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Charles D. Ferguson, Ph.D.
Board Director
Nuclear and Radiation Studies Board
Division on Earth and Life Studies
The National Academies of Sciences, Engineering, and Medicine
500 Fifth Street, NW
Washington, DC 20001

Dear Dr. Ferguson:

Oregon appreciates this opportunity to comment once again on the Academies' ongoing study of options for Supplemental Treatment of Low-Activity Waste (LAW) at the Hanford Nuclear Reservation. The State of Oregon retains a long-term interest in the safety of the Columbia River, which stands to be directly affected by the final end-state of Hanford wastes disposed on-site.

We have followed with interest the evolution of the Federally-Funded Research and Development Center's (FFRDC) report. The revised cost comparison between vitrification and grout appears to provide significant incentive to find an acceptable disposal context for a grouted waste form as a way to respond to the rising lifecycle costs at Hanford, which are outstripping even the most optimistic projections of future Congressional funding for cleanup.

We would like to credit both the FFRDC and the Committee for their fair and candid discussions at public meetings regarding both the tradeoffs between Supplemental LAW alternatives and the uncertainties that still remain regarding consistent long-term performance and the adequacy of current available data. We commend also the transparent and inclusive process that has supported the iterative nature of this study.

The conclusion in the FFRDC report of potential greatest concern to us – that Hanford LAW could be safely disposed as grout at Hanford – hinges predominantly on two major lines of evidence. First, the FFRDC compiled recent laboratory test results of short-term performance of reducing grout and grout with getters and proposes to extend these results toward long-term waste form performance in a dynamic disposal facility environment. Second, the FFRDC developed a Performance Evaluation to estimate the potential risk to a future receptor, based on a Performance Assessment (PA) for the Hanford Integrated Disposal Facility (IDF). We echo the point raised by members of the National Academies' Study Committee that until this PA is available for rigorous public review, the ability to judge the veracity of the FFRDC's analysis is severely hindered.

Within the FFRDC report, and in the many informational meetings, we lost count of the number of times a member of the Committee or the FFRDC made statements along the lines of, "This is the best we could do given the time available, the resources available, or other constraints." These caveats do not instill great confidence that the scope and resources of the study commissioned by Congress were equal to the significance of the decision it is intended to support. We strongly encourage the Committee to emphasize in its review the extent and importance of these limitations of the analysis so that a decision-maker may weigh the study's findings accurately.

This report becomes a rumination on what could be accomplished if the many assumptions underlying the analysis are true. The key question is whether they are in fact true and reliable over long time periods. If we treat the FFRDC analysis as a thought experiment and ask whether Oregon could accept grouted LAW disposal at Hanford under the best-case performance scenario, then we would likely answer yes. Our review of the state of the science, however, would suggest that such an assertion cannot be made with sufficient certainty yet, nor is the path of technology development to get us to that point certain to succeed within an expedited timeframe.

DOE's previous commitments on Hanford tank waste treatment included certain conditions to ensure protectiveness. As described in Appendix D to the 2012 Hanford Tank Closure and Waste Management EIS, Hedges (2008)[1] documents the agreement to eliminate technetium-99 removal in the Waste Treatment Plant (WTP) Pretreatment Facility because it was shown that glass would be able to safely confine these wastes. Now the FFRDC asserts that pretreatment is not necessary for onsite disposal of grout, yet for both technetium and iodine they state that in order to obtain best results (or indeed acceptable results for iodine), getters must be added to the mixture. These getters perform a similar function to pretreatment – separating the long-lived constituents into a sub-form within the larger waste form structure of grout. The difference between pretreatment and getters is the final resting place: above an aquifer in communication with a critical river (at Hanford); deep underground (at a geologic repository); or over 600 feet of redbed clay with no underlying drinking water resource (at the Waste Control Specialists disposal site in Texas)?

The FFRDC appears to have concluded that additional pretreatment is not necessary because getters can provide adequate waste form performance for onsite disposal in grout. However, the opposite is also true: getters are not necessary if additional pretreatment of technetium and iodine is pursued. The FFRDC report does not provide an explanation why getters have been given preference over pretreatment. Additionally, because getters represent a "sub form" to a larger grout waste form, their long-term performance should be evaluated with the same rigor and scrutiny as the primary waste forms in the study before they are endorsed as a viable option.

Much discussion in this study has focused on the definition and legal enforceability of the term, "as good as glass," as an expected standard for any supplemental LAW waste form other than glass. Tri Party Agreement Milestone M-062-00, for which Washington Department of Ecology is named the lead regulatory agency, directs DOE to, "Complete pretreatment processing and vitrification of Hanford High Level (HLW) and Low activity (LAW) Tank Wastes." This legally binding milestone gives the State of Washington the discretion to determine the acceptability of any waste form other than glass.

