SELECTION OF PRETREATMENT PROCESSES FOR REMOVAL OF RADIONUCLIDES FROM HANFORD TANK WASTE

Rudy Carreon and Billie M. Mauss,
U.S. Department of Energy, Office of River Protection
Richland, Washington, 99352

Mike E. Johnson,
CH2M Hill Hanford Group, Inc.
Richland, Washington, 99352

Langdon K Holton,
Pacific Northwest National Laboratory
Richland, Washington, 99352

G. Todd Wright, Reid A. Peterson and Ken J. Rueter
Washington Group International
Richland Washington, 99352

ABSTRACT

The U.S. Department of Energy’s (DOE’s), Office of River Protection (ORP) located at Hanford Washington has established a contract (1) to design, construct, and commission a new Waste Treatment and Immobilization Plant (WTP) that will treat and immobilize the Hanford tank wastes for ultimate disposal. The WTP is comprised of four major elements, pretreatment, LAW immobilization, HLW immobilization, and balance of plant facilities. This paper describes the technologies selected for pretreatment of the LAW and HLW tank wastes, how these technologies were selected, and identifies the major technology testing activities being conducted to finalize the design of the WTP.

INTRODUCTION

Hanford tank waste consists of approximately 54 million gallons of highly radioactive and mixed hazardous waste stored in underground storage tanks at the Hanford Site. The radiochemical inventory of the tanks waste is approximately 190 million curies, mainly consisting of the radio-isotopes of Cs, Sr, and transuranium elements (TRU). The tank waste includes solids (sludge), liquids (supernatant), and salt cake (dried salts that will dissolve in water forming supernatant). The tank waste will be remediated through treatment and immobilization to protect the environment and meet regulatory requirements.

The U.S. Department of Energy (DOE) determined that the preferred alternative to remediate the Hanford tank waste is to:

- Pretreat the tank waste to separate it into two fractions, Low-Activity Waste (LAW) and High-Level Waste (HLW);
- Immobilize the LAW as glass for on-site disposal; and
- Immobilize the HLW as glass for ultimate disposal in the national repository.

The first waste fraction, LAW, is comprised of the tank waste liquids (and dissolved salt cake) and contains the bulk of the tank waste chemicals and certain radionuclides (e.g., cesium, technetium and a limited amount of strontium and transuranics) that must be recovered prior to immobilizing this fraction of the waste. LAW is a mixed, characteristic, and listed waste regulated under the Resource Conservation
and Recovery Act of 1976 (RCRA), and must meet certain treatment standards and performance standards for on-site disposal of the final waste form.

The second waste fraction, HLW, is comprised of tank waste solids consisting primarily of iron and aluminum hydroxides as oxides and insoluble radionuclides. The radionuclides separated from the LAW fraction are combined with the HLW fraction prior to vitrification. HLW is a mixed, characteristic, and listed waste regulated under RCRA, and must meet specific treatment and performance standards for storage and repository disposal of the final waste form.

The U.S. Congress directed DOE to establish the Office of River Protection (ORP) at Hanford, Washington to perform the activities necessary to remediate the Hanford tank waste. Through a contract established between ORP and Bechtel National Inc., ORP will manage and oversee the design, construction, and commissioning of a new Waste Treatment and Immobilization Plant (WTP) that will treat and immobilize the waste for ultimate disposal. The WTP is comprised of four major elements, pretreatment, LAW immobilization, HLW immobilization, and balance of plant facilities. This paper identifies the processes that are planned to be used in the WTP Pretreatment Facility and describes the major activities being conducted to complete the technology development.

DESCRIPTION OF THE HANFORD WASTE TREATMENT PLANT PRETREATMENT FLOWSHEET

A simplified depiction of the tank waste pretreatment flowsheet for the WTP is depicted in Figure 1. The pretreatment facility receives from the tank farm two basic waste types that are specified in the WTP Contract. These are a LAW and a HLW waste feed.

The LAW fraction is comprised of the tank waste liquids (and dissolved salt cake) and contains the bulk of the tank waste chemicals and certain radionuclides that must be mitigated prior to immobilization. The principal non-radioactive components of the LAW stream are dissolved sodium salts found in the waste (e.g., sodium nitrate, nitrite, hydroxide, carbonate, phosphate, aluminate [at high pH] and fluoride and some of their mixed double salts). The pretreatment steps for the LAW fraction include: (a) evaporation to accommodate concentration adjustments in the feed to the radionuclide separation processes, and to concentrate aqueous recycle to maintain the process water balance; (b) strontium removal through isotopic dilution; and transuranic precipitation utilizing sodium permanganate which results in precipitated manganese hydroxide are combined with any insoluble solids transferred with the LAW feed from tank farms; (c) ultrafiltration for solids removal using crossflow filters; and (d) cesium and then subsequent technetium removal using an elutable SuperLig® (SuperLig® is a registered trademark of IBC Advanced Technologies, Inc.) ion-exchange resins.

