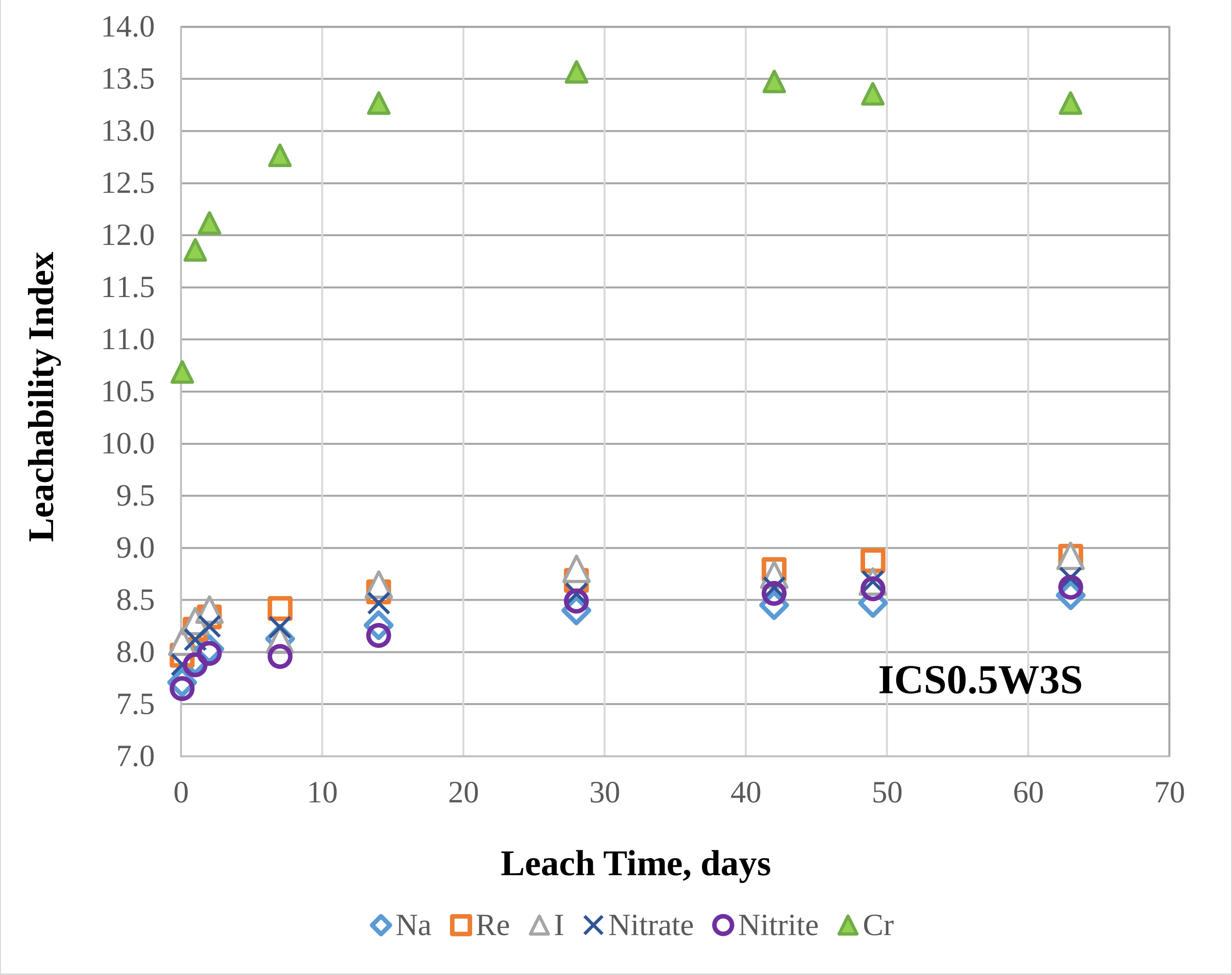

Figure 5.14. Leachability Index values as functions of time and COC for ICS0.5W3S from Phase 2 testing.

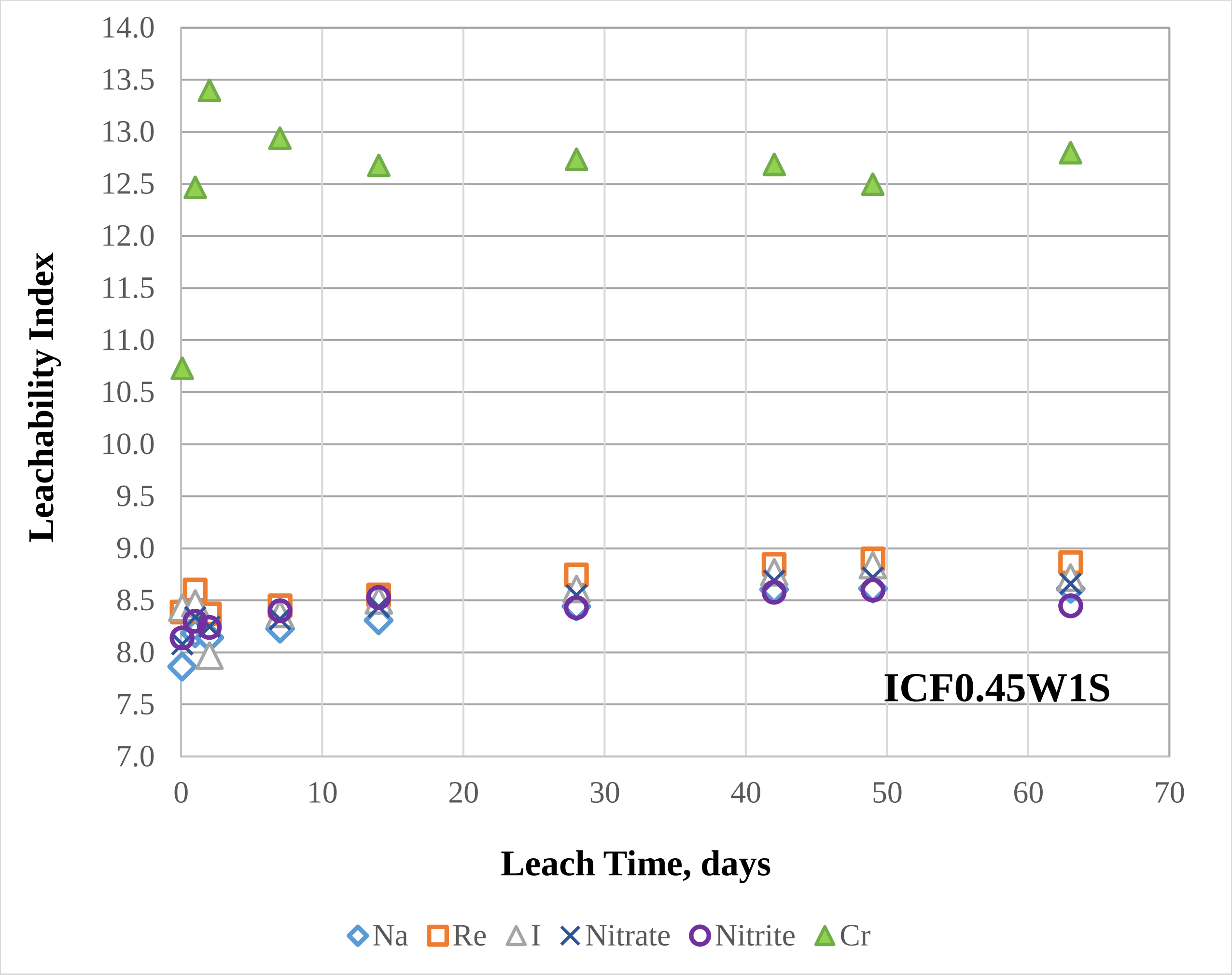

Figure 5.15. Leachability Index values as functions of time and COC for ICF0.45W1S from Phase 2 testing.

