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Technical Assessment of Proposed LAW Simulant for Cold Commissioning

September 2015

DK Peeler
GJ Sevigny

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

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Richland, Washington 99352

Executive Summary

Prior to radioactive operations, the Hanford Tank Waste Treatment and Immobilization Plant (WTP) will implement a cold-commissioning plan or strategy that will include water runs and other melter feed simulants to not only test the various engineering systems, unit operations, and processing strategies with respect to safety and performance, but to also allow facility operations to gain operational experience before introducing radioactive material into the vitrification facilities. Based on direction from Bechtel National, Inc. to eliminate nitrogen oxide (NO_x) generation, Energy*Solutions* has recommended the use of a simple NaOH solution with glass formers to support this stage of testing during cold commissioning.

The proposed simulant excludes any NO_x-generating components, hazardous species (e.g., Cl, F, I, S-based gases), and *Resource Conservation and Recovery Act* metals such as Hg. Based on a review by Pacific Northwest National Laboratory (PNNL), the use of a simple NaOH solution with glass formers will provide more insight into the formation of the cold cap compared to the alternative of frit and water. However, the use of this simple simulant may underestimate the dynamics of the cold cap that would eventually be present during radioactive operations. The low potential for direct comparison to radioactive operations is being driven by the requirement that the simulant be void of NO_x and other hazardous components.

A key question to be addressed was the ability of the simple NaOH-based simulant to allow WTP to tune the off-gas system. It is PNNL's position that the use of the simple tuning feed will not fully challenge the off-gas system compared to a more complex feed. The simple NaOH simulant will not allow WTP to tune specific unit operations within the off-gas system. Key concerns include: (1) the inability to demonstrate the performance of the selective catalytic reduction for NO_x control, (2) not sufficiently challenging the mercury adsorbers to demonstrate needed temperature control, (3) the potential impacts of hydrocarbons, CO, and CO_2 on the catalytic oxidizer may not be evaluated, and (4) off-gas system monitoring and control system could be calibrated, tuned, and operated but not fully demonstrated for all the complex feeds planned for WTP. These four concerns cannot be fully resolved until a more challenging feed (hazardous off-gas producing simulant or actual radioactive tank waste) is introduced into the system.

Acknowledgments

The authors gratefully acknowledge the financial support from Peter Benson of Bechtel National, Inc. under Contract No. DE-AC27-01RV14136 – Hanford Tank Waste Treatment and Immobilization Plant, Memorandum of Agreement (MOA) 24590-HC9-WA49-00001. The authors also thank Pavel Hrma and Nick Soelberg (Idaho National Laboratory) for their constructive feedback and discussions associated with this review. The authors would also like to thank Matt Wilburn for technical editing.

Acronyms and Abbreviations

BNI	Bechtel National, Inc.
ES	Energy*Solutions*
HEPA	high-efficiency particulate air
HLW	high-level waste
IHLW	immobilized high-level waste
ILAW	immobilized low-activity waste
LAW	low-activity waste
PCT	product consistency test
PNNL	Pacific Northwest National Laboratory
RCRA	*Resource Conservation and Recovery Act*
REDOX	reduction/oxidation
SBS	submerged bed scrubber
SCR	selective catalytic reduction
VHT	vapor hydration test
VOC	volatile organic carbon
VSL	Vitreous State Laboratory
WESP	wet electrostatic precipitator
WTP	Hanford Tank Waste Treatment and Immobilization Plant

Contents

1.0 Introduction

About 55 million gallons of high-level mixed waste is currently stored in underground tanks at the U.S. Department of Energy Hanford Site in the State of Washington. Bechtel National, Inc. (BNI) is constructing the Hanford Tank Waste Treatment and Immobilization Plant (WTP) to separate the tank waste into high-level waste (HLW) and low-activity waste (LAW) fractions, which will then be vitrified respectively into immobilized low-activity waste (ILAW) and immobilized high-level waste (IHLW) borosilicate glass products (DOE 2000). The ILAW product will be disposed in an engineered facility on the Hanford Site while the IHLW product is designed for acceptance into a deep geological disposal facility for high-level nuclear waste. The ILAW and IHLW products must meet a variety of requirements with respect to protection of the environment before they can be accepted for disposal.