The HLW fraction is comprised of tank waste solids and the long half-life radioactive solids that form the generally water insoluble fractions of alkaline fuel reprocessing wastes. This waste sludge is concentrated through the use of metallic cross filters and leached with water, and if needed caustic washed to leach the bulk of the soluble waste components from the waste. The radioactive materials recovered from the LAW waste stream (Cs, Tc, Sr, TRU) are blended with the washed HLW sludge prior to immobilization.

Since disposal of the immobilized HLW fraction as a glass product is significantly more expensive on a cubic meter of waste basis, than for disposing of the immobilized LAW, part of the processing of this waste stream is aimed at lowering the mass of nonradioactive components in the HLW stream. These include the oxyhydroxides of aluminum, insoluble metal phosphate salts, and various silica containing minerals. The high solids loaded waste stream is first water washed to remove the soluble sodium salts in solution in which it is suspended. The planned facility is designed so that those solids can then be caustic leached [3M NaOH at 80 to 90°C] to remove non-radioactive process chemicals.
Fig. 1. Simplified Pretreatment Process Flowsheet
DEFINITION OF WASTE TREATMENT REQUIREMENTS

The pretreatment requirements for the WTP have been established to ensure that the Immobilized Low Activity (ILAW) and Immobilized High-Level Waste (IHLW) waste form can meet specific acceptance criteria defined in applicable Federal and Washington State requirements for disposal and ensure that the operation of the WTP is optimized with respect to cost. The treatment processes are established to meet the requirements for the production of waste forms. A portion of the treatment steps, those associated with radionuclide and chemical removal are conducted in the pretreatment process. Other treatment requirements such as the treatment for destruction of organic tank waste constituents and immobilization of heavy metals are achieved in the LAW and HLW vitrification processes. The major separation requirements for the production of the ILAW and IHLW waste forms are summarized in Table I.

Table I. Summary of Major Waste Separation Requirements for the WTP Pretreatment Facility.

<table>
<thead>
<tr>
<th>Pretreatment Process</th>
<th>Treatment Requirement</th>
<th>Basis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Removal of Solids/Support washing of Sludges</td>
<td>Remove solids from LAW and soluble salts from the sludge</td>
<td>Ensure the ILAW glass will meet the radionuclide concentration limits</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Avoidance of Ion Exchange Column plugging</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Reduce the volume of IHLW to minimize treatment and disposal costs</td>
</tr>
<tr>
<td>Cs-137 Removal</td>
<td>Cs-137 less than 0.3 Ci/m3 in the ILAW product</td>
<td>Ensure the ILAW glass will adhere to 10 CFR61 Class C LAW concentration limits and the ILAW Performance Assessment (2) for shallow land burial</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Operational dose rate for LAW melter</td>
</tr>
<tr>
<td>Tc-99 Removal</td>
<td>Tc-99 less than 0.1 Ci/m3 in the ILAW product (On average 80% of the Tc shall be removed from the tank wastes.)</td>
<td>Ensure the ILAW glass will adhere to 10 CFR61 Class C LAW concentration limits and the ILAW Performance Assessment (2) for shallow land burial</td>
</tr>
<tr>
<td>Sr-90 Removal</td>
<td>Sr-90 less than 20 Ci/m3 in the ILAW product</td>
<td>Ensure the ILAW glass will adhere to 10 CFR61 Class C LAW concentration limits and the ILAW Performance Assessment (2) for shallow land burial</td>
</tr>
<tr>
<td>TRU Removal</td>
<td>Less that 100 nCi/gram in the ILAW product</td>
<td>Ensure ILAW glass can meet Class C LLW limits</td>
</tr>
</tbody>
</table>
SELECTION OF PRETREATMENT TECHNOLOGIES

The pretreatment technologies for the WTP were selected based upon evaluations and assessments conducted by the WTP Contractor during the time period 1996 to 2000. The selected technologies were experimentally evaluated (i.e., small scale proof of principle tests) using actual tank wastes, to provide a proof of principal demonstrations that the technologies would meet the technical requirements specified by the ORP. In one case; the originally selected ferric nitrate precipitation process (ferric floc) for removal of TRU elements from the tank wastes, was revised to use sodium permanganate precipitation. The technologies considered and the reference technology for each major pretreatment step is identified in Table II. The final selected technologies were specified in the WTP Contract.

Table II. Candidate and Selected Technologies for the WTP Pretreatment Process Flowsheet.