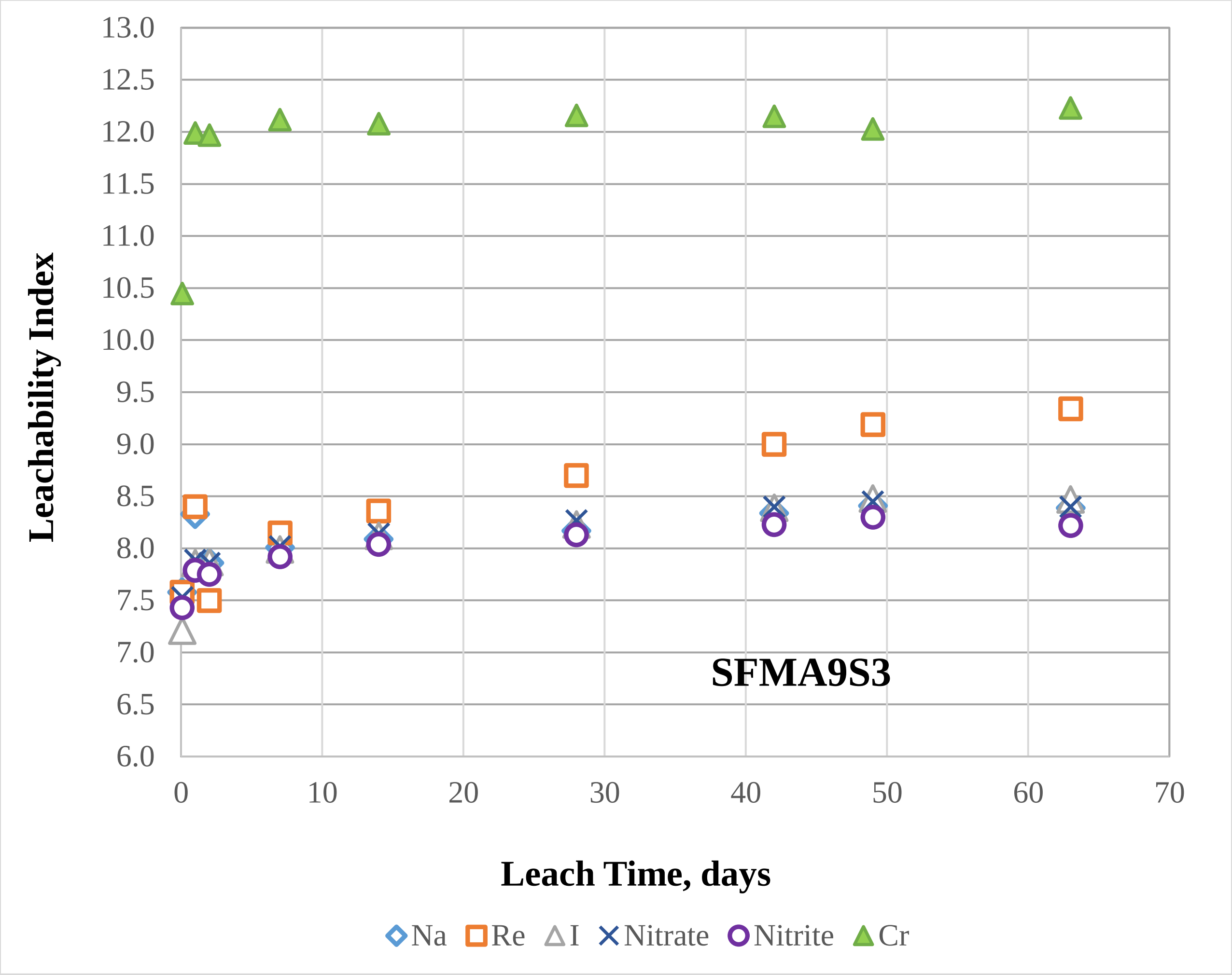

Figure 5.16. Leachability Index values as functions of time and COC for SFMA9S3 from Phase 2 testing.

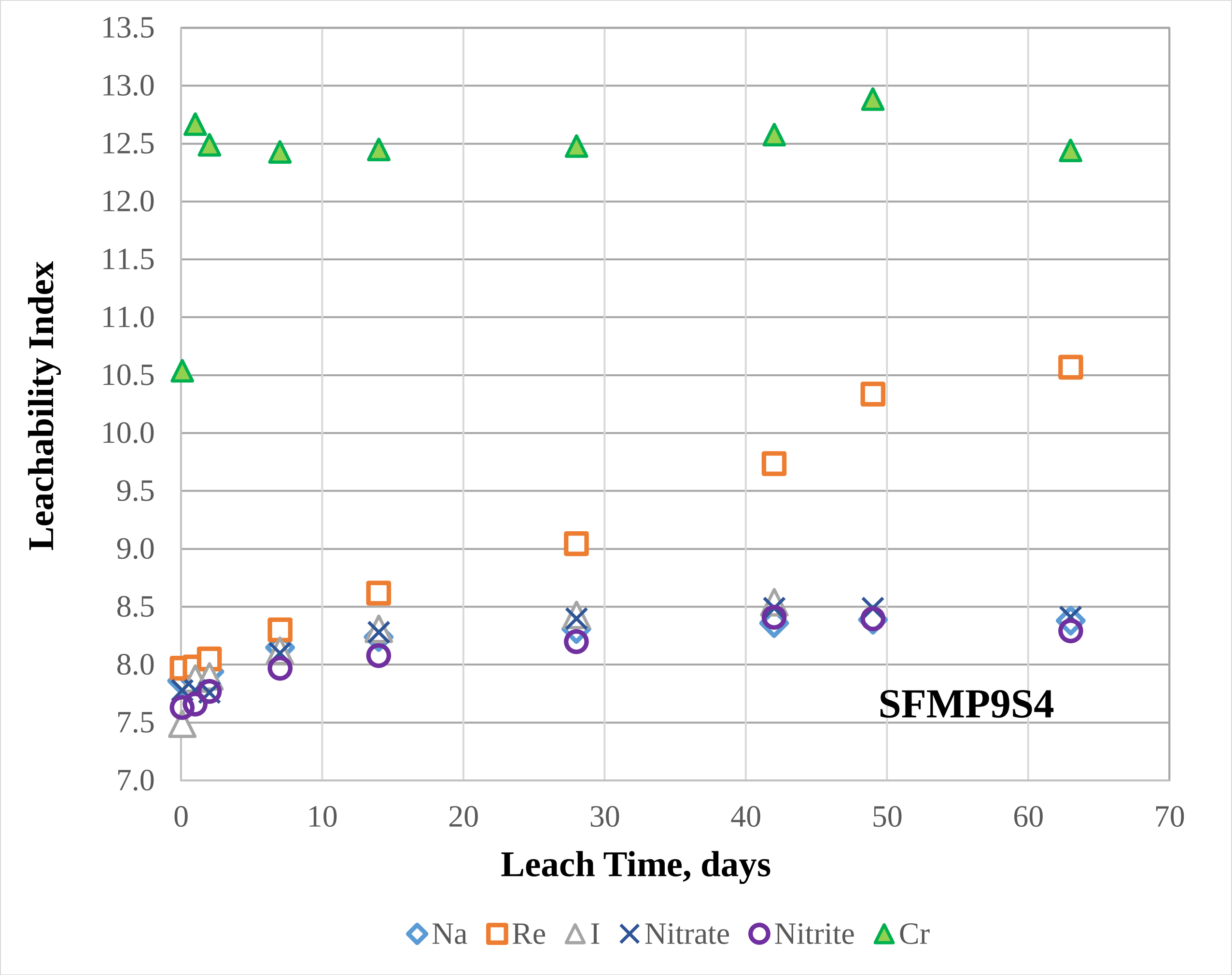

Figure 5.17. Leachability Index values as functions of time and COC for SFMP9S4 from Phase 2 testing.