We continue to stand by the comments we made to the Committee[2] more than a year ago regarding long-term uncertainty in grout performance and the need to exercise a responsible precaution when there is threat of irreversible harm to an irreplaceable resource. We ask the Committee to revisit our

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[1] Hedges, J.A., 2008, Washington State Department of Ecology, Richland, Washington, personal communication (letter) to S.J. Olinger, U.S. Department of Energy, Office of River Protection, Richland, Washington, D.A. Brockman, U.S. Department of Energy, Richland Operations Office, Richland, Washington, and W.S. Elkins, Bechtel National, Inc., Richland, Washington, "Draft Waste Treatment and Immobilization Plant (WTP) Dangerous Waste Permit," October 15. https://pdw.hanford.gov/document/0810160765

[2] https://energyinfo.oregon.gov/blog/2018/03/07/odoes-ken-niles-weighs-in-on-hanford-waste-treatment-we-must-remain-vigilant-informed-and-involved

specific statements regarding, “Here’s what we would need to see to buy into the idea of grouted Hanford tank waste being disposed on site.” Despite the optimistic results of the FFRDC’s grout scenario for disposal at Hanford, we maintain that given the remaining uncertainties today, a precautionary approach would include removal of technetium-99 and iodine-129 prior to disposal of these wastes at Hanford in any form other than glass.

We hope that the Committee will view the current state of grout performance projection with a critical eye and in its final report specify the type and scale of validation studies that are still necessary before a grout alternative would be tenable for Hanford. We would expect such studies to account for different waste chemistries with and without Land Disposal Restriction (LDR) treatment additions; harmonization of the laboratory results with real-world grout degradation studies; studies of grout setting performance in light of the complex chemistry of Hanford tank waste; greater specificity regarding the additional LDR treatment research needed; long-term performance of getters specific to the disposal context in question; and comprehensive uncertainty analysis regarding waste form performance relative to overall disposal facility performance.

We do not envy the challenge ahead for the Committee as you attempt to explain the complexity and necessary context of the FFRDC’s work for a decision-making audience. We urge you to critically evaluate the perceived urgency of a decision for Supplemental LAW treatment given the shifting sands of the tank waste treatment mission today, the potential improvements in glass production rate on the horizon for the existing LAW vitrification facility, and the uncertainties in the technical analysis upon which this study stands. We wonder instead if it might be a wise course of action to continue seeking improvements to secondary waste forms, reevaluate the separation of technetium and iodine from grouted LAW, and ultimately ensure that the long-lived hazardous constituents are placed in the appropriate disposal context.

Our specific technical comments follow.

If you have any questions about our comments, please contact Jeff Burright of my staff at 503-378-3187 or at jeff.burright@oregon.gov.

Sincerely,

Ken Niles
Assistant Director for Nuclear Safety

Long-Term Grout and Getter Performance

Grout Performance Parameter Values and Water Chemistry

- In our research, we discovered that the 2012 Tank Closure and Waste Management EIS (TCWM-EIS) also assumed a Cast Stone formulation using the same percentages of Portland Cement, fly ash, and blast furnace slag as the more recent laboratory experiments. However, the effective diffusion coefficient for grout used in the 2012 EIS did not include blast furnace slag as a reductant in its experiments (DOE (2005)[3], which in turn was based on Mattigod et al. (2001)[4]). We acknowledge that this apparent discrepancy in the EIS modeling does provide support for the idea, forwarded by the FFRDC, that while the grout formulation has not changed since 2012, the underlying experimental data that provided the basis for effective diffusion coefficients for Tc-99 retention in grout in particular was likely out of date.
- Since the improved grout performance (represented by the effective distribution coefficients for Supplemental LAW grout) is based on only five papers in the FFRDC report, with the majority of the parameters coming from Cantrell et al. (2016), it would have seemed prudent for the NAS to evaluate these works separately and seek testimony from the authors themselves. Ultimately the future of Hanford, billions of dollars, and potential future risk to water resources may rest on these works of scholarship that are three years old or newer, and which may have not been strenuously tested. We note that these cited works are also careful to caveat their results, for example:
    - Cantrell (2016) states: "*The data package presents the information that is available at this time, but recognizes that there is more work to be done to reduce the uncertainty in the measured properties and to provide perspective on the relevance and scalability of the laboratory work conducted to date and the performance of production-scale Liquid Secondary Waste (LSW) grout waste form in their containers in the disposal facility*."
- The FFRDC report does not provide diffusivity information for the "low" performing grout analyzed in the IDF PA, which they report could not meet regulatory requirements without 92% Tc-99 removal (p. 64). Instead, the "low performing" grout in the FFRDC Performance Evaluation corresponds to the most recent laboratory data. More information is needed to understand this discrepancy between the values and results in the IDF PA and the FFRDC Performance Evaluation.
- The report contains no formal assessment of the Technology Readiness Level (TRL) of reducing grout or grout with getters relative to waste form performance, only describing a high TRL (7) for the implementability of a grout treatment path. The FFRDC and the Committee should include an evaluation of the necessary timeline to get to a high enough TRL for all aspects of a grout alternative, per DOE policies. We note that the November 2018 public meeting did include some of this discussion, and Cast Stone performance was judged to be "medium" (4-6) because additional research is needed to confirm the understanding of retention characteristics. A getter TRL was not discussed.
- We note an observation made during the November 2018 public meeting that we still do not know the mechanisms of release over time for Cast Stone (e.g., diffusion limited versus other mechanisms) and can only infer "suggestions" from the research, which may not be the true conceptual model. A member of the FFRDC responded that they did not have the resources or

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[3] DOE, 2005. Technical Guidance Document for Tank Closure Environmental Impact Statement Vadose Zone and Groundwater Revised Analyses. https://www.hanford.gov/files.cfm/TCEIS-Vadose.pdf

[4] Mattigod et al., 2001. Diffusion and Leaching of Selected Radionuclides (Iodine-129, Technetium-99, and Uranium) Through Category 3 Waste Encasement Concrete and Soil Fill Material. PNNL-13639. https://www.pnnl.gov/main/publications/external/technical_reports/pnnl-13639.pdf

enough data in the literature to be able to tackle the question of the exact mechanism [for release]. A disposal decision with this degree of permanence should be based on a better understanding of the mechanisms influencing long-term waste form performance. Without confidence in the conceptual model, the "effective diffusion coefficient" approach (or in the words of one Committee member, "an amalgamation of all the real processes going on") represents only what has been observed for as long as we have been able to look. If we cannot say with reasonable certainty why a technology works today, it is not possible to say with confidence that it will continue to work for 1,000 or more years.

