Abatement of Mercury and Iodine in WTP LAW Off-Gas Streams

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Mission Need/Challenge

Continuation Project (TCR: HQ221814), **Abatement of Mercury and Iodine in WTP LAW Off-gas Streams.**

NNLEMS Hanford R&D Roadmap (PS-9, SW-9, IM-5), Hanford Risk Register (ID: DFLAW-0232-T)

Project Description

Significant flowsheet risks continue to exist for melter off-gas systems at the Hanford Waste Treatment and Immobilization Plant (WTP) because of low removal efficiency for mercury (Hg) and iodine (^{129}I) in glass, uncertainty in partitioning, and projected poor iodine retention in the carbon bed. Identifying candidate sorbent materials for individual or dual capture capability also mitigates issues with the current Kombisorb BAT-37 material, including lack of future commercial availability, fire safety risk due to exothermic heat generated by adsorption reactions between the carbon bed adsorbent and Hg, and the risk of ^{129}I bypassing the carbon bed to impact downstream facilities (i.e., the Liquid Effluent Treatment Facility and Effluent Treatment Facility).

This work seeks to evaluate and demonstrate commercially available and, as warranted, developmental materials for highly efficient capture and abatement of Hg and I in melter off-gas streams in the WTP Low-Activity Waste (LAW) and High-Level Waste (HLW) facilities. In FY23, an extensive review of literature and commercial manufacturers was completed to identify viable candidate materials for single and dual capture of these contaminants (Fountain et al. 2022). Screening testing of these materials was completed with static exposure tests to assess sorption capacity for Hg and I, followed by preliminary dynamic testing with a simplified off-gas composition containing Hg, I, air, and H_2O. A technology maturation study using down-selected candidate materials under dynamic and prototypic flow-through tests with complex gas compositions is now warranted. This scope will address near-term WTP LAW off-gas technology needs related to Hg and ^{129}I and also future WTP HLW off-gas abatement needs.

The proposed scope will continue evaluating candidate commercial materials and maturation of developmental materials while demonstrating Hg and I abatement in simplified, yet representative melter off-gas streams under dynamic conditions (i.e., Hg, I, air, and H_2O) and under prototypic complex gas compositions (e.g., NO_x, CO, HCl, SO_2). The candidate materials identified as the best performing and mechanically/chemically robust will be recommended for testing at larger-scale conditions and for subsequent waste form evaluations. Ideally, one material will abate both Hg and I simultaneously, but two materials can be considered in a mixed sorbent bed configuration.

Project Duration and Deliverables

This second year of work will build on the first year's success by continuing to screen out candidate materials and then move to more complex and prototypic gas compositions and off-gas conditions (i.e., residence time and superficial velocity) to demonstrate Hg and I abatement performance.

This second year will test the best commercially available material(s) identified (up to three) and viable developmental candidate materials (up to three) for subsequent larger-scale testing. Material characterization will be completed to investigate degradation mechanisms, as appropriate. The production of a waste form for at least one promising candidate material will also be demonstrated. A technical report summarizing these results and material recommendations for larger-scale testing will be completed.

Cost Estimate

- PNNL: $600K

Benefit to DOE-EM

Replacement Kombisorb BAT-37 with a dual-function material for capture of Hg and ^{129}I, or a combination of Hg- and I-specific materials, directly mitigates a risk of future material availability, but also addresses other operational risks in the carbon bed and to downstream secondary liquid treatment facilities at Hanford. The candidate materials advancing to final demonstration testing can replace and improve Hg and I abatement in the WTP HLW Facility and/or can be demonstrated and applied at other DOE sites requiring gaseous Hg and ^{129}I capture.

References

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Deployment of In-Line Sampling in Tank Farms

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Mission Need/Challenge

RPP Roadmap (MTW-76: Online Monitoring)

Deployment of in-line sampling within the tank farms at Hanford can address significant characterization and process control needs while reducing the number of (and cost associated with) needed sample collections. In-line monitoring based on Raman spectroscopy can provide quantitative analysis of multiple chemical species of interest, including but not limited to nitrate, nitrite, phosphate, hydroxide, aluminate, chromate, carbonate, oxalate, and sulfate (Lines et al. 2019; Tse et al. 2020). Real time analysis provided by Raman spectroscopy supports the remote characterization of process streams while relying on sensors that are hardened to radiation and corrosive chemical environments.

Specific applications include supporting chemical dissolution of waste for retrieval and aiding with feed waste qualification.

Project Description

Toward supporting deployment in the tank farms, the PNNL team proposes building and testing a spool piece to incorporate Raman probes. This will rely on leveraging existing technology and demonstrations of the applicability of Raman while expanding to show methodology of integrating Raman probes into representative-scale systems.

<u>Task 1: Development of spool piece</u> – A spool piece, or a large-scale flow cell, will be designed and fabricated to allow for connection into a process line as well as stable integration of a Raman probe. The team will work with process experts to identify ideal pipe diameters, target flow rates, and other integration concerns to ensure the spool piece will fit into target processes and meet system requirements.

<u>Task 2: Integration of Raman probe</u> – The team will procure and integrate a Raman probe into the spool piece. This probe will utilize customizable components to ensure ideal fit, focus, and sensitivity to target process streams.

<u>Task 3: Testing of spool piece</u> – The team will mock up a flow-loop to test spool piece and probe performance under flowing conditions.

<u>Task 4: Application of real-time analysis</u> – Chemometric models developed for quantifying target chemical species will be tested and applied to data collected from spool piece demonstration to evaluate ability to track concentrations of target chemical species in real time.

<u>Task 5: Reporting</u> – A summary of work will be presented to the client in the form of a letter report.

Project Duration and Deliverables

This will be a 1-year project

- Year 1 Deliverables: A report on design and performance of spool piece

Cost Estimate

- Task 1: $100K
- Task 2: $50K
- Task 3: $55K
- Task 4: $70K
- Task 5: $25K

Benefit to DOE-EM

The benefit to DOE-EM is to improve the efficiency of Hanford tank farm processing and characterization. More specifically, the integration of Raman-based monitoring can provide real-time feedback on a large number of chemical species of interest for process control and optimization. Utilization of this technology can not only reduce the needed number of grab samples (significant cost and time savings), but can help avoid process upsets while allowing for optimization of process performance.

References

Lines AM, P Tse, HM Felmy, JM Wilson, J Shafer, KM Denslow, AN Still, C King, and SA Bryan. 2019. "Online, Real-Time Analysis of Highly Complex Processing Streams: Quantification of Analytes in Hanford Tank Sample." *Industrial & Engineering Chemistry Research* 58(47):21194-21200.

Tse P, SA Bryan, NP Bessen, AM Lines and JC Shafer. 2020. "Review of on-line and near real-time spectroscopic monitoring of processes relevant to nuclear material management." *Analytica Chimica Acta* 1107:1-13.

Demonstrating Removal, Deployment, and Immobilization of Technetium and Iodine from Actual Hanford Waste

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Mission Need/Challenge

Continuation Scope (TCR: HQ221815), NNLEMS Hanford R&D Roadmap (SW-10, PL-6, IM-13)

Project Description

Supplemental low-activity waste (SLAW) immobilization and 200 West Area grouting activities are potential options DOE is considering in support of the Hanford mission. Demonstrating improved grout performance by removal of key radionuclides from the low-activity waste (LAW) using commercially available materials would show that a grouted SLAW inventory in the Hanford Integrated Disposal Facility (IDF) could meet performance objectives and build stakeholder confidence. The benefits of this scenario were described in the recent National Academies of Sciences (NAS) study of SLAW.

Technetium and iodine are two key risk drivers for disposal where a pathway to potable water is present. Removal of these radionuclides from LAW could greatly benefit a primary grouted LAW waste form where these radionuclides are the primary concerns for on-site disposal, as there is much uncertainty in the long-term performance of waste forms in the IDF (both glass and grout). Technetium removal was previously included in the Hanford Waste Treatment and Immobilization Plant and it was planned to use an elutable resin, Superlig 639, although iodine removal was not considered or evaluated. This technetium removal approach was abandoned in the early 2000s with an assumption that sufficient technetium retention would be achieved within the glass.

Since that time frame, a significant amount of development toward selective technetium and iodine removal from alkaline waste streams has been completed. The materials demonstrated are a combination of commercially available and newly developed materials. While individual technetium or iodine removal has been targeted the most, there are commercially available materials (e.g., Purolite A530e) that have recently been shown to remove both simultaneously. However, all recent work has been performed with simulated LAW or other alkaline simulants. In FY23, PNNL demonstrated, ***for the first time***, simultaneous removal of technetium and iodine from actual Hanford waste with a series of resins. This work highlighted that both species can be removed and the best performance in batch tests was achieved with the material SIR-110-MP, a gel strong-base anion-exchange resin. The SIR-110-MP was also tested in a column where 5 L of tank waste from tanks AP-105 and AP-107 was stripped of technetium but iodine uptake was limited compared to batch test levels. As only a single demonstration was performed, further refinement and understanding of resin performance for both technetium and iodine needs to be targeted. The original column tests were scaled based on the existing Tank Side Cesium Removal system, but these conditions may not be ideal for the resins. Based on the FY23 effort, there are four opportunistic tasks available to better target this technology development.

Subtask 1: Characterization of the resins tested in FY23 – This effort will include a detailed material balance of the loading onto the ion exchange material to help define a disposition path for the material. As well, the task will include targeted simulant column tests varying the flow conditions to optimize technetium and iodine removal.

Subtask 2: Processing of other opportunistic tank waste samples – The FY23 work tested a combination of waste from AP-107/AP-105. Other tank waste samples decontaminated of cesium are now available to test the effectiveness of the approach in other waste chemistries to show the universality of the approach. The conditions for the actual waste tests will be based on the Subtask 1 findings. The samples available are listed in the table below:

Waste	Volume	Issues
AW-102- 5.5 M Na	5.3 L	Treatability study ends 2023
AP-101- 5.2 M Na	2.1	Treatability study ends 2026
AP-105 (5.5 M Na)	3.7	Treatability study ends 2027
SY-101 (2.8 M Na)	8.5 L	Treatability study ends 2028
AN-107	TBD	Being processed in test platform in FY24

Subtask 3: Detailed isotherms on resins – For the most promising resins from FY24, the isotherms for technetium and iodine in tank waste matrices need to be determined to optimize column performance and understand the long-term viability of the resin removal.