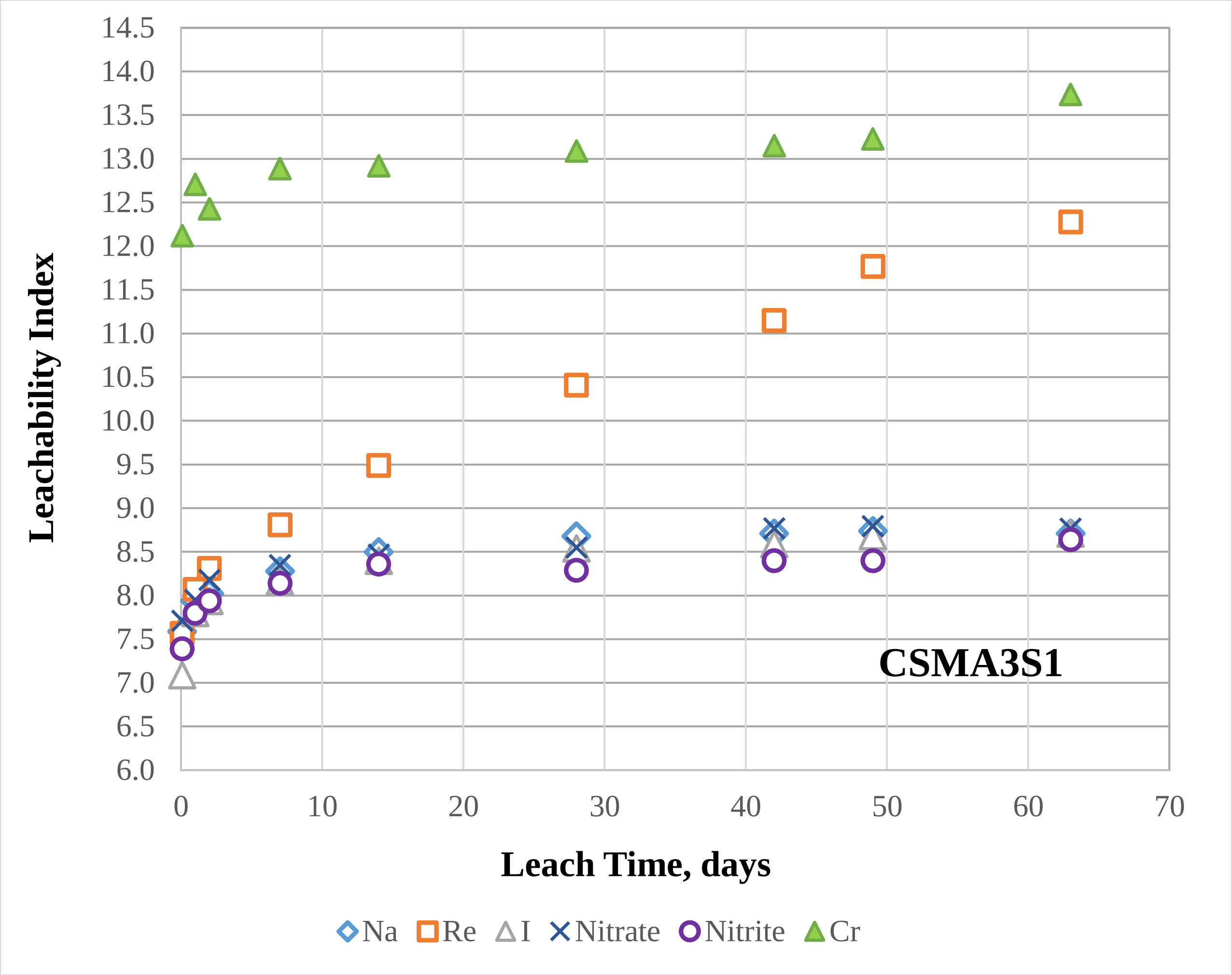

Figure 5.18. Leachability Index values as functions of time and COC for CSMA3S1 from Phase 2 testing.

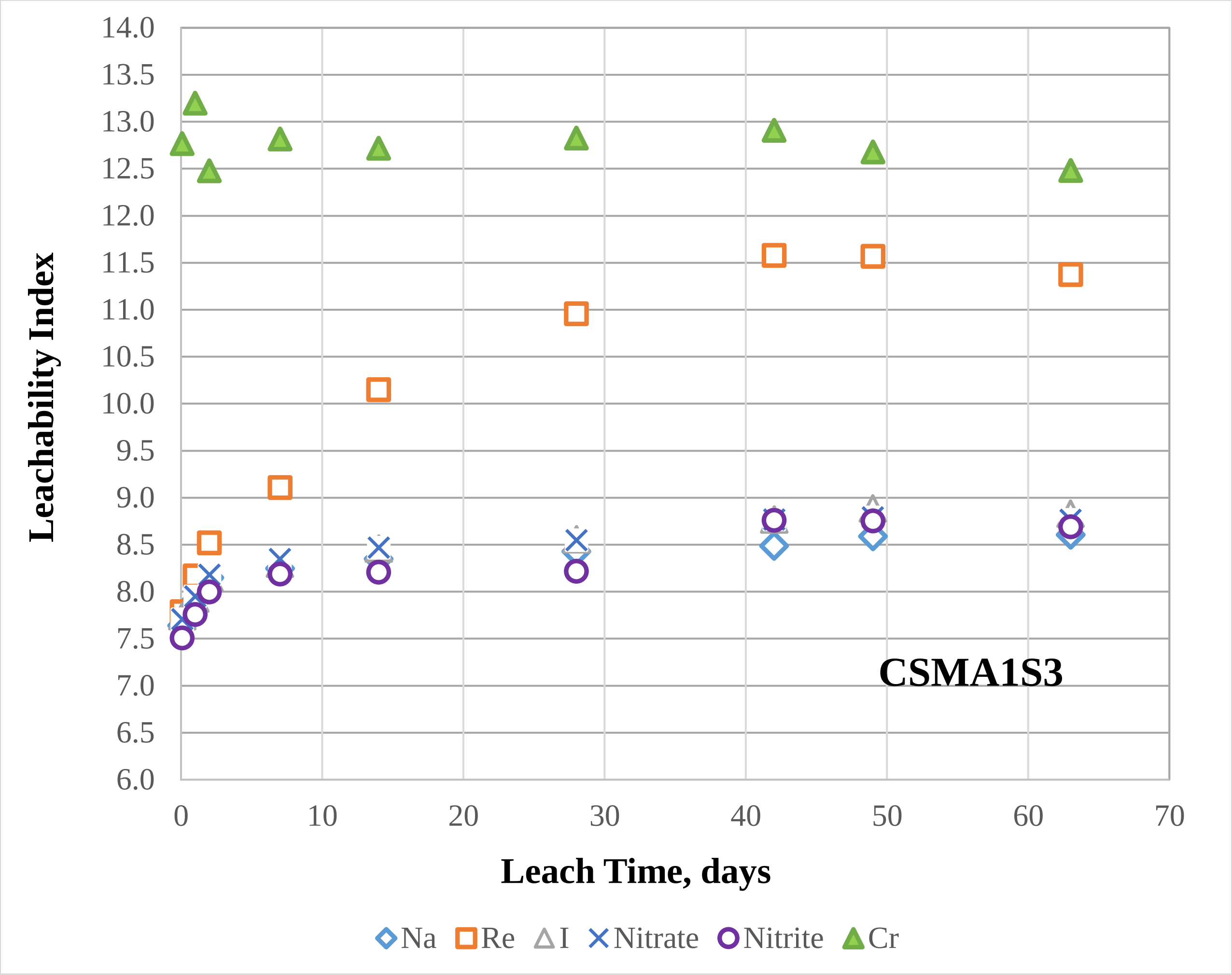

Figure 5.19. Leachability Index values as functions of time and COC for CSMA1S3 from Phase 2 testing.