- The risk of potential interaction between an oxidizing LDR treatment and a reducing grout does not appear to have been completely managed within the FFRDC report (page 110).
- The FFRDC report notes that the recent laboratory data on grout effective diffusion coefficient properties cited in the FFRDC report used two different kinds of water – deionized water (DIW) and vadose zone pore water (VZPW) – which showed markedly different results and essentially trends the Tc-99 leaching data toward "high performance" (Figure C-1 in the FFRDC report). We question whether either of these water chemistries are the appropriate benchmark for experimentation, and thus whether this data is useful as the fundamental basis for the FFRDC's waste form performance evaluation. As stated in Serne (2015)[1], the Vadose Zone Pore Water recipe is, "based on several direct measurements of actual VZPW removed from Hanford formation sediments from boreholes in 200 E where the IDF is located." These measurements were taken from samples at depths 48.5 and 82.5 feet below ground surface, averaged, and charged balanced. Based on the findings of Serne (2015), the VZPW created a secondary precipitate on the surface of the grout monoliths comprised of aragonite and brucite, which was credited for the lower Tc-99 leaching values. This is likely due to the CaSO4 (i.e., gypsum or Plaster of Paris) and magnesium (MgSO4 and MgCl2·6H20) added to the VZPW simulant[5]. We surmise that any water within the shallow disposal environment would be meteoric water (i.e., infiltrating precipitation), and the environment directly overlying waste packages – assuming an evapotranspiration barrier and unspecified backfill material - would not be representative of natural subsurface conditions. We reason also that the pH from infiltrating meteoric water would differ between the above scenario and deeper pore waters that have undergone buffering through native soils, as would the dilution and geochemical dissolution effects between shallow and deeper soils. Therefore, the water composition in the future IDF cannot be assumed to be similar to deeper vadose zone pore water. Last et al. (2015)[2] in their study of technetium and iodine Kds in IDF-specific sediments using VZPW would appear to acknowledge this distinction, stating, "The adsorption/desorption data presented in this report do not apply to the waste form environment itself." Finally, we note that there has been no discussion or experimentation related to the longevity of this secondary precipitate effect. We recommend additional experimental sensitivity analysis associated with this critical performance parameter.
- As noted in Cantrell (2016), work by Langton (2014) showed that, "*The leachability of technetium in slag-based sodium-salt waste forms may be greater in samples exposed to moist soil (representative of unsaturated vadose zone conditions) than that of samples submerged in deionized water." The potential effect of this finding is that the time to fully reoxidize waste forms is likely lower in a partially saturated environment compared to a fully saturated environment*," We note that leach tests commonly submerge samples in water, while true conditions in the IDF could instead involve partial saturation or gas-phase oxidation

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[1] Serne, RJ, et al., 2015. Extended Leach Testing of Simulated LAW Cast Stone Monoliths. PNNL-24297. https://www.pnnl.gov/main/publications/external/technical_reports/PNNL-24297.pdf

[5] Refer to Tables 2.8 and A.3 in Serne et al. (2016).

[2] Last, G.V., et al., 2015. Technetium, Iodine, and Chromium Adsorption/Desorption Kd Values for Vadose Zone Pore Water, ILAW Glass, and Cast Stone Leachates Contacting an IDF Sand Sequence. PNNL-24683.

mechanisms. This suggests that the current leach tests may not be sufficiently conservative. Cantrell notes that further research is needed on this front, but reasons that this uncertainty is bounded by the fact that his recommended effective diffusion coefficients are based on DIW, while VZPW generally resulted in lower effective diffusion coefficients. Our comment above regarding the applicability of VZPW in an engineered disposal environment would challenge this reasoning.

Grout Performance in the Field

- The DOE and Nuclear Regulatory Commission (NRC) have been working together since 2012 to resolve concerns associated with long-term grouted waste form performance, beginning with an NRC Technical Evaluation Report for the Saltstone Disposal Facility at the Savannah River Site[6]. Numerous study activities have taken place since then, including a 2015 NRC Technical Review[7] that identified many information needs regarding the long-term performance of Saltstone to retain Tc-99 in a field setting. A report from May 2018[8] reviewed the projected Technetium release from Saltstone in light of a DOE coring effort on field-emplaced Saltstone and concluded that most of its concerns remain open. A letter dated October 2018[9] includes a joint NRC-DOE plan to resolve remaining technical questions associated with Saltstone disposal at Savannah River, including: applicability of laboratory data to field-emplaced Saltstone; waste form matrix degradation; macroscopic fracturing; and radionuclide release from field-emplaced Saltstone. Most recently, a Technical Review from May 2019[10] concludes that some of the waste form degradation issues remain open. Additional studies related to this topic are available in the NRC ADAMS library under Docket# PROJ0734. We wish to draw the Committee's attention to the NRC's technical efforts, which are directly applicable to the study at hand. We further note that because the State of Washington is not covered under Section 3116 of the 2005 National Defense Authorization Act, there is currently no legally mandated mechanism for NRC review of a grouted waste form disposed in the IDF at Hanford.
- Concrete degradation via shrinkage and cracking is an expected mechanism that will affect the constituent release rate over time. Studies by the Center for Nuclear Waste Regulatory Analysis (CNWRA) (contracted to the NRC)[11] have shown that over relatively short time periods, concrete monoliths and drums develop multiple extensive crack/microcrack networks and experience permeability variations "ranging over five to seven orders of magnitude, whereas DOE maintains that they expect permeability of tank grout to vary over no more than one order of magnitude" (NRC, 2016; Dinwiddie et al., 2012)[12]. These networks both increase the localized diffusion rate