Subtask 4: Immobilization of loaded resin and column effluent – The column testing in FY23 has generated a valuable and unique tank waste sample that contains only non-pertechnetate species and residual iodine that passed the column. Grouting of this opportunistic waste sample would help several crucial areas: (1) inform, for the first time, on the behavior on non-pertechnetate in grout; (2) demonstrate leachability/waste acceptance of the resulting technetium/iodine-stripped and grouted waste; (3) demonstrate a total system mass balance for this disposal scenario by also immobilizing the loaded resin. Work at PNNL in FY23 funded by WRPS is screening candidate waste forms for the immobilization of spent organic-based ion exchange resins. **Note**: This subtask can be merged with tasks in the PNNL/SRNL proposal for "Non-pertechnetate Behavior in Grout" if funded.

Project Duration and Deliverables

This project will be performed over ~14 months to allow time for execution of the tasks as some tasks will feed information or materials to later tasks. The final deliverable will be submission of a draft journal article to EM-HQ and to a journal along with a presentation to DOE/site contractors on the findings.

Cost Estimate

$425K (All subtasks)

Benefit to DOE-EM

This task benefits DOE-EM by maturing a promising approach to manage the two most problematic radionuclides present in Hanford wastes destined for LAW immobilization. The most cost-effective, yet uncertain, disposal pathway considered by the recent NAS study for Hanford SLAW is the use of a primary grouted waste form disposed of at the IDF. The uncertainty, and subsequent risk, is drastically reduced if the technetium and iodine inventories in the grout are lowered significantly. This task is maturing a technology to achieve simultaneous technetium and iodine removal to meet this challenge.

Increased Hanford Tank Sidewall Integrity Inspections with Robotic Guided Wave & Magnetic Flux Leakage Sensors

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Mission Need/Challenge: Hanford contractor WRPS needs to increase the area of primary tank sidewall inspections from 1% to at least 10% to decrease risk of tank sidewall leaks and provide time to intervene with tank life extension measures such as repair. The inspection need is identified as Manage Tank Waste (MTW) 10: *Improved Inspection Methods for DST Primary Tank Walls* in the RPP Technology & Innovation Roadmap [1].

Project Description: Guided wave ultrasonic testing (UT) and magnetic flux leakage (MFL) sensor technology can inspect significantly larger tank sidewall areas in far less time than the traditional UT method currently used for sidewall inspections [2]. WRPS and PNNL propose to collaborate with sensor, robotics, and inspection service companies to leverage recent technology and machine learning advancements the teams have made to bring robotic guided wave UT and MFL sensor technology (equipped with machine learning algorithms for rapid analysis) to primary tank sidewall inspections. Three complementary inspection technologies are proposed, one per task.

<u>Task 1: Apply GWPA air-slot sensor for standoff inspection of large sidewall areas</u> – This task leverages work performed on guided wave phased array (GWPA) sensor iteration, requirement verification testing, nondestructive examination (NDE) reliability testing to qualify the sensor, and a GWPA machine learning model for floor plate scan image/data interpretation (would also be applicable to sidewall inspection data interpretation) under a WRPS primary tank floor inspection technology project. **Year 1**: Modeling to show GWPA sensor can inspect curved sidewall plates in at least the vertical sensor orientation. **Year 2:** Complete robotic wall crawler for GWPA sensor, integrate sensor with crawler, and complete requirement verification tests. Verification results must show the integrated system can at least detect simple geometry action-level corrosion test flaws in 1/2-in.-thick carbon steel plate (sensor limit but also represents majority of sidewalls). **Year 3**: Complete blind test point checks on existing qualification mock-up. Results must show that at least the same flaws can be detected during sidewall plate qualification tests as were detected during tank floor plate qualification tests to justify taking credit for full sensor qualification. **Year 4**: Deliver robotic GWPA sensor system and final report on GWPA sidewall inspection reliability (qualification to inspect tank sidewalls).

<u>Task 2: Qualify EMAT sensor for long-range standoff inspections of full-height sidewall plates</u> – This task leverages work performed on electromagnetic acoustic transducer (EMAT) sensor and robotic deployment system iteration and requirement verification testing under the WRPS primary tank floor inspection technology project. **Year 1:** Complete fabrication of sidewall test plates and attach to existing qualification mock-up. **Year 2**: Prepare test flaws in new sidewall test plates and complete first sidewall plate qualification test campaign. Results must show the EMAT can at least inspect the 7/8-in. and 3/4-in. plates – plate thicknesses the GWPA sensor cannot inspect and the MFL sensor may not be able to inspect – to warrant completing subsequent Stage 2 and 3 test campaigns. **Year 3**: Complete second sidewall plate qualification test campaign. **Year 4**: Complete third sidewall plate qualification test campaign. **Year 5**: Deliver report on EMAT sidewall inspection reliability.

<u>Task 3: Purchase and qualify MFL sensor for rapid inspection of discrete sidewall areas</u> – This task leverages commercially available MFL sensor technology, prior work by industry/academia to evaluate the NDE reliability of MFL sensors, and progress made on a DOE-FE project to train a hybrid physics-informed/data-driven machine learning model how to interpret MFL signals to predict corresponding flaw dimensions in carbon steel natural gas transmission pipelines. **Year 1**: Complete basic MFL sensor demo to show MFL can detect simple geometry action-level corrosion test flaws in at least 1/2-inch-thick carbon steel plate (potential limit of sensor but also represents majority of sidewalls). **Year 2**: Receive new MFL sensor and robotic wall crawler, integrate MFL sensor with wall crawler, and complete requirement verification tests. Verification test results must show the integrated system can at least detect simple geometry action-level corrosion test flaws in 1/2-in.-thick carbon steel plate. Also create a "digital twin" of the MFL sensor and sidewall qualification test plates in modeling software. **Year 3**: Complete blind test point checks on qualification mock-up. Results must show that complex geometry action-level corrosion test flaws can be detected by the MFL sensor in at least the 1/2-in.-thick sidewall test plates. Also use digital twin model to simulate MFL inspection of sidewall plates. **Year 4:** Deliver robotic MFL system and final report on MFL sidewall inspection reliability (qualification to inspect tank

sidewalls). Train the MFL machine learning model on MFL signal data collected during Year 3 blind tests and use the same signal data to validate MFL inspection simulations from digital twin. Real and simulated MFL signals must show agreement to justify using simulations to help train the MFL machine learning model to interpret inspection data and perform flaw characterization. **Year 5**: Train the MFL machine learning model on validated simulated MFL inspection data, perform blind test point checks of the MFL machine learning model to validate the model's predictions of flaw type and size, and issue report on model performance.

Project Duration and Deliverables

- Task 1 duration: 4 years. **Deliverables**: GWPA sensor integrated with a robotic wall crawler for tank sidewall inspections and reports on Year 1 modeling and simulation performed to determine the GWPA sensor orientation limitations, if any, for sidewall plate inspections; Year 2 verification test results; and Year 3 results of qualification point checks of flaw detection reliability (due Year 4).
- Task 2 duration: 5 years. **Deliverables**: Reports on Year 1 qualification mock-up expansion to facilitate sidewall inspection technology qualification tests; Year 2, Year 3, and Year 4 reports on the qualification/reliability testing of the Southwest Research Institute (SwRI) Robotic Remote EMAT Volumetric Inspection System (RREVIS) on the sidewall test plates; and a final Year 5 report on NDE reliability test results (qualification) of the SwRI RREVIS for sidewall plate inspections.[1,2]
- Task 3 duration: 5 years. **Deliverables**: MFL sensor integrated with a robotic wall crawler for tank sidewall inspections and reports on Year 1 MFL sensor demonstration; Year 2 verification test results; Year 3 results of qualification point checks of flaw detection reliability; Year 4 MFL modeling and simulation validation results; and Year 5 MFL machine learning model validation.

Cost Estimate

The estimated cost is itemized in the table below at the task (some spanning multiple years) and fiscal year level. Cost estimates include WRPS, PNNL, and subcontracts for various vendors (e.g., Guidedwave, Eddyfi Technologies, SwRI, and Onstream).

Task	*Cost ($K)*		*Fiscal Year*	*Cost ($K)*
1	$1,309		2024	$1,670
2	$1,462		2025	$1,286
3	$2,865		2026	$1,084
			2027	$952
Total	**$5,636**		2028	$644

Benefit to DOE-EM

Hanford double-shell tank (DST) life extension: Reduce risk of another tank failure and maximize service life of DSTs. Other DOE sites: The proposed technologies are intended for Hanford DST inspections but would be appropriate to extend to other DOE sites with tank inspection programs, such as the Savannah River Site.

References

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[2] Hede AL, DJ Reid, SR Doll, TA Wooley. 2023. *Technology and Innovation Roadmap*. RPP-PLAN-43988, Rev. 8, Washington River Protection Solutions, Richland, WA.

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[1] The EMAT sensor and robotic crawler are already deliverables under the tank floor plate inspection program. The same physical system would be used for simultaneous sidewall plate and floor plate inspection and therefore is not a separate deliverable here. Training a machine learning model to perform image/data interpretation is planned under the tank floor plate inspection program, and therefore is not a separate deliverable here.
[2] Tank sidewall test plates for sidewall inspection technology qualification would also be a capability/deliverable.

Mitigation of Contaminant Release from Residual Tank Waste

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Mission Need/Challenge

ORP-5. The residual waste that may remain unretrievable in Hanford's underground, single-shell storage tanks (SSTs) is a potential source of long-term contamination to the subsurface environment should leaks occur over time; and its impact is evaluated through performance assessments. Although the closure grout placed in the tanks can limit water intrusion, it has little reactivity toward migrating contaminants. Development of an effective mitigation strategy to prevent or slow the mobilization of radionuclides, Resource Conservation and Recovery Act (RCRA) metals, and toxic chemicals present in the residual waste is of interest to potentially improve closure approaches in performance assessments (PA's).

