

**RECOMMENDATION FOR SUPPLEMENTAL TECHNOLOGIES FOR HANFORD RIVER  
PROTECTION PROJECT POTENTIAL MISSION ACCELERATION  
(RPP-11838)**

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**ABSTRACT**

In May of 2002, the River Protection Project at Hanford proposed as part of the accelerated cleanup for the entire Hanford Site to “. . . accelerate waste stabilization by developing and deploying alternative treatment and immobilization solutions that are aligned with the waste characteristics to add assurance that overall waste treatment/immobilization will be completed 20 or more years sooner.” This paper addresses one of these elements: development of recommendations for the supplemental technologies that have the greatest potential to supplement the River Protection Project’s new Waste Treatment Plant throughput and achieve completion of waste processing by 2028.

Low-activity waste treatment in the Waste Treatment Plant needs either to be enhanced or supplemented to enable the full amount of low-activity feed in the single-shell and double-shell tanks to be processed by 2028. The supplemental technologies are considered for low-activity waste feed that represents the maximum effectiveness of treatment compared with Waste Treatment Plant processing.

During the Spring of 2002, over two dozen candidate technologies were assessed by staff from the U.S Department of Energy (DOE) Headquarters, Hanford Office of River Protection, representatives from the Washington State Department of Ecology and Region 10 of the Environmental Protection Agency, staff from many national laboratories, as well as contractor and independent experts.

Four technologies were down-selected by this group for further development beginning in fiscal year 2003. The four technologies are:

- ◆ **Sulfate Removal** consisting of sulfate precipitation using strontium nitrate addition, filtration, and solidification with grout-forming additives for immobilized waste suitable for land disposal. Sulfate removal would allow acceleration of cleanup by reducing the amount of glass produced in the Waste Treatment Plant by increasing the waste loading in the low-activity waste.
- ◆ **Containerized Grout** consisting of solidification with grout-forming additives to form immobilized waste suitable for land disposal. Containerized grout would allow acceleration of the tank waste cleanup by reducing the amount of sodium that the Waste Treatment Plant would need to process.
- ◆ **Bulk Vitrification** consisting of vitrification inside of the eventual disposal container suitable for land disposal. Bulk vitrification would allow accelerated tank waste cleanup by reducing the mass of sodium requiring vitrification in the Waste Treatment Plant.

- ◆ **Steam Reforming** consisting of denitration in a high-temperature fluidized bed with additives, then or later, to make an immobilized waste suitable for land disposal. Steam reforming would allow acceleration of the cleanup of tank waste by reducing the amount of waste requiring vitrification in the Waste Vitrification Plant.

The four selected supplemental technologies tended to rank higher than those not selected in nearly all of the major groupings of the criteria: compliance and safety, project utility, operability, technical risk, and programmatic risk.

The River Protection Project recommended that laboratory-scale demonstration and other investigations that would be required (e.g., follow-on engineering evaluations) for the four technologies should be pursued in fiscal year 2003. Adequate work is needed to obtain data necessary to determine merit and likelihood of successful deployment. If warranted, one or more of these technologies would then result in pilot testing during fiscal year 2004 and hot field deployment by fiscal year 2008. This schedule is currently being evaluated for further acceleration.

The River Protection Project also endorsed the continued investigation of promising, but not yet mature, technologies. Together with the Office of Science and Technology, they jointly agreed upon projects pertaining to immobilization alternatives to expedite cleanup, single-shell high-level waste tank disposition, and remediation of leaked high-level waste below Hanford Site tanks. These activities ensure that innovative technologies are available on a continuing basis to support the Mission Acceleration Initiative at the Hanford Site.

## INTRODUCTION

The U.S. Department of Energy (DOE), Office of River Protection (ORP), is responsible for the remediation and stabilization of the Hanford Site tank farms, including 53 million gallons of highly radioactive mixed waste contained in 149 single-shell tanks (SST) and 28-double-shell tanks (DST). This program is called the River Protection Project (RPP). The current plan calls for all wastes retrieved from the tanks to be transferred to a new Waste Treatment Plant (WTP) where they will be chemically partitioned to separate the highly radioactive materials requiring permanent isolation (high-level waste [HLW]) from very large volumes of chemical wastes. The HLW constituents will be vitrified, stored onsite, and ultimately disposed of in the offsite national repository. The less radioactive chemical waste, referred to as low-activity waste (LAW), will be vitrified and then disposed of onsite in trenches that comply with the *Resource Conservation and Recovery Act of 1976* (RCRA). Current estimates for this mission predict completion around 2070 if no additional processing facilities are deployed. A second LAW vitrification plant and expansion of the HLW vitrification capacity would be required to achieve commitments made in the *Hanford Federal Facility Agreement and Consent Order* (Ecology 1989), also known as the Tri-Party Agreement.

In May of 2002, the DOE drafted the *Performance Management Plan for the Accelerated Cleanup of the Hanford Site* (Performance Management Plan), a plan to transform and accelerate cleanup of the Hanford Site. This plan, issued in August 2002, provides a five-point acceleration strategy to complete cleanup of the entire Site by 2035. The second of these five strategies calls for accelerated closure of the Tank Farms by the year 2035 by means of three more initiatives. To meet the closure schedule, two of the three initiatives will be developed in parallel with the aim of completing all tank waste treatment by 2028.

