PNNL-32458 Rev 0

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Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

PACIFIC NORTHWEST NATIONAL LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC05-76RL01830

Printed in the United States of America

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Summary

Washington River Protection Solutions (WRPS) contracted subject matter experts at Pacific Northwest National Laboratory (PNNL) and Savannah River National Laboratory (SRNL) to perform a thorough screening of grout degradation mechanisms, the processes that drive the mechanism, and the likelihood that mechanisms and processes will impact grouted solid secondary waste (SSW) form performance after disposal. During operations of the Hanford Waste Treatment and Immobilization Plant (WTP) SSW will be generated that will be grouted and the resulting waste forms disposed of on-site at the Hanford Integrated Disposal Facility (IDF). The IDF performance assessment (PA) must make model assumptions that impact the predicted long-term ability of the waste forms to retain radionuclides for long periods of time (up to 10,000 years). However, there is limited data related to the long-term performance of grouted waste forms after disposal at the Hanford IDF, such as radionuclide retention. In the current IDF PA (USDOE 2018) the long-term performance of grouted SSW waste forms was not modeled to degrade over time based on technical information provided in the report "Solid Secondary Waste Data Package Supporting Hanford Integrated Disposal Facility Performance Assessment" (Flach et al. 2016a). In Flach et al. (2016), aging of the waste form was correlated with the amount of water that interacted with the waste form. The assessment of select degradation mechanisms indicated that SSW grout degradation from chemical attack was expected to be minimal under IDF disposal conditions. Although not included in full detail, the possible consequences of other aging assumptions were evaluated in the PA and found to not significantly affect the results ((USDOE 2018) Section 8.3.3, page 8-55).

A potential vulnerability of the PA is that the technical arguments used to describe waste form aging did not address all chemical, physical, and biological degradation processes that are known to influence cement materials and the ability of similar materials to retain radionuclides and hazardous chemicals over long disposal times. This lack of understanding results in uncertainty in the long-term contaminant release properties from grout waste forms and often results in overly simplistic and conservative assumptions being used in PAs (e.g., all grout waste forms turn to rubble at 500 years). The present report builds upon the technical arguments regarding cement aging mechanisms provided in Flach et al. (2016) to enhance the defensibility of the approach in the current and to future PAs and identify information gaps that could affect the PA conclusions, i.e., that there is a reasonable expectation that the grouted SSW will provide the necessary protection to human health and the environment for 1,000 years or more.

The overall objective of this work is to enhance the defensibility for the long-term performance of grouted Hanford SSW streams when disposed in a near surface disposal facility like the Hanford IDF. Providing defensibly for the long-term performance of the grouted waste forms is consistent with the technology maturation activities identified in the Performance Assessment Maintenance Plan, (Westcott et al. 2019), which are necessary to address the assumptions made in the PA. Specifically, this work addresses two areas identified for further technology maturation activities in the Performance Assessment Maintenance Plan: (1) "Evaluate ongoing research on transport characteristics of cementitious materials using accelerated tests to approximate the effects of aging/alteration/weathering"; and (2) "Evaluate ongoing research on microbial effects on transport processes in cementitious materials."

The effort considered three contemporary, candidate grout formulations and projected SSW types for Hanford. If new formulations are considered or alternate SSW emerge then a reevaluation should be performed using the approach discussed within.

The assembled subject matter expert team evaluated a list of degradation mechanisms and supporting processes and provided rankings of areas where further technology maturation is needed. From this assessment, high priority technology and maturation areas include: (1) the effects of carbonation, Ca leaching, and SSW dimensional change in grout waste forms; (2) updated model representations of grouted waste forms; and (3) scaled testing demonstrations. Moderate priority items including a paper study on possible microbial influence, reoxidation rates, radionuclide/contaminant dissolution and leaching from SSW in the grout and freeze thaw behavior. Other processes evaluated were deemed unlikely to occur, to have little impact on the SSW waste forms, or to occur at time frames beyond those considered (>10,000 years).

In addition, the geochemical evolution of grout and SSW was considered as aging plays a role in the change to waste form properties and CoPC availability for release. It was concluded that an effort should be made to incorporate simulations of the aging of grout waste forms into the analysis of the performance at the IDF. Any such development should include an understanding of radionuclide/CoPC leaching and dissolution from SSW in grout porewater conditions. This model development will capture dynamic grout aging and degradation relevant to the IDF.

The assessments and proposed R&D approaches are expected to support an update to the WRPS SSW roadmap.

Acknowledgments

The authors would like to thank the following people for their assistance. We thank Kent Rosenberger, (Savannah River Site) for information on the Savannah River Tank Farm Performance Assessments technical report on steel degradation. Dan Meess, (CHBWV), for West Valley experience on Waste Incidental to Reprocessing for West Valley Melter Grout Encapsulation. We thank Charmayne Lonergan (PNNL) for her peer review, David MacPherson (PNNL) for review, Chrissy Charron and Veronica Perez (PNNL) for document control and Nathan Johnson (PNNL) for graphics development. The authors would like to thank Kearn Pat Lee (Orano) for his review and commentary during the effort. The authors would also like to thank Grace Chen and Matt Landon (WRPS) and Alex Cozzi (SRNL) for involvement in the assessment discussions.

Acronyms and Abbreviations

Acronym	Definition
ACI	American Concrete Institute
AFm	aluminate ferrite monosulfate
AFt	aluminate ferrite trisulfate
Ag-GAC	silver impregnated granular activated carbon
AgIZ	silver iodine zeolite
AgM	silver mordenite
ASR	alkali silica reaction
BBI	Best-Basis Inventory
BFS	blast furnace slag
CASH	calcium aluminum silicate hydrate
CFR	Code of Federal Regulations
CM	cementitious materials
CoC	contaminant of concern (released from waste form)
CoPC	contaminant of potential concern (within waste form)
CSH	calcium silicate hydrate
DEF	delayed ettringite formation
DFLAW	direct feed low-activity waste
D_{obs}	observed diffusivity
DOE	U.S. Department of Energy
ETF	Effluent Treatment Facility
EXAFS	extended X-ray absorption fine structure
FA	fly ash
GAC	granular activated carbon
GWB	Geochemist's Workbench
HEPA	high efficiency particulate air
HGM-3	Hanford Grout Mix 3
HGM-5	Hanford Grout Mix 5
HLW	high level waste
IDF	Integrated Disposal Facility
ILAW	immobilized low-activity waste
ILW	intermediate level waste
K_d	distribution coefficient
LAW	low-activity waste
LLW	low level waste
NEUP	Nuclear Energy University Partnership
NRC	Nuclear Regulatory Commission
OPC	ordinary portland cement
PA	performance assessment

PNNL	Pacific Northwest National Laboratory
QA	quality assurance
RCRA	Resource Conservation and Recovery Act
RH	relative humidity
SCM	supplementary cementitious material
SDU	saltstone disposal unit
SF	silica fume
sRF	spherical resorcinol formaldehyde resin
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
SSW	solid secondary waste
TCLP	Toxicity Characteristic Leaching Procedure
TSCR	Tank Side Cesium Removal
UHPCC	ultra-high-performance cement composite
UHPG	ultra-high-performance grout
w/dm	water to dry mix
WAC	waste acceptance criteria
WRPS	Washington River Protection Solutions
WSU	Washington State University
WTP	Hanford Waste Treatment and Immobilization Plant
WWFTP	WRPS Waste Form Testing Program
XANES	X-ray absorption near edge structure
XES	X-ray emission spectroscopy
XRD	X-ray diffraction

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1.0 Introduction

1.1 Hanford Flowsheet

At the Department of Energy's Hanford Site, over 53 million gallons of chemically complex and radioactive wastes have been stored in 177 underground tanks. The Hanford Waste Treatment and Immobilization Plant (WTP) is under construction and is designed to treat and immobilize these wastes. Following retrieval from the tanks the liquid will be filtered and ion exchanged to remove Cs, generating a treated stream of low-activity waste (LAW). The solids are returned to the tanks and the majority of the sludge in the tanks will comprise the high-level waste (HLW) fraction of the waste. Both LAW and HLW streams will be sent to separate vitrification facilities within WTP to be vitrified, producing glass waste forms (Bernards et al. 2020).

During operations of WTP, solid secondary wastes (SSWs) will be generated as a result of waste treatment, vitrification, off-gas management, and supporting process activities. The SSWs produced through LAW and HLW operations are expected to include used process equipment, contaminated tools and instruments, decontamination wastes, the spent LAW melters, high-efficiency particulate air (HEPA) filters, carbon absorption beds (granular activated carbon, GAC), Ag-mordenite (AgM), and spent ion exchange resins (e.g., spherical resorcinol formaldehyde resin, sRF) (USDOE 2018)[1]. SSW treatment processes and resulting disposal pathways for the final disposition form of the SSW are needed to support direct feed low activity waste (DFLAW) operations and facilitate continued operation of WTP throughout the Hanford mission. These waste streams are planned to be immobilized by blending (non-debris) or encapsulating (debris) in grout (cementitious) waste forms that will then be disposed of on-site at the Hanford Integrated Disposal Facility (IDF). The IDF, which is a near-surface disposal facility that penetrates approximately 45 ft (14 m) into the subsurface of the 200 East area of the Hanford Site (Flach et al. 2016a).

1.2 Immobilization of SSW

The IDF is expected to receive over 72,000 containers of grout stabilizing or encapsulating SSW generated over the course of WTP's LAW mission (USDOE 2018). At the Hanford Site, grout is the common term used to describe a low temperature waste form that consists of paste made from ordinary portland cement (OPC), water and supplementary cementitious materials (SCM) (e.g., fly ash (FA) and blast furnace slag (BFS)). However, the actual formulation is tailored for both ideal processing and disposal performance properties once the paste has cured to stabilize/encapsulate the SSW material. When the desired properties cannot be optimized using various ratios of water, OPC, BFS, or FA; aggregate and/or other admixes may be included. By this process the final grout waste form provides improved structural integrity to the SSW material and attenuates the release of contaminants of potential concern (CoPCs)[2] to the surrounding environment.

There are two processes for the immobilization of SSW: stabilization (also termed blending, solidification or microencapsulation) and macroencapsulation. Stabilization of SSW materials of particle size < 60 mm that are considered non-debris and will be mixed into the fresh grout slurry prior to placement in a container for curing and disposal (Figure 1 (a) - (c)). Macroencapsulation of the larger SSW of particle size >60 mm particle size and termed debris waste, will first be compacted (if possible), placed in a container and then the grout slurry will be poured in the container to fill in the remaining voids in the container (Figure 1 (d)-(f)). The grout formulation used to encapsulate debris waste typically includes pozzolans and aggregates,

[1] Note: the spent ion exchange resins previously projected were the spherical resorcinol formaldehyde resins planned to be used in the LAW pretreatment system (LAWPS). However during DFLAW this system will be replaced with Tank Side Cesium Removal (TSCR).

[2] CoPC is used to describe a contaminant/radionuclide within the waste form, while the term contaminant of concern (CoC) is used for a species released from the waste form.

in addition to the binding cement paste, to provide a barrier around the encapsulated debris. Furthermore, in the final disposal container, a 5 – 10 cm barrier of neat grout (no SSW material) will encapsulate the debris-microencapsulating grout at the interior to meet performance metrics as modeled in the 2017 IDF performance assessment (PA) (USDOE 2018).

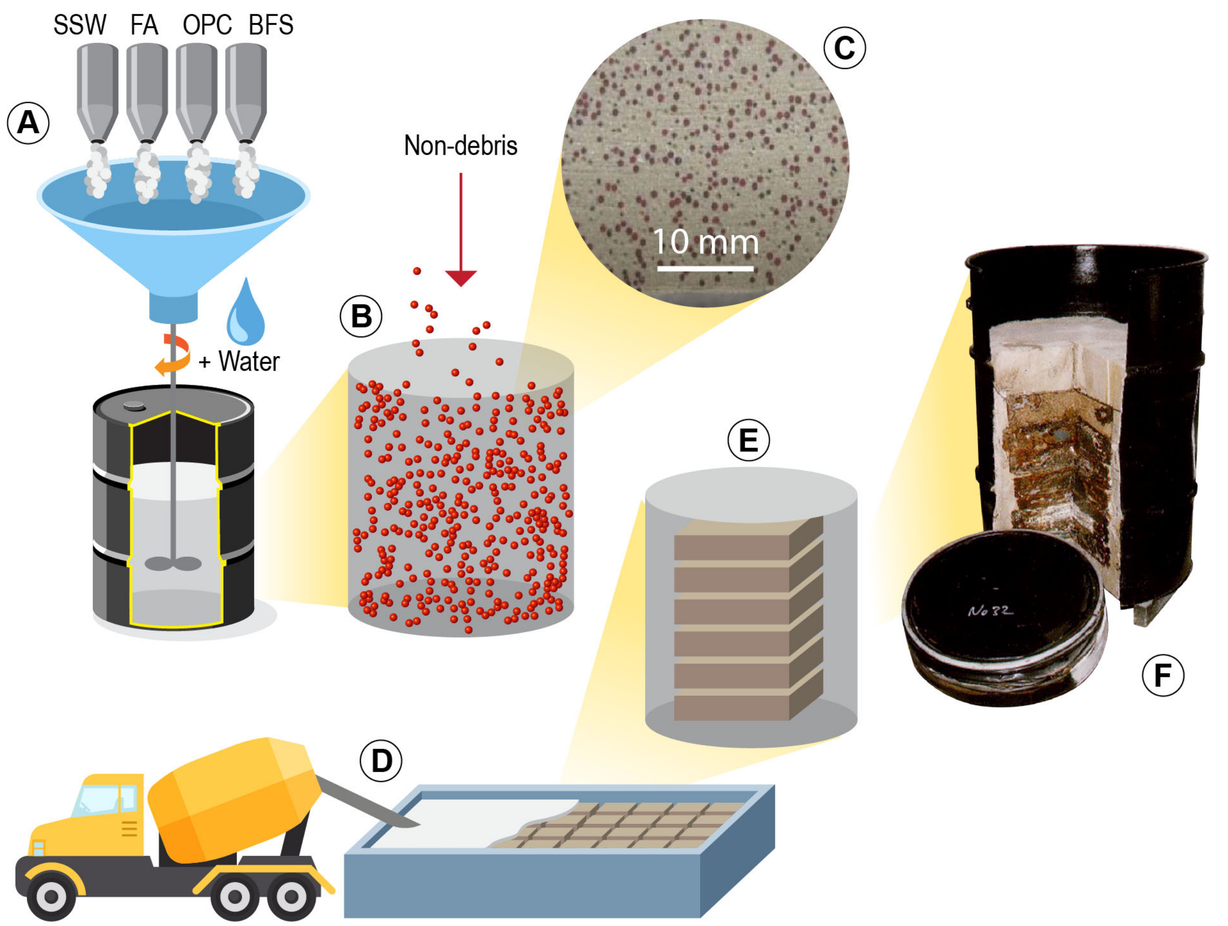

Figure 1. Conceptualized processes for solid secondary waste forms showing a stabilization/microencapsulation process and resulting waste form (a-c) and a macroencapsulation process and resulting waste form (d-f).

1.3 Grout Evolution

The resulting grout waste forms continually evolve with time as the internal hydration reactions continue and the waste form interacts with its environment. Initially, the pore solution in the hydrated grout is highly alkaline and includes soluble alkalis, e.g., Na^+ and K^+. Four chemical states are then experienced in the waste form as buffering conditions are generated and evolve due to decalcification of various minerals in the hydrated grout including the main binding phase, calcium-silicate-hydrate (CSH) (Ochs et al. 2016). The time frame for each state relative to the disposal time frames considered in this report (Section 3.1.2) are uncertain as they are highly dependent on the grout formulation used, the number of pore volume exchanges that occur, and the local chemistry.

- State I (13.5 > pH > 12.5), pH is controlled by dissolution of alkalis, (Na_2O/$NaOH$ and K_2O/KOH);
- State II (pH = 12.5), pH is controlled by dissolution of portlandite, $Ca(OH)_2$;

- State III (12.5 > pH > 10), more complex, pH and element concentrations are controlled by the sequence of dissolution and precipitation reactions (decalcification of calcium silicate and aluminate hydrates);
- State IV (pH < 10), CSH and other hydrated cement components have completely dissolved or carbonated. Pore fluid controlled by remaining aggregate minerals such as $CaCO_3$ and other carbonate phases and silica and alumina gels.

A technical report supporting modeling of liquid secondary waste grout waste forms in the 2017 IDF PA provided considerations for the evolution of pH through these states in the Hanford subsurface, transcribed below (Cantrell et al. 2016):

> *"Criscenti et al. (1996) performed calculations for three rows of 55-gallon cement-filled drums stacked on top of each other in a shallow land burial ground in the arid Hanford environment for various scenarios. For all scenarios modeled, the system pH did not decrease below 10 for 10,000 years because CSH gel remained to buffer the pH. For a scenario of one barrel filled only one-third with cement at the highest recharge rate (5 cm/yr), the CSH gel was completely depleted after 4,000 years, and the pH dropped to below 10. Possible container configurations for the secondary waste cementitious waste forms destined for burial in IDF include 55-gallon drums and 2.5 ft × 8 ft × 20 ft, as rectangular mild-steel burial boxes. It is acknowledged that the computer generated predictions by Atkinson et al. (1989) and Criscenti et al. (1996) did not address the potential for significant cement waste-form degradation, aside from a few simple thermodynamically controlled weathering reactions for the major cement phases. Thus, their results showing such long times for pH to be maintained at alkaline values close to 10 to 10.5 should be carefully considered. The network of chemical reactions (both thermodynamic and kinetically controlled) as well as the computer codes capable of solving the complex network of cement weathering reactions have vastly improved over the 20 to 25 years since these studies were performed (see Yabusaki et al. 2015 for more discussion). Despite this "warning," the low recharge rates expected for the IDF subsurface environment and the mass of cementitious secondary wastes to be buried are similar to those modeled by Criscenti et al. (1996); as a result, the IDF near-field Cast Stone leachate pH might be expected to remain caustic for millennia. In the example above with the barrel filled one-third with cement, at an IDF recharge rate of 0.35 cm/yr, it would take more than 55,000 years for the pH to drop below 10. This hypothesis is also offered by the saltstone PA documents for the more saturated SRS site. Although the environmental conditions at the Savannah River Site (SRS) are much different from those at Hanford (Savannah River has a nominal infiltration rate through a degraded closure cap of 31.6 cm/yr (SRR CWDA 2014), whereas Hanford will have a post-design infiltration rate of 0.35 cm/yr, that the transition from the high pH buffered by CSH to the lower pH buffered by calcite occurs between approximately 24,000 years for Saltstone Disposal Unit (SDU) 4 and >100,000 years for SDU 1 and SDUs that have diameters greater than 150 feet. In the SRS saltstone PA (SRR CWDA 2009), the source term release of contaminants of concern are based on both the degradation of the waste-form mineral forms from pore volume exchanges modeled using Geochemist Workbench® Release 6, incorporating Eh effects on technetium, and a hypothetically degraded saltstone condition. Degraded saltstone is assumed to take the form of cracked grout and has been modeled by increasing its hydraulic conductivity and modifying the characteristic curves."*

As the hydration reactions proceed coupled with other chemical processes and environmental interactions the mineralogy and chemistry within the waste form will also evolve. To predict this evolution, the solubility of mineral assemblages and grout chemistry of hydrated cement is used to establish the chemical constraints of the waste form environment. Then, alteration of the phase assemblages can be predicted as a function of the number of pore water exchanges that have occurred over time. Pore volume exchanges are used rather than infiltrating water or another metric because infiltration can vary significantly between disposal scenarios and over the lifecycle of a waste form. In this way the processes are more closely associated with the delivery of fresh infiltrating water to the waste form. Thermodynamic models are used to develop inputs for the relationship between chemical transport properties and pore volume exchange relationships (Flach 2021b).

1.4 2016 SSW Data Package

Recommendations for grout waste form physical and chemical properties to support the initial analysis of SSW disposal in the 2017 IDF PA were prepared and provided in the 2016 SSW data package (Flach et al. 2016a). At that time, specific formulations had not been identified for grout(s) for use to encapsulate or solidify SSW, and no IDF-specific experiments were conducted to obtain data for the PA. Thus, recommended property values were provided for a range of candidate materials based on a review of existing literature and a formulation currently used at Hanford. The 2017 IDF PA did not consider ultra-high performance grout waste forms.

Four key SSW streams were identified for emphasis due to expected inventories for CoPCs and contemporary flowsheets: HEPA filters, ion exchange resins (like sRF), GAC and AgM. Compacted HEPA filters were considered a debris waste and were assumed to be encapsulated while the other three key waste streams were considered non-debris blended and solidified in a cementitious matrix.

The data package included recommended inputs for the physical properties of the cured grout waste forms (e.g., saturated hydraulic conductivity, bulk density, porosity, water characteristic curves), assumptions governing the release of CoPCs from the key waste streams, and properties associated with mass transport of the CoPCs through the cured grout materials (e.g., distribution coefficients, solubility, diffusion coefficients). As would be expected, there were differing amounts of information available for specific input parameters. Variability in the information gathered represented uncertainty due to measurement error, variability from multiple samples using a given mix, and differences in properties associated with different mixes. Depending on available information, some recommendations were provided in the form of best estimates and statistical distributions, others were provided in the form of best estimates with a range of potential values, and others were addressed based on simplifying assumptions and expert judgment. Collectively the recommendations were representative of the available data and some will need to be confirmed or modified to reflect information specific to the actual mixes that are selected for IDF grout waste forms and when site specific data become available.