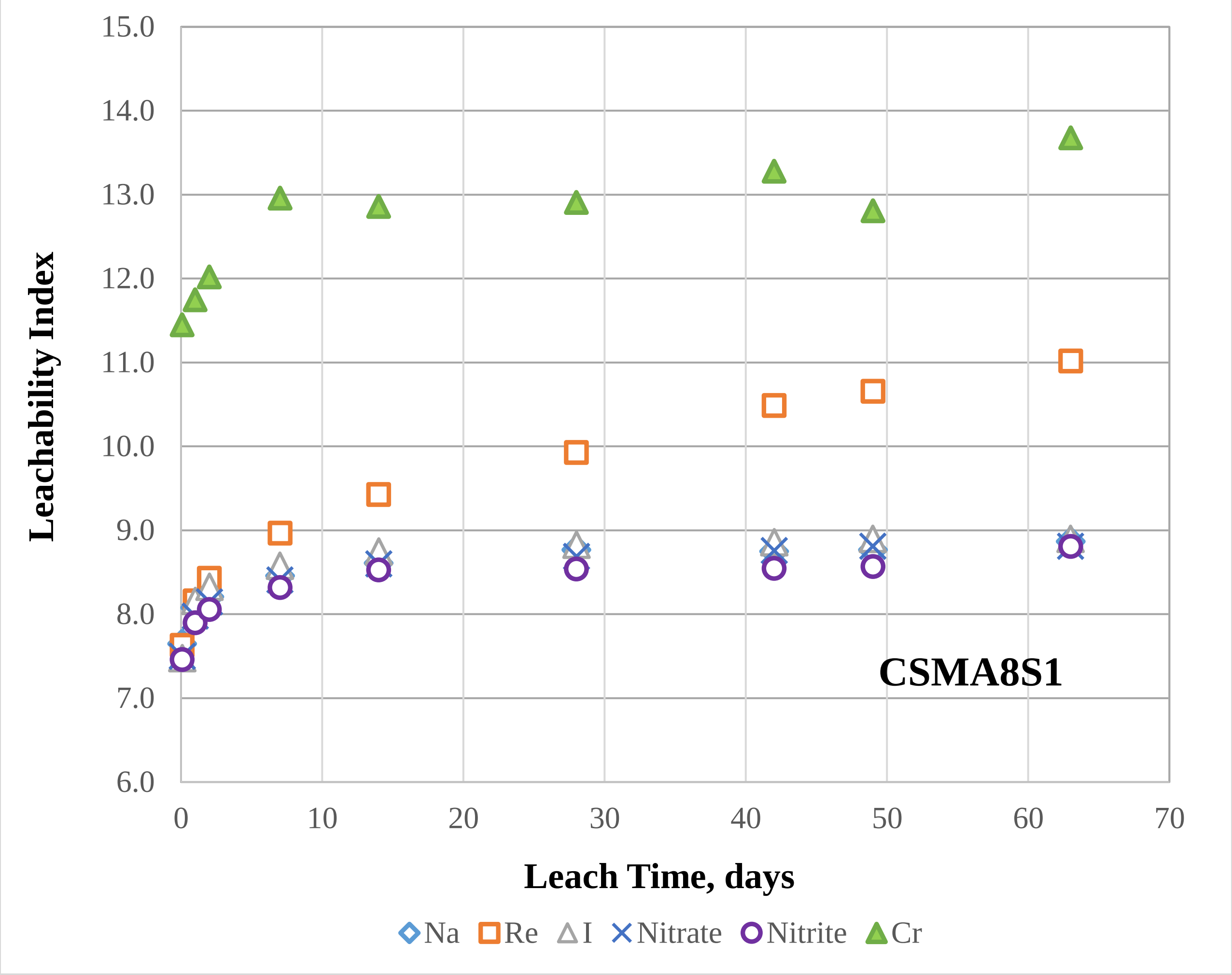

Figure 5.20. Leachability Index values as functions of time and COC for CSMA8S1 from Phase 2 testing.

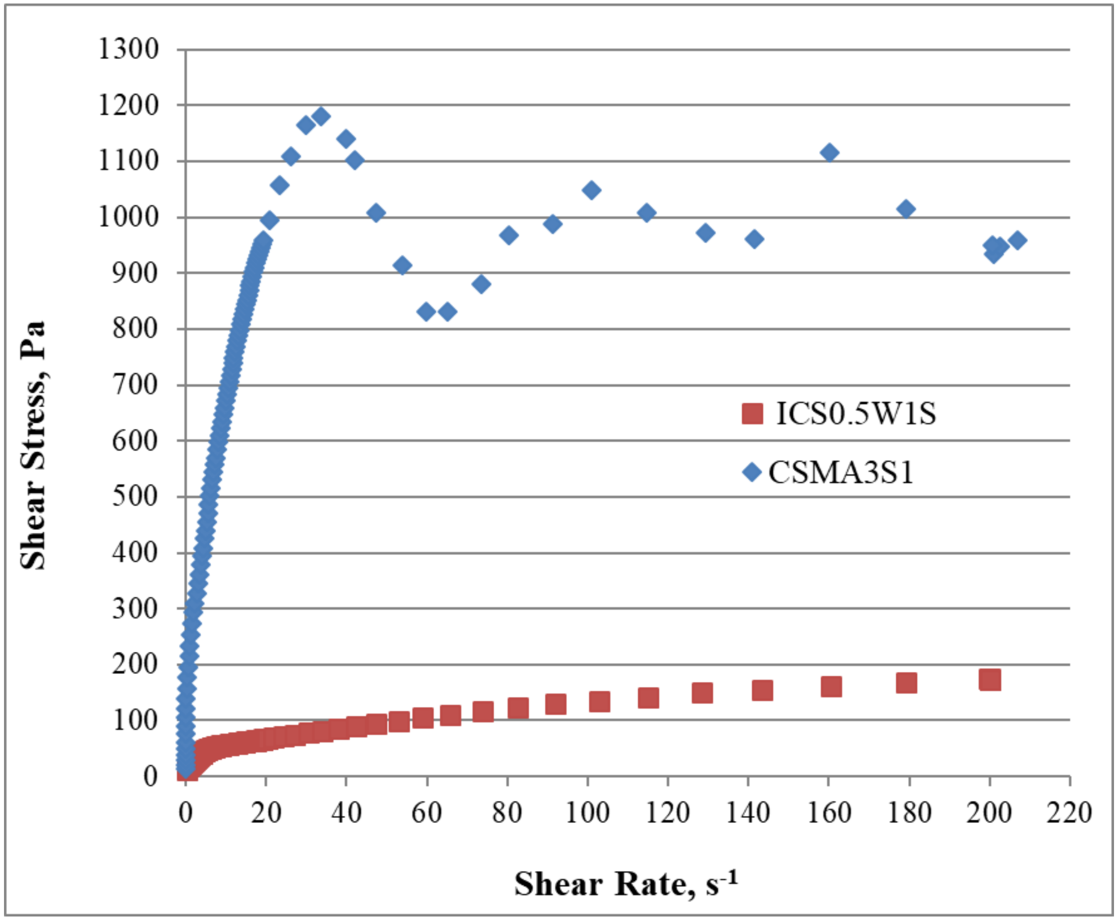

Figure 5.21. Shear stress versus shear rate for fresh grout samples selected for Phase 4 testing.