## FRAMING THE PROBLEM

The Performance Management Plan describes three key elements of accelerated treatment to complete tank waste processing by 2028:

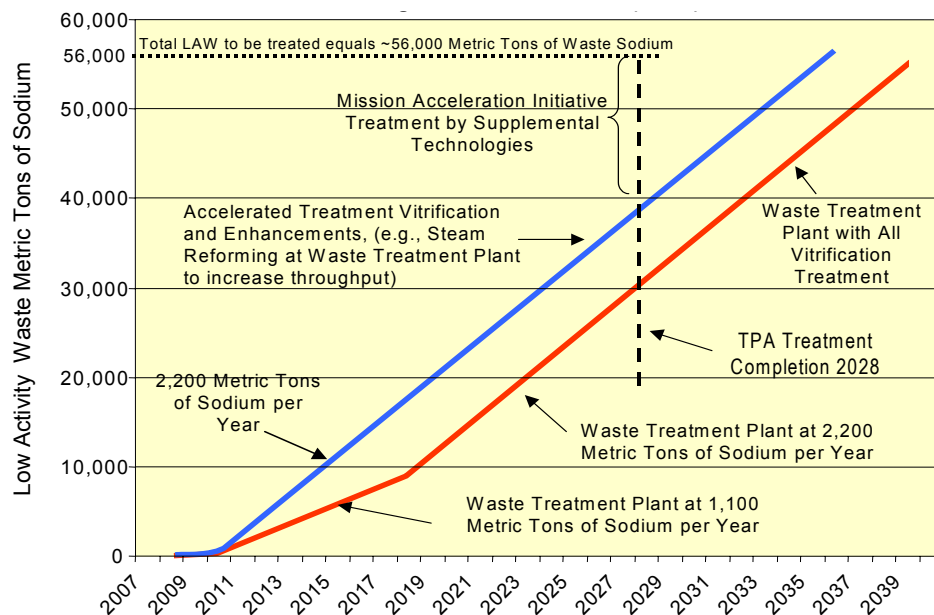
1. Build only one WTP facility but enhance its throughput.
2. Provide a potentially suitable LAW alternative to glass that could be used to supplement the LAW pretreated in the WTP.
3. Provide a supplement to WTP treatment for wastes that can be suitably treated and immobilized using non-WTP treatment approaches.

From these three elements, it is clear that in order to complete tank waste processing by 2028, the RPP must establish an integrated approach to selecting supplemental technologies.

Figure 1 (based on Figure 8 of the Performance Management Plan) shows how the synergy between WTP enhancements and supplemental treatments can achieve the 2028 milestone. The basic plant design supports a 1X capacity of 30 metric tons of glass per day (MTG/D) LAW, which corresponds to 1,100 metric tons (MT) of sodium processed per year. WTP pretreatment features support a 2X throughput, and improvements in LAW immobilization capacity are expected to support the same 2X rate by some combination of increased melter capacity and use of in-plant improvements such as steam reforming. As shown in Figure 1, the 2X WTP would complete treatment after 2035. Supplemental treatments on selected LAW feeds allow completion by 2028. As the figure implies, before selecting appropriate supplemental technologies it is important to understand which waste should be targeted.

The selection of appropriate target waste took into consideration several factors in anticipation of technology comparisons. CH2M HILL Hanford Group Inc. (CH2M Hill) performed a comprehensive analysis of tank waste in order to provide a rational basis for the technology selection process. Target waste was selected according to the following logic:

1. No DST waste and waste included in WTP phase 1 (although the analysis did consider some DST waste that, if treated by a different technology, could show significant cost and schedule savings over the baseline)
2. Waste that contained species non-optimal for processing in the WTP (such as sulfates)
3. Waste that existed in sufficient quantity such that the deployment of a minimum set of right-sized technologies (preferably one) could provide a complete treatment solution by 2028 alongside WTP
4. Waste that did not compromise the retrieval demonstration and Tank Closure Program
5. Waste that was located as centrally as possible so that a minimum number of deployments could achieve the desired effect
6. Waste that was representative of LAW because treating this fraction simplified retrieval and made the largest contribution to overall treatment commitments.



The combination of accelerated LAW treatment in the WTP and supplemental technologies provides a pathway to complete waste treatment by 2028.

Figure I. Comparison of Baseline and Accelerated Cases for Treating Low-Activity Waste and Other Non-High-Level Waste.

This target analysis provided the basis for the selection of supplemental technologies.

- The primary strategy was focused on treating the waste contained in 68 SSTs. These tanks contain predominantly saltcake, and at least 50,000 gallons of saltcake waste each. Cumulatively, these tanks contain over 20 million gallons of saltcake, approximately 85 percent of the total saltcake inventory for all tanks. These tanks contain about 60 percent of the sodium and over 70 percent of all the nitrates and sulfates in the total tank waste inventory. If processed through the WTP, the amount of immobilized LAW (ILAW) glass produced from the saltcake waste contained in these 68 SSTs would be about 65 percent of the total ILAW glass produced. This represents enough waste to ensure the parallel achievement of the 2028 completion alongside WTP. Twelve tanks were identified as not containing HLW using a source-based definition. These wastes will need to be classified as mixed-transuranic (mixed-TRU) wastes and could be treated and sent to the Waste Isolation Pilot Plant (WIPP).