The LAW waste stream is composed primarily of sodium salts with several constituents that complicate the vitrification process due to the formation of separate, low-viscosity, alkali-based salt phases on the surface of the glass melt and drive the performance assessment of the Integrated Disposal Facility. The salt phase that can be produced during the melting process is primarily Na_2SO_4 with small concentrations of halides, Cr, Tc, and alkali other than Na. Technetium-99 (^{99}Tc), iodine-129 (^{129}I), and cesium-137 are of particular concern for salt phase incorporation because their high volatilities can result in low retention in the glass. Therefore, there are two key or primary components that are anticipated to limit waste loadings for LAW vitrification: (1) Na_2O (or total alkali) content in glass and (2) SO_3 concentration in the melter feed.

Prior to radioactive operations, WTP will implement a cold-commissioning plan or strategy that will include water runs and other melter feed simulants to not only test the various engineering systems, unit operations, and processing strategies with respect to safety and performance, but to also allow facility operations to gain operational experience before introducing radioactive material into the vitrification facilities. Energy*Solutions* (ES) is under contract to BNI to provide technical expertise to support facility operations. One of the recent scopes contracted to ES by BNI was to develop a method to operate the LAW melters so that "process control loops can be tuned prior to introducing waste or feed materials that produce nitrogen oxides (NO_x)." The method to be developed includes not only the non-NO_x generating simulant but also a system configuration (including equipment operation). To support that scope, WTP, ES, and Vitreous State Laboratory (VSL) discussed the types of feed materials that could be used to support this objective. Diener (2015) summarizes two options that were considered (a frit-water mixture or a modified melter feed) and discusses the advantages and disadvantages of each. The report ultimately recommends an NaOH solution with glass formers without any NOx-generating components or hazardous species (e.g., Cl, F, I, S-based gases, *Resource Conservation and Recovery Act* [RCRA] metals such as Hg) to support this stage of testing during cold-commissioning.

BNI has requested that Pacific Northwest National Laboratory (PNNL) perform a technical review of the Diener 2015 report and comment on the proposed tuning material and strategy for impacts on glass formulation and plant equipment. More specifically, will the proposed non-NO_x simulant meet its intended objective?[a] Per Diener (2015) this objective (refer to Section 1.1 of that report) is to develop a

[a] Contract No. DE-AC27-01RV14136 – Hanford Tank Waste Treatment and Immobilization Plant, Memorandum of Agreement (MOA) 24590-HC9-WA49-00001, WA-45, Subcontract Change Notice (SCN) No. 157, Glass Formulation Training, effective June 15, 2015.

non-NO_x producing LAW tuning feed that will allow the melter system to operate and be tested while producing significantly less hazardous off-gas. Again, as part of the phased cold-commissioning strategy, BNI would like to implement a tuning feed (after water runs) that does not generate toxic or hazardous emissions (nitrogen oxides, acid gases, organic compounds, etc.). Through additional discussions between PNNL and BNI as part of the memorandum of agreement, another goal of this tuning simulant is to process a melter feed that will provide WTP operators with operational experience that is more similar to conditions to be seen under radioactive operations.

The PNNL technical review is based on the following objectives or questions:

(1) Does the proposed simulant eliminate NO_x and other hazardous components?

(2) Will the simulant provide WTP operators with experience indicative of actual LAW radioactive processing (not only focusing on melter and off-gas operations but feed systems as well)?

(3) Will the simulant allow WTP to tune the off-gas system?

The PNNL review will also provide feedback on the down-selection between frit-water mixture and the use of the NaOH solution with glass formers as they relate to each objective. Note that the response to these three primary questions may not be mutually inclusive. That is, the proposed simulant may meet one of the objectives while providing partial (if any) insight into the other technical issues. PNNL was also asked not to comment on the proposed experimental program by ES-VSL.

2.0 Technical Review

2.1 Tuning Simulant and Melter Feed System

The 5M NaOH solution with glass formers is the preferred choice relative to the frit-water mixture. The proposed tuning simulant will allow WTP to operate and gain experience with the different unit operations within the LAW vitrification facility. More specifically, operations of the glass forming system silos, reagent systems, and transfer techniques will be required, which will provide operational experience and potentially help to identify any process changes that may be needed prior to radioactive operations. In addition, mixing and sampling protocols could also be evaluated as warranted (assuming rheological characteristics are representative of actual radioactive waste streams or melter feeds).

Comparison of Table 2, Table 5, and Table 6 from Diener (2015) provides insight into the various raw materials sources used in the LAW Sub-Envelope A1 simulant versus that proposed for the tuning simulant. In short, ES-VSL has removed all constituents that would produce NO_x or other sources of off-gas generators (e.g., acetate, formate, oxalate, as well as sugar used for reduction/oxidation [REDOX] control). The tuning simulant is simply a NaOH solution with glass forming chemicals that meets one of the programmatic objectives (Objective 1).