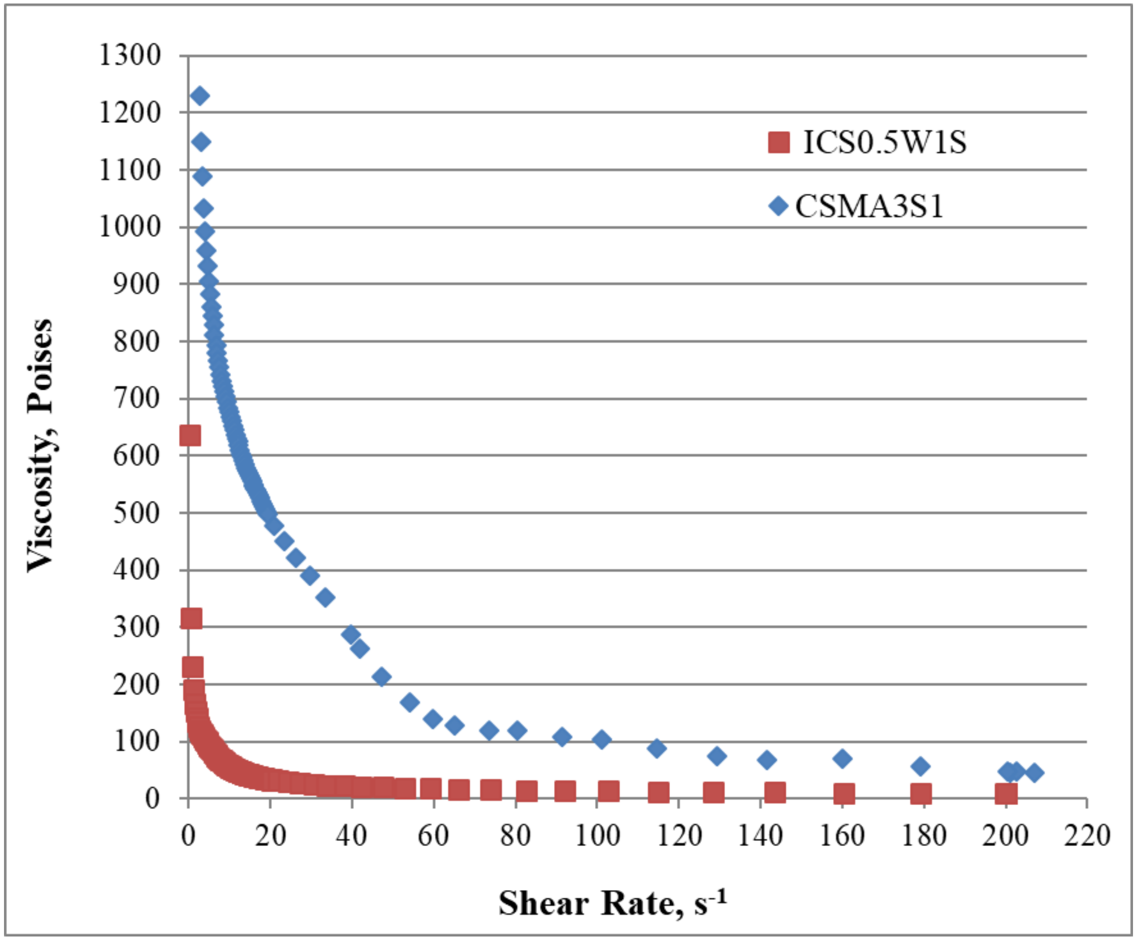

Figure 5.22. Viscosity versus shear rate for fresh grout samples selected for Phase 4 testing.

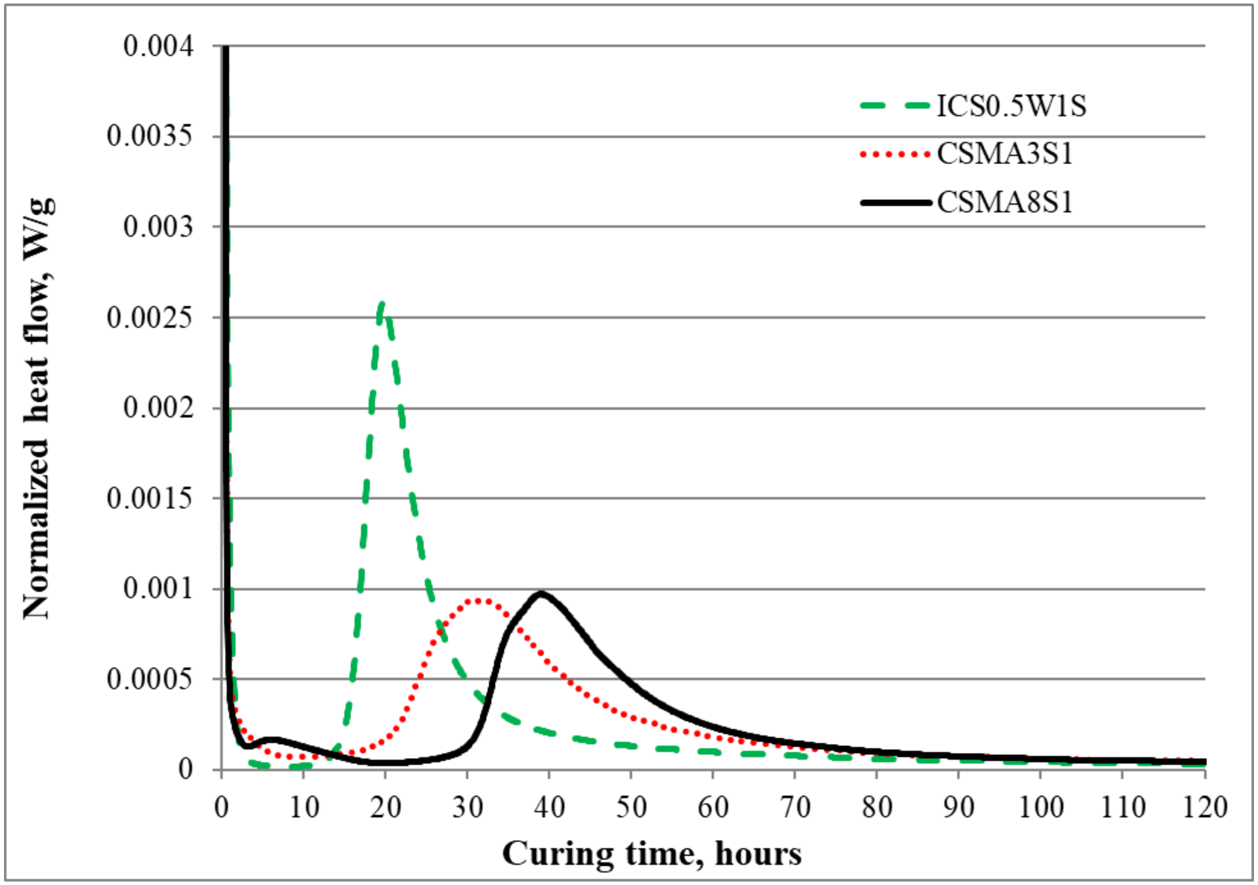

Figure 5.23. Normalized heat flows as a function of curing time up to 120 hrs for grout samples selected for Phase 4 testing.