Project Description

Most of the waste stored in SSTs will be retrieved and vitrified; but a small layer that contains several contaminants of concern (including U, ^{99}Tc, ^{90}Sr, Pu, and Cr^{VI}) is expected to be retained on the bottom of tanks (Deutsch et al. 2011; Cantrell et al. 2008, 2011; DOE 2006). U, ^{99}Tc, and Pu are long-term environmental risk-contributing radionuclides due to their long half-lives and toxicity (Khaleel et al. 2010). Additionally, the constituents possess a high mobility in the subsurface, even for their most stable species under aerobic conditions, adopting such oxidation states as U^{VI}, Tc^{VII}, and $Pu^{V/VI}$. The presence of other redox-dependent contaminants such as Cr^{VI} could influence their sequestration and diffusional release behavior from the residual waste (Cantrell et al. 2006). The reduction of aqueous U^{VI}, Tc^{VII}, Pu^{VI}, and Cr^{VI} to the sparingly soluble U^{IV}, Tc^{IV}, $Pu^{III/IV}$, and Cr^{III} reduces their mobility, and therefore risks associated with their migration in the subsurface. Characterization of residual waste samples from various 241-C tank farm (TF) SSTs suggests that concentrations of contaminants vary by multiple orders of magnitude (Deutsch et al. 2011), and release models have been developed in support of performance assessment PA's and closure (McMahon et al. 2016). However, the presence of numerous mineral phases and their contaminant associations, which are tank-specific, introduce uncertainty in forecasting the performance of these models. Therefore, temporal uncertainty remains in PA's; primarily due to infiltrating pore water that can contact the residual wastes and leach contaminants further into the vadose zone and groundwater. Developing approaches to reduce this uncertainty in contaminant migration from residuals can support current and future PA activities for the U.S. Department of Energy Office of Environmental Management (DOE-EM).

The PNNL-FIU team has extensively investigated economical zero-valent iron (ZVI) materials produced from cast iron, which have been shown to effectively sequester the radionuclide Tc-99 from high-salt and complex matrices (Boglaienko et al. 2019, 2020, 2021; Boglaienko and Levitskaia 2019; Kandel et al. 2022). Experimental evidence has demonstrated that ZVI can sequester a wide range of radioactive, RCRA, and toxic chemicals. The sorption efficiency of ZVI can be further tailored for specific applications at high pH by attachment of functional groups, such as sulfur or phosphorus modified iron (SM- or PM-ZVI).

The objective is to investigate the efficiency of ZVI, modified SM-ZVI, or PM-ZVI within cementitious grout formulations used to immobilize key redox-sensitive contaminants found in the residual waste of the 241-C TF SSTs under challenging conditions of alkaline pH (e.g., grout pore water) and high ionic strength. In addition, this study will quantify contaminants leaching from augmented grout materials by infiltrating water or vadose zone pore water. This testing targets high-priority closure of the 241-C-TF using representative compositions of simulated residual wastes derived from the wastes found in the 241-C TF SSTs. It is projected that the addition of ZVI or SM/PM-ZVI reductants/sequestration agents to the grout will control the release of key contaminants. The anticipated quantitative measurements from the study comparing the contaminant release from native and amended grouts align with the DOE-EM priorities to complete safe immobilization of the environmental legacy waste and closure of Hanford TFs. The specific tasks include:

- Task 1: Evaluate ZVI, SM-ZVI, and PM-ZVI for sequestration of contaminants of concern (U, Tc, Pu, Cr) under relevant conditions and down-select candidate material(s) using batch contact tests.
- Task 2: Formulate and test closure grouts compatible for ZVI, SM-ZVI, and PM-ZVI addition to assess changes in fresh or cured properties from the presence of ZVI agents.

- Task 3: Evaluate the effect of the selected candidate ZVI material(s) on the retention of contaminants of concern in cementitious grout using saturated leach testing.

Project Duration and Deliverables

- Task 1 Deliverables: Demonstrate the efficiency of ZVI materials to immobilize redox active contaminants and summarize results in a peer-reviewed manuscript.
- Task 2 Deliverables: Formulate grout composition compatible with ZVI, SM-ZVI, and PM-ZVI amendments.
- Task 3 Deliverables: Demonstrate improvement of the performance of the cementitious grout by introducing ZVI amendments mitigating leaching of radioactive contaminants from the simulated residual waste and summarize results in a peer-reviewed manuscript.

Cost Estimate

- Task 1: $160K (includes FIU subcontract)
- Task 2: $90K
- Task 3: $240K (includes FIU subcontract)

Benefit to DOE-EM: The closure of the TF involves grouting the retrieved SSTs to structurally stabilize tanks, immobilize residual wastes, minimize the infiltration of water, and prevent the dissolution of hazardous contaminants and radionuclides from further impacting the vadose zone and groundwater. The proposed work aims to improve the long-term performance of the cementitious grout by introducing amendments that can prevent or slow the release of contaminants from the residual waste, improving long-term containment of the residual waste within the tanks during closure and post-closure periods.

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Optimizing Tc-99 and Cr(VI) Retention in Grouts Using Ferrous Iron

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Mission Need/Challenge: ORP-5, NNLEMS Hanford R&D Roadmap (IM-13, SW-1, SW-10), Hanford Risk Register (ID: DFLAW-00363-T)

Project Description: Recent National Laboratories and companion National Academies of Sciences (NAS) studies evaluating supplemental treatment of low-activity waste at Hanford was supported by an extensive analysis of uncertainties around the behavior of various waste forms that could be disposed of at the Hanford Site (including grout). One of the main needs identified to address uncertainty (Vol II Appendix E of Bates et al. 2022) was an improved understanding and projection of the stability of phases/materials that may be used to immobilize technetium-99 (Tc) and other redox-sensitive contaminant species such as hexavalent chromium (Cr(VI)). A similar need was identified in the Hanford Mission Acceleration Roadmap for improved grout waste forms. However, this need truly extends beyond waste forms and is relevant to the long-term behavior of any residual solids in a closed tank where a reactive grout is placed as a base-layer to immobilize hazardous species.

One of the most promising and economical routes for stable, long-term retention of Tc and Cr(VI) is through the use of ferrous iron (Fe(II))-containing materials. In the most extreme conditions of the Hanford tank waste, where soluble Tc is expected to persist in tank sludges, enhanced stability of Tc associated with Fe has been identified with limited leachability (Cantrell et al. 2006). Prior work has shown that Tc and Cr(VI) can be effectively removed from Hanford liquid waste streams using $Fe(OH)_2$ to form Fe-Tc complexes such as Tc-containing magnetite, even in alkaline environments. These Fe-Tc complexes were then shown to improve Tc retention in a glass melt due to the stability of the Fe-Tc complexes (Um et al. 2017). One of the critical mechanisms for improved Tc stability is the reduction of Tc-99 to stable Tc(IV) and its incorporation into the resulting Fe-(oxyhydr)oxide structure. In this reduced and incorporated form, the release of Tc becomes dictated by both its redox state and the solubility of the Fe-(oxyhydr)oxide. In each of these successful cases, the functional variable in capturing the Tc/Cr is Fe(II). Tc and Cr(VI) reduction by Fe(II) and incorporation into iron spinel minerals has been well documented (Marshall et al. 2014; Lukens et al. 2016; Saslow et al. 2017; Wang et al. 2022). Studies in similar, alkaline environments using zero-valent iron (Fe(0)) have shown limited success. Fe(II) studies in representative grout environments are limited until recently. PNNL has shown that the use of $Fe(OH)_2$ as a Tc getter or using Tc-containing iron (oxyhydr)oxide minerals as the Tc source can enhance Tc retention in the grout waste form (Asmussen et al. 2023; Wang et al. 2023). As such, a <u>significant opportunity exists to expand the understanding of Fe-based capture and retention of Tc/Cr(VI) for use in grout waste forms and tank closure applications</u>. ***The primary challenge arises from the use of $Fe(OH)_2$ in all prior studies, which loses its reduction capacity toward Tc/Cr over time with exposure to air, thus presenting challenges with its deployment without maintenance of an inert atmosphere during storage.***

This effort will evaluate variable forms of Fe(II) that are stable against oxidation in air (e.g., ferrous chloride, ferrous sulfide, ferrous sulphate) capable of capturing Tc/Cr(VI) from various Hanford liquid waste streams (comparing against performance of the air sensitive $Fe(OH)_2$). The resulting complexes will be characterized using spectroscopy and scattering methods, including those available at X-ray synchrotron facilities, that are capable of identifying and understanding the Fe phases and stabilization mechanisms that lead to improved Tc/Cr(VI) capture and retention. The stability of the resulting Fe-(oxyhydr)oxides in grout conditions will be evaluated to optimize stability in a grout waste form. This effort will be used to further realize the promise of Fe(II) to provide economically friendly solutions for the long-term stabilization of redox-sensitive contaminants. Upon completion, this task would identify candidate materials for further maturation by site contractors in both waste forms and tank closure mission areas. To achieve these technical objectives, the following tasks are proposed:

<u>Task 1: Tc/Cr(VI) removal by Fe(II)</u> – This task will perform contact tests in simplified and complex simulated waste streams using candidate Fe(II) materials; many of the Fe(II) compounds will be tested for the first time. The removal of

both Tc and Cr will be monitored. Successful compounds based on total Tc and Cr removal will be carried forward to Task 2.

Task 2: Characterization of Fe-complexes from Task 1 – A combination of spectroscopic and scattering techniques at PNNL (e.g., X-ray diffraction, X-ray photoelectron spectroscopy), electron microscopy, and X-ray synchrotron capabilities will be used to identify the associations between the Fe and Tc/Cr(VI) in the resulting products from Task 1. This characterization will allow an assessment of the level of stability induced during capture and project stability in waste forms based on known chemistry behavior of the Fe-oxy(hydr)oxide complexes formed. The assessment will be made by collaborating with WRPS staff on data showing Tc-Fe interaction in tank sludges and other environments.

Task 3: Grout demonstration – The final task will take the most promising Fe phases from Task 2 and evaluate their stability when included in grout. A combination of leach testing and solids characterization will be used to monitor Tc/Cr(VI) retention and potential physicochemical transformations of the Fe-Tc/Cr(VI) complexes in a grout waste form.

Project Duration and Deliverables: This project will be performed over ~14 months to allow time for execution of the tasks and for gaining access to appropriate synchrotron beamlines, sample measurement, and subsequent data analysis. The final deliverable will be submission of a draft journal article to EM-HQ for subsequent submission to a peer-reviewed journal and a presentation to DOE/site contractors on the findings.

Cost Estimate: PNNL: $395K

Benefit to DOE-EM: The most recent evaluations directed by DOE-EM toward Hanford (the NAS and HMAT studies) both highlighted the need for efforts that reduce uncertainty and improve the performance of grout used as waste forms and in tank closure applications. This task directly meets these needs by furthering the technical understanding of one of the most promising approaches in recent years for immobilizing redox-sensitive contaminants, Tc and Cr(VI), while pursing directly implementable solutions. This task can mature the Fe(II)-based approach out from the developmental stage to where it can be supported for further development by the site contractors.