1.5 Modeling summary from IDF PA

The 2017 IDF PA (USDOE 2018) considered SSW as part of the full disposal inventory within the IDF along with the immobilized LAW (ILAW) glass, and solidified liquid secondary wastes from the Effluent Treatment Facility (ETF). The key contaminants considered across these waste form types were I-129, Tc-99, U, Cr and nitrate, and their inventory splits are shown in

Table 1 for Case 7 which can be considered the base case in the IDF PA. The SSW contained a large amount of the I-129 (41.2%) and minor amounts of Tc-99 (0.08%) and Cr (0.13%). Within the SSW inventory the contaminants and radionuclides were then distributed amongst the HEPA filters, ion exchange resins, GAC, AgM and other debris. The distribution of the contaminant and radionuclide inventory across the SSW types used in the 2017 IDF PA (Case 7, base case) are shown in

Table 2. The HEPA filters contained the majority of Cs-137 and Tc-99, the ion exchange resins contained mainly Cs-137, the GAC primarily I-129 and Hg, and the AgM had the majority of I-129.

Table 1 – Comparison of the inventory splits of the key contaminants across the waste form types considered in the 2017 IDF PA (Case 7). Adapted from Table 5-1 of USDOE (2018).

Key Contaminant	**Unit**	**ILAW Glass % (Ci or kg)**	**LAW Melter % (Ci or kg)**	**SSW Grout % (Ci or kg)**	**ETF Grout (Ci or kg)**	**Total Inventory to IDF (Ci or kg)**
I-129	Ci	56.2% (16.5)	0.08% (<1)	41.2% (12.1)	0.22% (<1)	28.6
Tc-99	Ci	99.6% (26400)	0.14% (37.5)	0.08% (20.0)	0% (<1)	26500
U Isotopes	Ci	1.4% (15.8)	0% (<1)	0% (<1)	0% (<1)	15.8
Cr	kg	83% (490000)	0.13% (744)	0.13% (743)	<1% (430)	491,000
U Total	Ci	1.3% (8100)	<1% (11.5)	0% (<1)	<1% (8.30)	8120
NO_3	kg	0% (0)	0% (0)	0% (0)	0.29% (164,000)	164,000
Note: Radionuclides are reported in curies and chemicals reported in kilograms and expressed as percentages of the 2002 or 2014 Best-Basis Inventory (BBI) as applicable. Note that these IDF inventories include only waste streams that are disposed of at the IDF and therefore do not represent perfect mass balance. Differences can be attributed to destruction during treatment, stack losses, and disposal offsite at a geologic repository.						

Table 2 – Comparison of the contaminant and radionuclide inventory for SSW used in Case 7 of the 2017 IDF PA. Adapted from Table 6-3 of USDOE (2018).

SSW Type	**I-129 (Ci)**	**137-Cs (Ci)**	**Sr-90 (Ci)**	**99-Tc (Ci)**	**Cr (kg)**	**Hg (kg)**	**Pb (kg)**
HEPA Filters	0.13	2031.17	17.29	17.45	699.62	0.00	7.27
Ion Exchange Resins	0.02	370.76	0.02	2.36	39.77	0.02	2.33
GAC	4.42	0.00	0.00	0.00	0.00	1001.95	0.00
Other Debris	0.00	1595.89	8.98	0.11	3.47	0.00	2.31
AgM	7.56	0.00	0.00	0.00	0.00	0.01	0.00
Total	12.12	3997.82	26.29	19.92	742.86	1001.98	11.91

Within the IDF PA there were four relevant cases where the radionuclide and contaminant inventory were varied across the waste forms beyond the base case (Case 7 above). Case 8 included Tc removal from the WTP off-gas and thus lowered the Tc inventory in the IDF. Case 10A split a larger amount of iodine and technetium from the primary glass waste form (20% and 32% respectively) with the difference landing in the secondary wastes. Case 10B had higher Tc retention in the glass (68%) compared to case 10A. It should be noted that Cases 10A and 10B are hypothetical operating scenarios that will be removed in future IDF PA iterations. The resulting splits for I-129 and Tc-99 are shown in Figure 2

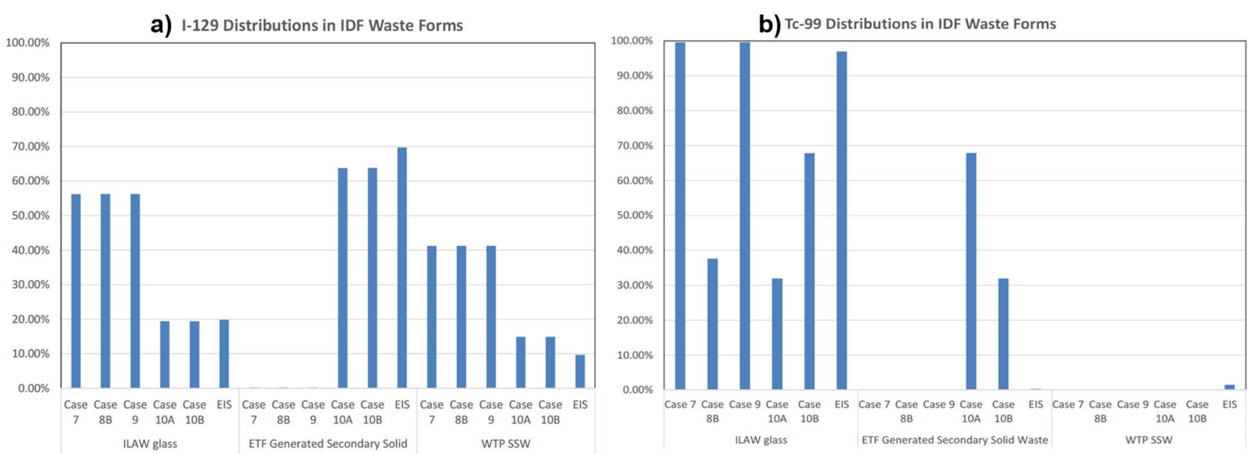

Figure 2 – Distribution of a) I-129 and b) Tc-99 across the different waste forms in the alternate cases in the IDF PA. Adapted from Figure 9-1 and Figure 9-3 of USDOE (2018).

The SSW was a primary contributor to radionuclide concentrations modeled at the point of compliance in the IDF PA for both Tc-99 and I-129. The breakthrough curves for the total release of I-129 and Tc-99 along with the contributions from each waste form type in the IDF PA are shown in Figure 3. For I-129, Figure 3a, the SSW contributed nearly all the I-129 simulated at the point of compliance; while for Tc-99, Figure 3b, the SSW was the largest contributor up to 7000 years. The main SSW waste form contributing to the I-129 release was the HEPA filters up to 5000 years followed by the AgM and GAC beyond 5000 years due to the depletion of the HEPA inventory, Figure 4a. The HEPA filters were the largest contributor of Tc-99 release, Figure 4b. It should be noted that the simulations performed used the information from the 2016 SSW data package (Flach et al. 2016) where site-specific information was limited. Efforts to obtain site-specific information have been ongoing since the 2017 IDF PA, Section 1.6. These results highlight that both the importance of accurate prediction of SSW grout performance in the IDF and the need to ensure any possible failure mechanisms are incorporated into the simulations (without unnecessarily conservative assumptions).

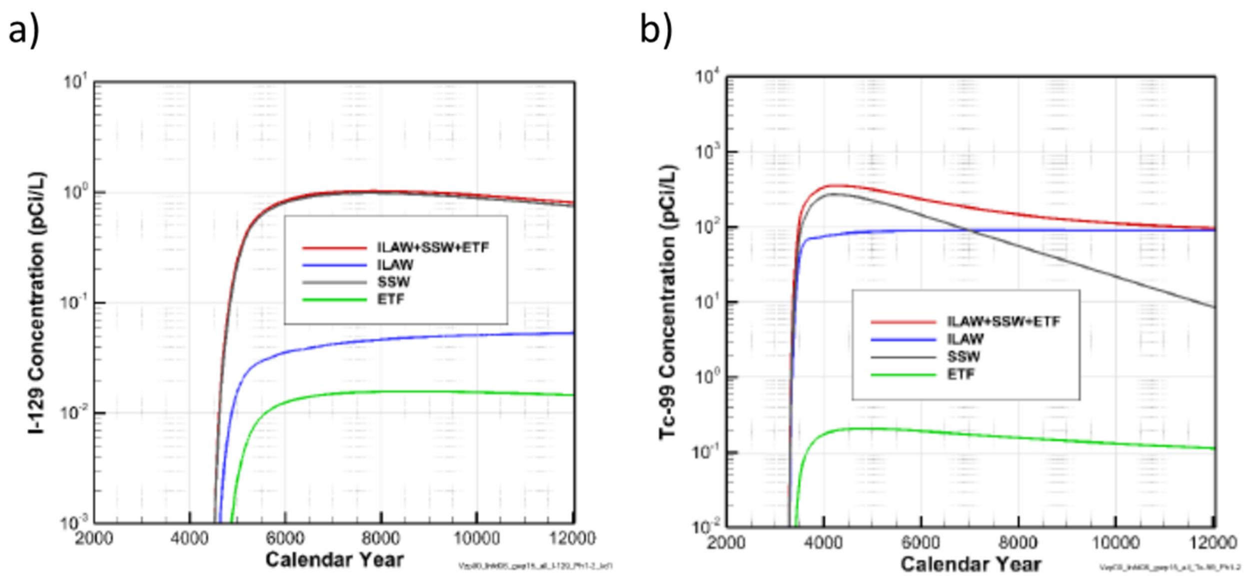

Figure 3 – Base case breakthrough curves at the point of compliance from the three waste form types in the IDF PA for a) I-129 and b) Tc-99. From Figures 5-98 and 5-99 of USDOE (2018).

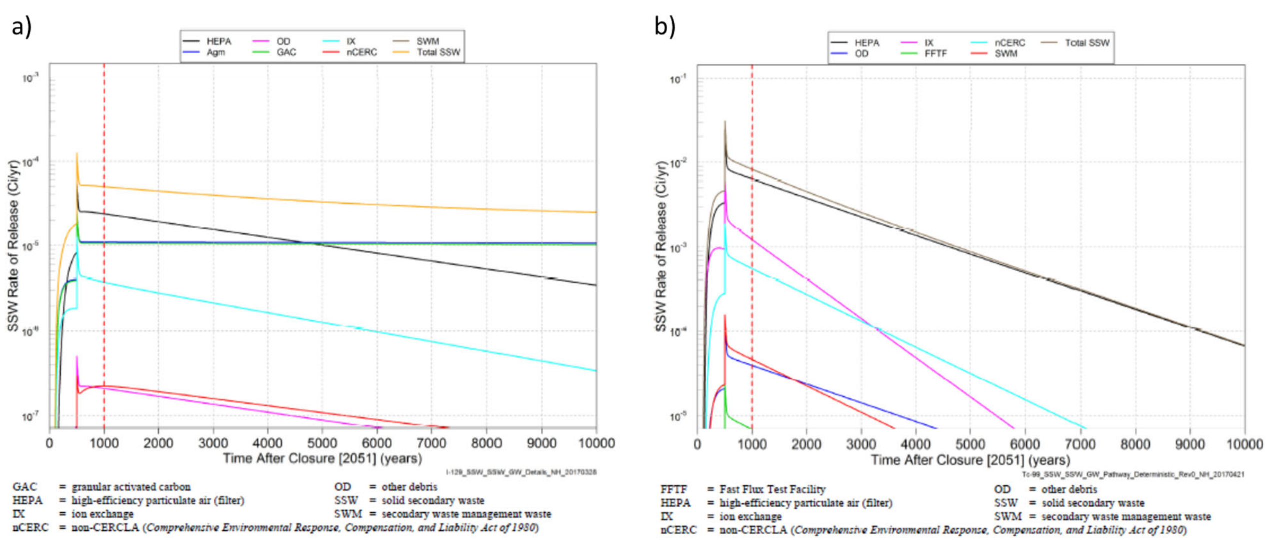

Figure 4 – The release to the vadose zone from the IDF for a) I-129 and b) Tc-99 for the various SSW waste forms. From Figures 6-56 and 6-57 of USDOE (2018).

1.6 Relevant Program Documents to SSW Since Data Package

The Washington River Protection Solutions, *LLC* (WRPS) SSW program has evaluated over the last few years the performance of site-specific Hanford SSW waste forms and evaluated options for disposal. This section presents a summary of the works performed to date.

1.6.1 2017 - Benchmarking of DFLAW Solid Secondary Wastes and Processes with UK/Europe Counterparts

A joint report between WRPS and DBD Inc (United Kingdom) was prepared to compare US and UK SSW (Brown et al. 2017). The intent of this report was specifically to compare waste practices in the UK and Europe to those wastes arising at the Hanford site, with a view to (1) provide additional information to assist the design and planning for the treatment of SSWs at Hanford; (2) introduce relevant UK and Europe best practices and possible innovations that could be brought to the site; (3) build on lessons learned from UK experience; (4) outline and compare the US and UK radioactivity thresholds for solid waste classifications; (5) review the Hanford SSWs and how they fit within the US and UK waste classifications; and (6) review equivalent SSWs, their conditioning, and storage within the UK and Europe.

The report presented findings that the basis behind the US and UK waste classification regulations are similar in that they consider activity concentrations and thresholds for key radionuclides; however, the US and UK categories are not directly comparable. In general, it appeared that for the majority of cases US Class A is the equivalent of UK Low-Level Waste (LLW), US Class C is the equivalent of UK Intermediate-Level Waste (ILW) and US Class B fits across both UK LLW and UK ILW categories. The waste classifications in the USA are defined in 10 Code of Federal Regulations (CFR) Part 61.55 *Waste Classification*[3]. A summary level review of average activity concentrations across each of the DFLAW waste streams indicates that the non-debris wastes are likely to be (US) Class A / (UK) LLW and debris wastes are likely to be a combination of (US) Class A, Class B, Class C / (UK) LLW, ILW.

1.6.2 2017 - Solid Secondary Waste Testing for Maintenance of the Hanford Integrated Disposal Facility Performance Assessment

In 2017, WRPS requested the SRNL support development of waste form formulations and testing to address performance requirements and waste form characteristics of SSW expected to be generated during the Hanford tank waste treatment mission (Nichols et al. 2017). This report contained the results of Phase 1 of a testing program defined in the report. In Phase 1, ten grout mixes were successfully prepared and tested for fresh and cured properties. Fresh properties were within the range expected for these mixes and all mixes in this study had fresh properties that would generally make them suitable for use in solidification and encapsulation of SSW based on contemporary compliance properties. The cured properties assessed were compressive strength and saturated hydraulic conductivity. One candidate mix contained polypropylene fibers proposed to improve compressive strength but were observed to clump in the waste form and caused their use to be questioned in the report.

1.6.3 2018 - Stabilization of Spherical Resorcinol Formaldehyde Resin in Grout-Maintenance of the Hanford Integrated Disposal Facility Performance Assessment FY 2018

This report was the follow-on to SRNL Phase 1 work (Section 1.6.2) and documented the results of studies performed by the SRNL to evaluate the stabilization of cation exchange sRF resin (Nichols et al. 2018).

[3] https://www.nrc.gov/reading-rm/doc-collections/cfr/part061/part061-0055.html

The sRF was previously considered as part of the LAW pretreatment system (LAWPS). Three different mixes were tested with different relative water to cementitious materials (CM = FA:OPC:BFS) (water:CM) ratios: 1) a CM of 75:25:0 with a water:CM of 0.29 (Hanford Grout Mix 5), 2) a CM of 45:10:45 with a water:CM of 0.45, and 3) a CM of 20:5:75 with a water:CM ratio of 0.45. Batches of each grout mix were prepared containing 10% and 30% volume fraction drained sRF resin. Selected fresh (flow, bleed, set time, and heat of hydration) and cured (hydraulic conductivity, water retention characteristics, compressive strength, dry bulk density, and porosity) properties were tested on waste forms from each of the formulations. The resulting waste forms met contemporary guidelines selected for fresh (flow and bleed) and cured properties (compressive strength). Additionally, hydraulic properties were similar to those recommended in the Solid Secondary Waste Data Package Supporting Hanford Integrated Disposal Facility Performance Assessment by Flach et al. (2016). Adsorption and desorption tests measured site specific Tc-99 and I-129 partition coefficients and the Tc-99 distribution coefficient (K_d) values for two of the formulations (w/ and w/o BFS) and these values were higher than those recommended by Flach et al. (2016) for the IDF PA. K_d values for I-129 were similar to those recommended by Flach et al. (2016) for the IDF PA.

1.6.4 2017 - Examples of Disposition Alternatives for Solid Secondary Waste

This report was a literature review of potential cradle-to-grave operational considerations and examples of waste form, container and disposal alternatives for SSW (Seitz 2017). Cradle-to-grave waste management considerations that could offer areas for improved efficiency included determination of whether the waste requires treatment for hazardous characteristics, considerations related to the need for compaction of debris, and general perspective regarding the ability to implement a “one-touch” philosophy for any SSW streams where the SSW is only handled once in the conversion to a waste form. Some examples of waste form and container alternatives for SSWs were provided.

1.6.5 2019 (Revision issued in 2020) - Development and Characterization of Cementitious Waste Forms for Immobilization of Granular Activated Carbon, Silver Mordenite, and HEPA Filter Media Solid Secondary Waste

The objectives of this work performed by PNNL (Asmussen et al. 2020) were to supply information related to: (1) the sorption/desorption behavior of key contaminants (Tc-99, iodide (I-), iodate (IO3-), and Hg) expected to be found in Hanford SSW (GAC, AgM, HEPA filters) in simulated grout pore water conditions; (2) the leaching behavior of I- from blended GAC/AgM in oxidized and reduced grouts; (3) the ability of two down-selected grout mixes to stabilize GAC/AgM upon curing; and (4) providing additional solid characterization data on candidate grout mixes to immobilize SSW. Two grout formulations were selected for this work to represent an oxidized environment (similar to Hanford grout mix 5, HGM-5) and a reduced environment (formulation similar to that used to create the Cast Stone waste form). The grout selections of a reduced and oxidized formulation from the testing in this report will inform selection of a grout formulation for GAC and AgM. Of note the presence of slag (reduced grout) was studied for its effect on iodine retention. As well, reduced grouts will oxidize with time. In addition, comparison data sets between an oxidized and reduced grout can facilitate modeling of a reduced grout that oxidizes with time. A third formulation tested, a mortar, known as Hanford grout mix 3 (HGM-3) containing dry sand, was also evaluated for hydraulic properties to provide a comparative case against the other two aggregate-free systems.

The major findings of this work are as follows. All grout mixes were able to incorporate and suspend the GAC and AgM. Fresh and cured properties were comparable to previous test efforts. Hydraulic conductivity was constant, $<10^{-9}$ cm/s, for waste forms containing up to 30 wt% GAC and AgM. The AgM appeared to be involved in some degree of reaction during curing, and Ag was observed to migrate into the hardened grout matrix. In general, the measured K_d aligned with the 2016 data package with the exception of a nonzero Kd for iodide to Cast Stone, lower K_d for iodide to GAC, high K_d for iodide to AgM, and a high Tc-99 K_d to GAC. Leach testing showed that observed diffusivity (D_{obs}) values for iodine in GAC containing samples were below the "optimistic" range in the data package while for AgM containing samples the D_{obs} were over four orders of magnitude lower. Lower D_{obs} indicates a waste form that will have lower release upon disposal - an ideal property.

1.6.6 2020 - Ultra-High-Performance Cementitious Composite (UHPCC) as Encapsulation Grout for Hanford Solid Secondary Waste

The purpose of this study performed by Washington State University (WSU) was to assess the characteristics of ultra-high-performance cement composite (UHPCC) as a possible encapsulation grout material for Hanford SSWs[4]. A UHPCC base mix (from literature) was used to measure physical properties and compared with baseline Hanford Grout Mix 3. Hanford Grout Mix 3 was chosen as the baseline for comparison because of the inclusion of sand (aggregate) as a component, which is also a component of UHPCC. The study also sought to optimize the UHPCC formulations to provide a formulation that will consist of easily available (locally sourced) components, with desirable fresh and physical properties along with cost-efficient production. Formulation optimization involved replacing the silica fume (SF) in the UHPCC with the more affordable FA and replacing the base sand particles with nominal-sized sand to lessen the effort of sieving with minimal impact on the UHPCC properties. The overall goal was to optimize the UHPCC formulation but still maintain the ultra-high strength and very low porosity that are characteristics of the UHPCC base formulation which can be beneficial to SSW disposal; the preliminary testing was promising in this regard.

1.6.7 2021 - Ultra-High-Performance Grout for Encapsulation of HEPA Filters

This report was a follow-on study to the WSU UHPCC report (Section 1.6.6) performed by the SRNL to determine the K_d and D_{obs} of Tc-99 and I-129 in what is now termed ultra-high-performance grout (UHPG) (Nichols et al. 2021). This grout was referred to as UHPG to preserve the relationship with UHPCC technology while recognizing it does not meet the definition of UHPCC and does not imply the required properties (i.e., compressive strength and flow) of UHPCC. Additional tests including compressive strength, bulk density, porosity, and water retention were also conducted. The low water to dry mix (w/dm) UHPG mix produced grout with low porosity and high bulk density. The UHPG required much higher pressure than the baseline grout to drain pores and allow air entry which is reflected in the moisture retention curve. Based on the low porosity, water retention characteristics and previously measured chloride penetration the size and number of connected pores in the UHPG can be expected to be smaller than in the baseline mix resulting in a low saturated hydraulic conductivity, $<1 \times 10^{-9}$ cm/sec.