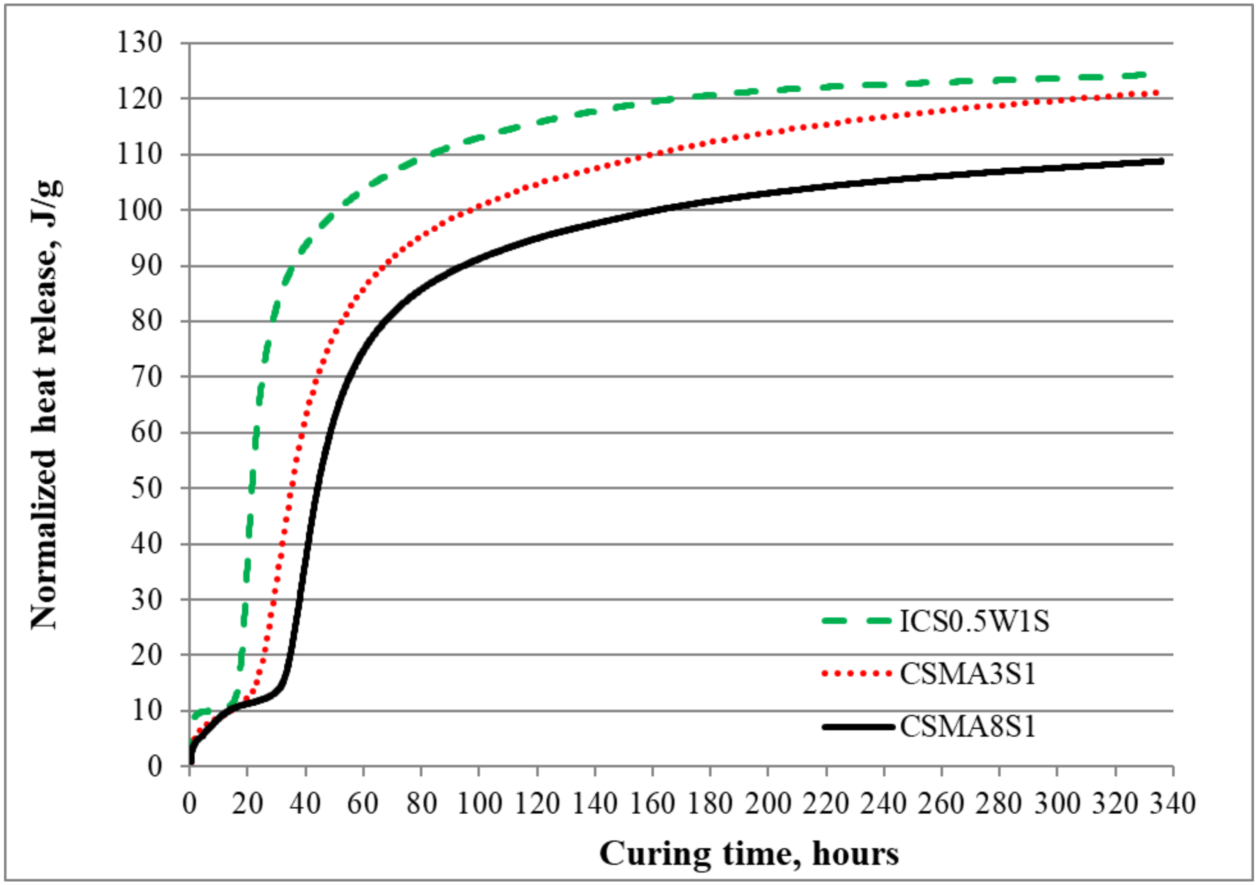

Figure 5.24. Normalized heat release as a function of curing time up to 14 days (336 hours) for samples selected for Phase 4 testing.

APPENDIX A

WASTE LOADINGS OF SELECTED WASTE FORMS

Table A1. Waste Loadings of Selected Waste Forms with 5.6 M Na SLAW.

Grout I.D.	**Description**	**w/dm**	**Formulation Type**	**Grams of Waste Sodium per Liter of Waste Form**
CSMA1S3	Mortar	0.425	NSAS	47.03
CSMA3S1	Mortar	0.425	NSAS	44.42
CSMA8S1	Mortar	0.425	NSAS	41.38
CSMP3S5	Paste	0.45	NSAS	70.69
CSMP8S2	Paste	0.45	NSAS	71.42
CSMP3S4	Paste	0.45	NSAS	73.16
ICS0.5W1S	Paste	0.50	Cast Stone	76.11
ICS0.5W3S	Paste	0.50	Cast Stone	77.03
ICF0.45W1S	Paste	0.45	Cement-Free	67.53
SFMA9S3	Mortar	0.425	ASAS	39.18
SFMP9S4	Paste	0.425	ASAS	59.78

APPENDIX B

EPA METHOD 1315 CONCENTRATION DATA

Table B1. Initial Concentrations of Contaminants in Phase 2 Waste Forms (C_0, kg/m^3).

COCs	**Improved Cast Stone/Cement Free**			**Alkali Activated Slag**		**Neutral Salt Activated Slag**			
	ICF0.45 W1S	ICS0.5W 3S	ICS0.5 W1S	SFMA9 S3	SFMP 9S4	CSMA 3S1	CSMA 1S3	CSMA 8S1	CSMP 8S2
Na	67.54	77.04	76.20	38.56	59.78	63.71	65.88	59.02	99.65
Re	0.18	0.21	0.21	0.10	0.16	0.12	0.13	0.11	0.19
Cr	0.65	0.75	0.74	0.38	0.58	0.43	0.46	0.40	0.69
I	0.18	0.21	0.21	0.10	0.16	0.12	0.13	0.11	0.19
Nitrate	58.74	67.00	66.26	33.54	51.99	38.63	40.90	35.98	62.13

Note: These concentrations are based on the sample recipes, the spiking levels and activator compositions. They do not include any contribution from the dry mix materials such as slag, fly ash, MgO, XYPEX, silica fume, zeolite and KOH.

Table B2. Concentrations of Sodium in the Leachate (Phase 2), mg/L.

Leach Time, days	**Leach Time, hrs**	**Improved Cast Stone/Cement Free**			**Alkali Activated Slag**		**Neutral Salt Activated Slag**			
		ICF0.45 W1S	ICS0.5W 3S	ICS0.5 W1S	SFMA9 S3	SFMP 9S4	CSMA 3S1	CSMA 1S3	CSMA 8S1	CSMP 8S2
0.08	2	84.01	115.35	98.27	66.71	74.78	109.21	106.50	93.94	126.37
1	24	143.16	222.27	131.78	69.45	182.07	178.08	193.26	141.20	289.09
2	48	87.31	114.17	72.824	69.45	97.53	95.423	84.77	71.02	175.09
7	168	235.20	303.38	186.73	173.23	228.97	209.88	223.04	156.95	520.42
14	336	191.29	233.13	147.91	140.91	182.22	144.48	178.77	118.27	372.24
28	672	231.56	277.89	200.46	180.24	237.63	167.04	229.94	139.51	ND
42	1008	147.50	202.10	176.71	114.88	172.51	123.32	164.55	109.10	ND
49	1176	63.57	86.10	79.683	46.25	73.14	52.221	64.36	46.67	ND
63	1512	115.20	142.64	130.91	85.07	133.26	96.89	112.99	74.87	ND

ND: Not determined due to sample cracking

Table B3. Concentrations of Rhenium in the Leachate (Phase 2), mg/L.