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The Behavior of Non-pertechnetate Forms of Technetium in Grout

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Co-PI: Dan McCabe[2]

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Mission Need/Challenge: ORP-5, NNLEMS Hanford R&D Roadmap (TC-4, TC-5, TC-3, IM-13, SW-1, SW-10), NAS SLAW Study, Hanford Risk Register (ID: DFLAW-0232-T)

Project Description: In recent National Laboratories and companion National Academies of Sciences (NAS) studies, on supplemental low-activity waste (SLAW), significant uncertainty was identified for the potential disposal of grouted low-activity waste forms at locations with a pathway to potable water (such as the Hanford Integrated Disposal Facility, IDF) related to the behavior of non-pertechnetate species in grout (Vol II Appendix E, Bates 2022). Technetium-99 (Tc) can adopt multiple oxidation states in aqueous solutions ranging from +1 to +7. While oxidized Tc(VII) in the form of pertechnetate (TcO_4^-) is expected to dominate in highly alkaline Hanford low-activity waste (LAW), high fractions of Tc in low oxidation states are found in double-shell tanks (DSTs) (the highest concentrations are in the high organics tanks in the AN- and SY-farms); overall experimental data on redox speciation of Tc is available for only 13 DSTs and no single-shell tanks have been assessed (Serne et al. 2014). One study (Serne et al. 2015) tested Cast Stone waste forms prepared using LAW simulant containing either Tc(I) or Tc(VII), and only an order of magnitude increase in Tc observed diffusivity was measured for the low-valent Tc in comparison with TcO_4^-. Because no speciation of Tc in the grout or leachate was tested, this accelerated leaching was speculatively attributed to the oxidation of Tc(I) to Tc(VII) and release of TcO_4^-. Better characterization of the behavior of low-valent Tc within grout waste forms is required to determine the potential impact of low-valent Tc on overall release in the IDF if a grout-immobilized pathway with on-site disposal is implemented. PNNL's recent analysis of AN-102 tank waste demonstrated that Tc redox speciation is complex and Tc species in several different oxidation states can be simultaneously present in LAW (Chatterjee et al. 2020). These forms of Tc can incorporate into the grout waste form differently and therefore have different release rates, resulting in poor predictability of the overall Tc behavior. PNNL's extensive work in characterizing Tc-species and developing detection methods can be leveraged to assess this uncertainty (Branch et al. 2018; Chatterjee et al. 2018a,b, 2017, 2015; Hall et al. 2015; Levitskaia et al. 2015, 2014).

The uncertainty related to low-valent Tc behavior in grout can be evaluated by assessing Tc behavior in a grout matrix and correlating the redox transformation with Tc leaching. Oxidative stability of the low-valent Tc greatly increases upon complexation with small organic chelators, most notably polydentate iminodiacetic acid and gluconate. The resulting forms complex with Tc(I) tricarbonyl (the likely most abundant non-pertechnetate species in the tank waste), have unknown behavior in grout (e.g., may not be reduced by slag in the same manner as Tc(VII)), and may simply diffuse to the surface, oxidize to Tc(VII), and subsequently leach out. Quantitative understanding of this behavior will provide technical information toward understanding the actual impact of low-valent Tc on the performance of grout waste forms.

The analytical determination of the Tc speciation can be done in the bulk grout samples directly using solid-state ^{99}Tc nuclear magnetic resonance for diamagnetic Tc species in oxidation states of +1 and +7, ^{99}Tc electron paramagnetic resonance for paramagnetic Tc species in oxidation states of +4 and +6, and X-ray adsorption spectroscopies (Chatterjee et al. 2020, 2018a,b; Hall et al. 2016; Levitskaia et al. 2015). The same techniques can be applied to speciate Tc in the liquid prior to grouting and in the resulting leachates from the grout. The surface analysis of Tc speciation can be achieved using X-ray photoelectron spectroscopy measurements. Comparing bulk solid, surface, and liquid measurements will provide mechanistic information regarding the redox transformation of non-pertechnetate species through the grout system. Analyzing grout samples at different curing stages and following leach testing of various intervals, a time-resolved understanding of Tc speciation evolution can be determined without further method development.

The speciation of Tc will be tracked in the initial solution, the spiked simulant, within the cured grout, in the resulting leachate, and in the leached grout to track the speciation behavior and compare to leach performance. PNNL will perform the fabrication and leaching with the SRNL collaborators assisting with experimental planning, prior literature analysis, and possible sample sharing. This study would improve confidence in the behavior of non-pertechnetate species in grout as no valuable data exists to date. The planned workflow for this task is presented in Figure 1.

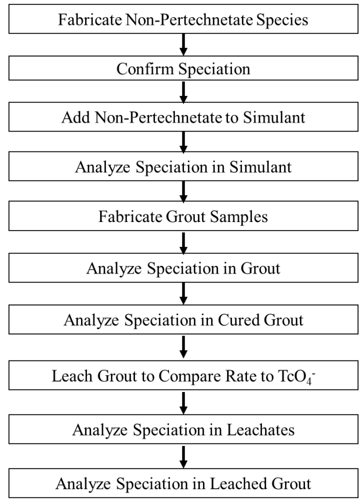

Figure 1. Planned workflow for studying evolution of non-pertechnetate species in waste through a leached grout.

Project Duration and Deliverables: This project will be performed over ~12 months to allow time for fabrication and curing of non-pertechnetate species and grout samples. Leach testing will require ~3 months. The final deliverable will be a draft journal article submitted to EM-HQ and to a journal along with a presentation to DOE/site contractors on the findings.

Cost Estimate: $400K PNNL, $25K SRNL (funded directly)

Benefit to DOE-EM: This task reduces the uncertainty associated with the on-site disposal of grout containing Tc that was highlighted in the recent NAS study. There have been sporadic efforts to identify and understand non-pertechnetate species in Hanford tank waste dating back to the 1990s; however, only now are adequate tools available.

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Ultrasonic Denitrification of Radioactive Waste Streams

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Mission Need/Challenge

RPP Roadmap (PTW-49); NNLEMS Hanford R&D Roadmap (PS-9, PL-8)

The nitrates/nitrites present in the radioactive waste stored in the Hanford tanks have a significant impact on the efficiency of technologies and facilities employed for immobilization. For low-activity waste (LAW), nitrates/nitrites in the melter feed must be countered with addition of reducing agents such as sugar to achieve reliable and successful processing in the melters. However, reaction of nitrates/nitrites and sugar results in the formation of organic compounds such as acetonitrile, which are released into the off-gas system and must be treated and removed from the effluent systems. ***Decomposing nitrates/nitrites in the waste or feed before charging into a melter may eliminate the need for sugar and hence the production of problematic organics, allowing control of the source and efficient management of the treatment systems.*** For high-level waste (HLW), DOE is considering the option of Direct Feed High-Level Waste processing which could potentially accelerate sludge processing but would significantly increase the concentration of nitrates/nitrites in the feed going to the HLW melter over the original plant design. This would mean a similar "reducing agent" issue as observed on the LAW side and would require plant modifications to handle the added NO_x from the HLW vitrification process. ***The ability to control, reduce, or eliminate nitrates/nitrites in the feed prior to vitrification could significantly reduce plant modification costs and prevent the negative impact of NO_x on sorption performance of sorbent materials.***

Project Description

This proof-of-concept project will demonstrate the feasibility of a high-power, focused ultrasound for denitrification waste streams. Current commercially available ultrasound systems use unfocused, low-frequency ultrasound for small-scale treatment of wastewater. They remove contaminants such as pharmaceuticals and organic compounds (Méndez-Arriaga et al. 2008; Hoffman et al. 1996) or break down inorganic contaminants such as sulfates or ammonia (Patil et al. 2021; Flannigan et al. 2005; Flint and Suslick 1991; Davies et al. 2015) over periods of hours to days. Several U.S. patents, e.g., 7,624,703 (2009) and 8,858,805 (2014), have been issued that describe a multi-tiered approach to ammonia/ammonium reduction. These typically follow a two-pronged approach. First, ultrasound is used to decompose ammonia/ammonium to NO_3^- and NO_2^-. Then, a carbon source such as methanol is added while applying ultrasound, reducing NO_2^- to NO, N_2O, and ultimately producing N_2.

The effect of ultrasonic denitrification will be studied with a high-power focused ultrasound capable of generating a strong cavitation in a dynamic flow system, allowing a complete and fast breakdown of nitrates/nitrites to N_2 in a continuous process. A small-scale recirculating system will be built and tested with water solution containing nitrates/nitrites of defined concentration and with liquid simulated waste and feed. The progress of decomposition of nitrates/nitrites will be monitored in real time with nitrate/nitrite and pH probe sensors. In addition, at the head space of the system, the gas species released from solution will be swept with He carrier gas and the gas composition will be analyzed in real time for NO_X and N_2 with a gas analyzer. The goal is to determine the efficiency of ultrasonic denitrification from time-dependent data on concentration of remaining nitrates/nitrites in the solution and on nitrogen gas speciation in the off-gas stream. Three tasks are planned for the project.

- Task 1: Build a small-scale recirculating system – Instruments and parts will be purchased to assemble a dynamic flow testing system. Shakedown testing will be performed, and instrumentation validated.
- Task 2: Test runs with nitrate/nitrite solutions in water – Nitrate/nitrite solutions will be prepared and exposed to a high-power focused ultrasound (different frequency and power level). Concentration of nitrates/nitrites ions will be monitored in real time with nitrate/nitrite probe. The pH probe sensor will be used to monitor increase in alkalinity due to production of NaOH. Off-gas composition will be analyzed in

real time for NO_X and N_2 with a gas analyzer.

- Task 3: Test runs with simulated waste and slurry feed simulant – Simulated waste and slurry feed simulant will be prepared. The same approach as for Task 2 will be used. The focus will be on investigating the effect of more complex composition and particle interaction on efficiency of ultrasonic denitrification.

Project Duration and Deliverables

This scope runs through to the end of FY24. A final report will be published at the end of the project summarizing results from ultrasonic denitrification study. Depending on the success of this proof-of-concept, additional work to evaluate scale-up and efficiency may be warranted.

Cost Estimate

Total funding of $370K is requested to cover cost of instruments, a small-scale recirculating dynamic flow system, labor, project management and miscellaneous consultations, and a final report.

Federal Champion

Albert Kruger (DOE-ORP)

Benefit to DOE-EM

Decomposition of nitrates/nitrites in the waste or feed to N_2 prior to vitrification would eliminate/reduce production of problematic organics into the off-gas system, prevent the negative impact of NO_x on sorption performance of sorbent materials, and may significantly reduce plant modification costs. It is envisioned that this technology could be implemented as a small footprint in-line or recirculation treatment capability, potentially in the vault or similar location between the tank farms and the vitrification process.