Initial studies have shown that considerable savings over the baseline are possible. Additionally, three of these tanks are DSTs and their early treatment would free up DST space during a time frame that may be valuable in mitigating risks with WTP startup. This alternative treatment would contribute about 3 years reduction in HLW vitrification duration to the 2028 commitment.

## PROCESS FOR TECHNOLOGY SELECTION

Technologies for treating the Hanford Site tank wastes, including the saltcake waste, have been researched and evaluated for a number of years. All candidate technologies and the assembly of those technologies into flow sheet options were screened to ensure that they met the criteria defined as closing the LAW treatment gap by accelerating cleanup and reducing risk while maintaining cleanup quality.

During the month of March of 2002, candidate technologies were grouped into families that met the basic screening principles but differed in implementation. Table I contains the candidate technologies separated by function: pretreatment or immobilization. SST 241-S-112 was selected as a good representative for the targeted LAW source stored in the SSTs. Technology experts were asked to prepare short briefings on their technology and how it could be applied to tank 241-S-112-type waste with the objective of a tank-scale (approximately 5 gal/min throughput) demonstration with real waste in 2005 or 2006. Additionally, separation technologies were combined with immobilization technologies to constitute complete treatment options.

At the Mission Acceleration Initiative (MAI) Technology Demonstration Workshop held on April 2 and 3, 2002, technical and programmatic experts from the DOE complex assembled to review this relatively high level information on technologies proposed for LAW treatment, to discuss how these technologies could be combined into viable treatment flow sheet options other than the current baseline WTP process, and to screen out technologies and combinations that did not appear viable for short-term demonstrations. Screened out technologies with longer term potential were referred to the Office of Science and Technology for further development. Experts were invited to make presentations describing their approach for treating a representative tank of LAW saltcake waste in a demonstration to be conducted within 4 years that would be applicable for addressing the WTP LAW processing capacity gap.

Table I. Treatment Technologies Candidates.

<b>Pretreatment Options</b>	<b>Immobilization Options</b>
Selective dissolution	Ex situ, bulk, mobile vitrification
<sup>137</sup> Cs ion exchange	Grouting/sorption
Cesium and technetium removal by solvent extraction	Microencapsulation
Thermal denitration by steam reforming, fluidized bed, or rotary kiln	Other ambient temperature immobilization
Active metal reduction of nitrate	Thermal processes for immobilization (steam reforming; active metal reduction)
Electrochemical denitration with or without NaOH recovery (by electrochemical or solvent extraction)	None
Fractional crystallization for sodium salt removal	None
Sulfate removal by precipitation or fractional crystallization	None

The results of the workshop were reviewed by ORP, CH2M HILL, Pacific Northwest National Laboratory, and the Cleanup Constraints and Challenges Team (C3T) MAI Subgroup to agree upon those flow sheets for which more detailed evaluation would be conducted with the purpose of submitting the selected flow sheets for evaluation by the C3T MAI Subgroup by the end of May of 2002.

During April and early May of 2002, CH2M HILL developed flow sheets for the six selected treatment options (plus two variants). Sulfate separation by strontium precipitation in acidic conditions was added as a seventh option during that period.

Figure 2 summarizes the process used in the nine flow sheets options for which mass balance and other data were developed.