Table 7 of Diener (2015) summarizes the predicted processing and product performance properties (based on the baseline WTP models) for the LAW glass to be produced from the tuning simulant. Key properties predictions include viscosity at 1150°C of 76 poise; electrical conductivity at 1100°C = 0.36 S/cm and at 1200°C 0.52 S/cm; a product consistency test (PCT) normalized release for boron (B) =

0.349 g/m^2 and for sodium (Na) = 0.412 g/m^2; and a vapor hydration test (VHT) response of 1.69 g/m^2/day. Table 8 of Diener (2015) compares these predicted values to the various LAW constraints or acceptance criteria, which shows that for those properties provided (except viscosity at 1150°C), the tuning glass should be processable and meet product specifications (i.e., durability as defined by PCT and VHT). The predicted viscosity of the tuning glass at 1150°C is 76 poise as compared to the 30 to 50 poise range as an "optimal." Although the predicted viscosity falls outside the "optimal" range, it is within the 20 to 80 poise constraints as reported by Kim and Vienna (2012), although the 76 poise prediction is provided without uncertainty relative to the upper limit of 80 poise.

That said, and as pointed out by Diener (2015), the proposed target glass composition (Table 3 of Diener 2015) is very similar to LAWA44, which was developed by ES-VSL (Muller et al. 2001) and has been processed through the DM-series of melters at VSL.

2.2 Melter Operations

One of the objectives described by Diener (2015) is to gain operational experience with the process of forming and maintaining a cold cap that supports efficient melter operations. Key factors (not inclusive) that influence cold cap formation and its stability are feed rate and melter feed rheology. Operationally, typically a balancing act has to be achieved to gain experience with how these factors control the cold cap formation and its stability. As stated by Diener (2015), these are operational issues that must be determined during commissioning.

With respect to a review of melter operations, the question is: Will the NaOH solution with glass former chemicals provide a basis from which that experience can be obtained? Without experimental data in hand, this question can only be answered based on knowledge of the complex reactions and processes in the cold cap and what components may influence its formation and stability.

The removal of a major off-gas contributor (NO_x) as well as other, even minor components (e.g., SO_3 and other halides) makes it difficult to apriori determine if the simple tuning solution will perform identical (or even similar) to actual radioactive operations with respect to cold cap behavior and responsiveness. PNNL's position is that the use of the simple simulant would likely underestimate the dynamics of the cold cap that would eventually be observed during radioactive operations. For example, because of the absence of nitrate/nitrite in the melter feed and the potential impact of foam formation, cold cap behavior and stability cannot be evaluated; although it is recognized that sugar is added to NO_x-based melter feeds, which can mitigate these issues.

Although it could potentially underestimate the dynamics of the cold cap, the use of a simple NaOH solution and glass formers will provide more insight into the formation and behavior of the cold cap as compared to the use of a frit-water solution. However, the low potential of having a direct comparison to radioactive operations is being driven by the requirement to use a simulant void of NO_x and other hazardous components (Objective 1), which basically drives the use of the simple NaOH-based simulant that has been proposed. Even though a direct comparison to radioactive operations would not be anticipated, the use of the simple simulant during cold commissioning is a step in the right direction as it will provide additional operational experience with feeding the melter and help to form a foundation of knowledge about the various feeding systems and strategies and the resulting melter response. The proposed testing by Diener (2015) (see last paragraph in Section 3.0 of Diener 2015) would provide some insight into the potential differences between the more complex, NO_x-based simulants used by VSL to support DM-series assessments and the simple, NaOH-based simulant proposed for portions of cold commissioning.

2.3 Off-Gas Operations

As previously mentioned, the simple tuning simulant is void of all constituents or additives that would produce NO_x or other sources of off-gas generators (e.g., acetate, formate, oxalate, as well as sugar used for REDOX control). In addition, the glass forming chemicals proposed, with the exception of boric acid and sodium carbonate, are oxide based. Based on the tuning simulant makeup, the primary off-gas components to be generated include H_2O (steam) and CO_2. Since the simple NaOH based tuning feed does not contain any hazardous off-gas producing constituents (nitrates, nitrites, Cl, F, I, S-based gases, or RCRA metals), it is expected that portions of the WTP LAW off-gas system will not be challenged. These sub-systems will not be challenged until a more complex based feed(s) is introduced. Operation with the simple NaOH-based melter feed would enable demonstration of the LAW primary off-gas process system and LAW secondary off-gas/vessel vent process to flow, scrub, and filter the off-gas and control the melter pressure, under those operating conditions. With respect to tuning, the key off-gas system unit operations, monitors, and controls are listed below, with comments about how operation with the NaOH-based simulant feed might challenge or enable tuning of their operation.