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Coatings for Bubbler Life-Extension

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Needs Statement:

Bubbler failure is the single most important event expected to interrupt Hanford LAW melter operation. There is a recognized need for understanding and reducing corrosion in process equipment (e.g., melter wear surfaces, bubblers, etc.) in order to extend the life of individual and component systems.

Scope of work:

This proposal is for the development of ceramic coatings/materials that can extend the service life of Hanford melter bubblers. Available literature and experimental tests will be used to assess material chemistry and surface properties correlations needed to design a ceramic coating capable of increasing the corrosion resistance of melter bubblers. The work will be performed in three successive Tasks, with each phase providing the go/no-go decision for each subsequent Tasks:

- Task 1 - Bubbler corrosion/failure mechanism study
- Task 2 - Materials development and testing
- Task 3 - Scale-up and prototype testing

The proposed budget is for performing Task 1 activities only. Subsequent Tasks will be revised as appropriate. Project management costs are included in the cost estimate.

Background:

Hanford melters will have bubblers that are expected to be replaced every 3-6 months due to corrosion of the bubbler materials. Although the bubbler material (Inconel) is relatively inexpensive, the cost of replacement is manifest in the labor to replace the bubblers and lost production time.

It is well known that ceramic materials such as K-3 or YSZ or (Mg, Ca)-PSZ are more corrosion resistant than Inconel metal; indeed oxide layers that develop on metal surfaces during operation can increase their corrosion resistance. In practice, it is common to apply protective barrier coatings to metal parts to combat corrosion in operating environments. This proposal adopts the concept of the thermal barrier coating (TBC) to improve corrosion resistance of the bubblers via reducing the nominal temperature of the bubbler surface, while simultaneously providing added resistance to chemical corrosion.

The wetting behavior of the glass melt and the temperature at the contact surface with the bubbler are critical to its corrosion resistance. Generally, corrosion resistance increases as the wetting and operating temperature decrease. Conceptually, a coating that thermally insulates the bubbler and that decreases the wetting of the glass to the bubbler would result in reduced corrosion. This concept is realized in applications where TBCs have been used for decades to reduce corrosion failures in Ni-alloy turbine blades/vanes and extend their useful service life. TBCs function both as a chemically unreactive surface and an insulator, enabling forced cooling to decrease the operating temperature of the metal components. A similar concept will be explored to extend melter bubbler service life.

It is recognized that TBCs are designed for conditions and operations significantly different from those that bubblers will experience in a glass melter. Understanding this, the dual role of the TBC will be explored and developed with consideration to thermal mechanical properties and corrosive resistance.

Goal:

The proposed Task will focus on the development of ceramic coating materials for Inconel bubblers to reduce corrosion and increase the service life of the bubblers by a factor of up to 5 times.

Technical Approach:

Available literature will be used in combination with experimental work to assess material chemistry and surface properties correlations needed to design a coating capable of increasing the corrosion resistance of melter bubblers. Equilibrium phases in contact with glass melts at operational temperatures will be used to tailor coating/material design to improve corrosion resistance. The technical scope will be accomplished across a multi-year effort involving three Tasks outlined below:

Task 1 - Bubbler corrosion/failure mechanism study
This activity will identify, through literature survey or experiment, critical surface properties (wetting, adhesion, etc.) of materials in contact with glass melts. This activity will include a survey of available corrosion information and glass composition envelope to ensure the subsequent activities are applicable. In addition, the method of application of the coating will be considered, as the fabrication of a coated bubbler tube will require additional processing. The result will be a technical data package with mechanical and chemical stability requirements for a bubbler coating.

Task 2 - Materials development and testing
This activity will identify candidate materials with favorable properties and compatibility. To reduce the experimental load, research will focus on known systems (e.g., YSZ, (Mg, Ca)-PSZ, etc.) or other known coatings for extreme environments (e.g., spinel). Coupons of candidate materials will be prepared and tested for surface properties (e.g., wetting angle) and corrosion (e.g., ASTM C621). Further down-selection will then be used to identify the most promising candidate materials for testing as a coating.

Task 3 - Scale-up and prototype testing
This activity will evaluate performance of Inconel coated bubblers using accelerated testing (e.g., ASTM C621). These tests will use laboratory experiments scaled to match production parameters accordingly. Further scaleup will be considered as well as cyclic performance testing.

Deliverables:

Description	Estimated Duration
Data package describing bubbler coating requirements for corrosion resistance and compatibility with Inconel bubbler	12 months (after start of Task 1)
Report: Properties and Performance testing of candidate coating materials applied to Inconel bubblers for improved corrosion resistance	18 months (after start of Task 2)
Report: Performance testing in a relevant environment	12 months (after start of Task 3)

Budget (Task 1): $200,000

Benefit to DOE-EM:

A direct benefit of a successfully developed bubbler with increased corrosion resistance would result in cost and risk reductions associated with nuclear waste vitrification. The information gained and the associated technology development would have foreseeable applications across the DOE complex, specifically with respect to life extension of components in extreme environments.

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PROJECT TITLE: <u>CONSOLIDATED WASTE GLASS DATABASE</u>

PRINCIPAL INVESTIGATOR: CORY L. TRIVELPIECE, PHD
COST: $300K (12 MONTHS)

NEEDS STATEMENT: A key technology area for EM's cleanup strategy is vitrification. Glass is the waste-form selected for high level radioactive tank waste at both the Savannah River and Hanford sites, and for low activity waste at Hanford. General research areas include advanced glass formulations, understanding process dynamics in the melter, developing integrated processing strategies, and understanding glass durability and corrosion mechanisms as a waste form. Significant strides have been made in glass composition-structure-property relationships over the past decade with researchers at universities, private companies, and national laboratories. The advanced machine learning tools has streamlined the data mining, analysis, interpretation and modeling. Furthermore, physics-driven machine learning (PDML) coupled with tools like molecular dynamics and Toy Landscapes will introduce a paradigm shift in waste glass design and processing. As such, DOE-EM's cleanup mission can be greatly assisted by the efforts of researchers world-wide working on these applications. The advancements can bring significant improvements in the design, processing, and qualification of glasses, broadening composition envelopes and thereby increasing processing flexibility.

BACKGROUND: DOE-EM has invested tens of millions of dollars in nuclear waste glass research resulting in thousands of report and papers. As many as a dozen distinct, locally managed glass property databases are held by labs, universities, field offices, and contractors. As contractors change, researchers and federal staff retire or change fields, the intimate knowledge of these databases are being lost. The rate of loss will only accelerate since the majority of the glass testing and database collections were conducted more than a decade ago. Many fields of science and engineering have experienced significant growth in understanding and capability by opening data to all potential developers. To leverage this potential for significant advancement in the understanding and modeling of nuclear waste glass properties, a glass property database will be developed and made openly available. Several semi-private datasets of properties exist at the national laboratories and supporting universities with specific purpose and limited distribution. These datasets will be compiled, screened, and formatted for easy access and use by those supporting the DOE Office of Environmental Management and their contractors. An initial launch of the database is planned for fiscal year 2024. This launch will include a large cross-section of data collected in support of the Defense Waste Processing Facility, the Hanford Tank Waste Treatment and Immobilization Plant, and the West Valley Demonstration Project.

GOALS: Compiling a single, controlled open access, database of glass properties and compositions can enable EM's mission. The following points highlight the overarching goals of the proposed efforts:

1) Document data in a systematic and useful manner to ensure access to future nuclear waste glass practitioners.
2) Make consolidated data available to researchers for development of advanced glasses which may enable a step function improvement in glass design.
3) Enable the local management of datasets that are immediately available for all DOE field offices, laboratories and contractors eliminating the need to search and locate data in

grey literature and transpose numbers from existing reports.

4) Build the foundation from which advanced tools can be integrated for the development of new concepts in composition control (e.g., through artificial intelligence).

TECHNICAL APPROACH: Collaboratively with PNNL, support the creation of an online database to manage waste glass data. These efforts will be a continuation of previous years' work and include the following activities for FY23:

1. Finalize the database framework (Figure 1) and establish beta hosting site online.
2. Maintain efforts to consolidate data and ensure quality assurance pedigrees for database.
3. Engage with external partners to test modeling tools' interface capabilities with database and troubleshoot beta version of database with modelers.

DELIVERABLES:

1. Beta version of database for testing of online software hosted by an appropriate entity.
2. Report outlining the initial testing and troubleshooting of the online database by external partners.
3. Journal article describing the application of PDML models to the dataset.
4.

IMPACT: The online database will serve as a universal resource, providing universal access (to both DOE and academia) to qualified data and predictive modeling that can be used to advance waste glass loading. The ability to increase the waste loading of HLW and LAW glasses will shorten the EM mission. Furthermore, the utilization of AI tools will enable the exploration of novel compositional spaces will drastically reducing the number of experiments required to qualify new compositions. In addition, we will partner with external entities to enable a significantly broader reach and access to data that will enhance the applicability of the legacy databases to problems beyond the current EM mission and impact the broader glass science community as a whole.

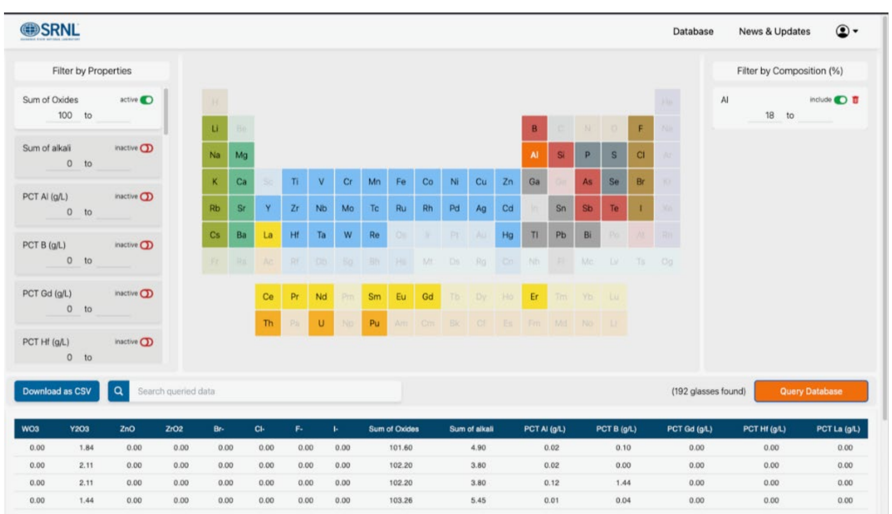

Figure 1: Screenshot of the initial GUI for the database developed by SRNL and Clemson University. The GUI ("landing page") initiates access to the database by enabling users to specify glass components and properties that the users may be interesting in studying.