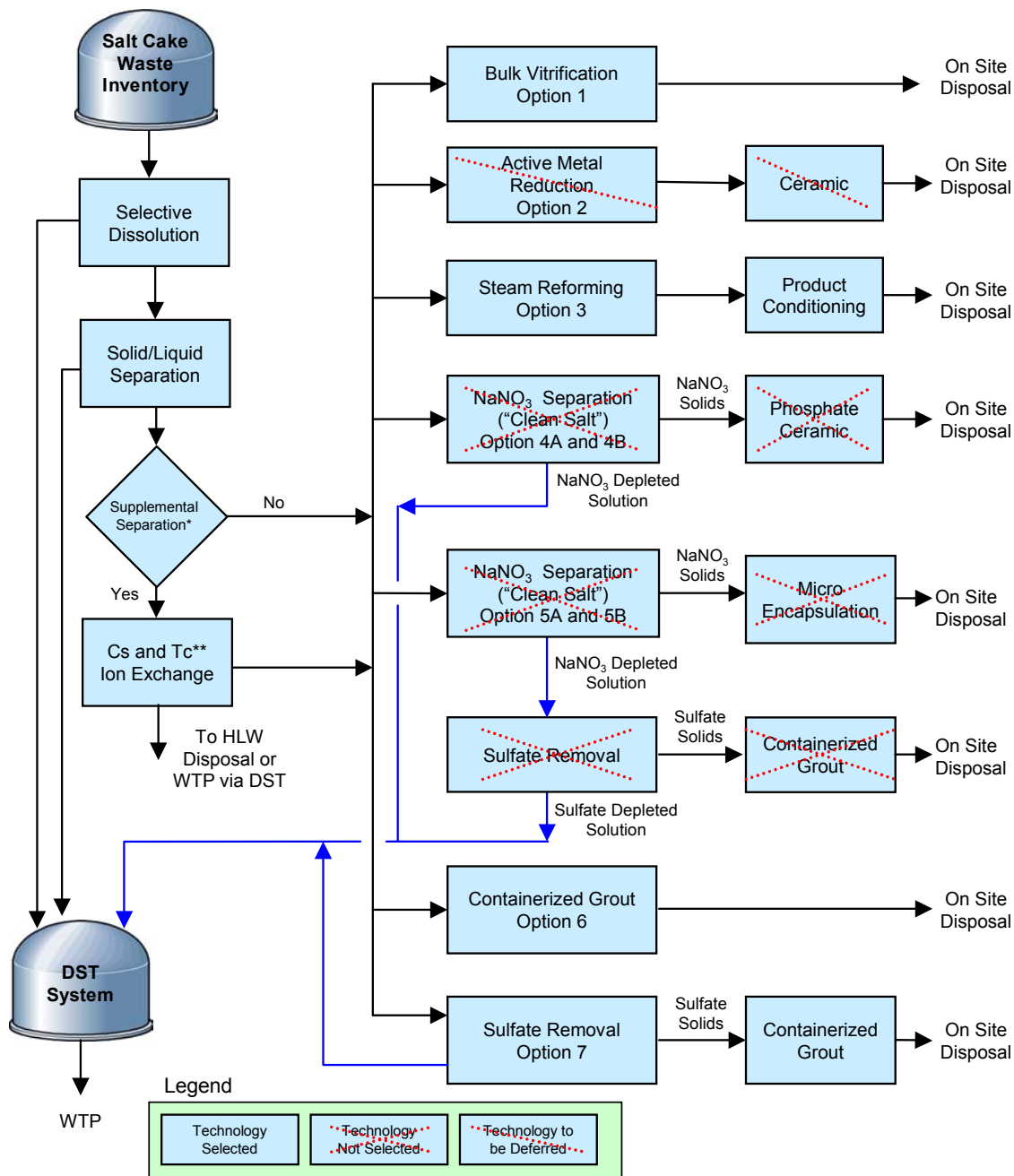
A three-day workshop was held on May 21, 22, and 23, 2002, to evaluate selected supplemental treatment options for Hanford Site tank waste.

### **PRETREATMENT COMMON TO ALL FLOW SHEET OPTIONS**

Participants at the C3T workshop conducted April 2-3, 2002, recommended that the saltcake waste be pretreated using selective dissolution, solid-liquid separation, and ion exchange to separate analytes (e.g., sulfate and sodium),  $^{137}\text{Cs}$ , and other radionuclides from the saltcake waste before conducting further treatment process steps. Participants at the C3T workshop conducted May 21-23, 2002, recommended that in addition to cesium separation;  $^{99}\text{Tc}$  should be separated from the saltcake waste. The participants at the C3T workshops assumed  $^{137}\text{Cs}$  and  $^{99}\text{Tc}$  needed to be separated from the saltcake waste. A combination of selective dissolution and ion exchange was assumed necessary to achieve a high degree of  $^{137}\text{Cs}$  and  $^{99}\text{Tc}$  separation from the dissolved saltcake solution.

### **FLOW SHEET OPTIONS RECOMMENDED**

The flow sheet options were evaluated by the May 21-23 C3T MAI Subgroup and associated expert group. The C3T MAI Subgroup recommended that these options be pursued for FY 2003 bench-scale or cold testing. The expert group and the C3T MAI Subgroup regarded these options as having the best potential to accelerate risk reduction and shorten RPP mission completion time. In examining the supplemental technologies, reduction in the length of time needed to complete tank waste treatment was used as a surrogate measure for life-cycle cost.



\* Clean Salt Option 4A and Option 5A don't include Cs and Tc removal.  
 \*\* Tc Ion Exchange added as a result of May 21-23 Workshop

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Figure 2. Low-Activity Waste Supplemental Treatment Alternatives.

The C3T MAI Subgroup recommended the following four technologies:

- Sulfate removal
- Containerized grout
- Bulk vitrification
- Steam reforming.

CH2M HILL recommended that ORP fund each of the four alternative technologies on a limited scale in FY 2003 to obtain data needed to determine merit and likelihood of successful deployment, potential mission acceleration, and risk reduction. These data include those that can be gathered from the following sources:

- Hot and cold laboratory testing
- Related input to establish the requirements for radionuclide removal on a tank by tank basis
- Related input for regulatory analysis to establish the requirements for hazardous waste constituent removal or immobilization

Facility configuration and approaches for demonstration and deployment.

## **SULFATE REMOVAL**

### **Process Description**

High concentrations of sulfate in the LAW feed solutions present problems for the current WTP baseline LAW vitrification process using joule-heated melters. These problems can lead to a reduction in waste incorporation in the ILAW glass. Additionally, preliminary testing of the LAW vitrification system indicated that a separate molten sulfur layer would form in the melter at the maximum sulfate-to-sodium mole ratio in the LAW solutions. This molten sulfur layer is highly corrosive to the melter components. The sulfate removal process is beneficial in the reduction or removal of sulfate from LAW that requires vitrification in the WTP. The sulfate removal process is not proposed for use on waste that is provided as feed to the other recommended MAI supplemental technology alternatives: ex situ bulk vitrification, containerized grout, or steam reforming.