- **Film cooler:** Challenge and tuning of the film cooler should be adequate during operation with the NaOH-based melter feed; except for some uncertainty remaining due to possible impact on its operation if the amount and consistency of particulate/condensable matter changes for more complex feeds.

- **Submerged bed scrubber (SBS) and wet electrostatic precipitator (WESP):** Operation with the NaOH-based simulant would demonstrate operational efficiencies of the SBS, which serves to condense steam and remove coarse particulate matter in the off-gas stream, and demonstrate overall performance of the WESP. In LAW, most of the particle matter will be associated with the glass forming chemicals and, given their use in the simple NaOH-tuning simulant, may be adequate to evaluate the SBS. If significant differences exist between the simple simulant and more complex feeds with respect to cold cap coverage or dynamics, this may affect the degree of particulate matter being carried into the off-gas system which could lead to different entrainment – primarily in the WESP.

  However, challenging the operation of SBS and WESP with the impacts from NO_x or other acid gases, such as the impacts on the scrub solution pH, specific gravity, and resulting species solubilities would not be achieved, as pointed out by Diener (2015). Scrub solution pH, specific gravity, and solubilities of scrubbed and condensed material could change considerably for more complex melter feeds, which could affect SBS and WESP operation and scrub solution handling and recycle or disposal.

- **HEPA filters**: Operation with the NaOH-based feed should provide adequate demonstration of the high-efficiency particulate air (HEPA) filters; recognizing that more complex feeds will change the composition of the gas passing through the HEPAs, and possibly the amounts and properties of particulate matter not captured in the SBS and WESP. These changes should be within the reasonable HEPA filter operating envelope that would be demonstrated by the NaOH-feed operation as long as the corrosive atmosphere or higher dew point temperature produced by actual feed does not affect the overall HEPA operation.

- **Mercury adsorbers**: Without the complex off-gas stream containing NO_x, other acid gases, CO, and hydrocarbons, the mercury adsorbers will not be sufficiently challenged to demonstrate needed temperature control, which the presence of NO_x and hydrocarbons could affect. This demonstration, plus the demonstration of Hg and acid gas control performance, would need to be done at another time to assure safe and effective operation during actual feed LAW operations. This is one of the most significant unit operations (along with the volatile organic carbon [VOC] catalyst and the selective catalytic reduction (SCR) NO_x control system) that would not be adequately challenged or tuned by operation with the NaOH-based feed.
- **VOC catalyst**: The absence of a reductant (sugar) given no nitrates/nitrites would not provide insight into the potential impacts of hydrocarbons, CO, and CO_2 on the catalytic oxidizer. The VOC catalyst demonstration and tuning would need to be done during other operation with more complex feeds.
- **SCR NO_x control system**: NO and other nitrogen species such as N_2O are less soluble and will mostly pass through the SBS and WESP. If these components are not present in the off-gas stream (due to removal of all NO_x generating components from the melter feed), it will not be possible to demonstrate the performance of the SCR for NO_x control. Demonstration of NH_3 addition and control to achieve the desired NO_x control efficiency without excessive NH_3 slip would not be possible. This would need to be tuned during other operations with more complex feeds.
- **Caustic scrubber**: Since the caustic scrubber is downstream of all other unit operations, its normal operation should be adequately demonstrated during NaOH-based melter feed operation. This is because most of the reactive constituents in the off-gas from more complex feed would be scrubbed or otherwise removed from the off-gas by the time the off-gas reaches the caustic scrubber. Two caustic scrubber conditions or parameters would not be adequately demonstrated: (1) pH control and (2) scrubber operation any time there are upstream process upsets (in particular, of the SCR NO_x control) that could result in larger-than-normal amounts of some gas species that could temporarily affect the caustic scrubber operation. These would need to be demonstrated or tuned during other operations independently.
- **Other off-gas system components such as the preheater and the heat recovery exchanger**: Operation with the NaOH-based melter feed will provide a generally adequate demonstration and tuning. The need for some fine-tuning should be expected for more complex melter feeds.
- **Off-gas system monitoring and controls including the passive gas analyzers, active safety analyzers, and continuous emissions monitors**: Without hydrocarbons, CO, NO_x, or Hg in the off-gas, it is not possible to demonstrate the performance of these monitors and controls under real conditions, although they can be calibrated and operated. These would need to be demonstrated and tuned during other operations with more complex feeds.