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[6] NRC, 2012. Final Technical Evaluation Report for the Revised Saltstone Disposal Facility at the Savannah River Site. ML121170309. https://www.nrc.gov/docs/ML1211/ML121170309.pdf

[7] Nuclear Regulatory Commission, 2015. TECHNICAL REVIEW: OXIDATION OF REDUCING CEMENTITIOUS WASTE FORMS, DOCKET NO. PROJ0734. https://www.nrc.gov/docs/ML1509/ML15098A031.pdf

[8] NRC, 2018. TECHNICAL REVIEW: UPDATE ON PROJECTED TECHNETIUM RELEASE FROM SALTSTONE. ML18095A122. https://www.nrc.gov/docs/ML1809/ML18095A122.pdf

[9] Nuclear Regulatory Commission, 2018. JOINT PLAN FOR THE SAVANNAH RIVER SITE SALTSTONE DISPOSAL FACILITY. Docket No. PROJ0734. ADAMS ACCESSION NO. ML18235A068. https://www.nrc.gov/docs/ML1823/ML18235A068.pdf

[10] NRC, 2019. TECHNICAL REVIEW: SALTSTONE WASTE FORM PHYSICAL DEGRADATION (DOCKET NO. PROJ0734). Accession No.: ML19031B221.

[11] Dinwiddie, C., et al., 2012. FISCAL YEAR 2012 MESO- AND INTERMEDIATE-SCALE GROUT MONOLITH TEST BED EXPERIMENTS: RESULTS AND RECOMMENDATIONS. https://www.nrc.gov/docs/ML1225/ML12251A305.pdf

[12] Nuclear Regulatory Commission, 2016. TECHNICAL REVIEW: U.S. DEPARTMENT OF ENERGY DOCUMENTATION RELATED TO TANKS 16H AND 12H GROUTING OPERATIONS WITH EMPHASES

of lower pH water into the concrete, as well as provide an advective pathway for constituent migration. Serne and Westsik (2011) also stated, "*The key process that must be addressed in the long-term analysis of Cast Stone performance is how long oxygen can be kept out of the waste form, and when oxygen does invade the waste form, how long does it take to fully reoxidize all the blast furnace slag and reduced 99Tc*." It is unclear how the FFRDC analysis factors these long-term degradation mechanisms into its Performance Evaluation.

- Another study (CNWRA, 2009)[13] estimated the radial penetration of the oxidation front from a concrete crack. Figure 3-2 of that report shows calculated oxidation front positions ranging between 2 and 8 cm from each crack, depending on sensitivity parameters, with a wider range of variability depending on the initial reductive capacity of the grout (which is depending on the sulfide content of the slag used in the formulation). These results neglect the effect of microfractures in the grout, which would "enhance the diffusion relative to unfractured grout." It is unclear to what degree of faithfulness these degradation mechanisms are represented by the effective diffusion coefficient approach used in the FFRDC report.
    - Langton et al. (2014) found, "The Tc-99 results indicate that the oxidation front is at least 38 mm below the exposed surface for a sample exposed to ambient laboratory conditions and humid air for 50 days. The total age of the sample was 98 days."[14]
- Serne (2015)[15] conducted extended leach tests on LAW Cast Stone samples. One finding of note was that the leach results for a few of the monoliths began to show an increased rate of release that the authors speculated was related to the formation of new surface micro-cracks visually observed after 790 days of leaching. The authors, "wonder if this observation is the first signs of some internal degradation of Cast Stone monoliths after a time period between 550 and 790 days of leaching." This finding casts further uncertainty on the long-term performance of reducing grouts as they begin to degrade.

Radionuclide Retention

- Asmussen (2016)[16] conducted particle digital autoradiography imaging of Cast Stone cross sections containing Tc-99 and found two distributions of the constituent: "a) congregation in a ring near the outer edge of the monolith, and b) isolation in discrete "hot spots"." This finding challenges the assumption that Tc-99 would be homogenously distributed within a grout monolith, and it suggests that a greater proportion of Tc-99 would be present closer to outer surfaces where they may be more likely to encounter oxidizing agents as the waste form degrades. Asmussen further supposes that the Tc-99 within the grout form may be migrating toward the outer walls, suggesting additional dynamics that may continue to develop over a longer period of time.
- On Page 101 of the FFRDC report, the analysis shows that the Cast Stone grout formulation containing blast furnace slag does not appreciably improve the retention of iodine on its own.