Separating sulfate from the saltcake waste contained in the 68 candidate SSTs has the benefit of reducing the amount of ILAW glass produced and thus reducing the duration of the RPP mission. Sulfate removal reduces by 8 the number of years (in the WTP) needed to complete ILAW treatment. The total ILAW volume is reduced from 205,000 cubic meters to 183,400 cubic meters.

Following solids-liquid separation to remove the entrained solids from the dissolved saltcake, the liquid LAW solution is acidified. Strontium nitrate is then added to the acidic waste to precipitate strontium sulfate. The strontium sulfate precipitate is separated from the acidic solution. The strontium sulfate precipitate is washed with water and processed again through the solid-liquid separation step to remove residual acidic solution. The strontium sulfate precipitate is solidified in a low-temperature waste form such as grout or phosphate-bonded ceramic. The solidified sulfate precipitate would be disposed of in the Hanford Site disposal trenches for mixed low-level waste.

The wash solution is combined with the acidic filtrate from the solid-liquid separation step, neutralized by addition of sodium hydroxide solution, and returned to the DST system for eventual processing in the WTP. If the sulfate removal process is conducted integral to the WTP, the acidic filtrate may not need to be neutralized before processing in the LAW vitrification system, further reducing the amount of ILAW glass produced.



### **Implementation for Demonstration**

Sulfate removal needs to be demonstrated on representative tank waste at the laboratory scale to evaluate the process and its parameters. Feed for this process evaluation needs to have undergone solids–liquid separation. The resulting sulfate precipitate then needs to be processed into a waste form and demonstrated to meet the LDR. This can be done at engineering scale followed by cold pilot-scale activity. Since the actual sulfate removal step for deployment is most likely to occur integral to the WTP pretreatment facility, no large demonstration-scale effort is anticipated. An annex facility would likely need to be constructed to contain the sulfate removal process if this process were integrated with operation of the WTP.

### **Implementation for Deployment**

Most of the saltcake waste that is sent to the WTP will benefit from sulfate removal after the baseline pretreatment steps and before being sent to the LAW vitrification facility. Only a handful of tanks have waste that would not benefit from such supplemental processing. Any waste going into the supplemental immobilization processes described in this document (e.g., bulk vitrification, containerized grout, or steam reforming) would not be sent through the sulfate removal process.

### **Summary**

This option supports the treatment of the dissolved saltcake waste from 68 SSTs in less time than the baseline by allowing an increased glass loading to be achieved in the LAW vitrification facility. The sulfate removal process supplements the WTP pretreatment activities for those wastes being provided to the WTP.

## **CONTAINERIZED GROUT**

### **Process Description**

The containerized grout supplemental treatment process includes the pretreatment steps for solids removal and cesium and technetium removal. To produce grout, the pretreated dissolved saltcake solution is mixed with a Portland cement-type grout solid, pumped into disposal containers, and allowed to cure or solidify. The cured product may now be managed with handling equipment for intermediate storage and disposal.

Use of the containerized grout process has the potential to reduce by 15 the number of years (in the WTP) to complete ILAW treatment. Total ILAW volume is increased from 205,000 cubic meters to 358,400 cubic meters.

## **Technical Analysis**

Historically the inorganic additives that have been successfully used for grout are Portland cement, fly ash, and slag. The following are the main reasons for the widespread use of these materials:

- Relatively low cost
- Good long-term stability, both physically and chemically
- Documented use on a variety of wastes for a period of over 20 years
- Widespread availability
- Non-toxicity of the chemical ingredients
- Ease of use in processing (processing is done normally at ambient temperature and pressure with no special equipment)
- High resistance to biodegradation
- Low water solubility and permeability for most isotopes and chemicals
- Good mechanical and structural characteristics.

Testing of specific grout formulations is needed to determine the leachate of constituents of concern (e.g., radionuclide RCRA metals, nitrate) for conducting a performance assessment of the grouted waste. Much of this data is available from the former Hanford Grout Disposal Project.

## **Disposal of Containerized Grout**

Grout containers would be disposed in disposal trenches on site.

## **Summary**

Use of containerized grout allows treatment of the alternate stream from 68 SSTs in less than 20 years and would achieve the 2028 completion date for processing. The disadvantage of containerized grout is that the volume of waste disposed of onsite is about 1.5 times more than the volume of glass, and the retention of alkali metals and nitrates is lower than glass, although release limits may still be met because of the reduced inventory and the use of engineered barriers. Additional performance assessment work is required.

## **BULK VITRIFICATION**

### **Process Description**

The bulk vitrification process converts low-level mixed waste into a solid glass form by mixing the waste with soil and applying electrical current. The configuration and approach analyzed involved a vitrification step conducted within a large steel container via the GeoMelt in-container vitrification (ICV) process licensed by AMEC Earth and Environmental.