Partitioning experiments were conducted under desorption conditions (as compared to adsorption conditions), making them more representative of a waste-form in the IDF environment scenario. Both grouts had similar K_d's for I-129 of ~100 mL/g. Based on aqueous Tc-99 concentrations in the UHPG desorption experiments, the Tc-99 appeared to be controlled by solubility. Physical stabilization of Tc-99 and I-129 was much better for the UHPG. I-129 and Tc-99 D_{obs} values for UHPG were orders of magnitude lower than baseline grout, e.g., Hanford Grout Mix 3. Results from testing of UHPG indicate it may have some advantages over traditional grout formulations for encapsulating contaminated HEPA filters. Specifically, the grout has low porosity, desirable moisture retention characteristics, low diffusivity, and favorable partition coefficients for Tc-99 and I-129. Recommendations to improve the technical defensibility and scale-up of the use of UHPG for waste forms containing radionuclides were provided.

[4] Hasan, TM, S Allena, L Gilbert, MR Choma. 2019 "Investigating Ultra-High Performance Cementitious Composite (UHPCC) as a Possible Encapsulation Grout for Hanford Solid Secondary Waste" Washington State University Tri-Cities, Richland, WA (Client report to WRPS)

1.6.8 2017-present – Other Relevant Literature (Non-WRPS Funded)

Kaplan et al. performed a study to: 1) quantify the effectiveness of two grout waste forms for disposing of the used silver iodine zeolite (AgIZ); and 2) determine the I speciation after leaching from AgIZ encapsulated in grout (Kaplan et al. 2019a). A 60-day kinetics batch experiment demonstrated that AgIZ encapsulated in slag-free grout was extremely effective at immobilizing I and Ag. However, AgIZ encapsulated in slag-containing grout was entirely ineffective at immobilizing I due to destabilization of the AgI. Thermodynamic calculations showed the strongly reducing conditions of the slag-containing system promoted the reductive dissolution of the AgI. The slag-free grout system was maintained under more oxidizing conditions and a minimal amount of I was released from the grout. In both grout systems, the aqueous I, originally added to the AgZ as I^-, was composed primarily of I^- and organo-iodine (org-I) and essentially no IO_3^- was detected. More org-I was detected in the slag-free than the slag-containing grout system because the high redox potential of the former system was more conducive to the formation of oxidized I species which may be intermediates in the covalent bonding of I with organic C in grout. Iodine K-edge X-ray absorption near edge structure (XANES) spectroscopy indicated that I likely existed exclusively as AgI in both samples. Together, these results indicate that subsurface grout disposal of AgIZ waste should be done under oxidizing conditions and that radioiodide released from AgIZ can undergo speciation transformations that have important implications on subsequent mobility and estimated risk.

In a related study Li et al. studied the efficacy of Ag-impregnated GAC (Ag-GAC) to remove I^-, IO_3^- and org-I from grout leachate. Grout materials containing the iodine-loaded Ag-GAC were characterized by iodine K-edge XANES and extended X-ray absorption fine structure (EXAFS) spectroscopy to provide insight into iodine stability and speciation in these waste forms (Li et al. 2019). The Ag-GAC was very effective at removing I^- and org-I, but ineffective at removing IO_3^- from slag-free grout leachate under oxic conditions. I^- or org-I removal was due to the formation of insoluble AgI(s) or Ag-org-I(s) on the Ag-GAC. When I^--loaded Ag-GAC material was cured with slag-free and slag grouts, I^- was released from AgI(s) to form a hydrated I^- species. Conversely, when org-I loaded Ag-GAC material was cured in the two grout formulations, no change was observed in the iodine speciation, indicating the org-I species remained bound to the Ag. Because little IO_3^- was bound to the Ag-GAC, it was not detectable in the grout. Thus, grout formulation and I speciation in the waste stream can significantly influence the effectiveness of the long-term disposal of radioiodine associated with Ag-GAC in grout waste forms.

Kaplan et al. also performed a study to determine iodine speciation in cementitious materials with slag (Grout+slag) and without slag (Grout–slag) and its impact on iodine immobilization (Kaplan et al. 2019b). Irrespective of which iodine species was amended to the aqueous phase, there were no significant differences in uptake-K_d values. However, when the various iodine species were hydrated with the grout, the release-K_d values (6.1–121.8 L/kg) were significantly greater than the uptake-K_d values. Both the iodine speciation ($I^- \ll$ org-I $\leq IO_3^-$) and grout formulation (Grout–slag < Grout+slag) had a significant impact on release-K_d values. In grout samples amended with I^- and IO_3^-, org-I was formed and comprised a majority of the iodine in the leachate after 28 days of equilibration. The formed org-I originated from organic carbon in the grout material (~1200 mg/kg C). For the first time, these studies demonstrated that multiple iodine species can co-exist simultaneously in grout porewater, the iodine species initially added to the grout can greatly affect iodine immobilization, and the addition of slag to the grout formulation increased iodine immobilization. These results may have important implications on radioiodine waste disposal however require further analysis with site-specific materials and with liquid wastes.

Dyer et al. developed an equilibrium reaction path model using The Geochemist's Workbench® (GWB) software to estimate the timescales (expressed as number of pore volumes) for chemical degradation of the reducing cementitious materials as indicated by changes in redox potential (Eh) and pH (Dyer 2018). The grout was modeled off of the properties of saltstone and SDU concrete. Three different GW infiltration scenarios were considered for the saltstone waste form simulations. GWB React model simulations were conducted for nine saltstone cases. The React simulations considered advective flow only and were executed in "flush" mode (i.e., an entering reactant fluid displaces an equal volume of previously equilibrated fluid from the system). This work is relevant to the modeling discussion related to SSW waste form in Section 4.2.

1.7 Summary of NRC Waste Form Degradation Document (2009)

Evaluating the possible failure or degradation mechanisms of waste forms has not been an exclusive interest to SSW. A review of failure mechanisms related to tank closure grouts was prepared in 2009 for the Nuclear Regulatory Commission (NRC) (Pabalan et al. 2009). The review was not specific to any disposal site but general activities to close the emptied tanks by filling the tanks, pipework, and concrete vaults with grout. In this case the cement-based material is expected to provide structural support, encapsulate and stabilize the residual tank waste and tank heel, act as a physical barrier to inhibit the flow of groundwater through the waste, and serve as a barrier to plant roots or to inadvertent intrusion by burrowing animals or humans drilling or excavating at the site. The review was driven by the acknowledgement that although much research has been done on the use of cement-based materials for immobilizing and stabilizing radioactive waste, the ability of these materials to maintain the low permeability and other properties necessary to retain radionuclides over the long time periods required for nuclear waste disposal is uncertain. This report reviewed cement fundamentals, covered degradation mechanisms, broadly classified into chemical and physical processes, and the role of the service environment in the degradation of cement-based materials. A similar list of mechanisms was considered in this SSW report. The NRC report also reviewed published modeling approaches.

1.8 NRC Technical Position on Waste Forms (1991)

The U.S. NRC developed and issued their initial technical position on low-level waste forms in 1983. This document provided both nuclear fuel cycle and non-nuclear fuel cycle waste generators guidance on waste forms and testing methods acceptable to NRC staff to demonstrate compliance with 10 Code of Federal Regulations (CFR) Part 61[5] waste form stability requirements (USNRC 1991). In 1991 the U.S. NRC (Technical Branch, Division of Low-Level Waste Management and Decommissioning) provided more comprehensive guidance on stabilization of low-level radioactive waste using cementitious (grout) waste forms via a revision (NRC Staff Technical Position titled "Technical Position on Waste Form (Revision 1)) and addition of Appendix A.

> "*Information and guidance on cement waste form specimen preparation, statistical sampling and analysis, waste characterization, process control program specimen preparation and examination, surveillance specimens and reporting of mishaps are provided in Appendix A.*"

Appendix A, Cement Stabilization, provides guidance to waste generators and processors intending to use cementitious materials such as portland and pozzolonic-type cements to solidify and stabilize low-level radioactive wastes in waste forms for disposal in shallow-land disposal sites, e.g., the Hanford IDF. Short descriptions of test procedures and recommended acceptance criteria for cementitious materials (grout) to solidify and stabilize low-level radioactive wastes follow below. It should be noted that the processes evaluated in this report do relate to these criteria, although this report will discuss the likelihood of occurrence in the IDF and does not necessarily negate the NRC guidance. The related topic in the SSW program or this report is given in parentheses:

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[5] 10CFR61. *Licensing Requirements for Land Disposal of Radioactive Wastes*. https://www.ecfr.gov/current/title-10/chapter-I/part-61?toc=1

- Grout Formulation – Demonstrate that the formulation compositions "…*of the waste form specimens used in the qualification testing adequately covers the range of waste compositions that will be encountered in the field.*", e.g., testing at maximum and minimum waste loading as well as target values. (This effort is a part of formulation development and scaled testing to determine maximum waste loadings).

- Compression – Demonstrate waste forms are structurally stable so as to maintain its physical dimensions under disposal conditions… "*a mean compressive strength equal to or greater than 500 psi is recommended for waste form specimens cured for a minimum of 28 days*." "*Compressive strengths of cement-stabilized waste forms should be determined in accordance with procedures described in ASTM Standard C39: Compressive Strength of Cylindrical Concrete Specimens (Ref. A2)*." (Compressive strength is regularly measured in laboratory testing).

- Thermal Cycling – Demonstrate waste form structural resistance to thermal degradation "*By cycling between the maximum and minimum temperatures called for in the test, any cracks initiated in the test specimen may propagate and eventually measurably weaken the waste form*." "*Test specimens suitable for performing compressive strength tests in accordance with ASTM C39 should be used. The specimens should be tested bare; i.e., not in a container. Specimens should be placed in the test chamber, and a series of 30 thermal cycles should be carried out in accordance with Section 5.4.1 through 5.4.4 of ASTM B553, with the additional proviso that the specimens should be allowed to come to thermal equilibrium at the high (60 degrees C) and low (-40 degrees C) temperature limits.*" "*If there are no significant visible defects, the test specimens should be subjected to compression strength testing in accordance with ASTM C39 and should have mean compressive strengths that are equal to or greater than 500 psi.*" (Calorimetry has been performed and Thermal Degradation is discussed in Section 3.2.2.1)

- Irradiation – Demonstrate waste form structural resistance to irradiation to a minimum dose of 10E+8 rads if "… *(1) the waste forms contain ion exchange resins or other organic media or (2) the expected cumulative dose on waste forms containing other materials is greater than 1OE+9 rads. Testing should be performed on specimens exposed to (1) 10^8 rads or the expected maximum dose greater than 10E+8 rads for waste forms that contain ion exchange resins or other organic media or (2) the expected maximum dose greater than 10^9 rads for other waste forms.*" "*Following the irradiation exposure the specimens should be examined visually and should be free of any evidence of significant cracking, spalling, or bulk disintegration; i.e., visible evidence of significant degradation would be indicative of failure of the irradiation test. If there are no significant visible defects (see Section II.C for discussion of significant degradation"), the test specimens should be subjected to compressive strength testing in accordance with ASTM C39 and should have mean compressive strengths that are equal to or greater than 500 psi.*" (Radiation effects are discussed in Section 3.2.5.2).

- Biodegradation – Demonstrate waste form structural resistance to microbial activity. "*Experience in biodegradation testing of cement-stabilized waste forms has shown (Refs. A7-A9), however, that they generally do not support fungal or bacterial growth. The principal reason for this appears to be that the fungi and microbes used in the G21 and G22 tests require a source of carbon for growth, and in the absence of any carbonaceous materials in the waste stream, there is no internal food source available for culture growth. Consequently, for cement-stabilized waste forms, biodegradation qualification testing need not be conducted unless the waste forms contain carbonaceous materials (e.g., ion exchange resins or oils)*." *"The test specimens (at least three for each organic waste stream formulation being qualified) should also be free of any evidence of significant cracking, spalling or bulk disintegration; i.e., visible evidence of significant degradation would be indicative of failure of the test. If there are no significant visible defects* *following the test exposures (see Section II.C of this Appendix for discussion of significant degradation%), the test specimens should be subjected to compression strength testing in accordance with ASTM C39 and should be shown to have mean compressive strengths equal to or greater than 500 psi."*(Biodegradation is discussed in Section 3.2.5.1)

- Leach Testing – Determine waste form resistance to leaching of radionuclides. "*The leach testing procedure specified in Section C.2.e. of the main body of this Technical Position is ANSI/ANS 16.1: Measurement of the Leachability of Solidified Low-Level Radioactive Wastes by a Short-Term Test Procedure (Ref. A10). ... The leachability index, as calculated in accordance with ANSI/ANS 16.1, should be greater than 6.0.*" Of note, although the standardized leach test leachant specified is deionized water, testing of other leachants is recommended to demonstrate radionuclide leach resistance to relevant leachant media to make sure the most aggressive leachant is tested. (Leach testing is regularly performed in laboratory testing to generate data to support the IDF PA.)

- Immersion Testing – At this time (1991), no standardized test method has been adopted by the NRC. However, immersion testing of cement-stabilized low-level waste is called out, and it should be performed for a minimum of 90 days on at least three (3) test specimens that have been cured for a minimum of 28 days. Leach testing should identify the most aggressive relevant immersion leachant media for use. "*Following immersion, the specimens should be examined visually and should be free of any evidence of significant cracking spalling, or bulk disintegration. If there are no significant visible defects see Section II.C of this Appendix for discussion of "significant degradation"), the specimens should be subjected to compressive strength testing in accordance with ASTM C39 and should have post-immersion mean compressive strengths that are equal to or greater than 500 psi and not less than 75 percent of the pre-immersion test (i.e., as-cured) mean compressive strength*." For post-immersion mean compressive strengths less than 75 percent of the pre-immersion testing results consult the NRC guidance. (Leach testing is regularly performed in laboratory testing to generate data to support the IDF PA.)

- Free Standing Liquids – Demonstrate compliance with 10 CFR 61 in terms of free liquid in waste disposal package. After low-level waste cement-stabilization "*…waste test specimens should have less than 0.5 percent by volume of the waste specimen volume as free liquids as measured using the method described in Appendix 2 of ANSI/ANS 55.1 (Ref. A13). Inasmuch as cement is an alkaline material, evidence of acidic free liquids is indicative of improper waste form preparation or curing. Therefore, any free liquid from cement-stabilized waste forms should have a minimum pH of 9*." (Free liquids measurements are regularly performed in laboratory testing.)

In addition to the laboratory-scale testing discussed above, full-scale testing is expected by the NRC. Full-scale testing is necessary to correlate full-size products to laboratory-scale test specimens. Full-scale testing will demonstrate mixing, curing, and storage of test specimens generated are sufficient to meet processing and disposal requirements. Once at this final waste form demonstration stage, researchers and engineers will need to review the "*Information and guidance on cement waste form specimen preparation, statistical sampling and analysis, waste characterization, process control program specimen preparation and examination, surveillance specimens and reporting of mishaps* [which] *are provided in Appendix A*."

2.0 Programmatic Approach and Objective

2.1 Programmatic Approach to SSW

There are two primary drivers for SSW work: (1) risk mitigation for the IDF PA; and (2) provide processing and formulation information for the stabilization and immobilization of SSW. First, SSW development and testing are needed to provide support for IDF PA maintenance to validate or update the literature-derived parameters used in the IDF PA and to provide data to minimize and manage uncertainties in the analysis. Second, testing results will establish grout formulations that are appropriate for effective stabilization and solidification of SSW that will be implemented for SSW waste form production operations.

Risk DFLAW-0206-T, "Secondary Solid Waste Management Less Than Adequate (Tank Farms and WTP)" is applicable. That is, if there is no storage or treatment pathway for SSW, then ILAW production will be delayed, and the mission duration will be increased. This plan addresses the identified risk and opportunity related to development and maturation of technology for the SSW streams. DFLAW SSW risks include the following:

- More waste volume will be generated and treated,
- Disposal and/or new treatment methods will be required above those planned,
- Waste may need to be remote-handled or may be transuranic,
- Waste may not be able to be disposed of at the IDF,
- Waste may exceed the volume or type of wastes that licensed commercial facilities can handle,
- No designated place to repackage waste is available, if required; and,
- Spent and failed melter disposal does not meet IDF waste acceptance criteria (WAC).

Therefore, the goal of the technology development in the WRPS SSW program is to develop, characterize, and recommend cementitious-based formulation for effective solidification and stabilization of SSW to enable disposal that supports timely and cost-effective completion of the RPP cleanup mission.

The following are benefits of the WRPS SSW waste form technology maturation program:

- Validates literature-based parameters and data that was provided to support the IDF PA and minimization/management of uncertainties in the results.
- Obtains long-term waste form performance data and information on degradation and release mechanisms to support the IDF PA and PA maintenance.
- Demonstrates that the waste form will have properties sufficient to meet the IDF WAC and IDF PA performance objectives.
- Demonstrates the equivalency of waste form performance through scale-up of the solidification process and with waste forms prepared with actual and/or spiked radioactive wastes.
- Establishes effective stabilization/immobilization of SSW, mitigating mission Risk DFLAW-0206-T, "Secondary Solid Waste Management Less Than Adequate (Tank Farms and WTP).
- Identifies waste form formulations that can be used to effectively encapsulate SSWs, even anticipating possible high-risk (could contain significant CoPC inventory) SSWs.

2.2 Evaluation Objective

The disposal of radioactive waste in a near-surface disposal facility on the Hanford Site in Southeast Washington State must meet U.S. Department of Energy (DOE) requirements for protection of human health and the environment for at least 1,000 years. A PA that uses computer models to simulate the fate and transport of radionuclides in the waste for 10,000 years and longer has been conducted, reviewed, and approved by DOE. Because there is limited data available to inform the models that evaluate the long-term performance of the grouted waste forms to retain radionuclides once disposed of at the Hanford IDF, the IDF PA made assumptions about the long-term ability of the waste forms to retain radionuclides for long periods of time. In the IDF PA (USDOE, 2018) the long-term performance of grouted waste streams did not degrade over time based on technical arguments provided in Flach et al. (2016). In Flach et al. (2016), aging of the waste form was correlated with the amount of water that interacts with the waste form. The assessment of potential degradation mechanisms indicated that SSW grout degradation from chemical attack was expected to be minimal under IDF disposal conditions due to the limited amount of recharge pore volumes that are expected to be exchanged within the waste form. In addition, although physical degradation of the waste form due to deformation cracking may be significant, the adverse effect of cracks was expected to be minimal with respect to moisture and solute transport due to the low saturation in the surrounding backfill material. The associated enhanced migration of oxygen into the waste form as the waste form aged was considered by assuming oxidizing conditions for redox-sensitive CoPCs. As a result, the potential effects of degradation of the waste form were simplified in the process modeling in the PA. Although not included, the possible consequences of other aging assumptions were evaluated in the PA and found to not significantly affect the results (USDOE (2018) Section 8.3.3, page 8-55).

A potential vulnerability of the PA is that the technical arguments used to describe waste form aging did not address all chemical, physical, and biological degradation processes that are known to influence cement materials and the capability of similar materials to retain radionuclides and hazardous chemicals over the long periods of time that DOE requires to protect human health and the environment. This lack of understanding results in uncertainty in the long-term contaminant release properties from these waste forms and often results in overly simplistic and conservative assumptions being used in PAs (e.g., all grout waste forms turn to rubble at 500 years). The present work builds upon the technical arguments regarding cement aging mechanisms provided in Flach et al. (2016) to enhance the defensibly of the assumed approach in the PA and identify information gaps that could affect the conclusion in the PA, i.e., that there is a reasonable expectation that the grouted secondary wastes will provide the necessary protection to human health and the environment for 1,000 years or more.

The overall objective of this work is to provide defensibility for the long-term performance of grouted Hanford SSW streams when disposed of in a near surface disposal facility on the Hanford Site. To improve the defensibility of the modeled performance, a review of the mechanisms that could affect the performance of the grouted waste forms to retain radionuclides and hazardous chemicals is needed. Providing further defense in depth for the long-term performance of the grouted waste forms is consistent with the technology maturation activities identified in Westcott et al. (2019), that are necessary to address the assumptions made in the PA. Specifically, this work addresses two areas identified for further technology maturation activities in the Maintenance Plan"

1) "Evaluate ongoing research on transport characteristics of cementitious materials using accelerated tests to approximate the effects of aging/alteration/weathering" and,

2) "Evaluate ongoing research on microbial effects on transport processes in cementitious materials".

2.3 Quality Assurance

This work was funded by WRPS under contract 349490, *Program Plan to Evaluate Grout Waste Form Durability and Degradation Mechanisms.* The work was conducted as part of PNNL Project 78623 and SRNL Project 55220-59.

This work was performed in accordance with the WRPS Waste Form Testing Program (WWFTP) quality assurance (QA) program. The WWFTP QA program is based on the requirements of NQA-1-2008, *Quality Assurance Requirements for Nuclear Facility Applications*, and NQA-1a-2009, *Addenda to ASME NQA-1-2008 Quality Assurance Requirements for Nuclear Facility Applications*, graded on the approach presented in NQA-1-2008, Part IV, Subpart 4.2, "Guidance on Graded Application of Quality Assurance (QA) for Nuclear-Related Research and Development." The WWFTP QA program consists of the WWFTP Quality Assurance Plan (QA-WWFTP-001) and associated procedures that provide detailed instructions for implementing NQA-1 requirements for research and development work.

The WWFTP QA Program works in conjunction with PNNL's laboratory-level Quality Management Program, which is based upon the requirements as defined in the DOE Order 414.1D, *Quality Assurance,* and 10 CFR 830, *Nuclear Safety Management*, Subpart A, "Quality Assurance Requirements." Performance of this work and preparation of this report were assigned the technology level "Applied Research". All staff members contributing to the work have technical expertise in the subject matter and received QA training before performing quality-affecting work. The "Applied Research" technology level provides adequate controls to ensure that the activities were performed correctly and that all client QA expectations were addressed in performing the work.