ON SPECIFICATIONS, TESTING, RECOMMENDATIONS AND PLACEMENT PROCEDURES (PROJECT NO. PRO0734). https://www.nrc.gov/docs/ML1623/ML16231A444.pdf

[13] Center for Nuclear Waste Regulatory Analysis, 2009. ESTIMATED LONGEVITY OF REDUCING ENVIRONMENTS IN GROUTED SYSTEMS FOR RADIOACTIVE WASTE DISPOSAL. https://www.nrc.gov/docs/ML1011/ML101160513.pdf

[14] Langton, C.A. et al., 2014. Comparison of Depth Discrete Oxidation Front Results and Reduction Capacity Measurements for Cementitious Waste Forms. http://www.wmsym.org/archives/2014/papers/14330.pdf

[15] Serne, RJ, et al., 2015. Extended Leach Testing of Simulated LAW Cast Stone Monliths. PNNL-24297. https://www.pnnl.gov/main/publications/external/technical_reports/PNNL-24297.pdf

[16] Asmussen, RM, et al., 2016. Solid State Characterizations of Long-Term Leached Cast Stone Monoliths. PNNL-25578. https://www.pnnl.gov/main/publications/external/technical_reports/PNNL-25578Rev0.pdf

Serne and Westsik (2011) stated, "*The available leach data suggest that iodide is not retained in Cast Stone waste forms as well as 99Tc, sodium or nitrate, the latter is generally used to represent a contaminant that has no chemical interaction with the cementitious minerals and is simply retained by the physical properties of the waste form that hinder diffusion*."

- The new Cast Stone formulations are intended to create a reducing environment, which is not expected to decrease iodine diffusion and may in fact increase the migration of the primary form at Hanford, iodate (Zhang et al. 2013[17]; Truax et al., 2015)[18] [note: the cited literature states that on average, 70% of the iodine found in Hanford groundwater samples is in the iodate form]. When iodate is reduced to iodide, it becomes more mobile[19].
    - Recent research at Savannah River National Laboratory[20] also found that, "Both iodide and iodate existed in grout porewater, however, the proportion of each species varied with the grout formulation; slag grout contained 99% iodide and 1% iodate, whereas slag-free grout contained 39% iodide and 61% iodate. Furthermore, iodate bound more strongly to grouts than iodide." These findings suggest that the iodine speciation may be an important factor not currently captured by the effective diffusion coefficient methodology of predicting future environmental release.
- Given that Cast Stone does not appear to adequately improve retention of iodine, the FFRDC assumes the effectiveness of "getters" to retain iodine, while acknowledging that limited data exists regarding the effectiveness or implementability of this technology. As the FFRDC report focuses on silver-containing getters for iodine, our comments will similarly focus on this technology, though we note that several other options are currently under development.
- Silver is the active iodine getter ingredient discussed in the FFRDC report, yet the analysis does not consider the regulatory acceptability of introducing additional RCRA-regulated toxic metal (silver) into the Supplemental LAW waste form. Pierce et al. (2010)[21] includes a discussion of the regulatory difficulty of disposing iodine-loaded silver adsorbent products in grout.
- Asmussen et al (2017)[22] conducted tests with both Tc and I getters and concluded, "It is clear that the presence of the I getter simultaneously with the Tc getter negatively effects (sic) the Tc getter." Additionally, this work found that sulfur-containing Tc getters can displace and re-release the iodine on the silver iodide (AgI). The report suggests that the interference between Tc and I getters can be overcome through sequential treatment of the waste solution, but the long-term effectiveness of this process adjustment does not appear to have been tested.
- Asmussen (2017) also suggests that the complex chemical environment of technetium getters and the Cast Stone itself may be interfering with iodine retention in silver-containing getters. It states, "From the dissolution experiments, it is likely that the instability of the AgI within the Cast Stone is most likely caused by the sulfide component of the BFS with the alkalinity of the LAW simulant and grout playing a minor role in the dissolution." The paper points out that previous examples of Ag based materials in less aggressive cementitious waste forms have

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[17] Zhang, S. et al., 2013. Iodine-129 and iodine-127 speciation in groundwater at the Hanford site, US: iodate incorporation into calcite.

[18] Truex, MJ, et al., 2015. Conceptual Model of Iodine Behavior in the Subsurface at the Hanford Site. PNNL-24709. https://pdfs.semanticscholar.org/bef3/53433dbb6ef3fdf68bd742dd474302acba2c.pdf

[19] Strickland, CE, et al., 2017. Evaluation of Iodine Remediation Technologies in Subsurface Sediments: Interim Status Report. PNNL-26957. https://pdfs.semanticscholar.org/18da/fa52c017e24b56c3aee7447e461f9b4d8dc6.pdf

[20] Savannah River National Laboratory, 2017. 2017 Laboratory Directed Research and Development Program Annual Report. P. 35. https://srnl.doe.gov/LDRD/pdf/FY17_SRNL_LDRD_Report.pdf

[21] Pierce, EM et al., 2010. Review of Potential Candidate Stabilization Technologies for Liquid and Solid Secondary Waste Streams. PNNL-19122. https://www.pnnl.gov/main/publications/external/technical_reports/PNNL-19122.pdf

[22] Asmussen, RM, et al., 2017. Preparation, Performance and Mechanism of Tc and I Getters in Cementitious Waste Forms – 17124. WM2017 Conference, March 5 – 9, 2017, Phoenix, Arizona, USA. http://www.wmsym.org/archives/2017/pdfs/FinalPaper_17124_0317021325.pdf

shown good iodine retention, "However, we have identified processes which will ultimately interfere with AgI stability, and thus alternate encapsulation technologies should be considered as well." These findings nevertheless cast uncertainty on the ability of Cast Stone grouts to obtain consistent long-term performance for iodine with getters.