The saltcake waste is pretreated to remove solids, cesium, and technetium before feeding the bulk vitrification module. The bulk vitrification module consists of a drying step, a mixing step, and an ICV step. The drying unit blends process soil with the waste and removes water through evaporation. The remaining process soil is then mixed with the evaporated soil/waste stream and delivered to the vitrification container by a screw auger. A temporary off-gas hood is placed over the container and electrodes inserted. Power is applied to the electrodes to melt the waste/soil mixture. After cooling, the resulting vitrified product is sent to a disposal site.

The bulk vitrification process has the potential to reduce by 15 the number of years (in the WTP) to complete ILAW treatment. The total volume of the ILAW is reduced from 205,000 cubic meters to 148,200 cubic meters.

### **Technical Analysis**

The melting process is initiated within a waste and soil mixture. Electrical power is directed to the treatment zone via graphite electrodes and regulated to maintain the desired melt rate. The melt temperature typically ranges from 1,400 °C to 2,000 °C depending on the materials being treated and the process configuration. The melt grows downward and outward until the target waste volume has been treated and the electrical power is shut off.

The size and configuration of the container used for the ICV process depends on the application of the treatment technology. Two roll-off boxes are typically processed in parallel. The boxes can be staged to accommodate melts in the 25 to 30 metric ton range. Typical melt time is 2 to 3 days per pair of melts.

### **Product Description**

The vitrified waste form normally consists of a mixture of glass and crystalline materials and often has an appearance similar to volcanic obsidian. The product is typically five to ten times stronger than concrete and ten or more times more durable and leach resistant than typical borosilicate glasses used to immobilize HLW. The durability and leach resistance of the glass is due to a high concentration of glass formers ( $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ ).

Based on the assumptions used in this analysis, the estimated waste loading of the product is 20 wt% sodium oxide.

### **Process Chemistry**

Organic contaminants are destroyed via pyrolysis and dechlorination reactions at elevated temperatures in reducing conditions around the melt. No organic contaminants remain in the melt due to the inability of organics to exist at the temperatures involved. The melt incorporates most heavy metal and radionuclide contaminants resulting in permanent immobilization in the resulting vitrified product.

### **Process Experience**

Bulk vitrification has been successfully used to treat a wide range of contaminated wastes and debris including mixed low-level radioactive wastes, mixed TRU wastes, polychlorinated biphenyls, pesticides, dioxins, and a range of heavy metals. The ICV treatment configuration has been used in Australia and Japan and is being developed for DOE and commercial applications. The batch technique involves staging and treating wastes in refractory-lined steel containers. The containers can vary in size and shape from 208-L (55-gal) drums to large roll-off boxes. After each batch is treated, the melted waste is allowed to cool and solidify in the container. The container can be reused or disposed of after each melt.

After each batch of waste is treated, the vitrified waste solidified, and the off gas hood removed, a lid is placed on the container and the vitrified waste is transported to the disposal site.

### **Secondary Waste Generation**

Off-gases that evolve from the melt are typically collected in a steel containment hood and directed to an off-gas treatment system. The off-gas treatment steps vary depending on the particular requirements of the project but generally consist of an initial step of particulate filtration followed by quenching, wet scrubbing, two stages of high-efficiency particulate filtration, and carbon adsorption or thermal oxidation.

### **Implementation for Demonstration**

The number and size of the ICV containers processed would be determined in conjunction with the engineering studies and hot laboratory tests carried out in FY 2003.

### **Summary**

The use of bulk vitrification treatment for the waste from 68 SSTs allows the WTP to complete ILAW processing of the other tank waste in approximately 20 years. Bulk vitrification has two other advantages. One advantage is the production of a high-quality waste form that is equivalent to or better than the ILAW borosilicate glass. The second advantage is a reduction in the total volume of low-level waste glass for onsite disposal.

### **STEAM REFORMING**

This option utilizes a high-temperature fluidized bed to destroy nitrates and, with the help of additives, to incorporate radioisotopes together with sodium, sulfate, chlorine, and fluorine in a granular material that can be placed in containers or grouted. DOE has identified steam reforming for a variety of pretreatment and immobilization applications at the Hanford Site and at other DOE sites. To support the broad application of this technology, DOE has established a team to evaluate deployment and testing of the technology. As their strategy for deployment becomes more detailed, additional information will become available for evaluation.

For this evaluation and recommendation, one of the potential candidate processes for steam reforming is used: the Thermal Organic Reduction (THOR), steam reformer technology. THOR is a service mark held by Studsvik, AB.

The steam reforming process has the potential to reduce by 15 the number of years (in the WTP) to complete ILAW treatment. The total volume of the ILAW is increased from 205,000 cubic meters to 248,900 cubic meters.

### **Process Description**

In the THOR process, waste is fed directly to the steam reformer as slurry or as shredded solids through a lock hopper. The reforming reactor consists of a vertical vessel containing a fluidized bed of alumina sand that is designed to operate at temperatures of up to 800 °C. For safety reasons and to ensure containment of steam-reformed products and gases within the processing equipment, the bed operates at a negative pressure. Heat is supplied to the bed through the injection of superheated steam. Additional energy is supplied by injecting oxygen into the bed where it reacts exothermically with reductant compounds present in the waste or added to the waste. The reformer alumina bed is fluidized and heated with superheated steam. Any organic compounds in the waste are destroyed through pyrolysis and through reaction with hot nitrates, steam, and oxygen. Other reactions include reaction with carbon

sources to produce hydrogen, carbon monoxide, carbon dioxide, and water. The temperature of the bed is thus controlled by adjusting the inlet temperature of the fluidizing steam and by regulating the amount of oxygen and reductant injected.