Project Title: TMFD Online Alpha Monitors

Principal Investigators: David DiPrete, david.diprete@srnl.doe.gov

Rusi Taleyarkhan(Purdue)

Project Description

NEEDS STATEMENT:

TMFD's could make an ideal at-process-line gross alpha/alpha spectrometry sensor or make rapid gross alpha measurements in hot cells to support, for example, characterizations of CST resin performance and not be affected by the high beta gamma dose fields found in those environments.

BACKGROUND:

Gross alpha measurements are typically conducted in radiochemistry laboratories using a number of conventional methodologies. Existing methods have difficulty measuring samples with high beta content or high salt content, conditions that are both present in Hanford and SRS tank wastes. For these tank wastes, extensive radiochemistry is required prior to the gross measurements by any of the existing technologies. These technologies also require locations in low dose environments to maintain low backgrounds and thus high measurement sensitivities.

Tension Metastable Fluid Detectors (TMFD's) have been studied for the past decade in the Purdue University's TMFD laboratory [1-5] and more recently have been studied under a Purdue/SRNL collaboration focused more on the neutron detection potential of these devices.

The fluids in the devices for the testing at Purdue were tensioned centrifugally using centrifugal metastable fluid detectors (CTMFD) (figure 1). These detectors operate on the premise of spinning the fluids, causing an area of controlled tension in the receptacle at the base of the vessel. When tensioned, the fluid becomes metastable and the bonds holding the molecules together can be weakened sufficiently so that external stimuli can break these bonds and create audible-visible-recordable cavitation detection events (CDEs) in the form of vapor bubbles that quickly (within microseconds) grow from a few nanometers to several millimeters in diameter. TMFDs exploit this behavior of fluids at negative pressures to monitor for high linear energy transfer (LET) ionizing radiation such as neutrons, alphas, and fission fragments to enable spectroscopic detection while remaining 100% blind to low LET ionizing radiation (e.g., gammas and betas). Using these CTMFD devices, the Purdue/SRNL collaboration demonstrated that not only gross alpha measurements could be made, but also alpha spectrometry measurements could be made[6].

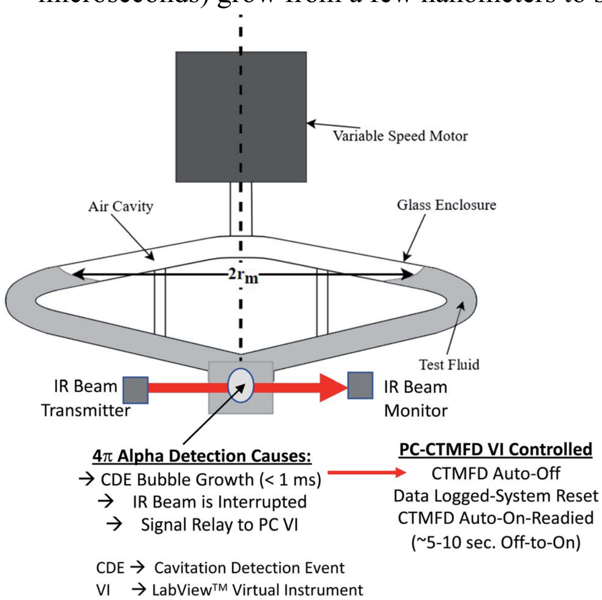

Figure 1. CTMFD

The TMFD devices are beta/gamma blind, so don't suffer from the beta/gamma spillover of the aforementioned gross alpha measurement methodologies. The devices also don't suffer from the dissolved solids of a salt matrix as liquid scintillation counting is not affected. The devices can be located in high dose fields, and sensitivity would not suffer.

In addition to the CTMFD devices, the Purdue/SRNL team have made progress in developing an acoustically tensioned device. These devices tension the fluids by sending an ultrasonic wave thru the fluids. The resulting cavitation is audible and is measured with acoustic sensors. This acoustic tensioned metastable fluid detector (ATMFD) has all the properties of the CTMFD but without the mechanical mechanism required to generate the tension. The form factor for the device is a cylindrical vessel, rather than having the involved wing structure of the CTMFD making for a viable potential form that could be deployed out into the field for a field at-line sensor, or in a hot cell for a rapid gross alpha measurement.

Goal:

The goal of this project is to raise the TRL level of the ATMFD developed to date to generate a fieldable gross alpha measurement device. The project will explore technologies to aliquot sampled process streams and introduce the aliquots into the ATMFD's non-hazardous, non-flammable measurement fluids.

TECHNICAL APPROACH

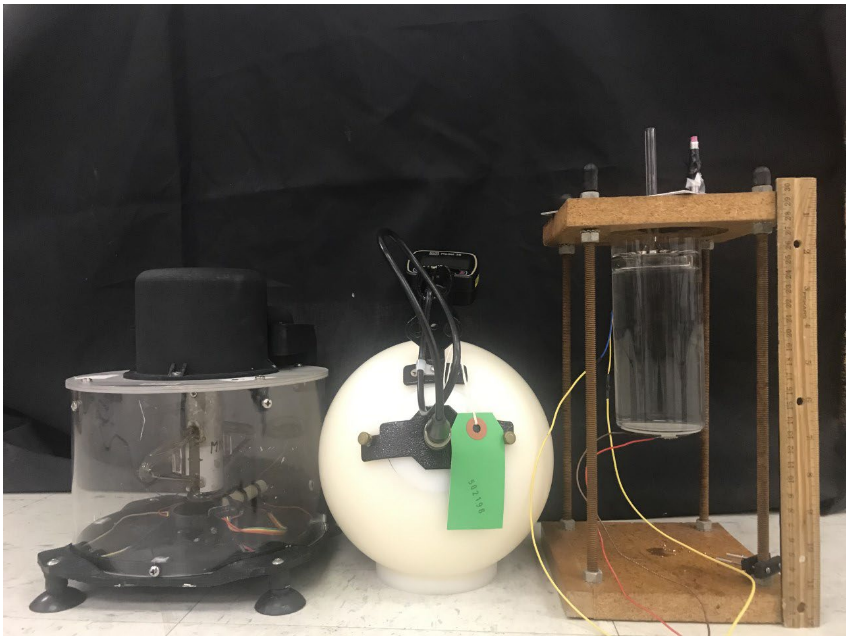

Figure 2. From Left to Right CTMFD, He-3(Ludlum 30-7B), ATMFD

The current ATMFD prototype is shown in figure 2. In year one, this project will attempt to scale the size of the ATMFD down to a 20ml volume or smaller size. Purdue University will continue to engineer the device, testing it with actinide solutions on hand. Purdue will deliver a prototype to SRNL, which will test the device. Tests will be made using known high Cs-137, high salt, low actinide simulants and using real SRS Tank waste quantified previously via the SRNL Nuclear Measurements Radiochemistry Laboratories. In year two of the project, SRNL and Purdue will also work to engineer an aliquot delivery system to the device to demonstrate the potential to make an at-line gross alpha measurement device out of the ATMFD.

Deliverables

1. Report describing the performance of a current ATMFD with gross alpha standards at Purdue and with high beta/high salt/low actinide matrices at SRNL
2. Development and testing of a slimmed down ATMFD device
3. Construction of a sample aliquot delivery system to an ATMFD device
4. Report describing the viability of an on-line alpha measurement system using TMFD's.

Budget and Schedule: $300,000 per year for 2 years.

Benefits to DOE-EM

Development of an acoustically tensioned metastable fluid detector (TMFD) to serve as a real time at-line alpha activity monitor or a rapid alpha measurement hot cell device for Hanford and Savannah River Site high Cs-137 activity salt wastes would decrease analytical cycle times and decrease personnel exposure by eliminating the need for the extensive electrochemistry steps prior to sample measurement. Gross alpha measurements that are beta/gamma blind could be invaluable to track the alpha concentrations in high Cs-137 caustic salt feeds to operations at Hanford and the Savannah River Site. The at-line alpha spectrometry potential of these devices could provide real-time data on plutonium, americium and curium concentrations on high beta activity streams at concentrations well below those provided by alternate technologies such as UV/Vis.

References

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April 25, 2023

Project Title: Continuous Improvement of Cement Waste Form Technology - Measurement of Ultra-low Relative Permeability for Grout

Principal Investigator: **Christine Langton, christine.langton@srnl.doe.gov**

Project Description

Background

The Department of Energy is currently responsible for treating radioactive and mixed waste resulting from nuclear weapons production during the Cold War. Cementitious reagents are the most widely used materials for (1) chemically stabilizing and encapsulating radionuclides and hazardous metals and (2) solidifying radioactive wastewater. Ambient temperature radioactive waste cementation is by far the lowest cost technology for producing waste forms final disposal. The current practice of designing and testing waste forms is based on a mid to late 20th century technology approach, i.e., materials, characterization and test methods for generating parameters for risk assessments. DOE technology development is needed to address both current, long term, and emerging issues in this area as new waste streams come online and as regulations, performance knowledge, and risk assessment methodology continue to evolve. Consequently the use of cementation as a means of treating chemically challenging radioactive liquid waste streams and reactive debris requires an enduring effort to (1) advance technology both in chemical compatibility between the waste and matrix (2) optimize of the waste form ingredients with respect to chemical and physical properties to support long-term durability predictions, (3) address growing concerns about future availability and cost of conventional cementitious waste form ingredients, Portland cement, alternative cements and supplemental reagents such as low pH cements, slag and Class F fly ash, respectively, in addition to innovative chemistries that could be tailored for enhanced performance, (4) develop new methods for measuring performance parameters for advanced materials, and (5) investigate new ambient temperature solidification/stabilization systems. Improved understanding of waste form performance and property measurements will support disposal of cementitious waste forms in near surface facilities and reduce long-term performance uncertainty.

Cementitious waste forms have been used to condition aqueous radioactive waste in the DOE complex since the 1980s. Over 17 million gallons of radioactive tank waste have been stabilized in a cement waste form, saltstone, at the Savannah River Site since 1991 and new process are being developed for new waste streams such as future Hanford ETF waste. Over the past 30 years, advancements in characterization, test methods, materials, and risk assessment methodology have supported the development and deployment of cementitious waste forms for ambient temperature radioactive waste treatment and conditioning process. DOE technology development is needed to address both current and emerging needs in this area as new waste streams come online and as regulations and performance knowledge continue to evolve.