3.0 Mechanisms and Processes for Grout Aging

The American Concrete Institute (ACI) defines durability as "*the ability of a material to resist weathering action, chemical attack, abrasion and other conditions of service*".[6] As opposed to concrete structures, waste form durability also includes the material's ability to retain CoPCs. A durable waste form retains CoPCs to limit releases at a rate that is protective of the surrounding environment. Aging of grout waste forms may degrade the properties leading to accelerated release of CoPCs but it could also improve other properties influencing CoPC retention. As noted in Section 1.5, predicting whether a grout waste form will remain durable throughout a 10,000-year life-cycle requires a comprehensive understanding of the different aging mechanisms that improve or degrade release of CoPCs. Such understanding would then lead to more carefully designed waste forms and disposal strategies that reduce the potential for identified significant degradation processes.

This section presents an overview of degradation mechanisms and processes expected to occur in the IDF and affect the durability of SSW grout waste forms. For the purpose of this report, we are defining process and mechanism as follows:

Process: a material evolution or environmental interaction with the waste form matrix that causes a mechanism. These can be physical (e.g., freeze thaw) or chemical (e.g., oxidation) in nature.

Mechanism: leads to a behavior or a bulk change in the waste form that is different from the unaltered state and projected aging. Examples include cracking or chemical changes to the radionuclides/CoPC.

Processes can be initiated through a variety of environmental conditions or the waste form processing history but can be mitigated. For example, adequate curing can reduce delayed ettringite attack or careful selection of aggregate can reduce alkali silica reactions, etc. These factors will be discussed below. Also, grout waste forms are designed to have low permeability and in turn low leach rates of CoPCs to minimize their release to the surrounding environment. Thus, grout formulation designs may aim to further minimize the potential for degradation by minimizing porosity and permeability through changes in the grout mix that: (1) target specific bulk chemistries, (2) consider the mineralogy and internal surface chemistry, and/or (3) minimize corrodent accessibility. However, these properties can also be altered by the various processes leading to mechanistic changes.

3.1 Mechanism and Evaluation Layout

3.1.1 Likelihood of Mechanisms and Processes

The review team considered a list of possible mechanisms and subsequent processes that can influence SSW waste forms to screen for relevancy. The likelihood of a processes or mechanism occurring in the IDF was judged against the prevalence of necessary conditions for the mechanism/process and the susceptibility of the individual grout formulations. Consideration was also given to four distinct time frames listed below. In all time frames there would be open exchange to some degree between the atmosphere and/or water:

[6] American Concrete Institute. 2021. Concrete Terminology. CTI-21. Available at: https://www.concrete.org/store/productdetail.aspx?ItemID=CT21

1) Cured/predisposal (0-1 years after fabrication) – Waste form from slurry state through young curing. Waste form exposed to the environment and container assumed to be intact.

2) Pre-closure (1-50 years after fabrication) – Waste form in IDF and under backfill but no cap on IDF and water infiltration is higher. Corrosion of waste form container starts.

3) Post-closure (50-550 years after fabrication) – The IDF is filled, the cap and liner are in place and water infiltration is low and container corrosion continues.

4) Long-term – Cap Failure (>550 years) – After closure, loss of institutional control and cap/liner failure leading to higher water infiltration rates. Waste form container presumed to be fully corroded.

These four stages are described in more detail in Section 3.1.2. The review team of subject matter experts (SMEs) compiled an initial list of possible mechanisms and processes that may influence SSW grout waste forms based on prior durability reports (Tovena 2002, Pabalan et al. 2009, Flach et al. 2016a). The list of mechanisms and processes compiled is shown in Table 3. These processes are presented for their relevancy within the four distinct time frames.

The SMEs were provided complete freedom to provide their own assessment of each mechanism and process. Process specific information was gathered to describe the process, provide the current state of literature, the likelihood of a process to occur during the time frame in the IDF based on assumed conditions, its applicability to grout/mortar and UHPG formulations, and how to handle R&D or modeling gaps. A summary of these assessments is provided in Section 3.2.

Table 3 – Summary of the proposed degradation mechanisms and processes evaluated for SSW waste forms in the IDF. These columns list if the mechanism/process relevant to the grout (cured) or to the encapsulated SSW (in the cured grout). Green is relevant, grey is not relevant. The timeframe where the process is likely to occur is also listed.

Mechanism	**Processes**	**Component Involved**		**Active Timeframe**
		Involves the Grout	***Involves the Encapsulated SSW***	
3.2.1 Unaltered Evolution	*Natural and Predicting Evolution*			All
3.2.2 Environmental Driven Cracking	*Deformation/Cracking (Moisture driven)*			> 1 year
	Deformation/Cracking (Thermal driven)			0-1 year
	Dimensional Change of SSW			All
	Freeze Thaw Cycling			0-50 years
	Alkali-Silica Reactions (ASR)			>50 years
	Corrosion of Steel			All
	Phase Segregation (aggregate or SSW)			0 – 28 days
	Rheological Properties/Molding Issues			0 – 28 days
	Creep – Storage Mechanical Compression			>50 years
	Scaling			>50 years
3.2.3 Cracking and Chemical Change from Mineral Evolution	*Carbonation*			>1 year
	Ca Leaching			>50 years
	Sulfate Attack			>50 years
	Delayed Ettringite Formation (DEF)			>50 years
3.2.4 Chemical/Waste Specific	*Reoxidation*			All
	Radionuclide Leaching (general)			All
	Dissolution of CoPC			All
	RCRA Metal Leaching (e.g., Ag-M)			>1 year
3.2.5 Environmental Changes	*Microorganisms*			>50 years
	Radiation Damage			All
	Fire Resistance			All
	Acid Attack			>1 year

3.1.2 Assumptions

Solid secondary waste forms will go through several stages during their life cycle that range in duration from days to centuries, Figure 5. Physical and chemical changes that occur in an earlier stage may impact the performance of a waste form in a later stage. For example, cracking that occurs early increases saturated hydraulic conductivity and the potential for leaching during a later stage due to increased water infiltration. The conditions within the IDF may vary during these timeframes. A summary of IDF conditions considered in this evaluation is given in Table 4 for the various time frames. These conditions were used in the considerations by the review team to assess the likelihood of a failure mechanism to occur within the IDF within a set time frame.

The IDF is expected to receive SSW for 50 years prior to closure by installation of a cap. Stages in the SSW disposal lifecycle can thus be combined into phases based primarily on operating conditions of SSW disposal. The first phase runs from 0-1 years for the waste form and covers the period wherein the waste form is fabricated, sealed in its container, staged and then moved to the IDF. The importance of mitigating early degradation during the stages prior to being buried in the IDF are illustrated in Flach (2018)'s related study of a disposal vault concrete floor that developed modified material properties leading to observable cracks by time of use in flow and transport simulations.

The second stage runs 1-50 years and covers the period from preparation of the first SSW waste form (t=1 yr) through storage in the open IDF (with backfill) until completion of disposal in the IDF and the IDF is capped closed (t=50 yr). During this period SSW waste form containers are exposed to the open environment and subject to atmospheric temperature fluctuations, infiltration of rainfall, and atmospheric levels of O_2 and CO_2.

The third stage begins with completion of the cap on the IDF and extends until the cap fails, covering years 50 – 550. It is at this time the period covered by the IDF PA begins. During this period the SSW is exposed to relatively stable soil temperature (~15 ºC), low saturation of the surrounding sediment beneath the cap, reduced O_2 levels and increased CO_2 levels relative to the first phase. Exposure to moisture is greatly reduced during this phase compared to the first phase, however the chemistry of the moisture is expected to be changing due to the presence of other waste forms and equilibration with the backfill and corrosion of the container will occur.

The final stage (550 - 10,000 years) begins when the IDF cap and liner are assumed to fail in the IDF PA resulting in increased moisture input and flux of atmospheric gasses, i.e., O_2, CO_2, and N_2. The primary differences between this phase and the second are the increase in moisture input and flux of atmospheric gasses and the container is corroded. Degradation processes generally result in cracking of the matrix in grout and separation of paste from aggregates and solid waste allowing moisture to enter the waste form causing further degradation and increased CoPCs release to the surrounding environment.

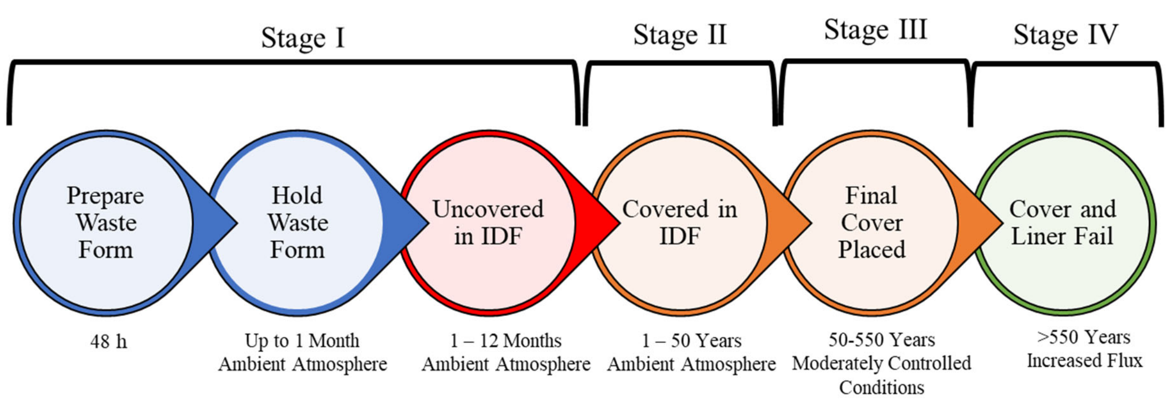

Figure 5. Stages in the SSW disposal life cycle.

Table 4 – Comparison of the properties of the IDF environment during the four timeframes considered in this evaluation.

Condition	**Cured/Pre-disposal (0-1 years)**	**Pre-closure, Assume Under Backfill (1-50 years)**	**Post Closure (50-550 years)**	**Long-term – Cap Has Failed (>550 years)**
Temperature	-0.5 °C – 25.1 °C (average) Table 3-1 of RPP-RPT-59958 Can assume 0.2 °C change per decade for climate change (page 3-24 of RPP-RPT-59958)	-0.5 °C – 25.1 °C (average) Table 3-1 of RPP-RPT-59958 Can assume 0.2 °C change per decade for climate change (page 3-24 of RPP-RPT-59958)	15 °C (average) from Figure 3.2 of PNL-7558 (note, not well documented)	15 °C (average) from Figure 3.2 of PNL-7558 (note, not well documented)
O_2	Atmospheric	2.65E-4 mol/L (Table 2 of WSRC-RP-2003-00362) From page 5-64 of RPP-RPT-59958. *The reference case of IDF near-field conditions (RPP-RPT-59341) assumes that partial pressures of reactive gas species CO2(g) and O2(g) are fixed at atmospheric values.*	2.65E-4 mol/L (Table 2 of WSRC-RP-2003-00362) From page 5-64 of RPP-RPT-59958. *The reference case of IDF near-field conditions (RPP-RPT-59341) assumes that partial pressures of reactive gas species CO2(g) and O2(g) are fixed at atmospheric values.*	2.65E-4 mol/L (Table 2 of WSRC-RP-2003-00362) From page 5-64 of RPP-RPT-59958. *The reference case of IDF near-field conditions (RPP-RPT-59341) assumes that partial pressures of reactive gas species CO2(g) and O2(g) are fixed at atmospheric values.*
[CO_3] (as CO_2 fixed)	Atmospheric	3E-4 mol/L Page B-8 of RPP-RPT-59341	3E-4 mol/L Page B-8 of RPP-RPT-59341	3E-4 mol/L Page B-8 of RPP-RPT-59341
[SO_4]	N/A	Not in PA lithology card, PNNL-14121 shows ~200 mg/L in H2 formation on Page 4-25	Not in PA lithology card, PNNL-14121 shows ~200 mg/L in H2 formation on Page 4-25	Not in PA lithology card, PNNL-14121 shows ~200 mg/L in H2 formation on Pg 4-25
[Ca]	N/A	1E-7 mol/L Page B-8 of RPP-RPT-59341	1E-7 mol/L Page B-8 of RPP-RPT-59341	1E-7 mol/L Page B-8 of RPP-RPT-59341
[Si]	N/A	1E-5 mol/L (as SiO_2) Page B-8 of RPP-RPT-59341	1E-5 mol/L (as SiO_2) Page B-8 of RPP-RPT-59341	1E-5 mol/L (as SiO_2) Page B-8 of RPP-RPT-59341

Condition	Cured/Pre-disposal (0-1 years)	Pre-closure, Assume Under Backfill (1-50 years)	Post Closure (50-550 years)	Long-term – Cap Has Failed (>550 years)
[Al]	N/A	1E-6 mol/L Page B-8 of RPP-RPT-59341	1E-6 mol/L Page B-8 of RPP-RPT-59341	1E-6 mol/L Page B-8 of RPP-RPT-59341
pH	Dependent on grout formulation	pH 7 (fixed) Page B-8 of RPP-RPT-59341 cites pH 6.97 to 7.74	pH 7 (fixed) Page B-8 of RPP-RPT-59341 cites pH 6.97 to 7.74	pH 7 (fixed) Page B-8 of RPP-RPT-59341 cites pH 6.97 to 7.74
Eh	(Slag) reducing (non-slag) oxidizing	TBD	TBD	TBD
Infiltration Rate/Cycles	18.14 cm/yr (Annual avg precipitation) Table 3-2 RPP-RPT-59958	18.14 cm/yr (Annual avg precipitation) Table 3-2 RPP-RPT-59958	0.4 mm/yr	1.7 mm/yr - 3.5 mm/yr RPP-RPT-59958
Hydraulic Properties (K_{sat} etc.)	N/A	4.91E-3 cm/s from Page B-2 of RPP-RPT-59341 (Backfill soil value)	4.91E-3 cm/s from Page B-2 of RPP-RPT-59341 (Backfill soil value)	4.91E-3 cm/s from Page B-2 of RPP-RPT-59341 (Backfill soil value)
Saturation	N/A	0.065 cm^{-1} (nonhysteric van Genuchten) Page B-2 of RPP-RPT-59341	0.065 cm^{-1} (nonhysteric van Genuchten) Page B-2 of RPP-RPT-59341	0.065 cm^{-1} (nonhysteric van Genuchten) Page B-2 of RPP-RPT-59341
[Mg], [Fe]	N/A	Fe (1E-10 mol/L) Page B-8 of RPP-RPT-59958 Mg (~40 mg/L) Table 4.4 of PNNL-14121	Fe (1E-10 mol/L) Page B-8 of RPP-RPT-59958	Fe (1E-10 mol/L) Page B-8 of RPP-RPT-59958
Container State	Steel	Steel	Corroding	Corroded
RPP-RPT-59958 (USDOE, 2018) PNL-7558 (Campbell et al. 1990) WSRC-RP-2003-00362 (Kaplan et al. 2003) RPP-RPT-59341 (Intera 2016) PNNL-14121 (Lindenmeier et al. 2003)				

3.1.3 Hanford SSW Grouts

Hanford Grout Mix 5 (HGM-5) is currently the baseline grout being considered for stabilization of SSW at the Hanford Site; however, a mortar mix known as Hanford Grout Mix 3 (HGM-3) has also been considered. More recently results from a new UHPG mix indicated it may be a good alternative to HGM-5 due to its low porosity and diffusivity. Several laboratory studies have been completed to characterize the initial properties of HGM-5 and HGM-3 (Nichols et al. 2017, Asmussen et al. 2020), and UHPG (Nichols et al. 2021). Table 5 compares the formulations for HGM-5, HGM-3, and UHPG. For evaluation purposes, the mechanisms and processes potential impacts on UHPG was assessed separately from the grout (HGM-5) and mortar (HGM-3).

Table 5. Grout formulations under consideration for use in SSW waste forms to be disposed of in the IDF.

Mix	H_2O:CM[a] (m/m%)	H_2O:DM[b] (m/m%)	FA/OPC/BFS/Sand (m/m%)	Admixture:H_20 (m/m%)
HGM-5	45	45	20/5/75/0	none
HGM-3	41	41	14/14/0/72	none
UHPG	18[a]	7[b]	6/17/17/6	24[c]

Note: [a] CM = OPC+FA+BFS, [b] DM = OPC+FA+BFS+Sand, [c] BASF Masterglenium 3030

3.2 Mechanism and Process Descriptions

The degradation of cementitious materials can occur through several mechanisms driven by different processes (Table 3). This section and its subsections will provide information on the mechanisms and processes that were considered in this work for their potential to impact SSW grout waste forms in the IDF.

3.2.1 Mechanism: Unaltered Evolution

A grout waste form is a dynamic system that continually evolves and interacts with its environment over time. A schematic showing the evolution of grout waste forms is shown in Figure 6. Upon combining the dry ingredients with water, a slurry is generated and the formation of the mineral assemblages that will create the hardened grout begins (t=0). These mineral assemblages continue to form throughout the curing process. At 28 days it is commonly presumed that the grout is now cured and in its young state (t=28 days). However, a common misconception is the grout is in its final state and static beyond this point. Instead, the grout matrix (e.g., the CSH) will continue to equilibrate, mineral evolution will continue, and the interior pore water will evolve. These processes continue through the time periods described in Figure 5. However, environmental factors and conditions within the waste form can induce additional processes that may alter the waste form beyond the natural evolution. It is these other processes that were considered in this effort and natural evolution was assumed to occur regardless. The following sections will present these various mechanisms and potential processes that could lead to the identified degradation mechanism initiating.

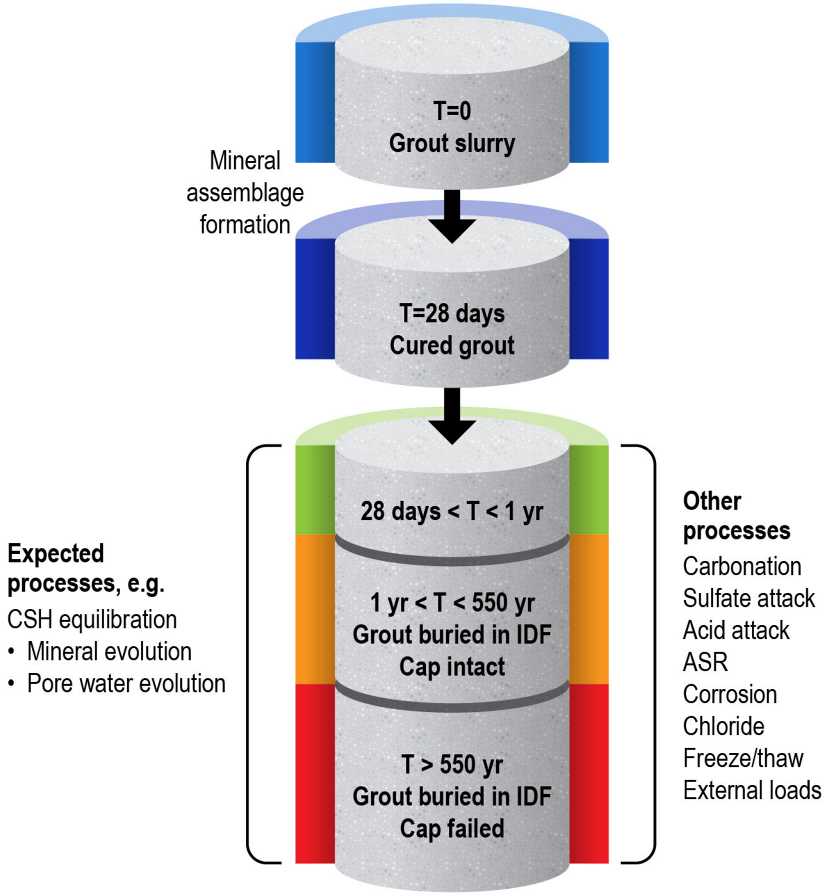

Figure 6 – Schematic of the general lifetime, natural evolution (expected process) and the processes considered in this work (other processes) of a grouted waste form in the IDF. (CSH = calcium silica hydrate, ASR = alkali silica reaction).

3.2.2 Mechanism: Cracking

The most common mode of physical degradation in cementitious materials is the generation of cracks and fractures. In fact, cracking was highlighted in the 2016 SSW data package (Flach et al. 2016) as a main possible failure pathway leading to CoPC release. However, the impacts of cracking on SSW grout hydraulic transport properties were estimated in the 2016 report to be minimal. in the IDF was est. The justifications from the SSW data package for this assertion was as follows: Saturated cracks can alter the physical properties controlling the hydraulic parameters of the waste form (permeability, diffusion coefficient). However, for cracks with apertures below a certain threshold size, minimal impact may be observed. In unsaturated conditions, modest capillary tension is typically required to dehydrate cracks, which can negate their influence on bulk flow and transport properties. Previous works suggest apertures >100 µm are required to impact waste form hydraulic and transport properties, which control CoPC retention (Ismail et al. 2004, Ismail et al. 2008). Within the data package a projection for IDF conditions predicted capillary pressures of approximately 1000 cm. At capillary pressures > 15 cm the cracks are considered unsaturated; therefore, limited water transport through the cracks is expected. Although limited, unsaturated cracks are still able to transport water and dissolved species through other mechanisms (e.g., film flow). For a grout waste form with macrocracking (cracks visible to the naked eye), theoretical studies of granular material surrogates suggest that a significantly fractured grout will not exceed a hydraulic conductivity of 1.0×10^{-9} cm/s; however, no direct testing of unsaturated grout waste forms backs this hypothesis. An upper limit of 1.0×10^{-8} cm^2/s was therefore proposed for a diffusion coefficient. With the low infiltration rate of the IDF no advective flow is expected.