- Saslow et al. (2017)[23] tested one grout formulation with iodine getters (using hydrated lime instead of the fly ash used in the Cast Stone formula[24]). This experiment showed very low effective diffusion coefficients for iodine, yet this grout form was the worst performing for Tc-99 retention, resulting in effective diffusion coefficient of $10^{-7.9}$ versus $10^{-10.9}$-10^{-12} for the other tests without the iodine getter. This discrepancy is attributed to severe cracks that formed after 7 days of leaching, but this theory is not tested nor is the reason for the crack formation explained. Crawford (2017)[25] also found that silver zeolite getter material increased retention of iodide at the expense of chromium and Tc-99. The only explanation offered for this result was that the silver-zeolite could have expended some of the reducing capacity of the blast furnace slag in the premix. These results raise uncertainty regarding compound effects of getters for retention of multiple constituents, and the Saslow results are also interesting in light of the uncertainty regarding the effect of grout degradation on constituent release.

Long Term Getter Performance

The final conclusion of the FFRDC analysis appears to be that grout will only provide adequate performance at Hanford for iodine-129 if the best-case grout from today's lab testing proves feasible to bring out of the lab. The best case relies on effective getters for iodine, LDR treatment, and the Cast Stone reducing grout formula all to work in concert as well as is hoped. The long-term performance of getters in reduced grout is a key scientific uncertainty that would complicate selection of grout for disposal of Supplemental LAW at Hanford.

- Serne and Westsik (2011) stated: "*Past studies using iodide getters containing silver-based reagents show they do reduce iodide leaching significantly in short-term leach tests; however, long-term thermodynamic-based constructs raise concerns whether low solubility silver iodide will remain stable. Thus, iodide getters that do not rely on precipitation of low solubility silver iodide will probably be required to meet the currently desired effective diffusion coefficient of* 1×10^{-11} cm^2/s*.*"
- Dr. Jim Krumhansl of Sandia National Laboratory noted in Serne and Westsik (2011) that, "*At the Earth's surface the calculations indicate that AgI is transformed to the much more soluble AgIO3, while under strongly reducing conditions AgI releases iodide as it breaks down to form silver metal . . . It should be noted that none of these reactions occur rapidly enough to be easily observed in the short-term lab waste form leaching studies performed to date. Hence, short-term studies will generally just reflect the extremely low solubility of AgI*."
- Atkins et al. (1990), as summarized by Pierce et al. (2010): "*They concluded that even though AgI is stable in Portland cement in the near term, after disposal in a repository, the oxidation/reduction conditions will cause the AgI to release* I^- *and render the* Ag^+ *inert as* Ag^0 *. From their evaluation of Portland cement and Portland cement containing 85% [blast furnace*

[23] Saslow, SA, et al., 2017. Updated Liquid Secondary Waste Grout Formulation and Preliminary Waste Form Qualification. PNNL-26443. https://www.pnnl.gov/main/publications/external/technical_reports/PNNL-26443.pdf
[24] The hydrated lime formulation is intended to address high-sulfate Liquid Secondary Wastes. The one Cast Stone sample in this study failed to set properly.
[25] Crawford, CL, et al., 2017. Analysis of Hanford Cast Stone Supplemental LAW using Composition Adjusted SRS Tank 50 Salt Solution. https://sti.srs.gov/fulltext/SRNL-STI-2016-00619.pdf

slag] as S/S agents for iodine, they conclude that even within 300 years, added silver will have no benefit with respect to iodine release."

- Maddrell et al. (2019)[26] discussed alternate waste forms for silver-zeolite loaded with iodine. The report remarks, "*While the silver sodalite wasteform produced is, like the popular AgI-based wasteforms, highly leach resistant to leaching by deionised water it was unstable under highly reducing conditions, which are likely to occur in most geological disposal facilities. Post leaching characterisation revealed the redeposition of AgI and the formation of an aluminosilicate alteration layer under some leaching conditions. Appropriate precautions are required should a silver sodalite wasteform for iodine immobilisation be exposed to reducing groundwater conditions*."
- Kaplan et al. (2019) found that encapsulation of iodine-loaded silver-impregnated zeolite in slag-free grout was "extremely effective" at immobilizing iodine, but encapsulation in slag-containing grout was "entirely ineffective." They state, "*Based on thermodynamic calculations, the strongly reducing conditions of the slag-containing system (Eh was −392 mV) promoted the reductive dissolution of the AgI, forming Ag0(*aq*) and releasing iodide (I−) into the aqueous phase. . . these results indicate that subsurface grout disposal of AgIZ waste should be done under oxidizing conditions*." If it can be reasoned that the grouted waste form would begin as a reduced environment and oxidize over time, it is unclear why these results are so seemingly different from the best-case scenario in the FFRDC report.
- A discussion of AgI disposal in deep boreholes[27] notes that AgI is redox sensitive, giving the example that iron can reduce AgI to silver metal and release iodide ions.
- Qafoku et al. (2015)[28] states in its section on future study: "*We will continue our focused efforts to determine if there is an appropriate getter that when used in Cast Stone formulations will significantly decrease the Tc and I diffusivities and their overall release. To achieve this short-term objective we will work in parallel to answer the question of <u>how and why</u> the getter is effective so that we can assess whether or not [it] will exhibit a good long-term performance. In addition, we will continue working in the future to 1) determine an acceptable formulation for the LAW Cast Stone waste form with getters; 2) demonstrate the robustness of the formulation in terms of Tc and I release diffusivities; and 3) provide Cast Stone contaminant release data for risk assessment evaluations.*" These research and development goals seem to be a tall order on a short timeframe.
- Qafoku et al. also states, "*The long-term performance of the getters as part of monolithic waste forms, which is currently unknown, should be also evaluated (Pierce et al. 2010)*," and, "*Currently, only a limited number of studies have thoroughly investigated interactions between getters and waste forms (Pierce et al. 2010), and additional experimental work is needed in this area*."
- The FFRDC report (p. 31) notes that silver adsorbents for iodine pretreatment, "represent work at a very low TRL," and, "If iodine removal is determined to be required, extensive R&D will be required to develop and mature the technology needed." Yet, when silver grout additives are incorporated as getters to obtain the "best performance" necessary for grouted iodine to be compliant with applicable regulations, the team judged a low risk that the necessary technology R&D could be completed within the project timeframe (p. 110). This is a confusing discrepancy.