Leach Time, days	**Leach Time, hrs**	**Improved Cast Stone/Cement Free**			**Alkali Activated Slag**		**Neutral Salt Activated Slag**			
		ICF0.45 W1S	ICS0.5W 3S	ICS0.5 W1S	SFMA9 S3	SFMP 9S4	CSMA 3S1	CSMA 1S3	CSMA 8S1	CSMP 8S2
0.08	2	0.124	0.230	0.235	0.180	0.178	0.210	0.172	0.182	0.189
1	24	0.240	0.428	0.222	0.173	0.433	0.291	0.274	0.244	0.413
2	48	0.182	0.216	0.134	0.282	0.234	0.129	0.107	0.104	0.199
7	168	0.495	0.587	0.360	0.399	0.518	0.214	0.161	0.167	0.400
14	336	0.391	0.434	0.290	0.277	0.320	0.087	0.043	0.087	0.168
28	672	0.443	0.543	0.413	0.267	0.277	0.043	0.024	0.069	ND
42	1008	0.302	0.369	0.331	0.144	0.096	0.014	0.009	0.028	ND
49	1176	0.124	0.146	0.152	0.051	0.021	0.003	0.004	0.010	ND
63	1512	0.233	0.251	0.263	0.077	0.029	0.003	0.009	0.012	ND

ND: Not determined due to sample cracking

Table B4. Concentrations of Chromium in the Leachate (Phase 2), mg/L.

Leach Time, days	**Leach Time, hrs**	**Improved Cast Stone/Cement Free**			**Alkali Activated Slag**		**Neutral Salt Activated Slag**			
		ICF0.45 W1S	ICS0.5W 3S	ICS0.5 W1S	SFMA9 S3	SFMP 9S4	CSMA 3S1	CSMA 1S3	CSMA 8S1	CSMP 8S2
0.08	2	0.030	0.036	0.004	0.024	0.033	0.004	0.002	0.008	0.005
1	24	0.010	0.023	0.004	0.010	0.007	0.005	0.003	0.014	0.004
2	48	0.002	0.010	0.002	0.006	0.005	0.004	0.004	0.006	0.004
7	168	0.010	0.014	0.006	0.015	0.016	0.007	0.008	0.006	0.002
14	336	0.012	0.007	0.006	0.014	0.014	0.006	0.008	0.006	0.002
28	672	0.016	0.007	0.005	0.018	0.019	0.007	0.01	0.008	ND
42	1008	0.013	0.006	0.006	0.014	0.013	0.005	0.007	0.004	ND
49	1176	0.007	0.003	0.004	0.007	0.004	0.002	0.004	0.003	ND
63	1512	0.009	0.006	0.006	0.010	0.012	0.002	0.009	0.002	ND

ND: Not determined due to sample cracking

Table B5. Concentrations of Iodine in the Leachate (Phase 2), mg/L.

Leach Time, days	**Leach Time, hrs**	**Improved Cast Stone/Cement Free**			**Alkali Activated Slag**		**Neutral Salt Activated Slag**			
		ICF0.45 W1S	ICS0.5W 3S	ICS0.5 W1S	SFMA9 S3	SFMP 9S4	CSMA 3S1	CSMA 1S3	CSMA 8S1	CSMP 8S2
0.08	2	0.118	0.198	0.315	0.276	0.310	0.363	0.183	0.217	0.218
1	24	0.278	0.389	0.231	0.322	0.485	0.397	0.360	0.243	0.399
2	48	0.290	0.200	0.136	0.184	0.278	0.196	0.164	0.117	0.270
7	168	0.541	0.827	0.375	0.476	0.641	0.456	0.407	0.262	1.094
14	336	0.414	0.401	0.287	0.367	0.459	0.305	0.302	0.190	0.672
28	672	0.519	0.479	0.412	0.455	0.564	0.367	0.381	0.246	ND
42	1008	0.330	0.390	0.350	0.292	0.381	0.267	0.231	0.183	ND
49	1176	0.133	0.184	0.171	0.115	0.182	0.106	0.088	0.076	ND
63	1512	0.275	0.250	0.305	0.210	0.358	0.183	0.168	0.138	ND

ND: Not determined due to sample cracking

Table B6. Concentrations of Nitrate in the Leachate (Phase 2), mg/L.

Leach Time, days	**Leach Time, hrs**	**Improved Cast Stone/Cement Free**			**Alkali Activated Slag**		**Neutral Salt Activated Slag**			
		ICF0.45 W1S	ICS0.5W 3S	ICS0.5 W1S	SFMA9 S3	SFMP 9S4	CSMA 3S1	CSMA 1S3	CSMA 8S1	CSMP 8S2
0.08	2	57.27	82.40	91.53	61.08	70.99	81.81	61.07	67.88	68.69
1	24	104.25	153.56	92.03	100.27	175.29	122.35	113.75	96.23	176.89
2	48	67.44	77.13	52.96	60.24	105.05	60.01	50.73	46.15	112.19
7	168	184.19	232.56	139.10	149.09	209.14	140.31	123.75	101.66	384.87
14	336	143.28	158.72	108.60	115.32	151.74	96.01	95.74	72.85	223.42
28	672	179.01	201.74	156.36	139.81	186.35	130.68	124.74	93.18	ND
42	1008	116.45	144.79	133.68	92.70	129.14	82.78	73.53	65.75	ND
49	1176	48.88	59.11	59.86	38.35	56.69	33.82	31.40	27.09	ND
63	1512	95.00	102.55	107.20	72.90	111.69	59.79	58.53	48.90	ND

ND: Not determined due to sample cracking

Table B7. Concentrations of Nitrite in the Leachate (Phase 2), mg/L.

Leach Time, days	**Leach Time, hrs**	**Improved Cast Stone/Cement Free**			**Alkali Activated Slag**		**Neutral Salt Activated Slag**			
		ICF0.45 W1S	ICS0.5W 3S	ICS0.5 W1S	SFMA9 S3	SFMP 9S4	CSMA 3S1	CSMA 1S3	CSMA 8S1	CSMP 8S2
0.08	2	13.78	27.64	28.29	17.89	21.85	21.42	19.90	18.44	45.87
1	24	28.14	52.25	31.02	28.97	52.33	32.96	36.55	27.24	120.51
2	48	17.64	26.95	16.59	17.64	26.68	16.4	16.08	13.23	73.36
7	168	43.39	83.1	45.03	43.39	63.14	38.75	38.82	29.39	270.55
14	336	33.40	58.86	32.92	33.40	49.61	26.68	33.47	20.45	110.29
28	672	52.76	56.86	41.98	42.78	60.79	40.73	46.67	28.41	ND
42	1008	34.17	39.97	36.18	29.03	36.64	27.74	19.33	21.60	ND
49	1176	14.59	16.55	15.91	11.72	16.31	12.04	8.48	9.26	ND
63	1512	31.29	29.39	28.43	23.33	33.18	16.49	16.45	12.69	ND

ND: Not determined due to sample cracking

Table B8. Cumulative Percent Mass of Na Released.