From these analyses, the SSW data package originally proposed that the intact properties recommended will remain largely valid under physical degradation conditions, provided the capillary tension head in the subsurface exceeds approximately 1000 cm. It must be understood though that unsaturated cracks will enhance gas-phase transport, which could indirectly influence aqueous transport through altered Eh or pH conditions affecting CoPC sorption and/or solid phase solubility and reducing conditions. However, at modestly lower capillary suctions, e.g., capillary pressures equal to 100s of centimeters, the effects of fractures are projected to be significant compared to an intact matrix under the same conditions (Jensen et al. 1996, Lee et al. 2006, Bentz 2007). Pore size can change throughout the lifetime of the waste form (and is also altered by w/dm and cement fineness) and impact the capillary behavior. Considering the sensitivity of the above analyses to capillary tension, general uncertainty in the analysis methods, and reliance on surrogate behaviors rather than direct measurements, the conclusion that cracks will have little direct impact on aqueous transport for capillary pressures ≥ 1000 cm is considered tentative. However, this report was prepared to assess areas where improved confidence can be put around assumptions such as these.

As cracking can occur at any stage of a waste form's life, this mechanism is a continual source of uncertainty in predicting the performance of grout waste forms with the effect dependent on the process that leads to cracking (described below in subsections 3.2.2.1 to **Error! Reference source not found.**). To complicate this matter, cracks are generally characterized as either microcracks (< 0.1 mm aperture) and macrocracks (visible to the naked eye) (Pabalan, 2009). Works to date have often focused on "standard" formulations (e.g., containing OPC, FA) where there is significant porosity in the waste form and microcracks will not have significant impact (Pabalan, 2009). However, the low permeability target of the UHPG may be impacted more by microcracks, though little data is available on the impact of cracks on CoPC release from UHPGs. Works have shown that the use of silica fume to reduce pore space induces higher capillary suction (McGrath et al. 1990, Jensen et al. 1996). Modeling of cracks within grout waste forms can be handled with different approaches for microcracks and macrocracks as discussed below.

Microcracks

Due to the ubiquitous nature of microcracks, their influence on fluid permeation and chemical diffusion is likely to be included with uncracked properties in laboratory measurements of concrete permeability and diffusion coefficients (Young 1988, Truc et al. 2000, Samson et al. 2005). Pabalan et al. (2009) stated that segregating the role of microcracks from the bulk waste form for radionuclide release may not always be appropriate for several reasons.

- *"The residence time of fluids within the waste form matrix can be reduced from preferential flow through microcracks."*
- *"The concentration of radionuclides in the microcracks may be overestimated as their transport from the waste matrix is likely diffusion limited."*
- *"Radionuclides traveling through the microcracks may not be immobilized, because chemical equilibrium with the matrix is not achieved."*
- *"Laboratory measurements already likely include the influence of microcracks."*

If microcracks are explicitly represented in a model, then the intact matrix flow and transport values should likely be lowered to exclude the influence of microcracks. The impacts of microcracking on CoPC release will likely be greater for waste forms where impermeability is targeted (e.g., UHPG) which accentuates the need to understand and model the phenomena separately from pore diffusion

Macrocracks

Macrocracks in a cured grout waste form can result from a variety of processes, described in the following sections or through the expansion of microcracks. While laboratory data likely includes the influence of ubiquitous microcracks, the macrocrack influence must be studied separately for input data to models and coupled with the occurrence rate of the processes which lead to cracking. The presence of macrocracks can influence the hydraulic conductivity and release properties by many orders of magnitude depending on crack size. As macrocracks have higher permeability than microcracks and the grout pores, most fluid flow through the grout will occur through macrocracks if present. Any macrocracks could act as rapid pathways into the waste form for water and air and out of the waste form for CoPCs. However, macrocracks can generate bypassing pathways that limit contact of infiltrating water with the encapsulated SSW. As such, scale effects of cracks should be considered in the development of transport modeling, with macrocracks modeled independently from microcracks.

From this standpoint, the primary R&D needs to further our ability to adequately model SSW waste forms are to understand the influence of microcrack progression in low permeability grouts and measurement of transport properties in candidate waste forms with macrocracks. The likelihood of macrocrack development will be controlled by the occurrence rate of the various degradation processes assessed below.

3.2.2.1 Process: Deformation Cracking (Wet Dry Cycling and Thermal Driven)

Cracking due to wetting and drying cycles is a common process that can affect the durability of cementitious materials. Drying causes removal of water from the pores, stimulating shrinkage and micro-cracking − both non-reversible changes. Subsequent wetting leads to regaining water and any swelling may further drive cracking (Wu et al. 2017a, Rangel et al. 2020). All formulations considered in this report could be susceptible to wet-dry cycling. The type and rate of moisture transport is influenced by the degree of saturation (Houst et al. 1994, Wong et al. 2007). For example, wet-dry cycling induces sorption hysteresis where the hygral state of cementitious materials exhibits a complex path (history) dependent behavior (Baroghel-Bouny 2007, Wu et al. 2017b). A separate report (Li et al. 2008) verified through modeling that the transport of moisture during drying is driven by evaporation and diffusion, while the transport of moisture during wetting is driven by absorption. To model wet-dry cycling effects, the change in waste form structure and properties upon cycling needs to be assessed to incorporate adequately modeled processes into the PA. For example, ASTM D559/D559M *Standard Test Methods for Wetting and Drying Compacted Soil-Cement Mixture* could be a potential basis for a development of a relevant test method for encapsulated SSW grout waste forms (ASTM D559 / D559M-15). Little discussion of wet-dry cycling on SSW waste forms was covered in the 2016 data package, limited to the following:

> "*Furthermore, drying time scales as the square of the characteristic length. For example, exposure conditions that would dry a centimeter-scale specimen over one day would require three decades (100^2 days) to dry a meter-scale SSW waste form in the same manner.*"

In deep nuclear waste repositories, changes in elevation of the groundwater can lead to flooding and allow water to infiltrate and contact the immobilized waste and subsequent drying if levels drop (Pabalan et al. 2009). However, an arid nuclear waste repository location could escape wetting for several hundreds of years (MacKenzie et al. 1985). Under the protective closure cap of the IDF and the use of metal containers to dispose of the SSW grout waste forms, the chances of the SSW waste form being exposed to wet-dry cycling is significantly reduced. Finally, despite surface precipitation rates that make the Hanford surface susceptible to several severe moisture loss and ingress cycles, at the depth of the IDF the moisture profile is expected to be uniform, making wet-dry cycling unlikely (Mallgren, 2019, Fayer et al. 1995).

Cement pastes used in the SSW waste forms can expand when heat is generated early during the curing phase. Specifically, stresses arise from thermal gradients generated during early hydration and formation of the cementing mineral phases. When this thermal gradient creates significantly greater temperatures at the center of a waste form compared to the exterior this process can lead to cracking. For example, thermal-induced water loss and drying can cause severe cracking. Based on lab-scale samples, thermally induced deformation and cracking is not expected due to the low temperatures generated during curing. In these tests, isothermal calorimetry is commonly used to measure heat generation as a function of time. However, scaled testing of SSW waste forms with temperature profiling and coupled solids analysis should be used to confirm any scaling effects from thermal stresses are captured in future PAs. Especially since total heat generation will increase at larger scales and the thermal gradient will be more pronounced.

Despite the potential impact of wet-dry cycling on cracking and the susceptibility of all formulations considered, as discussed above, the likelihood of wet-dry cycling occurring in the IDF is low. If needed, to model wet-dry cycling effects, the change in waste form structure and properties throughout these cycles needs to be assessed to incorporate adequately modeled processes in any simulation. For example, ASTM Method D559 / D559M-15 Standard Test Methods for Wetting and Drying Compacted Soil-Cement Mixtures could be used to study wet-dry cycling if required. Thermal stresses, also having a low likelihood, will be confirmed in the production of SSW waste form samples at scale with appropriate temperature profiling and solids characterization.

3.2.2.2 Process: SSW Dimensional Change

Degradation of grout waste forms often focuses on the physical and chemical processes originating from the grout matrix that led to mechanisms that increase the release of CoPCs. However, encapsulated SSW can also degrade and change with both time and the evolving matrix conditions. The non-debris SSW (e.g., resin, GAC) are not in equilibrium with the grout pore water when the waste form is fabricated. Coming to equilibrium may change the volume or properties of the SSW. These changes may include dimensional change from shrinking or swelling of the SSW. Figure 7 shows an example of sRF solidified in HGM5 where the crack around the resin bead is separating the bead from the bulk grout. This crack is believed to have formed due to shrinking of the resin caused by a substitution where the resin is originally in its H^+ form then converts to a Ca^{2+} when it equilibrated with Ca^{2+} rich pore water in the grout and shrinks (Nichols et al. 2018). It should be noted that sRF resin is not a part of DFLAW operations however other organic based resins being under testing for radionuclide removal from liquid wastes.

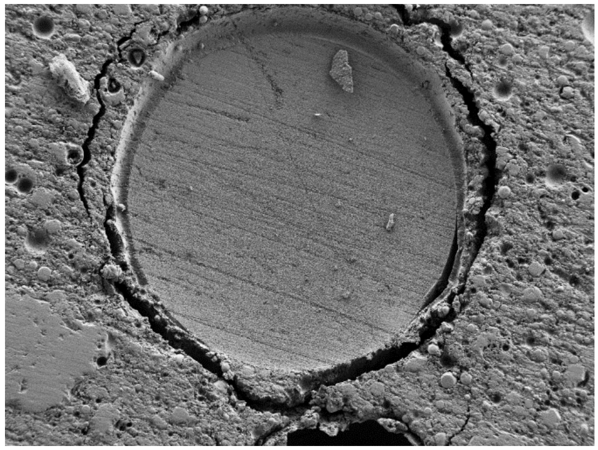

Figure 7. H^+ form of the sRF resin solidified in HGM-5 grout.

This level of dimensional change can induce void space (macrocracks) around a shrunken particle or drive cracking in the cured matrix due to particle swelling. All grout formulations considered may be susceptible to the resulting effects of SSW dimensional change. While organic based resins would be most susceptible to swelling/shrinking due to their water content, other non-debris SSW could also change in size due to degradation or hydration. The 2016 SSW data package did not consider the possible effects of SSW dimensional change. The SSW has only been observed in cursory laboratory observations and little data on the resulting effects has been produced. If needed, the final form of non-debris SSW for disposal can be modified (e.g., resin cation substitution) to reduce the potential for dimensional change. Studies of dimensional change in SSWs, should focus on monitoring SSWs within grout waste forms in different solution chemistries relevant to waste forms compatible with the IDF. Various water contents in the waste forms should also be assessed. The resulting impact on waste form properties based on the various states of the SSW would then be evaluated.

All formulations considered may be susceptible to SSW dimensional change, but the likelihood of this process occurring depends on the SSW type but is high for some. The rate of change and subsequent impact on the waste form is unknown. Studies equilibrating grout pore water with SSW (both bare and in grout) can provide insight in the severity of the potential for this form of degradation.

3.2.2.3 Process: Freeze Thaw Degradation

As the name implies, freeze-thaw cycling involves the exposure of a waste form to a wide temperature range and can lead to alteration of the physical state of the waste form. Unlike thermal cracking, which pertains only to thermal gradients generated in the waste form during curing (< first 28 days), freeze-thaw degradation involves cyclic temperature changes caused by the environment. Dimensional changes of water (9 % expansion of water when it freezes) trapped in the waste form pores can induce stresses leading to scaling and cracks if the stresses exceed the tensile strength of the material when freezing. During the thaw stage, more water from the environment can infiltrate the waste form, filling the cracks and pores to induce leaching of the cementitious hydrates and increase the amount of water present for the next freeze cycle. The more freeze-thaw cycles that happen, the more likely cracks develop and erode the matrix and potentially expanding pathways for leaching and decrease mechanical strength. Depending on the regularity and severity of freeze-thaw cycles, the waste form composition, and other applied stresses on the system, the impact of freeze-thaw cycling can be seen as early as one year (Tovena 2002). Freeze-thaw cycling has a greater effect on cement matrix durability when the w/dm ratio is high and the cement young (Wei et al.

2020). When exposed to freeze-thaw cycling at an early age, the waste form paste is not able to recover the pore structure achieved by continuous hydration. According to Cai and Liu, for OPC the freezing rate of a concrete pore solution is larger at temperatures > -10 ºC, meaning that frost damage mainly occurs above -10 °C (Cai et al. 1998).

Southeastern Washington State falls within the general geographic location where freeze-thaw failure is common, see Figure 8. Within the IDF freeze-thaw induced changes to the waste form will most likely occur during the early life of the waste form while it is in Stages 1 and 2 (up to 50 years). After closure of the IDF, the temperature of the Hanford subsurface remains close to 15 ºC. Due to the expected impact during the early life of the waste form, the 2016 SSW data package (Flach et al. 2106) recommends freeze-thaw effects on performance be considered

> *"A number of potential considerations have been identified that could influence the cementitious materials that will need to be addressed (e.g., initial saturation of a cured cementitious material, freeze-thaw, cellulose materials, microbial influences, impact of non-debris waste streams on the properties of a solidified cementitious waste form, controlling factors for release of Tc from a solidified waste form)."*

Figure 8 – Map showing the prevalence of freeze-thaw exposure on cement and concrete systems.

Dry ingredients used to formulate the SSW grout waste forms will have an impact on the degradation caused by freeze-thaw cycling. For instance, the use of limestone (Tsivilis et al. 2000, Dhir et al. 2007, Adu-Amankwah et al. 2021) and slag (Osborne 1999, Bleszynski et al. 2002) in grout materials, without the use of air entrainment admixes, are more susceptible to freeze-thaw damage. The addition of an air-entraining agent into cement paste is a way to limit freeze-thaw damage by creating air voids that accommodate volumetric expansion (Powers 1949); however, these same voids may come at the expense of increased CoPC release due to increased porosity. Alternatively, the use of polyvinyl alcohol reduces ice crystal growth in the pore space (Qu et al. 2020). Finally, in UHPG, the decrease in w/dm ratio and inclusion of SF, FA and steel fibers increase the resistance to freeze-thaw by decreasing the porosity of the cement relative to OPC-based cements (Russell et al. 2013, Alkaysi et al. 2016, Lu et al. 2021). This will be especially important as UHPG contains freeze-thaw susceptible BFS. The grout formulations considered (HGM5 and HGM3) have higher water contents that could also be susceptible to freeze-thaw cycling.

Possible test cases do exist to evaluate the potential freeze-thaw damage on containerized grout with the grout waste forms produced for disposal at the Hanford trenches, which remain above ground for a period of time. These forms could be examined directly. Laboratory studies for freeze-thaw cycling can be performed on SSW candidate formulations (e.g., ASTM Method D560/D560M-16 *Standard Test Methods for Freezing and Thawing Compacted Soil-Cement Mixtures* or ASTM Method C666/C666M-15 *Resistance of Concrete to Rapid Freezing and Thawing*). These measurements can be used to model the freeze-thaw process using a thermoporomechanical description of thermoporoelasticity theory while taking into consideration temperature, liquid pressure, and salt concentrations (Zeng 2011).

As freeze-thaw cycling early in life may change the waste form's properties before placement in the IDF and long-term susceptibility to freeze-thaw effects, some testing is warranted. Evaluations of existing Hanford grouts in the disposal trenches can be used as surrogates for SSW grout waste forms. Laboratory studies of freeze-thaw resistance can be measured (e.g., ASTM Method C666/C666M – 15 or ASTM D560/D560M-16) and used to model the freeze-thaw process using a thermoporomechanical description of thermoporoelasticity theory while taking into consideration temperature, liquid pressure, and salt concentrations.

3.2.2.4 Process: Scaling

Scaling is a process through which the hardened paste on the outer surface of the waste form is lost near aggregate and particles and commonly results from expansion during freeze-thaw cycling. While the process can degrade and crack the outer waste form surface it is not a bulk process. Instead, overall freeze-thaw cycling effects were considered in Section 3.2.2.3.

Scaling of SSW waste forms is not anticipated to significantly affect waste form performance as scaling is limited to the surface.

3.2.2.5 Process: Alkali-Silica Reaction

Alkali-silica reaction (ASR) occurs when alkali species in the portland cement or alkalis from the environment react with amorphous silica aggregates (e.g., opaline or chert), aggregates containing strained quartz grains, or reactive glassy aggregates. The reaction product is an expansive gel that is extremely disruptive to the concrete or grout and can lead to cracking. Specifically, the ASR between the alkaline solution in grout pores and aggregate produces a hydroscopic alkali-calcium silica gel in and on the aggregate grains resulting in material expansion (ACI 1968). The expansion results in stresses in the aggregate grains and ultimately cracks them and the surrounding cement paste. As the UHPG and HGM3 contain sand as a fine aggregate, they can be considered for ASR.

ASR was not discussed in the 2016 SSW data package and the likelihood of this process occurring is low. Hanford sand commonly used in concrete in the Richland Area has an ASR value of 0.034 (ASTM Method C1293-20a, ASTM Method C1778-20) and is considered acceptable for all concrete with no mitigation. The components of the formulations considered in this report (FA, SF, BFS) are used to mitigate ASR through alkali binding, mass transport reduction, increasing tensile strength, and reducing aggregate dissolution rate (Shafaatian et al. 2013). Low alkali cements (< 0.06% Na_2O) are also used to prevent ASR by lowering the alkalinity of the solution in the pore spaces (ACI 201.2R-08). Finally, alkali-carbonate aggregate reactions are also known to result in disruptive expansive reactions. However, Hanford Sand (basalt sand) is expected to be used in UHPG, HGM3, and the IDF fill, which does not contain carbonate. Therefore, this ASR process variation is not considered a significant contributor to the cracking mechanism leading to degradation. It should be noted that SSW (e.g., Ag-mordenite) may contribute to ASR in the SSW waste form and act as a dissolving aggregate. However, no supporting data is currently available.

ASR has a low likelihood of occurrence in the IDF as the Hanford sand (basalt sand) expected to be used in UHPG, HGM3 and the IDF fill has a low ASR value (0.034), meaning mitigation is not required, and does not contain carbonate. These properties minimize significant risk for ASR induced cracking in SSW grout waste forms.

3.2.2.6 Process: Corrosion of Steel

Corrosion of steel embedded within cement-based materials or in contact with cement-based materials (i.e., outer container) is an electrochemical process that degrades the metal and generates corrosion products as a result e.g., iron oxides/hydroxides. The corrosion products commonly occupy a larger volume than the original steel and such expansion can cause degradation and cracking (Pabalan et al, 2009). This cracking can lead to increased CoPC/radionuclide dissolution and release. Yet, migrating CoPCs and radionuclides can also interact with the corrosion products slowing the radionuclide and CoPC transport. The corrosion of steel can also alter the redox conditions of the waste form with implications for CoPC speciation and formation of stable and mobile phases.

The corrosion of metallic components can impact SSW waste forms by two primary methods:

- Corrosion of metallic components of the SSW themselves within the SSW grout waste form that can lead to cracking, e.g., debris waste (failed contaminated metals: tools, jumpers, melter bubblers, thermocouple wells, etc.), failed melters, and HEPA filters (note that a cage will likely be used to house compacted debris waste during encapsulation and this cage may be made of steel).
- Corrosion of the containers for the encapsulated SSW grout waste forms will dictate near field conditions that can influence CoPC and radionuclide transport.

Within, or when in contact with, cement-based materials, the corrosion of steel will proceed through two regimes—initiation and propagation. During the initiation period, the steel is passive with relatively low corrosion rates due to the alkaline nature of the cement and porewaters. The loss of passivity can occur due to carbonation changing the pH or chloride penetration creating a preference for localized corrosion. These two events lead to the propagation period where corrosion attack and subsequent corrosion product growth expand across the steel (Masi et al. 1997). The formulations considered for SSW immobilization will use SCMs like FA and BFS for a significant fraction of the dry ingredients as opposed an OPC-rich formulation. As such, the high pH gained by the presence of portlandite may not persist long term as fly ash and slag both react with portlandite to form the cementing matrix (Pabalan 2009). Therefore, the influence of steel corrosion on SSW waste forms performance is a long-term process that may persist throughout the waste form lifetime.

The 2016 data package contained some discussion of the role of corrosion on SSW waste forms. The data package discussed: (1) the likelihood of carbonation and chloride ingress to corrode embedded steel (related to debris waste or steel fibers); (2) the corrosion of the steel container; and, (3) the interaction of CoPCs and corroding steel. Absent from this discussion in the data package were the impact of steel corrosion on embedded HEPA filters in a low permeability formulation (e.g., UHPG, which at the time was not considered for SSW), corrosion of spent melters (both LAW and HLW), impact of steel corrosion on redox potential of the waste form (see Section 3.2.4.1) and modeling of the steel corrosion process (if needed).

From an infrastructure standpoint much research has been put into the corrosion rates of steel fibers in UHPG (or commonly UHPCC). However, with the importance of limited porosity and transport properties of the UHPG in retaining CoPCs, any risk of steel fiber inclusion leading to corrosion driven cracking should be eliminated and no steel fibers used. UHPG, as defined in Nichols et al (2021), **will not contain steel fibers.** Pabalan et al. (2009) stated "*If the exceptional strength of the UHP(G) is required other types of reinforcement are available, including glass and organic polymer fibers, but these are not common to disposal of radioactive wastes.*"

Several example exist for the modeling of chloride migration through cement systems (Masi et al. 1997, Nagesh et al. 1998) and cracking due to rebar corrosion (Bhargava et al. 2006, Chen et al. 2008). A guide for modeling of steel corrosion processes within SSW waste forms can be leveraged from the work at the SRS that evaluated progressive degradation model of steel corrosion in evolving grout environments work at the SRS (Wiersma 2021). The corrosion progression model has two key aspects: (1) assumes an immediate transition between corrosion regimes (e.g., anoxic, passive corrosion transitions to carbonation induced corrosion upon the arrival of the carbonation front); and, (2) the exterior and interior sides of a steel sample may experience different environments at the same time and thus different corrosion rates that are summed. The models developed make simple and generally conservative assumptions regarding the corrosion response to environmental fluxes induced by cracks on the steel corrosion rate. The models can be used to predict expansion rates and when the onset of cracking from steel corrosion could occur.