[26] Maddrell, Ewan & Vance, E.R. & Grant, Charmaine & Aly, Z & Stopic, Attila & Palmer, T & Harrison, J & Gregg, D.J.. (2019). Silver iodide sodalite – Wasteform / Hip canister interactions and aqueous durability. Journal of Nuclear Materials. 517. 10.1016/j.jnucmat.2019.02.002.

[27] https://www.osti.gov/servlets/purl/1109063

[28] Qafoku et al., 2015. "Technetium and Iodine Getters to Improve Cast Stone Performance". PNNL-23282 Rev 1. https://www.pnnl.gov/main/publications/external/technical_reports/PNNL-23282Rev1.pdf

Conclusion
On page 110 of the FFRDC report, the authors judge there to be a "low" risk that the technology research and development necessary to support onsite grout disposal will not be complete within budget or timeline. Given the uncertainties described above, a more substantial basis should be provided for this assertion, or it should be reconsidered.

FFRDC Performance Evaluation

- We note that the site-specific analysis for the Hanford IDF relies on a Performance Evaluation or "mini performance assessment" built on the more developed IDF PA, which has not yet been subject to public review. As members of the Committee have acknowledged, the public has not had an opportunity to validate the methods in the performance assessment or its approach to addressing model uncertainty.
    - For example, the FFRDC report (p. 171) states that the 2017 IDF PA and supporting documents "described in detail" why it is appropriate to decrease the total iodine-129 inventory in the tanks by 39% relative to that used in the 2012 TC&WM EIS, but that justification is not available for public scrutiny.
    - Given how the NRC has recently highlighted numerous potential issues with another recent Hanford performance assessment[29], which passed DOE's internal Low-Level Waste Disposal Facility Federal Review Group (LFRG) review, we emphasize the importance of fully vetting a performance evaluation, including independent expert technical review, before its results are condensed for decision-makers. To do otherwise would irresponsibly anchor their expectations and run the risk that potentially significant uncertainties are not given their due. It is unfortunate that the timing of the NAS study prohibits this crucial decision support step from taking place, and we urge the committee to strongly caution decision-makers against drawing a premature conclusion from the present study.
    - Example issues identified in the NRC review of the Waste Management Area-C PA included the projected speed of flow in the aquifer, which would affect contaminant concentrations in groundwater, and the approach to modeling uncertainties related to alternative future scenarios. These issues would also be relevant to the Supplemental LAW decision based on the IDF PA.
- Unlike performance assessments for other LLW facilities or tank closures, the report's performance evaluation appears to assume current site conditions persist. This decision provides an incomplete picture of waste form performance, as it does not evaluate each form's resilience to unexpected changes in the disposal environment. Given that the reader is unable to ascertain whether the majority of performance derives from the waste form or its disposal environment, the evaluation is incomplete. For example, pages 183 – 185 calculate release rates based on a baseline recharge rate from the IDF PA that assumes no recharge during the first 100 years, 0.5 mm/yr for the next 400 years, and 3.5 mm/yr thereafter. A sensitivity case should evaluate the effect of early disposal facility cap failure. To further illustrate this point, the Hanford Solid Waste Landfill Annual Monitoring Report for 2006-2007[30] includes a figure of cumulative lysimeter drainage from 1996-2007, which measured an average annual drainage of

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[29] NRC, 2019. Request for Additional Information on the Draft Waste Incidental to Reprocessing Evaluation for Closure of Waste Management Area C at the Hanford Site. ML19112A091. NRC Docket #PROJ0736.

[30] Hanford Site Solid Waste Landfill Annual Monitoring Report July 2006 Through June 2007. https://pdw.hanford.gov/arpir/pdf.cfm?accession=AR-02383

49.8 mm/yr, dominated by two wet winters in 1997 and 2003. It is reasonable to evaluate the effects of similar episodic conditions occurring in the event of future cap failure.