Leach Time, days	**Leach Time, hrs**	**Improved Cast Stone/Cement Free**			**Alkali Activated Slag**		**Neutral Salt Activated Slag**			
		ICF0.45 W1S	ICS0.5W 3S	ICS0.5 W1S	SFMA9 S3	SFMP 9S4	CSMA 3S1	CSMA 1S3	CSMA 8S1	CSMP 8S2
0.08	2	1.11	1.34	1.15	1.54	1.11	1.53	1.44	1.42	1.13
1	24	3.00	3.91	2.69	3.14	3.82	4.03	4.05	3.54	3.72
2	48	4.15	5.24	3.54	4.75	5.27	5.37	5.19	4.61	5.29
7	168	7.26	8.75	5.72	8.75	8.67	8.31	8.21	6.98	9.94
14	336	9.78	11.46	7.45	12.01	11.38	10.33	10.62	8.76	13.28
28	672	12.84	14.68	9.79	16.17	14.91	12.68	13.73	10.87	ND
42	1008	14.79	17.02	11.85	18.82	17.48	14.40	15.95	12.51	ND
49	1176	15.63	18.02	12.78	19.89	18.56	15.14	16.82	13.21	ND
63	1512	17.15	19.67	14.31	21.86	20.55	16.50	18.35	14.34	ND

ND: Not determined due to sample cracking

Table B9. Cumulative Percent Mass of Re Released.

Leach Time, days	**Leach Time, hrs**	**Improved Cast Stone/Cement Free**			**Alkali Activated Slag**		**Neutral Salt Activated Slag**			
		ICF0.45 W1S	ICS0.5W 3S	ICS0.5 W1S	SFMA9 S3	SFMP 9S4	CSMA 3S1	CSMA 1S3	CSMA 8S1	CSMP 8S2
0.08	2	0.61	0.99	1.01	1.54	0.98	1.56	1.20	1.45	0.87
1	24	1.78	2.82	1.97	3.01	3.36	3.72	3.12	3.39	2.78
2	48	2.66	3.74	2.55	5.42	4.64	4.68	3.87	4.21	3.70
7	168	5.08	6.26	4.11	8.83	7.49	6.27	4.99	5.54	5.54
14	336	6.99	8.12	5.36	11.19	9.25	6.92	5.29	6.23	6.32
28	672	9.15	10.44	7.14	13.47	10.77	7.24	5.46	6.78	ND
42	1008	10.62	12.03	8.57	14.70	11.30	7.34	5.52	7.00	ND
49	1176	11.23	12.65	9.22	15.14	11.41	7.37	5.55	7.08	ND
63	1512	12.37	13.73	10.36	15.79	11.57	7.39	5.62	7.18	ND

ND: Not determined due to sample cracking

Table B10. Cumulative Percent Mass of Cr Released.

Leach Time, days	**Leach Time, hrs**	**Improved Cast Stone/Cement Free**			**Alkali Activated Slag**		**Neutral Salt Activated Slag**			
		ICF0.45 W1S	ICS0.5W 3S	ICS0.5 W1S	SFMA9 S3	SFMP 9S4	CSMA 3S1	CSMA 1S3	CSMA 8S1	CSMP 8S2
0.08	2	0.04	0.04	0.00	0.06	0.05	0.01	0.00	0.02	0.01
1	24	0.05	0.07	0.01	0.08	0.06	0.02	0.01	0.05	0.01
2	48	0.06	0.08	0.01	0.09	0.07	0.03	0.02	0.06	0.02
7	168	0.07	0.10	0.02	0.13	0.09	0.04	0.03	0.08	0.02
14	336	0.09	0.11	0.03	0.16	0.12	0.05	0.05	0.09	0.02
28	672	0.11	0.12	0.03	0.20	0.14	0.07	0.07	0.11	ND
42	1008	0.13	0.12	0.04	0.24	0.16	0.08	0.08	0.12	ND
49	1176	0.14	0.13	0.04	0.25	0.17	0.08	0.09	0.12	ND
63	1512	0.15	0.13	0.05	0.28	0.19	0.09	0.11	0.13	ND

ND: Not determined due to sample cracking

Table B11. Cumulative Percent Mass of I Released.

Leach Time, days	**Leach Time, hrs**	**Improved Cast Stone/Cement Free**			**Alkali Activated Slag**		**Neutral Salt Activated Slag**			
		ICF0.45 W1S	ICS0.5W 3S	ICS0.5 W1S	SFMA 9S3	SFMP 9S4	CSMA 3S1	CSMA 1S3	CSMA 8S1	CSMP 8S2
0.08	2	0.58	0.85	1.36	2.35	1.70	2.70	1.28	1.72	1.01
1	24	1.93	2.52	2.36	5.10	4.37	5.66	3.80	3.66	2.85
2	48	3.35	3.37	2.94	6.67	5.89	7.11	4.94	4.59	4.09
7	168	5.99	6.91	4.56	10.74	9.42	10.50	7.79	6.67	9.14
14	336	8.01	8.63	5.80	13.87	11.94	12.77	9.90	8.18	12.24
28	672	10.54	10.68	7.58	17.76	15.04	15.50	12.57	10.13	ND
42	1008	12.15	12.35	9.09	20.25	17.14	17.49	14.18	11.59	ND
49	1176	12.80	13.14	9.83	21.24	18.14	18.27	14.80	12.19	ND
63	1512	14.14	14.21	11.15	23.03	20.10	19.63	15.97	13.28	ND

ND: Not determined due to sample cracking

Table B12. Cumulative Percent Mass of Nitrate Released.

Leach Time, days	**Leach Time, hrs**	**Improved Cast Stone/Cement Free**			**Alkali Activated Slag**		**Neutral Salt Activated Slag**			
		ICF0.45 W1S	ICS0.5W 3S	ICS0.5 W1S	SFMA9 S3	SFMP 9S4	CSMA 3S1	CSMA 1S3	CSMA 8S1	CSMP 8S2
0.08	2	0.89	1.10	1.23	1.62	1.21	1.89	1.33	1.68	0.99
1	24	2.52	3.14	2.47	4.29	4.21	4.72	3.80	4.06	3.53
2	48	3.57	4.17	3.18	5.89	6.01	6.11	4.91	5.20	5.14
7	168	6.44	7.27	5.04	9.85	9.58	9.35	7.60	7.71	10.66
14	336	8.67	9.39	6.50	12.91	12.17	11.57	9.68	9.51	13.87
28	672	11.46	12.08	8.60	16.62	15.36	14.60	12.40	11.82	ND
42	1008	13.28	14.01	10.40	19.08	17.57	16.51	14.00	13.44	ND
49	1176	14.04	14.79	12.20	20.10	18.54	17.29	14.68	14.11	ND
63	1512	15.52	16.16	12.64	22.04	20.45	18.67	15.95	15.32	ND

ND: Not determined due to sample cracking

Table B13. Cumulative Percent Mass of Nitrite Released.

Leach Time, days	**Leach Time, hrs**	**Improved Cast Stone/Cement Free**			**Alkali Activated Slag**		**Neutral Salt Activated Slag**			
		ICF0.45 W1S	ICS0.5W 3S	ICS0.5 W1S	SFMA9 S3	SFMP 9S4	CSMA 3S1	CSMA 1S3	CSMA 8S1	CSMP 8S2
0.08	2	0.81	1.42	1.47	1.84	1.44	1.91	1.67	1.76	1.42
1	24	2.46	4.11	3.08	4.81	4.90	4.86	4.75	4.36	5.16
2	48	3.49	5.50	4.94	6.62	6.66	6.32	6.10	5.63	7.44
7	168	6.04	9.78	6.28	11.07	10.83	9.79	9.36	8.44	15.84
14	336	8.00	12.81	7.98	14.50	14.11	12.17	12.18	10.39	19.26
28	672	11.10	15.74	10.16	18.89	18.13	15.81	16.10	13.10	ND
42	1008	13.10	17.80	12.04	21.87	20.55	18.29	17.73	15.17	ND
49	1176	13.96	18.65	12.87	23.07	21.62	19.37	18.44	16.05	ND
63	1512	15.79	20.17	14.34	25.47	23.81	20.84	19.82	17.27	ND

ND: Not determined due to sample cracking