Corrosion of the encapsulated steel debris is likely within the SSW, albeit at a slow rate. Materials encapsulated with grout or mortar would be more susceptible due to their increased porosity and perceived water transport. The influence of steel corrosion on a low permeability waste form requires investigation from a modeling (using IDF transport conditions and the SRS model) or an experimental standpoint (measuring corrosion rates in UHPG porewaters).

3.2.2.7 Process: Rheological, Molding, and Phase Segregation

Rheological properties are crucial to ensure adequate processing of the grout, homogenous distribution of blended/solidified non-debris wastes, and complete encapsulation of debris wastes. Laboratory data from slurry grout testing to date indicates limited concerns with the rheology of the candidate formulations, with most passing a modified slump test where the produced slurry pancake must have a diameter of at least 125 mm for the pre-defined form dimensions. Only secondary concerns related to the water content needed to pass rheological slump tests arise due to the effect hydration has on, for example, freeze-thaw cycling induced cracking.

When molding, defects within the grout waste form and between the cured grout and exterior container can be generated that lead to accelerated transport pathways for CoPCs and exposure to environmental elements that can induce cracking. No issues with molding behavior have been seen in the laboratory. However, scaled demonstrations are needed to confirm that any defects that do form do not lead to cracking or other degradation mechanisms. This will be especially important in a scenario where UHPG is used to create a clean barrier (grout lining the steel canister), that the SSW and grout waste form will be poured into (Nichols et al. 2021). This is a lower cost alternative to using UHPG in the entire grout waste form but would require tests to confirm a defect-free barrier can be prepared.

Phase segregation is a process through which the non-debris SSW, or aggregate, settle in the grout slurry leading to settling. Too much settling could potentially lead to structural failure or cracking in regions with concentrated SSW due to a lack of paste available to provide structural stability. Furthermore, concentrating SSW in a single location within the grout waste form would alter the CoPC release characteristics from those predicted based on a uniform distribution. Some of the non-debris wastes have low densities and there is evidence of segregation in lab testing (Asmussen et al. 2020). Any concerns with phase segregation, as well as rheology and mold defects, should be quantified during laboratory and scaled formulation testing.

Rheological and molding properties, along with any segregation behavior of SSW within the waste form will be confirmed during scaled testing when processing conditions are defined.

3.2.2.8 Process: Creep

Creep is a process through which a structure is deformed under a sustained load that could eventually lead to cracking. While the IDF will have stacking of waste forms, the minimum 500 psi requirement of waste forms suggested by the NRC Branch Technical position on waste forms (USNRC 1991) will exceed the expected load of 85 psi at the bottom of the IDF (Bourlag 2019) and the placement of low density backfill between forms is likely sufficient to prevent creep.

Creep in SSW waste forms is not anticipated to significantly effect waste form performance.

3.2.3 Mechanism: Cracking and Chemical Change from Mineral Evolution

The next processes presented are ones that primarily involve the evolution and interaction of the mineral assemblages within the waste from. The processes can lead to cracking or a chemical environment alteration mechanism.

3.2.3.1 Process: Carbonation

In the carbonation process a chemical reaction occurs in which Ca-containing hydrated phases in the waste form react (primarily the portlandite, $Ca(OH)_2$) with CO_2 in the air or HCO_3^-/CO_3^{2-} in infiltrating water producing insoluble calcium carbonate as shown in the equation 1 below:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \tag{1}$$

The degree of carbonation is highly dependent on the permeability of the waste form, the concentration of HCO_3^- and CO_3^{2-} ions in the matrix porewater and contacting aqueous phase, and CO_2 partial pressures. Because $CaCO_3$ has a higher specific gravity (2.71) compared to $Ca(OH)_2$ (2.23), this reaction results in shrinkage or an increase in matrix porosity that can provide pathways for CoPC diffusive release. The carbonation process also alters the waste form pH due to the loss of portlandite. As the pH decreases, leaching of the cement phases can occur (See Section 0). Carbonation is currently modeled in the SRS PA for the SDUs.

Hydrating cement phases like $Ca(OH)_2$, CSH and calcium-aluminum-silicate-hydrate (CASH) gels, aluminaferrite mono- or tri-sulphate (AFm and AFt) phases facilitate the carbonation reactions by contributing both water and Ca species. Since CoPCs may be bound within the mineral structure or adsorbed to these phases, the consumption of the phase(s) via carbonation reactions may accelerate CoPC release. Gas phase carbonation is also possible but is considered insignificant if the relative humidity (RH) is below 25%. Carbonation rates are highest when RH is between 50% and 75%. Above 75% RH moisture in pores restricts CO_2 penetration as a gas but not as the bicarbonate ion (ACI 201.2R-08). Low porosity and permeability cements may be useful in restricting carbonation in the IDF and in some cases surface carbonation is reported to seal the surface, i.e., lower the porosity (Branch et al. 2018, Zhang et al. 2022). As such, optimization of the carbonation process may be a useful tool in mitigating CoPC release from grout waste forms if adequately controlled over waste form life-cycles. The 2016 SSW data package considered the effects of carbonation on waste form stability and corrosion. Specifically, the data package stated that:

> *"Among the key geochemical processes that are especially influenced by a gas pathway is accelerated carbonation of cement as a result of providing a faster pathway for $CO_2(g)$ to come into contact with the cementitious material and accelerated oxidation of reducing cements as a result of providing a faster pathway for $O_2(g)$ to oxidize the reducing cement. Aside from their concentrations being different in air and porewater, they also diffuse 10^5 times faster through air than in porewater. Carbonation of cement by porewater or air has been extensively studied in relation to the construction industry and several books have been written on the subject (reviewed by Bertos et al. 2004; Parrott 1987). To our knowledge there is no quantitative or qualitative information about the oxidation of reducing cement through an air pathway. This lack of knowledge introduces uncertainty to the conceptual model. There will be a need to modify the existing conceptual geochemical cement model to account for the drier environment unique to Hanford."*

> *"Carbonation and chloride ingress may not directly damage cementitious materials, but can lead to accelerated corrosion of reinforcing or other embedded steel. Steel corrosion products (rust) are expansive and can cause cracking or spalling in sufficient volume. SSW encapsulation and solidification grout is not expected to contain any steel near environmental exposure surfaces, assuming a minimum thickness of encapsulation grout on the order of 10 cm (4 inches). Furthermore, reactive transport simulations performed by Brown et al. (2013) indicate that a carbonation front effectively stops advancing after initial penetration due to dissolved calcium migrating to the reaction front from unreacted zones. Also, SSW grouts are expected to fully saturated once equilibrated with surrounding backfill. Carbonation via dissolved CO_2 transport alone is extremely slow (Flach and Smith 2014) and typically neglected outright (e.g. Papadakis et al. 1989)."*

> *"Carbonation shrinkage differs from drying shrinkage in that the material gains mass and is densified. Water is released when calcium hydroxide is dissolved from presumably more highly stressed regions resulting in shrinkage and calcium carbonate crystallizes in the pores. The strength is typically increased and the hydraulic conductivity decreased as the result of carbonation."*

However, little data on carbonation rates for the candidate SSW grouts in Hanford subsurface conditions is currently available. The ongoing field lysimeter test at the IDF Test Platform will provide valuable information on carbonation rates under slightly accelerated conditions. However, laboratory testing can be used to supplement this information using exposures to differing environments coupled with phenolphthalein testing for monitoring pH changes and X-ray diffraction (XRD) analyses to assess mineral changes.

Carbonation is possible for waste forms within the IDF. The rate and impact of carbonation can be studied in the laboratory, but the most relevant data will come from the on-going Field Lysimeter test at the IDF Test Platform. Optimization of the carbonation process may be a useful tool in mitigating CoPC release from grout waste forms if adequately controlled over waste form life-cycles.

3.2.3.2 Process: Calcium Leaching

The leaching of primary constituents of the grout waste form matrix (i.e., Ca) is a potentially detrimental processes to cementitious materials (Berner 1992). This process occurs when contact with aggressive ions leads to a shift in the equilibrium between the cementing hydrate phases and the poral solution that induces dissolution of the hydrates or the precipitation of new phases. During portlandite ($Ca(OH)_2$) leaching, caused by chemical reactions or decreasing pH, the number of larger pores and overall porosity in the grout matrix increases (Choi et al. 2013). As portlandite is depleted, Ca leaching continues to progress through the dissolution of the CSH gel and ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$, also generally referred to as AFt), which begins to lower the mechanical strength of the grout (Carde et al. 1999, Glasser et al. 2008)(Berner 1992). making Ca-leaching a long-term process for consideration in the IDF (likely >1000 years). The 2016 SSW data package (Flach et al. 2016) discussed Ca leaching as follows:

> *"One means of chemical degradation is dissolution and leaching of the calcium-bearing minerals binding the cementitious material together, known as primary constituent leaching. The concentration of Ca^{2+} varies through the leaching process; alkali metals leach first, followed by $Ca(OH)_2$, and then CSH (Walton et al. 1990). In this assessment dissolution of CSH is assumed to control the concentration of Ca^{2+} over most of the leaching process, considering the relative abundance of CSH. CSH dissolves incongruently in that calcium leaches preferentially in comparison to silica. SIMCO (2012, Table 11) measured $[Ca^{2+}]$ = 1.8 - 2.0 mmol/L in a Savannah River Site concrete, which is similar to Clodic and Meike (1997, Table 15, Ca/Si= 0.9) with $[Ca^{2+}]$ = 1.1 - 1.8 mmol/L. At this low concentration (< 2.0E-6 mol/cm^3) and assuming diffusive transport, decalcification proceeds very slowly and is typically insignificant compared to other chemical degradation processes (e.g. Flach and Smith 2014)."*

In order to avoid the precipitation of calcite, the total CO_3^{2-} concentration in the infiltrating water must be below 1.1×10^{-5} mmol/L (Tovena 2002), which is orders of magnitude below the anticipated IDF groundwater concentration (0.3 mmol/L, Table 4). Because leaching of the cement constituents in the pore space is driven by a concentration gradient, the cement total pore volume affects the Ca dissolution phenomena. Haga et al. reported that for higher w/dm ratios, the larger the pore volume, the higher the portlandite leaching rate via a diffusion process (Haga et al. 2005). The addition of SCMs, (e.g., FA, BFS), improves the Ca leaching resistance of cement with less Ca^{2+} released and lowers the overall porosity as demonstrated in UHPCC (García Calvo et al. 2010, Cheng et al. 2013, Segura et al. 2013). Also, by starting with a high alkaline content in the pore solution, the common ion effect will reduce portlandite dissolution and Ca^{2+} leaching (Jain et al. 2009). However, as pH decreases leaching of the cement may then lead to increased porosity allowing other damage to occur such as freeze thaw or chloride and sulphate attack.

When Ca leaching does occur, increased porosity in the grout matrix can lead to damage caused by, for example, freeze-thaw cycling or chemical (chloride, sulphate) attack. This degradation process can be modeled using Fick's law diffusion and a shrinking unreacted-core model (Buil et al. 1992, Baker et al. 1997, Le Bellego et al. 2003, Nguyen et al. 2007, Kamali et al. 2008, Segura et al. 2013). In the model developed by Berner, one water exchange cycle corresponds to a lifetime between 1 to 100 years (Tovena 2002). The resistance of CoPCs to leaching depends on the solid phase containing the CoPC (e.g., matrix, or SSW). Yokozeki et al. modeled the Ca leaching at 1000 years between 20 °C to 80 °C, with a degradation of portlandite and CSH between 7 to 13 cm and 2 to 3.5 cm respectively for OPC at a w/dm ratio of 0.55. For a smaller w/dm ratio of 0.3, at 1000 years, portlandite is leached two times slower than for a 0.5 w/dm ratio while the CSH degradation seems to increase (Yokozeki et al. 2004). Based on thermodynamic laws, Feng et al. (2014) modeled the microstructure evolution during cement leaching, which could possibly be applied for all cement types. These examples point to the promising predictive capability current models may offer for long-term Ca leaching in grout waste forms disposed of at the IDF, especially when coupled with knowledge of the waste form history (formulation, curing environment, SSW immobilized, and storage) and characterization of similar or analog grout microstructures of variable age.

Based on this information, Ca-leaching as a potential long-term degradation mechanism should be considered, based heavily on the pH evolution of the waste form as this is integral to limiting Ca leaching. Upon identification of the SSW grouts to be used, the established models noted above should be performed to confirm sustained resistance to Ca leaching throughout the grout waste form life-cycle of 10,000 years.

3.2.3.3 Process: Sulfate Attack and Delayed Ettringite Formation (DEF)

Grout degradation spurred by sulfate attack is a process that occurs when water containing SO_4^{2-} ions infiltrates the cured grout matrix and reacts with calcium and aluminate phases to form sulfate phases (e.g., ettringite [$Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$] and gypsum [$CaSO_4\cdot 2H_2O$]). The formation of gypsum leads to matrix softening and loss of strength. The formation of sufficient ettringite, on the other hand, can result in matrix expansion and cracking, which increases porosity and permeability (described more in Section **Error! Reference source not found.**).

A sister process to sulfate attack is the process called delayed ettringite formation, or DEF. This specific process is linked to the heterogenous crystallization of ettringite that was unable to fully crystallize during the initial cement hydration and curing period (Damidot et al. 1992, Damidot et al. 1993, Barbarulo et al. 2005, Flatt et al. 2008). DEF can occur months to years after formulation of the grout waste form when exposure to wet conditions allow diffusion of SO_4^{2-}, Ca^{2+} and Al^{3+}. In these instances, an external supply of sulphate is not required to form ettringite. Grout waste forms susceptible to DEF exhibit crack development and growth, and in severe cases material spalling (Collepardi 2003).

The development of cracks in the cement paste or around the aggregates and solids if present, result in pathways that may increase water ingress from the outside environment. If sufficient SO_4^{2-} is present in the additional water, new ettringite crystals can form in the cracks resulting in even more cracking, loss of strength and increased permeability. However, the most severe degradation of the cement due to SO_4^{2-} ions happens at temperatures lower than 10 °C, when SO_4^{2-} combined with CO_3^{2-} and water move through the developed cracks and attack the portlandite and CSH phases to produce thaumasite ($Ca_3Si_6\cdot 12H_2O$). The produced material decreases strength and cohesion within the grout matrix, leading to a pulpy mass (Pauri et al. 1989). Data to date suggests temperatures will not be high enough to observe these effects, but this will be confirmed in scaled testing efforts.

The groundwater contacting the SSW waste form is expected to contain SO_4^- in the 150 – 500 mg/L range. ACI identifies exposure of concrete to external water with 150 mg/L < SO_4^- < 1500 mg/L as Class 1 exposure, low risk, (ACI 201.2R-08) and recommends the use of C150 Type II or equivalent formulation with a w/dm 0.45 by mass. Sulfate attack can also be controlled by using low alumina, low tricalcium aluminate portland cements (Type V, high sulfate resistance) or combining Type II cement (moderate sulfate resistance) with slag and / or pozzolans that provide a similar resistance as Type V portland cement when designed in accordance with ACI protocols. Mixes are considered sulfate resistant by demonstrating expansion <0.1% in 1 year by ASTM C1012-18b *Standard Test Method for Length Change of Hydraulic-Cement Mortars Exposed to a Sulfate Solution.* However, service life should also be considered when determining suitability for a particular application.

Sulfate attack was discussed in the 2016 SSW data package as follows:

> *“.....provide a qualitative indication of cementitious material susceptibility to chemical attack due to pH, carbon dioxide, magnesium, and sulfate exposure. The exposure concentrations identified in Section 4.3 of Flach 2016 correspond to at most “Weak” or “Mild” susceptibility using their descriptive terms.”*
>
> *“The rate of sulfate penetration into Saltstone Disposal Unit concrete was estimated by Flach and Smith (2014 Table 2-6) and Flach (2015 Table 4-4) to be approximately 0.02 cm/yr for an exposure concentration of 100 mmol/L. From Section 4.3 the sulfate concentration typical of Hanford vadose zone pore water is about 2 mmol/L, or 50 times lower, which suggests a prorated sulfate attack rate of roughly 0.0004 cm/yr. At this rate 10,000 years of exposure would result in a sulfate penetration depth of only 4 cm. Sulfate penetration does not necessary produce physical damage. Low sulfate exposure concentrations and high porosity in SSW paste materials may lead to no damage from sulfate ingress.”*

As such, sulfate attack can occur on the grout formulations considered in this report but likelihood is low due to the low sulfate concentrations. However, some waste streams containing high levels of sulfate (e.g., immobilized brines from the ETF) may be grouted and disposed of in the IDF. These waste forms have potential for high release of sulfate over time that increase groundwater and / or pore water sulfate concentrations and risk of sulfate attack. It is important to note though that the amount and rate of sulphate release from ETF grout is not well documented but could be studied by measuring the released SO_4^{2-} concentration changes from leached ETF grout waste forms. Furthermore, the ongoing lysimeter test at the IDF Test Platform includes two ETF grout formulations and concentrations of SO_4^{2-} will be measured in the backfill (it should be noted the lysimeter test does include the contemporary ammonia tolerant grout planned for ETF). If SO_4^{2-} concentrations exceed projected limits an operational constraint in the in IDF can be used as a mitigation approach to isolate the high-sulfate secondary waste forms from other grouted waste forms to prevent sulfate attack of low-sulfate grout waste forms.

The likelihood of sulfate attack from the SO_4^{2-} present in the IDF groundwater is low due to low sulfate concentration. However, the IDF is expected to receive waste forms from the ETF that contains a high concentration of sodium sulfate in its waste stream. A study of the release of SO_4^{2-} from these waste forms can be used to project increased sulfate concentrations and assess susceptibility to sulfate attack and DEF. Alternatively, sulfate release from the ETF waste forms used in the lysimeter test can be used for this assessment. If SO_4^{2-} levels exceed limits, the location of the ETF waste form in the IDF should be taken into consideration along with its effects on the other grouted waste forms in the disposal facility.

3.2.4 Mechanism: Chemical/Waste Specific Processes

3.2.4.1 Process: Reoxidation

Reoxidation is a process through which oxygen entry into the waste form, through air or water pathways, leads to a loss of reducing conditions due to oxidation. Certain grout formulations are designed to reduce certain metal CoPC species to less soluble forms by increasing the reducing capacity of the waste form via reductants, mainly using BFS that contains sulfide and ferrous iron reductants (Lukens et al. 2005). For example, Tc(VII) as the pertechnetate ion (TcO_4^-) is relatively soluble and highly mobile in oxidizing environments. When TcO_4^- is reduced to Tc(IV) by reductants naturally found in the BFS, these Tc(IV) species form relatively immobile and sparingly soluble solids, e.g., $TcO_2{\cdot}xH_2O$. However, exposure to oxygen or other oxidizing species can consume the reduction capacity in the waste form, which can allow reduced species to reoxidize and form mobile species which are then more rapidly released into the near-field environment. Pertaining to SSW, reduction capacity is crucial in waste forms where Tc(VII), or other redox active CoPCs like Cr(VI), are present on the SSW (e.g., HEPA filters). The corrosion of steel can also generate reducing conditions within cement matrices (Ma et al. 2019). Yet, of the formulations considered in this report for SSW, only the UHPG contains BFS.

At present, the reduction potential of the slag-containing cements is captured through empirical determinations of diffusion rates. Within the IDF PA K_d are used to represent the ability of a waste form to retain a CoPC in reducing vs. oxidizing conditions. This is accomplished by assuming a change from one K_d to another occurs at a discrete point in time. Recent works have investigated the use of equilibrium models to estimate the loss of reduction capacity (Chen et al. 2021) and dynamic reduction capacity is assessed in the SRS Saltstone performance assessment (Kaplan 2016).

Methods to measure reduction capacity and monitor the diffusion of oxygen into the cement matrix exist and can be used to quantify changes to candidate waste forms due to environmental exposure. For example, it is possible to measure the reduction capacity of various materials by dissolution and titration methods and this reduction capacity could be accounted for in a PA-type model (Angus et al. 1985, Roberts et al. 2009, Um et al. 2015, Arai et al. 2017, Abramson et al. 2022). Additionally, the rate of oxygen ingress into the cement matrix can also be directly monitored as a means to determine the rate of reoxidation of key species (Langton et al. 2013). Although, it is unknown if the rates of re-oxidation and use of reduction capacity proceed linearly through the performance lifetime of the IDF. The field lysimeter test on-going at the IDF Test Platform will provide valuable information on re-oxidation rates of BFS-containing waste forms in the IDF. A recent FY22 funded Nuclear Energy University Partnership (NEUP) project led by the University of Washington and PNNL aims to provide a rapid, reliable method for reduction capacity measurements through development of a non-destructive method using X-ray emission spectroscopy (XES) (Abramson et al. 2022). If successful, this approach will be able to probe redox sensitive elements to better understand aging cement redox chemistry and use this information to inform performance observations and predictive models.

The role of oxidation in reducing waste form behavior and proposed handling in modeling was discussed in the 2016 SSW data package in great detail (Flach et al. 2016). This discussion considered a shrinking core model for representing the process.