The fluidized bed is designed to be operated such that less than 5 percent of the total bed weight is due to waste solids. This design ensures that the inert part of the bed acts as a large heat sink, thereby avoiding problems with agglomeration caused by the presence of low-melting point salt eutectics in the waste. Recovery from an agglomeration of the bed media involves cooling the bed and washing the media with hot water. The bed is then dried and refluidized through the injection of superheated steam. Alternatively, a water-wash screw conveyor has been designed that could be installed on the bottom of the bed. Operation of the screw would augment the de-agglomeration process.

### **Technical Analysis**

Most of the nitrate and nitrite are reduced to nitrogen while reducing agents would be oxidized to carbon dioxide and water. The off-gas composition under these assumptions would be less than 500-ppm nitrogen oxides and less than 20-ppm chloride, sulfur and fluoride. At this nitrogen compound concentration, ammonia would not be required for the control of nitrogen oxides. Most of the chlorides, sulfur, and fluoride would be retained in the product along with greater than 99 percent of the cesium and technetium.

### **Salt Agglomeration**

When processing sodium saltcake waste, the reformer–fluidized bed tends to form agglomerates over the temperature where sodium salts exists in a molten state. These agglomerates range in size; but regardless of their size, they tend to plug the fluidized bed. To overcome this problem, substances are added to the saltcake feed to (1) lower the decomposition temperature of sodium nitrate or (2) to combine with the nitrate at a low temperature to form a compound that is stable at, and has a melting point above, the reformer operating temperature. The use of additives is proposed in the application of the THOR process to the treatment of saltcake waste.

The conversion of sodium nitrate to nepheline,  $\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ , would require addition of aluminosilicate clay (kaolin) to the steam reformer. The use of sucrose as an additive to enhance nitrate destruction has been tested extensively in related processes.

### **Steam Reformer Waste Product Acceptability for Low-Level Waste Disposal**

The waste produced from steam reforming saltcake waste is assumed to be a powder of nepheline, beta-alumina, sodium carbonate, and other minerals and salts. The MAI technology program should verify the expected composition of the steam reformer product through laboratory-scale testing of simulated saltcake waste. The steam reformer product should be tested to verify that the waste meets criteria for disposal. As with the other recommended technologies, this flow sheet and product must be evaluated against regulatory analysis and performance assessment requirements.

### **Implementation for Deployment**

The steam reforming capability can serve as a denitration step (supplement to pretreatment). The product may be suitable for packaging for land disposal at the Hanford Site or may require additional immobilization, either through the use of additives during the steam reforming process or the use of subsequent additives to form a compliant grout.

## Summary

The use of the steam reforming treatment for the waste from 68 SSTs allows the WTP to complete ILAW processing of the other tank waste in approximately 20 years. Steam reforming has two other advantages. The first advantage is that it allows the destruction of nitrates in the wastes and enables a stable mineral waste form to be produced. The second advantage is the elimination of waste recycles between facilities permitting a single-pass operation. Steam reforming would be deployed in conjunction with other MAI to achieve the desired 2028 tank farm mission completion. Steam reforming leads to an estimated 20 percent increase in the total volume of ILAW product for disposal at the Hanford Site.

## OTHER TREATMENT OPTIONS

Other processes were presented in the April 2-3 workshop and were included in the subsequent flow sheet analysis work to develop material balances and other information. All of these flow sheets were included in the evaluation done by the May 21-23 C3T MAI Subgroup. The C3T MAI Subgroup did not recommend that these flow sheets be pursued as part of the MAI in FY 2003. (RPP-11131, *Mission Acceleration Initiative Demonstration Information Package*)

While additional initiatives are not part of the analyses presented in this paper, for completeness please note that ORP is pursuing additional initiatives as part of its efforts to accelerate tank waste cleanup. ORP, as supported by CH2M HILL, is jointly pursuing with the Office of Science and Technology an initiative that could expedite both LAW and HLW immobilization. The goal of this initiative is to significantly increase the throughput of the WTP to enable accelerated cleanup and to achieve balance of mission treatment requirements beyond the current WTP contract. Waste loading improvements to vitrified HLW will significantly increase the capacity of the HLW vitrification plant as well as reduce the volume of immobilized waste requiring disposal.

## TRANSURANIC TANK WASTE SOLIDIFICATION FOR DISPOSAL AT THE WASTE ISOLATION PILOT PLANT

The Hanford Site underground storage tanks contain approximately 1.3 million gallons of waste that could potentially be classified as TRU waste. These wastes are stored in nine SSTs and three DSTs. The current baseline for treatment and disposal of the Hanford Site tank wastes, including the potentially TRU tank wastes, begins with pretreatment to separate the tank waste into LAW and HLW fractions. The HLW is to be vitrified and disposed of in the spent nuclear fuel-HLW repository. The LAW also is to be vitrified and disposed of at the Hanford Site.