The U.S. Department of Energy Office of Environmental Management (DOE-EM) sponsored the Cementitious Materials Technical Exchange (CMTE) in December 2019, which was organized and hosted by the Savannah River National Laboratory (SRNL). The DOE-EM expectation for this technical exchange was to (1) identify cementitious materials needs that support radioactive and mixed waste treatment for final disposal, tank closure, facility decommissioning, and environmental restoration that have the potential for a high technology development return on investment (ROI) and (2) prioritize research and development opportunities with respect to potential return on DOE-EM Technology Development investment. Optimizing cement waste form technology and maintaining an international leadership position in this areas was identified by the CMTE participants as having the greatest potential for high to medium return on investment (operating cost, life cycle cost, final disposal risk reduction, and site closure acceleration).

The overall program objective is to establish a multi-year, enduring program to address cementitious waste form needs identified by the CMTE and maintain expertise in this area with the goal of significantly reducing DOE site closure life-cycle costs, schedules, and risks. This proposal represents on task in this program.

Development of a schema to determine/measure ultra-low permeability of porous materials, specifically ultra-high-performance grout (UHPG) developed to encapsulate debris containing long-lived mobile radionuclides, e.g., I-219 and Tc-99 is needed since existing methods of measuring permeability, a key property related contaminant sequestration in waster forms, are not capable of determining the permeability of emerging cementitious materials being considered for waste disposal.

Task 1.

SRNL will work with Dr. R. Falta at Clemson University to implement the computational method to determine the permeability of porous materials with very low (<10^{-7} darcy) permeability. The model will be used to re-analyze laboratory data collected during moisture retention tests to determine the permeability. Samples of ultra-high-performance grout (UHPG) will be prepared and tested to generate data to use in the evaluation of the new computational tool. Current measurement methods over-estimate the permeability of ultra-low permeability materials (<10^{-7} darcy) by several orders of magnitude, inaccurately limiting the use of the new materials. Improved measurement of permeability in these emerging materials will improve the subsequent numerical modeling of contaminant transport in cementitious waste forms. This is key since the data from these efforts are used in the waste treatment and disposal risk-based decision-making processes.

Cost and Schedule

FY23 costs: 350k. Task schedule: Completion of listed scope within one year of funding receipt.

Deliverables

1. Monthly reports on integrated task progress, monthly calls, and integration of project activities.
2. Technical Report summarizing results of method development for measuring ultra-low unsaturated hydraulic conductivity for ultra-high-performance grout designed for debris encapsulation. Development of a computational tool capable of analyzing data from laboratory tests to determine permeability for use in subsequent numerical modeling of contaminant transport in cementitious waste forms.

Benefits to DOE-EM

The continuous improvement program for grout waste forms is expected to (1) support accelerated treatment/conditioning of liquid waste, solid waste, (2) reduce risk associated with final disposal of waste forms containing long-lived and highly mobile isotopes, and (3) reduce life-cycle costs associated with waste treatment and final disposal at several DOE facilities including Hanford, Idaho, Los Alamos, and the Savannah River Site.

April 25, 2023

Project Title: Continuous Improvement of Cement Waste Form Technology- Replacement of Fly Ash with Natural Pozzolans

Principal Investigator: **Christine Langton, christine.langton@srnl.doe.gov**

Project Description

Background

The Department of Energy is currently responsible for treating radioactive and mixed waste resulting from nuclear weapons production during the Cold War. Cementitious reagents are the most widely used materials for (1) chemically stabilizing and encapsulating radionuclides and hazardous metals and (2) solidifying radioactive wastewater. Ambient temperature radioactive waste cementation is by far the lowest cost technology for producing waste forms final disposal. The current practice of designing and testing waste forms is based on a mid to late 20th century technology approach, i.e., materials, characterization and test methods for generating parameters for risk assessments. DOE technology development is needed to address both current, long term, and emerging issues in this area as new waste streams come online and as regulations, performance knowledge, and risk assessment methodology continue to evolve. Consequently the use of cementation as a means of treating chemically challenging radioactive liquid waste streams and reactive debris requires an enduring effort to (1) advance technology both in chemical compatibility between the waste and matrix (2) optimize of the waste form ingredients with respect to chemical and physical properties to support long-term durability predictions, (3) address growing concerns about future availability and cost of conventional cementitious waste form ingredients, Portland cement, alternative cements and supplemental reagents such as low pH cements, slag and Class F fly ash, respectively, in addition to innovative chemistries that could be tailored for enhanced performance, (4) develop new methods for measuring performance parameters for advanced materials, and (5) investigate new ambient temperature solidification/stabilization systems. Improved understanding of waste form performance and property measurements will support disposal of cementitious waste forms in near surface facilities and reduce long-term performance uncertainty.

Cementitious waste forms have been used to condition aqueous radioactive waste in the DOE complex since the 1980s. Over 17 million gallons of radioactive tank waste have been stabilized in a cement waste form, saltstone, at the Savannah River Site since 1991 and new process are being developed for new waste streams such as future Hanford ETF waste. Over the past 30 years, advancements in characterization, test methods, materials, and risk assessment methodology have supported the development and deployment of cementitious waste forms for ambient temperature radioactive waste treatment and conditioning process. DOE technology development is needed to address both current and emerging needs in this area as new waste streams come online and as regulations and performance knowledge continue to evolve.

The U.S. Department of Energy Office of Environmental Management (DOE-EM) sponsored the Cementitious Materials Technical Exchange (CMTE) in December 2019, which was organized and hosted by the Savannah River National Laboratory (SRNL). The DOE-EM expectation for this technical exchange was to (1) identify cementitious materials needs that support radioactive and mixed waste treatment for final disposal, tank closure, facility decommissioning, and environmental restoration that have the potential for a high technology development return on investment (ROI) and (2) prioritize research and development opportunities with respect to potential return on DOE-EM Technology Development investment. Optimizing cement waste form technology and maintaining an international leadership position in this areas was identified by the CMTE participants as having the greatest potential for high to medium return on investment (operating cost, life cycle cost, final disposal risk reduction, and site closure acceleration).

The overall program objective is to establish a multi-year, enduring program to address cementitious waste form needs identified by the CMTE and maintain expertise in this area with the goal of significantly reducing DOE site closure life-cycle costs, schedules, and risks. This proposal represents on task in this program.

Natural pozzolans have been identified as a potential replacement for Class F fly ash and as a partial replacement for blast furnace slag in salt waste forms, e.g. saltstone and Cast Stone and as an ingredient in the Hanford ETF waste form. Bulk oxide composition, particle size, hydration chemistry and microstructure, and mechanisms of contaminant stabilization will be investigated. Volcanic pozzolans such as pumice and other volcanic ashes and calcined clay will be evaluated.

Task 1: Natural Pozzolan Evaluation

Samples of natural pozzolans will be obtained and analyzed for chemical composition, particle size and morphology, and mineralogy from representative sources in Idaho, Nevada, Oregon, and Georgia. Based on composition and mineralogy, processing properties of two of the volcanic pozzolans will be evaluated for processing using the Hanford Cast Stone and SRS saltstone formulations. One or two calcined clays will be evaluated as alternative ingredients in SRS saltstone. Depending on results, other ingredient adjustments may be required so that quality baseline samples can be prepared for cured property characterization. Waste loading, soluble ion and redox sensitive ion leaching, porosity, and hydraulic conductivity will be measured. A report summarizing results will be prepared. Future scope would be dependent on the results and will include measurement of unsaturated transport properties and scale up to 15 L scale.

Cost and Schedule

FY23 costs: 300k. Task schedule: Completion of listed scope within one year of funding receipt.

Deliverables

1. Monthly reports on integrated task progress, monthly calls, and integration of project activities.
2. Technical Report on evaluation of natural pozzolans as a replacement for Class F fly ash in cement waste forms.

Benefits to DOE-EM

The continuous improvement program for grout waste forms is expected to (1) support accelerated treatment/conditioning of liquid waste, solid waste, (2) reduce risk associated with final disposal of waste forms containing long-lived and highly mobile isotopes, and (3) reduce life-cycle costs associated with waste treatment and final disposal at several DOE facilities including Hanford, Idaho, Los Alamos, and the Savannah River Site.

OFFICE OF ENVIRONMENTAL MANAGEMENT - TECHNOLOGY DEVELOPMENT
WORK AUTHORIZATION / TASK CHANGE REQUEST (TCR)

Project Number:	**SR071301**	Date:	September 2022	AFP Change Month:	

Project Title:	**Cementitious Materials Studies - Continuous Improvement of Cement Waste Form Technology**

Site /Contractor:	SRNL	Project Area from Roadmap:	Legacy Waste	Work Proposal Attached:	Yes

Contract Number if other than National Laboratory or DOE site contractor:
Name of Principal Investigator: Christine Langton, Savannah River National Laboratory, 803-725-5806, christine.langton@srnl.doe.gov
Name of Budget Analyst at the site where the contract is held: Christopher Plunkett, 803-725-2614, christopher.plunkett@srnl.doe.gov

New BA ($K) Requested	Prior Funding ($K) in this FY	Total Estimated Un-costed ($K) as of beginning of this FY	Total Available Funding ($K) including this request (add first three columns)
$250K	0$	0$	**$250K**

Spend Plan for Total Available Funding (use actual costed funds for previous quarters)

1st Quarter of FY	2nd Qtr of FY	3rd Quarter of FY	4th Quarter of FY	Projected uncosted at the end of this FY
50$	**0$**	**$0K**	**$25K**	**$225K**

Funding Codes (To be Completed by Budget Office)

Fund	Year	Allotted	Reporting Entity	SGL	Object Class	Program	Project	Amount
01250	2020	1	410004	61000000	25400	1110676	0003920	$250,000

Short Description of Work Scope Authorized /Changed for input in AFP:	**Technical Area 1 – Replacement of Fly Ash with Natural Pozzolans** **Technical Area 2 – Reclaimed Coal Ash for Waste Forms and Other Beneficial Uses** **Technical Area 3 – Advanced Computational Method to Extend the Range of Low Permeability Data** **Technical Area 4 – Project Management** **Task 2, funded under this TCR/TTP, would characterize coal ash for use in grout, and identify sites that have this material for reuse in cementitious materials. The task also supports a collaboration with Oklahoma State University to apply machine learning to the characterization of coal ash material for this use.** **Note: This TCR has the technical scope listed for a number of tasks; only Task 2 is funded under this TCR.**