> *"It is anticipated that a cementitious waste form in a Hanford vadose zone may be unsaturated with respect to water. As such, there may be two pathways by which O_2 can enter the waste form and oxidize the system.*
>
> *1) A porewater pathway, where O_2(g) from the vadose zone partitions into porewater (via Henry's Law) and delivers O_2(aq) into the cementitious waste. The oxidation reaction of O_2(aq) with the reducing agents within the cementitious waste form are described by the Shrinking Core Model.*
>
> *2) An air pathway, where O_2(g)from the vadose zone enters directly into the cementitious waste form as the exterior of the waste form desiccates along the edges"*
>
> *"If necessary, these processes would be modelled as coupled processes. This approach requires advanced computational resources and developmental work. An alternative would be to decouple these processes and evaluate each process by itself that is to conduct a porewater pathway analysis and a separate air pathway analysis. The porewater pathway will be conducted assuming fully saturated conditions. The air pathway analysis would involve unsaturated flow modeling and will assume that the oxidation front will advance instantaneously through the cementitious waste form as it desiccates from the exterior towards the interior. The rate determining process will then be determined by identifying which process resulted in the oxidation front moving the fastest. There is significant uncertainty regarding how the dynamics of saturated/partially saturated conditions in the cementitious waste forms and surrounding backfill of the IDF will impact air pathway modeling and its impact on spatial evolution of the oxidation front."*
>
> *"To our knowledge there is no quantitative or qualitative information about the oxidation of reducing cement through an air pathway. This lack of knowledge introduces uncertainty to the conceptual model. There will be a need to modify the existing conceptual geochemical cement model to account for the drier environment unique to Hanford."*

To sustain reducing conditions of grout waste forms for as long as possible two primary approaches are used: (1) maintain a low Eh environment, or (2) limit cracking and fracturing, which may allow diffusion of oxygen or infiltration of oxygenated water and increase the rate of reoxidation. The excellent performance of UHPG in decreasing Tc release is attributed to these two approaches (Nichols et al. 2021). When oxygen enters the waste form it is consumed by the reducing capacity of the BFS that is also maintaining the desirable form of CoPCs. Once the reducing capacity is exhausted, CoPCs are susceptible to reoxidation and formation of more mobile species, like TcO_4^-. Studies of reducing waste forms that contain BFS indicate this happens in a stepwise manner due to evolution of the mineralogy in the grout matrix (SRR 2019). Figure 9 shows an example of stepwise evolution of redox potential during mineralogical evolution resulting from equilibration with multiple pore volumes of grout pore water (it should be noted that pore volumes displaced in the IDF is highly dependent on infiltration rates).

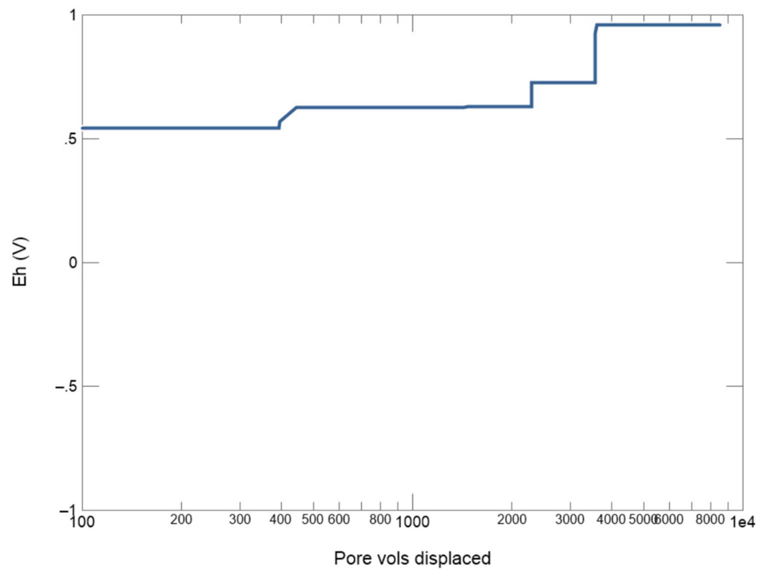

Figure 9 Example time series for Eh in grout pore water with reaction path modeling (SRR 2019).

Relationships similar to the one shown in Figure 9 are the basis for periodically changing chemical transport properties for redox sensitive CoPCs in numerical simulations of waste forms.

Further studies should seek to incorporate laboratory measurements of reduction capacity and oxygen ingress rates into IDF PA modeling and document the impact of oxidation on UHPG performance (or other candidate formulations) for the retention of Tc and other redox sensitive CoPCs. The lack of information on air-driven oxidation should be rectified so a coupled process model can be developed. The on-going lysimeter tests at Hanford will provide real world insight into these rates but near-term experimental data will be beneficial.

3.2.4.2 Radionuclide Leaching and Dissolution of CoPC

Well-designed stabilizing grouts sequester CoPCs (and radionuclides) in the waste form attenuating their release into the surrounding environment at acceptable rates to ensure environmental limits are not exceeded. In this context radionuclide leaching is the transfer of radioactive CoPCs from the waste form into the surrounding environment. CoPCs are sequestered in waste forms as a result of several physical and chemical properties including, low permeability, slow diffusion, sorption, entrainment (trapped within isolated pores or mineral crystal structures), and precipitation. As some SSW waste forms contain particulates of CoPCs removed from waste streams in the WTP, processes that increase porosity, permeability or diffusivity, change the form of CoPCs to a more mobile form, or reduce the sorptive properties of the grout matrix will increase the rate of CoPC leaching from the waste form. For example, HEPA filters have been selected to remove particulate forms of ^{99}Tc and ^{129}I in the secondary off-gas treatment system of the LAW facility (Jenkins et al. 2013). These particulates are anticipated to be soluble salts of ^{99}Tc and ^{129}I. CoPCs may not be in chemical equilibrium with grout pore water and as a result they may change form or speciation upon immobilization. Some changes may have a desirable result, e.g., Tc(VII) reduction to stable Tc(IV) phases, while other changes may be undesirable, i.e., becoming susceptible to transport via dissolution. Dissolution can be minimized by reducing contact of CoPC solids with liquids. These processes were not discussed in the 2016 SSW Data Package (Flach et al. 2016).

Dissolution of soluble CoPCs in the SSW waste form by grout pore water can increase the potential for CoPC leaching. This process can occur immediately upon mixing the SSW with the grout slurry. It is not known if the CoPC inventories on the SSW to be solidified/microencapsulated begin to leach their inventory upon mixing. Such behavior will be captured in current leach data but should be confirmed spectroscopically by analyzing samples for CoPC presence in the "clean" grout after curing. If immediate leaching is observed, then macroencapsulation of the non-debris wastes should be considered to limit distribution of CoPCs within the grout and any migration from a microencapsulated core of SSW during fabrication should also be studied.

The sorption/desorption behavior of CoPCs to the SSW and the grout matrix in realistic conditions is also critical to understand the dissolution behavior. Studies have been done on the sorption of species (Tc, I, Hg) to several SSW (sRF, GAC, AgM) in simulated grout pore waters for HGM5 and a reducing grout (Cast Stone) (Asmussen et al. 2020). As formulations are down-selected or new SSW identified similar studies are required to understand CoPC dissolution within these waste forms.

Many radionuclides and other CoPCs present on SSW exist as soluble salts that can immediately leach from the SSW during waste form fabrication. These processes are captured in current leach testing data but should be confirmed for representative SSW in down-selected formulations. This dissolution behavior should be understood to support development of models for SSW waste from aging. Rapid leach testing or solid phase characterization/microscopy can be used to observe the migration of dissolved CoPCs.

3.2.4.3 RCRA Metal Behavior

Resource Conservation and Recovery Act (RCRA) metals refers to a group of 8 metals that exhibit the characteristics of corrosivity, toxicity: As, Ba, Cd, Cr, Pb, Hg, Se, and Ag (Taylor 2010). Depending on the SSW, some RCRA metals may be present from capture during vitrification or on the SSW itself (i.e., silver mordenite). The 2017 IDF PA considered the presence of Cr (94% on HEPA filters, 5% ion exchange (IX) resins and 1% other debris), Hg (100% on GAC) and Pb (61% HEPA filters, 20% IX resins and 19% other debris). A substantial amount of Ag will be present in the IDF resulting from the disposal of Ag-mordenite from HLW vitrification. The other RCRA metals were not considered in this report due to either their low concentration in the Hanford wastes or projected high retention in glass and therefore not being present on the resulting SSW (USDOE, 2018).

The RCRA metals considered for SSW (Cr, Hg, Pb, Ag) behave differently due to their chemistry, but all are redox sensitive and can form various complexes. Within a reducing grout waste form, it would be expected that these four RCRA metals would be in a sparingly soluble reduced state or associated with sulfide. With reoxidation of the grout, they may oxidize and become mobile. However, the performance of a waste form for the RCRA metals is assessed against regulatory limits using the Toxicity Characteristic Leaching Procedure (TCLP)[7]. There is high confidence a grouted waste form for SSW would pass TCLP. One unknown is associated with the behavior of Ag upon stabilization of Ag-M. Recent work has shown that stabilization of iodine-loaded Ag-mordenite in a slag-free grout (oxidizing) leads to limited release of iodine compared to release from a slag-containing waste form (Asmussen et al. 2020). However, in an oxidizing grout the release of Ag may be higher and TCLP testing is required on example systems to ensure the waste forms still pass TCLP.

[7] https://www.epa.gov/hw-sw846/sw-846-test-method-1311-toxicity-characteristic-leaching-procedure

SSW waste forms are likely to pass TCLP to ensure RCRA compliance. Selection of a slag-free formulation would be desirable for a waste stream where I-129 release from an already oxidized cation, such as Ag, is the primary risk from an IDF performance standpoint (Asmussen et al. 2020). It is unknown how a slag-free formulation would perform for Ag release in TCLP testing.

3.2.5 Mechanism: Environmental Changes

The following subsections cover processes that can alter the local chemical environment, and in turn, can alter the behavior of the SSW waste form. The processes include microorganisms, irradiation, fire resistance and acid attack.

3.2.5.1 Process: Microorganisms

Microbial interaction/degradation of cementitious materials is an unavoidable, yet environmentally sensitive process that is challenging to accurately integrate into PA-type degradation models. Microbial influence is highlighted as a criterion in the NRC technical position on waste forms (See Section 1.8). Most often the microbes themselves do not degrade the cement matrix, rather the process by which they grow on the cement surface leads to waste form degradation. That being said, microbe growth degrades grout primarily through three physical mechanisms: (1) eroding the exposed concrete surface, (2) increasing concrete porosity, and (3) increasing the transport of other degradants into the cement matrix that are capable of inducing cracking and spalling (Wei et al. 2014). Slight shifts in the local environment, including pH, Eh, carbon (or other species) source and concentration, water content, and the availability of crucial elements, e.g., bioactive electron donors and electron acceptors, nitrogen, phosphorous, sulfur, potassium, magnesium, and iron, have dramatic impacts on the rate and extent to which microbes grow (Tovena 2002, Turick et al. 2016). In turn, changes in these properties can directly influence performance of the waste forms. Table 6 provides a summary of the most common bacteria growth mechanisms known to cause cement degradation. Microbial activity within the IDF is acknowledged and should be considered for its impact on waste disposal.

Table 6. Types of microbes known to degrade cement and the environments in which they thrive (Turick et al. 2016).

Microbe Type	Energy Source	Carbon Source	Products	Reacts with Cement to Form	Ideal Environment & Comments
Algae & Cyanobacteria	Light	CO_2	Organic acids, O_2, CO_2	Calcium Carbonate, Calcium Organic salts	Exposure to air and nutrients, e.g., Ca and Mg. Capable of growth in harsh environments. Bacteria adsorption of Ca and Mg from cements leads to drying and cracking.
Sulfur Oxidizing	Sulfide	CO_2	Organic acids, CO_2, H_2SO_4	Calcium Sulfate, Calcium Carbonate, Calcium Organic salts	Acidic to neutral (~pH 9); leads to dissolution of hydrated cement, formation of gypsum that weakens the cement structure. Eventually leads to delayed ettringite growth that causes cracking, allowing the bacteria colonies to spread. Inhibited by calcium formate.
Iron Oxidizing	Fe(II)	CO_2	Organic acids, CO_2, Fe(III), OH	Calcium Carbonate, Calcium Organic salts	Similar to sulfur oxidizing bacteria that favor acidic pH where Fe(II) is stable. Catalyzed by the corrosion of rebar, bacteria growth continues to drive down the pH thus facilitating faster rebar corrosion. Inhibited by calcium formate.
Nitrifying	NH_4, NO_2	CO_2	Organic acids, CO_2, HNO_3	Calcium Nitrate, Calcium Carbonate, Calcium Organic salts	Wide range of pH, tolerant of low water, facilitated by ordinary portland cement and blast furnace slag, promotes Ca dissolution
Aerobic Respirators	Organic Carbon	Organic Carbon	Organic acids (rare), CO_2	Calcium Carbonate, Calcium Organic salts	High tolerance for low water and wide pH ranges; capable of penetrating small cracks leading to greater degradation.

Microorganisms are notoriously adaptable and develop the capacity to thrive in harsh environments, including the alkaline environments typical of cement matrices (Smith et al. 2016, Turick et al. 2016). As such, approaches to modeling grout waste form degradation induced by microbial growth requires a detailed characterization of the environment, materials, and microbes historically and currently present (Turick et al. 2016). Equally important is the recognition that microbe adaptability means that they will persist in nearly any environment also occupied by cementitious waste forms at some point over the waste form's 10,000 year expected life cycle (Wei et al. 2014).

At the IDF depth, the mineralogy is comprised of the Hanford sediment formation (Xie et al. 2003, Lin et al. 2011, Kaplan et al. 2014), which is aerobic, composed of unconsolidated sediment ranging in size from silt to sand to gravel, and contains moderate levels of highly diverse bacterial biomass (Lin et al. 2011, Kaplan et al. 2014). The pH of the Hanford formation is generally 7.9 ± 0.1 and often has a rich Fe content compared to other sediment strata found at the Hanford site. Bacterial divisions that have been characterized for this area of the site include (in decreasing abundance) betaproteobacteria, gammaproteobacteris, alphaproterobacteria, deltaproteobacteria, acidobacteria, GAL15, nitrospirae, chloroflexi, NC10, actinobateria, SPAM, panctomycetes, gemmatimonadetes, bacteroidetes, and firmicutes (Xie et al. 2003). Under these conditions, the current knowledge gap is not if microbes will play a role in cementitious waste form degradation, but rather to what extent will microbes play a role in waste form degradation. This was concluded in the 2016 SSW data package (Flach et al. 2016) where a decrease in cement pore water pH over time will inevitably begin to promote microbe growth, yet routine biodegradation testing is not incorporated into current waste form development and testing efforts (Flach et al. 2016b). In fact, one of the recommendations for SSW was to study microbial influence:

> *"A number of potential considerations have been identified that could influence the cementitious materials that will need to be addressed (e.g., initial saturation of a cured cementitious material, freeze-thaw, cellulose materials, microbial influences, impact of non-debris waste streams on the properties of a solidified cementitious waste form, controlling factors for release of Tc from a solidified waste form)."*

Considering that bacterial impact on cement properties is in some cases on the order of 10s of days (Ehrich et al. 1996, Kamorny et al. 2021), performance assessment models need to be updated to include this degradation pathway or changes in waste form properties/near field conditions due to microbial activity. Microbial activity may impact waste forms from an early stage in life but would most likely be long-term processes to generate bulk differences. Such attempts will need to rely on tangential data from the published literature until enough microbe activity and degradation data is generated specific to grout waste forms specific to the Hanford site.

Filling the current cementitious materials microbial degradation knowledge gap for Hanford will require testing exercises that may be modeled using the current literature or derived from standard test methods that may not be specifically designed for cement-based materials (Pagga 1997). These efforts should be preceded by a review of the microbial data and an assessment of the "driving force" required from microbial activity to alter bulk properties of the waste form/near field.

3.2.5.2 Process: Radiation Damage

Radiation damage is a process through which ionizing radiation from decay of radioactive ions in the SSW can induce water radiolysis, degrade organic chemicals, and influence solid phases in the waste form. Radiation resistance is a criterion in the NRC technical position on waste forms (see Section 1.8) Radiolysis of organic admixtures which may be present in a relatively high concentration in the UHPG matrix is of particular concern because the reactions may generate hydrogen gas. Radiolysis of water in the hydrated cement matrix may also cause drying in addition to generating hydrogen. However, the projected SSW and other waste forms in the IDF will only contain low levels of radionuclides and any effects would be expected to be minimal.

Radiation damage of SSW waste forms is not anticipated due to the low levels from the SSW and other waste forms in the IDF.

3.2.5.3 Process: Fire Resistance

Exposure to high heat from fire can dehydrate and alter cementitious materials. However, the low likelihood of a fire and the containerization of the SSW waste forms minimize the risk associated with fire.

Fire resistance of SSW waste forms is not anticipated to be of concern.

3.2.5.4 Process: Acid Attack

Acid Attack is a process through which alkaline grouts and cements contact acidic solutions leading to congruent ($Ca(OH)_2$) or incongruent (CSH) decalcification. However, the infiltrating water and resulting IDF porewater is projected to be near neutral (pH 6-8) or alkaline from contacting the grout and/or glass. Calcium leaching and the resulting pH increase becoming more alkaline were considered instead as a separate mechanism in Section 0.

Acid attack of SSW waste forms is not anticipated to be of concern in the IDF.

4.0 Summary of Target Needs

The following section summarizes the primary needs identified in this assessment of mechanisms and processes relevant to SSW waste forms. Section 4.1 will cover the needs identified in the mechanism and process assessment. Section 4.2 will cover a clear need in updated model representations for grout waste forms. While Section 4.3 will cover needs in engineering or scaled testing. Figure 10 shows a schematic listing the key processes identified in each time frame considered in IDF disposal. The style of testing (engineering, lab/field or modeling) required to study the processes from each time frame are also shown. Engineering-scale testing is required to observe/confirm properties from the slurry state through the young, hardened waste form (1 year). Laboratory- and field-scale testing can be used for studying waste forms in ages from hours to decades. Modeling is required to predict the behavior of the waste form once cured through its entire disposal lifetime.

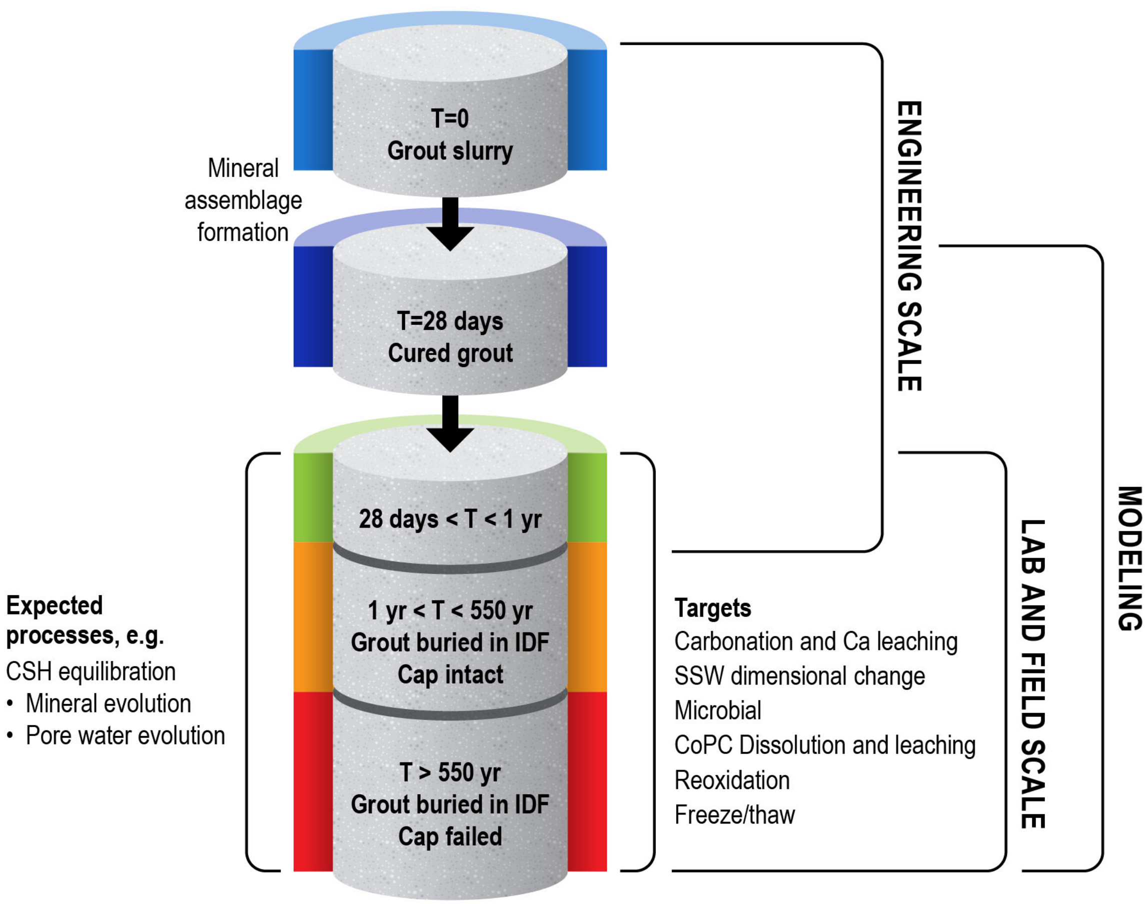

Figure 10 – Schematic showing examples of key processes identified in this effort and what type of testing will be required to study the processes in the listed time frames.