Pretreatment, LAW vitrification, and HLW vitrification processing of tank wastes will be conducted at the WTP. These wastes likely will require blending with HLW sludges before being vitrified in the WTP because they contain components (e.g., bismuth, chrome, and zirconium) that exhibit limited incorporation in borosilicate glass. If processed without blending in the WTP, the TRU tank wastes would produce an estimated 10,900 MT of glass. Instead, if processed in the WTP, these potentially TRU tank wastes would likely be blended with other sludges retrieved from other Hanford Site underground storage tanks. Assuming the potentially TRU tank wastes could be blended with other tank sludges to achieve a non-volatile waste oxide loading of 40 wt% (excluding sodium, potassium, and silicon), the amount of glass produced would be approximately 2,000 MT.

As an alternative to immobilizing the TRU tank wastes in glass, the TRU tank wastes could be immobilized in a low-temperature waste form and transferred to the WIPP for disposal.

## **Process Description**

The TRU tank wastes would first be retrieved from their underground storage tanks and transferred to a facility for separation of supernatants. The TRU solids would be separated from the liquids. Next, the TRU tank wastes would be washed with either water or dilute sodium hydroxide solution to remove soluble salts (such as NaF contained in the neutralized cladding removal waste stored in tanks 241-AW-103 and 241-AW-105) to reduce the mass of TRU tank waste. For the sludges stored in tanks 241-SY-102 and 241-AW-103, washing also separates the HLW supernatant from the TRU sludges. The wash solutions would be transferred to the DST system for treatment in the WTP. The washed TRU tank waste would be immobilized and packaged for disposal in the WIPP. Candidate alternative treatment processes that could be used to prepare the TRU tank wastes for disposal at the WIPP include immobilization in grout, immobilization in phosphate-bonded ceramic, and low-temperature drying.

The development program for the MAI supplemental technology alternative processes will need to determine whether the TRU tank wastes are CH-TRU or RH-TRU waste and conduct process verification testing to demonstrate compliance with the WIPP waste acceptance criteria for CH-TRU and RH-TRU wastes once the RH-TRU waste acceptance criteria have been developed.

## **Solidification of Tank 241-T-110 Low-Level Waste Solids**

As part of evaluating whether the SSTs and DSTs contain waste that could be classified as TRU waste, approximately 369,000 gal of waste contained in tank 241-T-110 was identified as potentially low-level waste according to criteria established in DOE M 435.1-1, *Radioactive Waste Management Manual*.

## **RECOMMENDATIONS AND PATH FORWARD**

### **Recommendations**

Four recommendations are presented for the acceleration of cleanup of tank wastes dealing with technology investigation, review of waste treatment and disposal requirements, TRU and low-level waste processing, and denitration. The detailed scopes for implementation of these recommendations are to be developed as part of planning for the target baseline.

### **Technologies for Investigation Fiscal Year 2003**

The pursuit in FY 2003 of the laboratory-scale demonstrations and other investigations that would be required (e.g., follow-on engineering evaluations) for the following supplemental technologies are recommended:

- Sulfate removal
- Containerized grout
- Bulk vitrification
- Steam reforming.

### **Sulfate Removal**

Sulfate removal allows for the acceleration of cleanup by reducing the amount of glass produced in the WTP by increasing the waste loading in the LAW. Though this technology could be deployed in conjunction with tank farm operations, it is envisioned that as a pretreatment step, sulfate removal would be best deployed in the WTP. This deployment would offer the potential benefit of not having to neutralize the waste, which would in turn reduce the amount of sodium to be vitrified.

### **Containerized Grout**

Containerized grout allows acceleration of tank waste cleanup by reducing the amount of sodium that the WTP needs to process. In deploying this technology, the testing can be conducted independently of the location selected for implementation. Containerized grout could be successfully deployed either in conjunction with tank farm operations or in conjunction with WTP operations.

### **Bulk Vitrification**

Bulk vitrification accelerates tank waste cleanup by reducing the mass of sodium requiring vitrification in the WTP. The technology could be deployed in a variety of configurations based on the module design of the equipment. The investigations for FY 2003 should focus deployment in conjunction with tank farm operations.

### **Steam Reforming**

Steam reforming allows acceleration of the cleanup of tank waste by serving as an additional method for immobilizing the LAW fraction of the waste. By reducing the burden on the WTP melters, the schedule could be significantly accelerated.

### **Supplemental Analysis of Denitration of Tank Waste**

If DOE's current strategy for treatment of the Hanford Site tank waste does not achieve its desired goals, development of one or more backup strategies would be prudent. To increase the range of application for these backup strategies, investigation of means to denitrate the waste would be advantageous. In the evaluation of technologies, the C3T MAI Subgroup found that active metal denitration appears to be promising and warrants further investigation. Thus, the recommendation is that the Office of Science and Technology perform investigations of denitration processes.

### **Transuranic Waste Treatment**

TRU waste treatment allows for acceleration of tank cleanup by reducing the amount of waste that requires vitrification as HLW. This treatment system would be deployed in conjunction with tank farm activities to minimize the impact on the WTP.

### **PATH FORWARD**

The current RPP path forward includes the following additional steps, which will be completed to implement the Performance Management Plan:

Complete hot laboratory testing of alternative technologies	8/31/03
Complete cold pilot demonstrations of selected technologies	8/31/04



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