- We note that the FFRDC report assumed that the leachate collection system at the IDF would not degrade for 500 years (p. 173), yet institutional controls are assumed to fail in 100 years. It stands to reason that a leachate collection system would eventually fail without human intervention via operations and maintenance activities. This discrepancy may be a sensitive parameter for waste form performance and the time of peak dose.
- Serne and Westsik (2011) acknowledged, "Long-term waste form leaching and durability studies and modeling need to be performed for environmental conditions relevant to the IDF disposal environment. Without such long-term waste form leaching and durability studies and complementary predictive modeling efforts using IDF disposal environment conditions, it will be difficult to create a credible performance assessment."[31]

Glass Performance and Production Rate

- We wish to call the Committee's attention to the progress that has been made toward improving the rate of glass generation in the current LAW vitrification facility. In a March 2019 Hanford Advisory Board Tank Waste Committee meeting[32], the DOE Hanford Glass Scientist remarked that with a number of prospective enhancements, Hanford is "within striking distance" of not needing a Supplemental LAW treatment capability. For example, the removal of the extra refractory in next-generation melters could increase the glass production rate for each melter from 15 metric tons per day to 50 metric tons per day[33]. Additionally, an increase in the tolerance of crystal formation in the glass from 1% to 1.5% could potentially reduce the total glass volume of the WTP mission by 20%[34]. However, discussions with other DOE staff revealed that the existing LAW facility likely does not have the support infrastructure (e.g., electrical wiring, offgas treatment) necessary to support a melter capacity increase of this scale. As a result, these potential advances were only partially considered in System Plan 8[35], which was a foundational information source for the FFRDC. With so much emphasis in the FFRDC report placed on the rewards of additional R&D on grout technology, we see the lack of a similar focus on future glass process improvement as a missed avenue of investigation in the NAS study. This

[31] Serne and Westsik, 2011. Waste Form Development and Optimization – Cast Stone. http://citeseerx.ist.psu.edu/viewdoc/download?doi=10.1.1.465.1951&rep=rep1&type=pdf

[32] https://www.hanford.gov/files.cfm/Enhanced_Waste_Glass_Effort_AJZ.PDF; https://www.hanford.gov/files.cfm/Final_3_13_19_Sum.pdf

[33] After the M-Area melter at Savannah River exhibited leaking, the design for the Hanford LAW melter included a second layer of refractory material as a precaution. Subsequently the root cause of the M-Area melter failure was determined, and the extra 12-inches of refractory around the LAW melter was determined to have been unnecessary. The 10m^2 melt pool 1st generation melter weighs 330 tons; a 2nd generation melter with refractory removed would also weigh 330 tons and have identical physical dimensions. (Albert Kruger, pers. comm., 2019).

[34] The origin of the 1% crystal tolerance derives from experiments at Mol Belgium performed by Germany in the 1970s-80s. The experiments used reprocessing wastes from a high burn commercial fuel that included high quantities of noble metals. The melter was a bottom electrode design and un-agitated. Due to shear flocculation, conductive metal crystals grew on the floor and walls of the melter, creating a path between the bottom and side electrodes. By contrast, the WTP melters do not use bottom electrodes, the defense wastes have a significantly smaller fraction of noble metals, and the melter uses bubbled agitation. DOE is developing information to support a potential decision that relaxing the crystal tolerance constraint would pose no risk to the WTP melters. (Albert Kruger, pers. comm., 2019).

[35] System Plan 8 assumes that next-generation melters will increase capacity by nominally 25% (i.e., 37.5 MT/d maximum) after five years of initial operation using the existing melters.

additional context may also complicate the underlying premise of the NAS study charge and the decision it is intended to support.

- The ability of the LAW vitrification facility to retain Tc-99 is another focus of continual glass improvement. Staff in DOE's Office of River Protection have claimed that their contractor has demonstrated greater than 99% retention of Tc-99 in their pilot vitrification facility if the condensed LAW overheads are recycled back into the feed, however this would result in a 7-15% increase in the total amount of LAW glass produced. As an alternative, DOE is working on ways to retain a "cold cap" at the top of the crucible melt via temperature and feed mass management, which would trap the Tc-99 and not allow it to escape as steam.[36] If these improvements are realized in the LAW facility, the liquid secondary waste would contain a significantly lesser quantity of Tc-99. This would improve the performance of glass relative to a grout alternative for Supplemental LAW.

Other Complicating Factors

- We note for the benefit of the Committee that DOE has initiated an Analysis of Alternatives for the WTP in accordance with DOE Order 413.3b. This analysis is in response to the 2018 US Army Corps of Engineers Parametric Evaluation of the Waste Treatment Plant, which concluded that the Pretreatment and high-level waste (HLW) facilities as currently envisioned cannot be completed on time or within a reasonable range of the current budget. The resulting analysis will include five scenarios for a new WTP system configuration, three of which would reconfigure or abandon the Pretreatment facility in favor of a direct-feed HLW configuration.[37] The FFRDC analysis explicitly does not evaluate the effects of direct-feed HLW on the LAW fraction of the waste, which demonstrates that the NAS study scope has already begun to depart from a reasonably foreseeable future reality.
- Similarly, the new DOE interpretation of the definition of high-level radioactive waste has the potential to significantly change the WTP mission, as it creates confusion regarding the level of radionuclide separation necessary to distinguish between "high-level" and "low-activity" waste. While we acknowledge that no overt steps have been taken to apply this interpretation to Hanford, a close reading of the newly interpreted definition suggests that the glass coming from the HLW vitrification facility as currently imagined could no longer strictly be high-level waste, but rather may qualify as greater-than-Class-C low-level waste. This development unfortunately casts the applicability of the Committee's chartered study into further doubt.

[36] Albert Kruger, DOE Glass Scientist. Pers. Comm., 1/2/18.
[37] https://www.hanford.gov/files.cfm/USACE_Parametric_Analysis_Final_ajz.pdf