4.1 Mechanism and Process Assessments

Based on the assessments above in Section 3, individual gaps and needs were identified for the evaluated processes. The likelihood of the process occurring in the IDF, the susceptibility of the grout formulations and the existence of data/modeling were assessed to guide a technology gap roadmap approach in Section 5. For the likelihood a ranking of high (very likely to occur, significant consequence or limited R&D),

moderate (possible, but conditions are uncertain, a preceding process is required), or low (feasible but long-term processes) were assigned. For each grout type those that are susceptible are listed. Existing gaps in modeling or site/material specific data are also presented. A process with a high likelihood, having a grout formulation(s) being susceptible to the process and with a lack of site-specific data or no current modeling approach would be identified as a high importance item. A final assignment of moderate importance was given to processes that are possible, but conditions are uncertain, waste forms impacted are few or little technology maturation is available. Those assigned a low importance are perceived long-term processes or ones where only minor technology maturation is needed. Some processes were eliminated as it was not likely to occur or impact waste form. The summary is given in Table 7.

Table 7 – Summary of the identified gaps and needs for the mechanisms presented in Section 4. The risk associated with the mechanism and the current gaps are listed as high, moderate, low, or eliminated.

Mechanism	**Processes**	**Active Timeframe**	**Likelihood (HML)**	***Grout Susceptibility***	**Existence of Site-Specific Data or Modeling**	**Importance**
4.2.1 Environmental Driven Cracking	***Deformation/Cracking (Moisture driven)***	> 1 year	L	All	Limited	Low
	Deformation/Cracking (Thermal driven)	0-1 year	L	All	Some	Low
	Dimensional change of SSW	All	H for Resins, mordenite, HEPA (steel)	Grout and Mortar. UHPG limited by porosity	Limited	High
	Freeze Thaw Degradation	0-50 years	H	All	Limited	High/Moderate
	Alkali-Silica Reactions (ASR)	>50 years	L	UHPG/Mortar	Limited	Low
	Corrosion of Steel (Chloride Driven)	All	M	Grout/Mortar, UHPG limited by porosity	Some from SRS	Low/Moderate
	Phase Segregation (aggregate or SSW)	0 – 28 days	M (microencapsulated materials)	None – will be confirmed in scaled testing	Yes – lab scale	Low
	Rheological properties/Molding issues	0 – 28 days	L	None – will be confirmed in scaled testing	Yes – lab scale	Low
	Creep - Mechanical compression in storage	>50 years	L	None – 500 psi requirement	Yes – strength data, but limited	Low
	Scaling	>50 years	L	N/A	Limited	Eliminated
4.2.2 Cracking and Chemical Change from Mineral Evolution	***Carbonation***	>1 year	H	All	Limited – lysimeter (not the same mixes)	High
	Ca leaching	>50 years	M	All	Limited – lysimeter (not the same mixes)	High
	Sulfate attack	>50 years	L (unless you store near ETF grout)	All	Limited	Low
	Delayed Ettringite Formation (DEF)	>50 years	L (long-term: unless you store near ETF route), can avoid with correct cement selection early	All	Limited – learn in scaled testing	Low
4.2.3 Altering CoPC/Radionuclides	***Reoxidation***	All	H	UHPG	No but can model as oxidized	Moderate
	Radionuclide Leaching and Dissolution of CoPC	All	H	All	Already captured in leach data, no spectroscopic proof and	Moderate

Mechanism	Processes	Active Timeframe	Likelihood (HML)	*Grout Susceptibility*	Existence of Site-Specific Data or Modeling	Importance
					limited data in grout conditions	
	RCRA metal behavior (e.g., Ag-mordenite)	>1 year	L – Ag unknown	All	Yes	Moderate
4.2.4 Environmental Changes	***Microorganisms***	>50 years	H	All	No	Moderate
	Radiation Damage	All	L	All	No	Eliminated
	Fire resistance	All	L	None	No	Eliminated
	Acid attack	>1 year	L	All	No	Eliminated

4.2 Updated Model Representation

Laboratory and field testing performed during the development of a grout waste form provides information useful in assessing early (0-50 years) aging and performance of grouts. Tests and characterization performed during the development of a grout formulation include fresh property tests to demonstrate processibility and cured property tests. The cured property tests demonstrate the waste form meets both regulatory disposal requirements and disposal site waste acceptance criteria. The tests also to provide base case parameters for long-term performance predictions. The cured waste form properties measured include bulk oxide composition, mineralogy, CoPC sorption, permeability, diffusivity, porosity, bulk density, dimensional stability, and compressive strength. CoPC sorption-desorption behavior in simulated grout porewaters from different times in the grout's age is a crucial input parameter to such models and must be studied experimentally. In addition, long-term performance assessments require characterization of the disposal facility including the near field environmental media in the vadose zone and aquifer. All of these properties control processes/mechanisms that drive CoPC behavior.

At the present time, test protocols to directly evaluate performance over 100s to 1000s of years have not been developed. Therefore, numerical simulations and sensitivity analyses are used to predict and evaluate long-term risks incurred as the result of specific waste and waste form disposal operations.

An approach used to simulate long-term (>50 years) performance of grout waste forms uses chemical transport of dissolved ions through pores in the grout matrix and chemical equilibrium models (Flach 2021b). Grout alteration is simulated using chemical equilibrium models with case specific thermodynamic databases. Multiple pore volume exchanges are used in the chemical equilibrium models to calculate reaction pathways. This approach yields the chemical and mineralogical evolution of a grout resulting from leaching of soluble components (alkaline and alkaline earth ions) in the grout matrix.

Results from chemical equilibrium modeling generate the mineral assemblages and estimates of pH and Eh, that affect radionuclide speciation and release. Flow modeling through the disposal facility can then be used to estimate the amount of time it takes for a given volume of infiltrating water to migrate through a waste form. Transport parameters for CoPCs can then be periodically updated at specific times based on Eh and pH time series generated from reaction pathway modeling that reflect mineralogical evolution in the grout. A report from the Savannah River Site SRS (2019) presents the application of this approach to varying partition coefficients based on Eh and pH time series from reaction pathway modeling. The IDF PA utilizes a more conservative approach where CoPC release is controlled by partition coefficients associated with bulk changes in waste form performance as the grout waste form moves from reducing to oxidizing conditions.

Figure 9 and Figure 11 are examples of results from reaction pathway modeling and show the evolution of mineral assemblages and master variables (e.g., pH) as a function of pore volume exchanges (Flach 2021a). Results like these from reaction pathway modeling are then used to establish the variability of transport properties such as partition coefficient in numerical simulations. Transport simulations are started and stopped at different times to update material properties throughout the lifecycle of waste form.

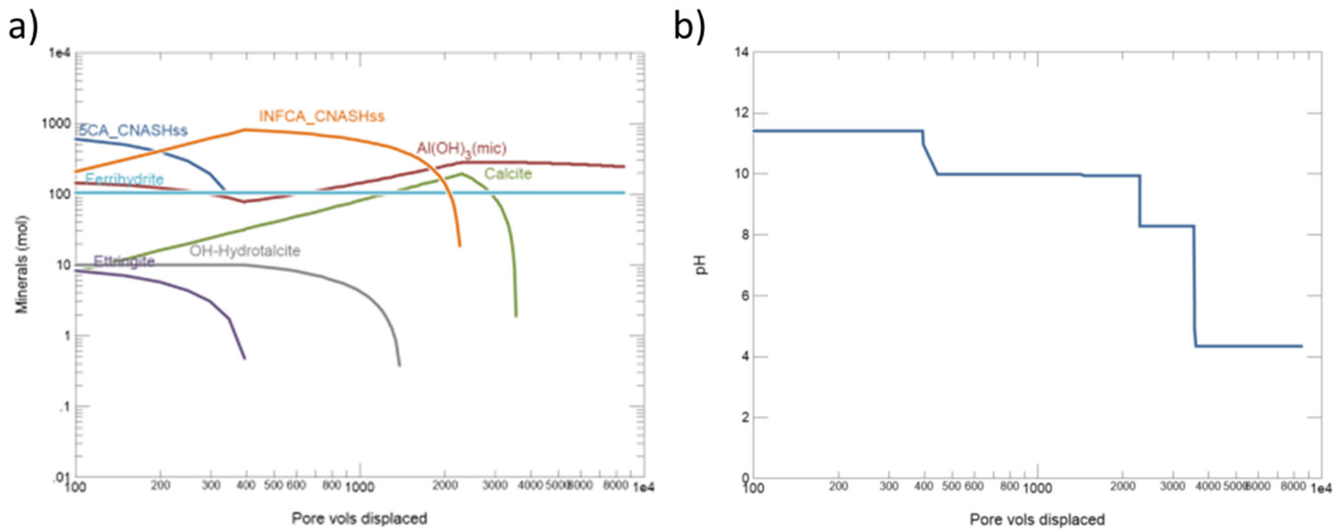

Figure 11 Example reaction pathway results as a function of the number of pore volumes of water that are equilibrated with the waste form; a) mineral evolution, b) pH of grout in a waste form.

Feng et al. (2014) reported development of a new model of 3-dimensional paste microstructure to simulate leaching of hydrated cement pastes and the resulting structural evolution. Structural evolution is tracked using digital models of the 3-dimensoinal microstructure to track changes in binder microstructure as leaching proceeds. Simulating the structural evolution reveals changes in porosity, diffusivity, etc. that occur over time due to mass removal from leaching. Figure 12 shows examples of the evolution of diffusivity as a function of changing porosity resulting from hydration and leaching of cement pastes. CRESP has also shown through equilibrium modeling the improvements gained by capturing coupled oxidation/carbonation processes in disposed grout waste forms.

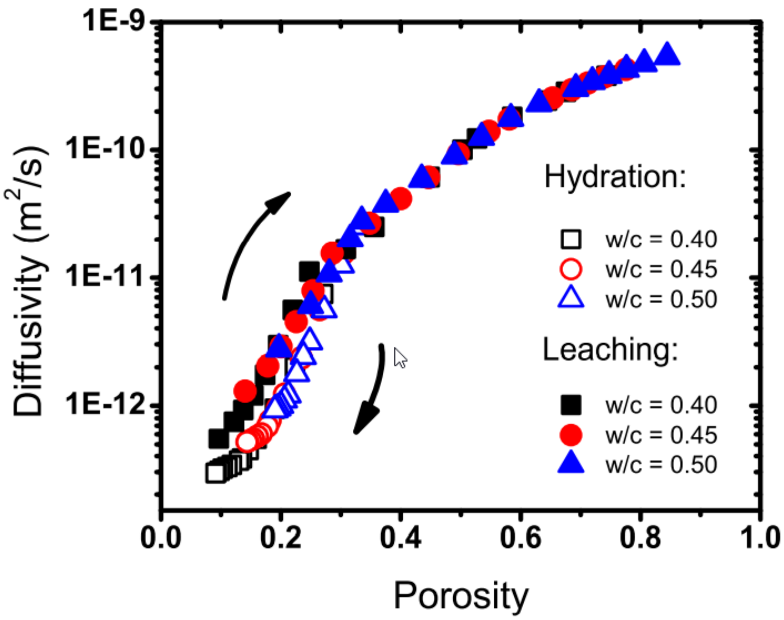

Figure 12 Illustration of the effective diffusivity of cement pastes during hydration and leaching as a function of capillary porosity.

In summary, much development has been accomplished toward improving the accuracy of simulations for aging grout waste forms and these adaptations are utilized in other performance assessments. An effort should be made to incorporate similar modeling approaches into performance assessments for SSW waste form in the IDF. Doing so would improve the accuracy of long-term performance predictions, capture processes specific to radionuclides and CoPCs, and potentially remove unnecessary conservatism.

4.3 Scaled Testing

Data generated during the development of grout formulations is used to initiate the assessment of aging and its impact on performance. Knowledge of mineral assemblages, pore water chemistry, permeability, diffusivity, partition coefficients, water retention, saturation, and environmental conditions is used to evaluate early waste form performance and should be consistent in waste forms produced at full-scale. Scaled testing is required to address the effects of standard industrial batching methods on waste form properties. It is also recommended in the NRC technical position on waste forms to perform scaled testing for all waste forms, Section 1.8. For example, weighing, mixing, curing, exothermic reactions, and resulting stresses are more controlled at the laboratory-scale than at full-scale. Design and test results obtained during development are used to establish initial conditions and develop a conceptual model for waste form aging.

Prior to any scaled testing, the formulation to be used for each SSW type needs to be identified through a down selection. The down-selection process should be documented in a report and include recent site and material specific data. Once the formulations are identified, scaled testing of the various waste forms should be performed. From the processes evaluated in Section 3.2, scaled testing was identified as being integral to confirming rheological behavior (including phase segregation, Section 3.2.2.7), thermal gradients (Section 3.2.2.1), delayed ettringite formation (3.2.3.3), and radionuclide leaching and dissolution of CoPCs (Section 3.2.4.2).

5.0 Future Work Planning

The effort considered three contemporary, candidate grout formulations and projected SSW types for Hanford. If new formulations are considered or alternate SSW emerge then a reevaluation should be performed using the approach within.

Based on the assessment of grout materials degradation mechanisms containing SSW provided in this report, the programmatic needs to improve the representation of SSW in the IDF PA falls into three categories:

1) *Waste Form Performance/Aging* – activities related to testing the degradation processes identified in this effort,

2) *Waste Form Modeling* – activities related to updating/enhancing the model representations for SSW, and

3) *Scaled Demonstrations* – activities supporting scaled demonstrations of SSW waste forms.

Figure 13 presents a schematic summarizing the program needs based on the assessment in this report. The activities are listed in order of priority and chronology. The following subsections will give expanded details on the technology maturation efforts needed to support each activity.

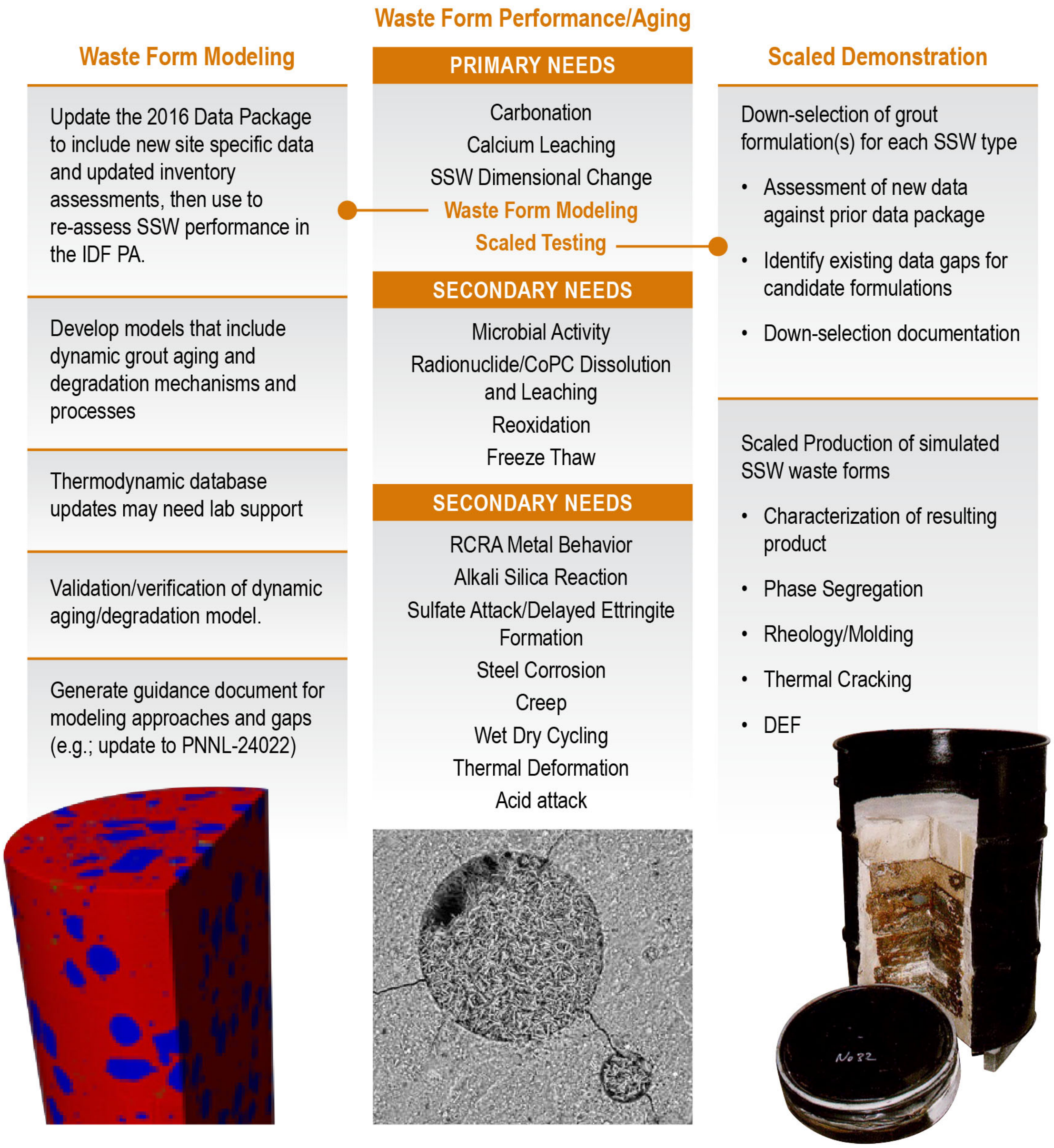

Figure 13 – Schematic showing the programmatic needs for SSW in order of priority. Note that the high priority items titled Waste Form Modeling and Scaled Testing in the left most list are further expanded in the second two lists.

5.1 Waste Form Performance/Aging

Several priority items were identified in this assessment to better predict SSW waste form performance and aging within the IDF and should be added to the WRPS-SSW roadmap. Primary and secondary needs were identified, and the proposed technology maturation approaches are briefly summarized below. The summary presented below are listed in order of priority and in chronological order to support an update to the WRPS SSW roadmap.

1) **Primary: Carbonation and Calcium Leaching**
    - **a.** Expose candidate formulations to various CO_2 vapor and CO_3^{2-} liquid environments and monitor carbonation movement with time using the phenolphthalein method coupled with XRD and waste form property, e.g., compressive strength, assessment.
    - **b.** Use ongoing lysimeter test to inform the natural progression of this degradation process in the IDF.
2) **Primary: SSW Dimensional Change**
    - a. Study dimensional change of SSWs within grout waste forms, in different solution chemistries relevant to grout and the IDF, and at various water contents (w/dm ratios).
    - b. Evaluate leaching of CoPCs from SSW (resin, GAC, AgM) in different grout pore water chemistries as a result of dimensional change.
    - **c.** Study changes to waste form properties in response to the variables above to assess the impact of dimensional change.
3) **Secondary: Microbial Activity**
    - **a.** Complete a paper study on microbial activity in the Hanford subsurface and what environmental changes can be induced from their activity.
    - **b.** Identify any experimental needs as part of the paper study and apply these tests to candidate SSW waste forms.
4) **Secondary: Radionuclide/CoPC Dissolution**
    - **a.** Prepare radionuclide- and CoPC-spiked SSW waste forms and prior to any leaching monitor for migration of radionuclides/CoPCs into the paste using spectroscopic methods.
    - **b.** Study sorption and desorption behavior of radionuclides and CoPCs to SSW and the grout matrix in realistic environments where data does not exist (e.g., UHPG pore waters).
    - **c.** Note that it is likely that these processes have already observed in leach tests of Hanford grout/mortar formulations, but not yet in UHPG tests.
5) **Secondary: Reoxidation**
    - **a.** Study reoxidation rate of UHPG using Langton/Almond method with single face exposures with different environments.
    - **b.** Couple measurements with updated reduction capacity experimental methods.
    - **c.** Use ongoing lysimeter test data to inform this process for other formulations.
6) **Secondary: Freeze Thaw**
    - **a.** Evaluate grouted waste forms prepared for the trench burial grounds for any evidence of freeze-thaw damage (e.g., cracking).
    - **b.** If any evidence exists, test candidate formulations (e.g., ASTM Method C666-15).

5.2 Waste Form Modeling

The WRPS SSW program has been focused on gaining site-specific and material-specific data for SSW grout waste forms to assess the assumptions made in the 2016 SSW data package for grout performance. A concluding effort should be performed before a programmatic switch to grout aging studies is made as suggested in this report. The 2016 SSW data package should be updated to include the data gained since 2016. Using the current modeling construct, IDF waste form simulations should be performed to assess any improvement on SSW performance in the IDF when including the new data.

Adoption of a dynamic, reactive front model for grout waste forms is desirable to better represent the actual aging of the grout and resulting disposal behavior. Several priority items were identified in this assessment of grout materials degradation mechanisms containing SSW to improve SSW waste form modeling and should be added to the WRPS-SSW roadmap. The proposed timeline for these efforts is as follows:

1) Develop models that capture dynamic grout aging and degradation relevant to the IDF and assess needs for further data (for example evaluating the leaching of CoPCs from SSW (in different grout pore water chemistries).
    a. Data to update thermodynamic databases as necessary which may involve laboratory studies.
2) Perform IDF waste form simulations using updated aging/degradation model constructs.
3) Validate/verify updated aging simulations against contemporary simulations.
4) Update guidance document for grout waste form modeling using information gained in above activities, (Yabusaki et al. 2015).

5.3 Scaled Demonstrations

Full-scale testing is required to demonstrate that the grout waste form properties observed and measured in laboratory-scale tests remain with an increase in waste form production size and should be added to the WRPS-SSW roadmap. The proposed timeline for these efforts is as follows:

1) Down-selection of formulations to use for each SSW waste form type.
    a. Assess against recent data.
    b. Identify remaining data needs to support individual selections.
    c. Generate down-selection report.
2) Identification of a fabrication method for macro-encapsulated waste forms.
    a. Can be supported with laboratory testing initially.
    b. Example: clean UHPG grout layer in box.
3) Prepare scaled samples (55-gallon drum, large box).
    a. During fabrication monitor for rheology, settling, heat generation, bleed, and swelling.
    b. Following curing assess for cracking and mineralogy (e.g., delayed ettringite formation (DEF)).

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