Therefore, it is PNNL’s position that using the simple NaOH-based tuning feed will not fully challenge the off-gas system in comparison to a more complex based feed. The use of the simple NaOH-based simulant would meet Objectives 1 and 2, but not all aspects of Objective 3. That being the case, the WTP operators will gain experience in operating the off-gas system with the simple tuning simulant; however, that experience is unlikely to encompass all the information or challenges that will be experienced during radioactive operations with more complex melter feeds.

It is understood that WTP is pursuing a phased commissioning strategy that includes transitioning to a more complex simulant melter feed (e.g., one that includes NO_x precursors and sugar) prior to radioactive startup. The use of the simple NaOH-based melter feed to meet Objectives 1 and 2 will be followed by processing of a more-complex melter feed (that at least contains NO_x precursors and the sugar reductant) to complete the off-gas system tuning (Objective 3). As the phased commissioning strategy nears the transition to radioactive operations, BNI should also consider transitioning the melter glass composition to a composition similar to the initial feeds to be immobilized.

3.0 Summary

Prior to radioactive operations, WTP will implement a cold commissioning strategy that will include water runs and other melter feed simulants to not only test the various engineering systems, unit operations, and processing strategies with respect to safety and performance, but to also allow facility operators to gain experience before radioactive material is introduced to the vitrification facilities. Based on direction from BNI to eliminate NO_x generation, Energy*Solutions* has recommended the use of a simple NaOH solution with glass formers to support this stage of testing during cold commissioning.

Subsequently, BNI has requested that PNNL perform a technical review of this recommendation with respect to meeting the following objectives:

1. Does the proposed simulant eliminate NO_x and other hazardous components?

2. Will the simulant provide WTP operators with experience indicative of actual LAW radioactive processing (not only focusing on melter and off-gas operations but feed, glass formers, and reagent systems as well)?

3. Will the simulant allow WTP to tune the off-gas system?

The proposed simulant excludes any NO_x-generating components, hazardous species (e.g., Cl, F, I, S-based gases), and RCRA metals such as Hg. Therefore, the proposed NaOH solution with glass formers accomplishes Objective 1. From a glass formulation perspective and as pointed out by Diener (2015), the proposed target glass composition is very similar to LAWA44, which was developed by ES-VSL (Muller et al. 2001) and has been processed through the DM-series of melters at VSL. Therefore, there is minimal risk associated with processing the simulant through the melter during cold commissioning.

With respect to Objective 2, the use of a simple NaOH solution with glass formers will provide more insight into the formation of the cold cap compared to the alternative of frit and water. However, the use of this simple simulant may underestimate the dynamics of the cold cap that would eventually be present during radioactive operations. The low potential of having a direct comparison to radioactive operations is being driven by the requirement to use a simulant that is void of NO_x and other hazardous components (Objective 1)—which basically drives the use of the simple NaOH-based simulant that has been proposed.

With respect to the ability of the simple NaOH-based simulant to allow WTP to tune the off-gas system (Objective 3), it is PNNL's position that the use of the simple tuning feed will not fully challenge the off-gas system in comparison to a more complex based feed—thus not allowing WTP to tune all of the unit operations within the off-gas system. Key concerns include: (1) the inability to demonstrate the performance of the SCR for NO_x control, (2) not sufficiently challenging the mercury adsorbers to demonstrate needed temperature control, (3) the potential impacts of hydrocarbons, CO, and CO_2 on the catalytic oxidizer may not be evaluated, and (4) off-gas system monitoring and control system could be calibrated and operated but not fully demonstrated. Demonstrating, challenging, and tuning of these key systems would require use of a more complex feed or separate unit operation testing.

In summary, the proposed use of a simple NaOH and glass former solution during the initial phase of commissioning is a step in the right direction when compared to the alternative of frit and water. This strategy will allow WTP staff to gain operational experience before the introduction of radioactive materials in the facility. Since the tuning feed does not contain any hazardous off-gas producing constituents (nitrates, nitrites, Cl- F, I, S-based gases, or RCRA metals) it is expected that portions of the WTP LAW off-gas system will not be challenged during this phase. These sub-systems will not be challenged until a more complex based feed is introduced. The tuning of these sub-systems will likely occur during a subsequent phase of commissioning when a more challenging simulant is introduced.

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