Submitted by:	**Nicholas Machara** Nicholas P. Machara	*Date:* 8/3/2022
	Headquarters Project Manager, (Please Print & Sign)	
Field:	**N/A**	*Date:*
	DOE Field Representative or HQ Site Liaison (Please Print & Sign)	
Approved by:	**Nicholas Machara** Nicholas P. Machara	*Date:* 8/3/2022
	TDO Program Manager, (Please Print & Sign)	
Approved by:	**Kurt Gerdes** KURT GERDES Digitally signed by KURT GERDES Date: 2022.08.10 12:02:46 -04'00'	*Date:*
	Director for Office of Technology Development, (Please Print & Sign)	
Approved by:	**Nicole Nelson-Jean**	*Date:* 8/11/22
	Associate Principal Deputy Assistant Secretary for Field Operations, EM-3, (Please Print & Sign)	
Submitted to:	**Angela Maddox** Angie Maddox	*Date:* 8/11/2022
	EM-HQ Budget Analyst for TDD to complete AFP change (Please Print & Sign)	

Technical Task Plan - Continuous Improvement of Cement Waste Form Technology

NEEDS STATEMENT

The Department of Energy is currently responsible for treating radioactive and mixed waste resulting from nuclear weapons production during the Cold War. Cementitious reagents are the most widely used materials for (1) chemically stabilizing and encapsulating radionuclides and hazardous waste containing dissolved metals and salts and (2) solidifying radioactive wastewater. Ambient temperature radioactive waste cementation is by far the lowest cost technology for producing waste forms that meet requirements for final disposal of Low-level waste. The current practice of designing and testing waste forms is based on a mid to late 20th century technology approach, i.e., materials, characterization and test methods for identifying processing equipment and for generating parameters for operational and long-term risk assessments. DOE technology development is needed to address current, long term, and emerging issues in this area as new waste streams come online and as regulations, performance knowledge, and risk assessment methodology continue to evolve. Consequently the use of cementation as a means of treating chemically challenging radioactive liquid waste streams and reactive debris requires an enduring effort to (1) advance technology both in chemical compatibility between the waste and matrix (2) optimize of the waste form ingredients with respect to chemical and physical properties to support long-term durability predictions, (3) address growing concerns about future availability and cost of conventional cementitious waste form ingredients, e.g., Portland cement, (4) identify alternative cements and supplemental reagents such as low pH cements, slag and Class F fly ash, respectively, in addition to innovative chemistries that could be tailored for enhanced performance, (5) develop new methods for measuring performance parameters for advanced materials, and (6) investigate new ambient temperature solidification/stabilization systems. Improved understanding of waste form performance and property measurements will support disposal of higher inventories of long-lived and/or highly mobile cementitious waste forms in near surface facilities and reduce long-term performance uncertainty.

BACKGROUND

Cementitious waste forms have been used to condition aqueous radioactive waste in the DOE complex since the 1980s. Over 17 million gallons of radioactive tank waste have been stabilized in a cement waste form, saltstone, at the Savannah River Site since 1991 and new process are being developed for new waste streams such as future Hanford ETF waste. Over the past 30 years, advancements in characterization, test methods, materials, and risk assessment methodology have supported the development and deployment of cementitious waste forms for ambient temperature radioactive waste treatment and conditioning process. DOE technology development is needed to address both current and emerging needs in this area as new waste streams come online and as regulations and performance knowledge continue to evolve.

The U.S. Department of Energy Office of Environmental Management (DOE-EM) sponsored the Cementitious Materials Technical Exchange (CMTE) in December 2019, which was organized and hosted by the Savannah River National Laboratory (SRNL). The DOE-EM expectation for this technical exchange was to (1) identify cementitious materials needs that support radioactive and mixed waste treatment for final disposal, tank closure, facility decommissioning, and environmental restoration that have the potential for a high technology development return on investment (ROI) and (2) prioritize research and development opportunities with respect to potential return on DOE-EM Technology Development investment. Optimizing cement waste form technology and maintaining an international leadership position in this areas were identified by the CMTE participants as having the greatest potential for high to medium return on investment (operating cost, life cycle cost, final disposal risk reduction, and site closure acceleration).

This technology will support DOE EM's site closure mission. The benefit to DOE-EM is expected to be realized by (1) supporting accelerated treatment/conditioning of liquid waste, solid waste, (2) reducing risk associated with final disposal of waste forms containing long-lived and highly mobile isotopes, and (3) reducing life-cycle costs associated with waste treatment and final disposal at several DOE facilities including Hanford, Idaho, Los Alamos, and the Savannah River Site.

GOAL

The overall program objective is to establish a multi-year, enduring program to address cementitious waste form needs identified by the CMTE and maintain expertise in this area with the goal of significantly reducing DOE site closure life-cycle costs, schedules, and risks.

The first-year effort will consist of project management and execution of projects in three technical areas that support enhancements of cementitious waste forms and continuity and reliability for DOE legacy waste management projects:

(1) Identifying replacement pozzolans for Class F fly ash to support seamless cost-effective transitioning from Class F fly ash to an alternative material as the supply of fly ash deceases due to closure of coal fired power plants. Candidate materials include natural pozzolans and reclaimed coal ash.
(2) Evaluating the potential and actions needed to reclaim SRS coal ash and thereby eliminate and waste stream through beneficiation and reuse.
(3) Developing an innovative method for determining relative permeability of very low porosity cementitious materials.

Technical Area 1. Natural Pozzolan Replacement: In FY 22/23, we will evaluate natural pozzolans as a potential replacement for Class F fly ash and as a partial replacement for blast furnace slag in salt waste forms, e.g. saltstone and Cast Stone and as an ingredient in the Hanford ETF waste form. Bulk oxide composition, particle size, hydration chemistry and microstructure, and mechanisms of contaminant stabilization will be investigated. Volcanic pozzolans such as pumice and other volcanic ashes and calcined clay will be evaluated.

Technical Area 2. Reclaimed Coal Ash Collaboration with SRS Area Closure Projects: In FY 22/23, we will evaluate use of coal ash currently stored at the Savannah River Site for use as an ingredient in a cementitious waste form or other beneficial use supplemental cementitious material application rather than having these byproduct materials being stored in basins or landfills. The bulk oxide composition, particle size, and hydration and contaminant chemistry will be evaluated for these materials. Other beneficiation options will also be evaluated. Activities in this space are supported by the SRS Area Completion Projects. In FY 22/23 SRNL will collaborate with T. Ley at Oklahoma State University to investigate new opportunities to apply machine learning approaches to coal ash characterization, with the goal of enabling beneficial use of these materials in the cementitious applications. For example, SRNL data of natural pozzolans and SRS coal ash will be incorporated in the database developed at OK State University.

Technical Area 3. Advanced Relative Permeability Measurement: In FY22/23, SRNL will collaborate with Dr. R. Falta at Clemson University, to develop a schema to determine/measure ultra-low permeability of porous materials, specifically ultra-high-performance grout (UHPG) developed to encapsulate debris containing long-lived mobile radionuclides, e.g., I-219 and Tc-99. Existing methods of measuring permeability, a key property related contaminant sequestration in waster forms, are not capable of determining the permeability of emerging cementitious materials being considered for waste disposal.

2022 TECHNICAL APPROACH

Task 1: Natural Pozzolan Evaluation (unfunded in this TCR)

In FY 22/23, we will obtain samples of natural pozzolans, perform chemical analyses, particle size analyses and determine mineralogy and morphology from representative sources in Idaho, Nevada, Oregon, and Georgia. Based on composition and mineralogy, processing properties of two volcanic materials will be evaluated for processing using the Hanford Cast Stone and saltstone formulations. One or two calcined clays will be evaluated as alternative ingredients in saltstone. Depending on results, other ingredient adjustments may be required so that quality baseline samples can be prepared for cured property characterization. Waste loading, soluble ion and redox sensitive ion leaching, porosity, and hydraulic conductivity will be measured. A report summarizing results will be prepared. FY23/24 scope will be developed based on FY22/23 results and will include measurement of unsaturated transport properties and scale up to 15 L scale.

Task 2: SRS Coal Ash Evaluation for a Beneficial Use ($250K)

In FY22/23, we will obtain and characterize samples of SRS coal ash from ash generated in the SRS F- and A- Areas. SRNL will consult with the DOE National Energy Technology Laboratory (NETL) to identify other DOE sites that have coal ash piles and to identify potential value-added reuse material streams, as well as determining the possibilities these materials could be employed in cementitious formulations. SRNL will work with Dr. Tyler Ley, at Oklahoma State University, to include SRS coal ash data in his Class F fly ash artificial neural network (ANN) and machine learning techniques to evaluate potential uses and options for these materials.

Task 3: Measurement of Ultra-low Relative Permeability for Grout (Unfunded in this TCR)

In FY22/23, SRNL will work with Dr. R. Falta at Clemson University to implement the computational method to determine the permeability of porous materials with very low (< 10^{-7} darcy) permeability. The model will be used to re-analyze laboratory data collected during moisture retention tests to determine the permeability. Samples of ultra-high-performance grout (UHPG) will be prepared and tested to generate data to use in the evaluation of the new computational tool. Current measurement methods over-estimate the permeability of ultra-low permeability materials (< 10^{-7} darcy) by several orders of magnitude, inaccurately limiting the use of the new materials. Improved measurement of permeability in these emerging materials will improve the subsequent numerical modeling of contaminant transport in cementitious waste forms. This is key since the data from these efforts are used in the waste treatment and disposal risk-based decision-making processes. The deliverable for this task will be a method and an equation the output of which will be verified in a follow on task.

FY22/23 DELIVERABLES – Schedule and Milestones

Tasking includes monthly reports on integrated task progress, monthly calls, and integration of project activities. Development of a web page documenting project results. There will be regular Status reporting to DOE EM-HQ through the Technology Development "Dashboard" as required (currently monthly).

Task 2: Status report on SRS coal ash beneficiation options, costs, and potential uses.

SCHEDULE / MILESTONES:

Technical Area/Task/Activity	Estimated Completion Date
Interim (letter) report on characterization of SRNL coal ash	TBD
Report (letter) and/or briefing on the status of the use of AI to evaluate options for fly ash materials with characterization data	TBD
Final Status report for Task 2 on SRS coal ash beneficiation options, costs, and potential sources and uses.	May 2023

Additional Deliverable: Regular Status reporting to DOE EM-HQ through the Technology Development "Dashboard" as required (currently monthly).

BUDGET

FY22 Monthly Spend Plan ($K)

Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sept	*Total*
$0K	$0K	$0K	$0K	$0K	$0K	$0K	$0K	$0K	$0K	$0K	$25K	*$25K*

FY23 Monthly Spend Plan ($K)

Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sept	*Total*
$25K	$25K	$25K	$25K	$50K	$50K	$20K	$5K	$0K	$0K	$0K	$0K	*$225K*

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