<table>
<thead>
<tr>
<th>Treatment Function</th>
<th>Candidate Technologies</th>
<th>Selected Technology</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solids Removal</td>
<td>• Ultra filtration&lt;br&gt;• Deep Bed Filtration&lt;br&gt;• Centrifugation&lt;br&gt;• Pressure Precoat Filtration&lt;br&gt;• Sedimentation (Tank Farm or Pretreatment Plant)</td>
<td>Ultrafiltration using crossflow filtration</td>
</tr>
<tr>
<td>Cs Removal</td>
<td>• Single Use Ion-Exchanger&lt;br&gt;• Regenerable Ion-Exchanger&lt;br&gt;• Solvent Extraction&lt;br&gt;• Ferrocyanide Precipitation&lt;br&gt;• Crystallization&lt;br&gt;• Tetraphenyl borate Precipitation</td>
<td>Regeneratable Ion-Exchange using Superlig® 644</td>
</tr>
<tr>
<td>Tc Removal</td>
<td>• Single Use Ion-Exchanger&lt;br&gt;• Regenerable Ion-Exchanger&lt;br&gt;• Activated Carbon Adsorption&lt;br&gt;• Precipitation with sodium sulfide</td>
<td>Regeneratable Ion-Exchange using Superlig® 639</td>
</tr>
<tr>
<td>Sr Removal</td>
<td>• Isotopic Dilution&lt;br&gt;• Single Use Ion-Exchanger&lt;br&gt;• Regenerable Ion-Exchanger&lt;br&gt;• Activated Carbon Adsorption&lt;br&gt;• Titania Adsorption</td>
<td>Isotopic Dilution with Sr nitrate</td>
</tr>
<tr>
<td>TRU Removal</td>
<td>• Decomplexation/Adsorption&lt;br&gt;• Solvent Extraction&lt;br&gt;• Ferric Floc Precipitation&lt;br&gt;• Activated Carbon Adsorption</td>
<td>Decomplexation/Adsorption using NaMnO4</td>
</tr>
</tbody>
</table>
The criteria used for the selection of the technologies was based upon:

- Technical Maturity
- Operability
- Safety
- Ability to meet the ILAW Specification
- Ability to meet the IHLW Specification
- Effluent Compatibility with existing Disposal Systems
- Plant Process Throughput
- Life Cycle Cost

Using these criteria, each of the candidate technology alternatives were evaluated and numerically scored based upon the following ranking criteria. Technologies ranked the highest, considering a combination of all criteria, were selected for the Pretreatment process baseline.

1. The process has been identified as having major hazards, significant maintenance requirements, or products or effluents would not meet technical specifications. Technology has a remote chance of being developed to meet the project timescale.
2. Process has been operated on a small scale, significant maintenance is required, or major hazards exist. Insufficient data is available to confirm that product and effluent specifications can be met.
3. Process successful with significantly different wastes types. May require significant solid material handling and disposal. Potential hazards exist. Product and effluents may fail to meet specified requirements, but additional processes may resolve this.
4. Process successfully demonstrated/operated with different wastes and has no safety or environmental issues. Confirmation or additional processing may be required to meet product and effluent specifications. Testing needed to confirm applicability of process to Hanford tank wastes.
5. Process has been successfully operated for many years, requires little downstream treatment, and is safe; products and effluents will meet specified requirement.

The basis for the selection of the preferred technologies is summarized below.

**Solids Removal and Sludge Washing**

The preferred technology for solids removal from supernatants and to support solids concentration is ultrafiltration using cross flow filters in the pretreatment facility. Cross-flow filtration was selected for use in the WTP flowsheet. This selection was based on previous test results and operating experience at the Sellafield plant in the United Kingdom and other DOE sites with similar applications (e.g., West Valley, Oak Ridge and Savannah River Site). Cross-flow filtration offers intrinsic advantages in its simple construction (i.e., no moving parts), and high chemical/radiation resistance that is important for WTP operation. It is also less sensitive to variability in the feed compared to other solids-liquid methods such as settling and decant or centrifuges. The baseline design uses a sintered metal filter with a nominal porosity of 0.1 micron. Previous operating experience has shown that a 0.1 micron filter produces a higher flux than a 0.5 micron filter under high solids loading conditions. The bases for selection of this technology approach also considered the following:

- Technology is well established.
- Ability to remotely restore the filtration flux demonstrated.
- No significant safety issues.
- High efficiency removal of solids (0.5, 0.2, 0.1 micron filter elements commercially available).
No significant secondary wastes produced.
In-facility sludge treatment reduces the chemical requirements of washing/leaching due to more efficient solid/liquid separations and separation at elevated temperatures (improved reaction equilibrium and kinetics).
Life-Cycle Cost savings result from in facility washing of sludges due to the reduction in secondary wastes requiring immobilization as ILAW or IHLW.

Removal of Radioactive Sr and TRU Elements

The preferred technology for the removal of Sr from the alkaline complexed supernatant is the use of the isotopic dilution using Sr-nitrate. Complexed wastes at Hanford (e.g. Double Shell Tanks 241-AN-102 and 214-AN-107) require both solids removal and Sr/TRU precipitation or removal. Chemicals are added into the ultrafilter feed vessels to precipitate the strontium and TRU elements contained in the waste feed stream. Soluble $^{90}$Sr is removed by adding 1 M Sr(NO$_3$)$_2$ to the ultrafiltration feed vessel, which causes the precipitation of Sr as SrCO$_3$. The Sr reacts with carbonate in the waste to form a precipitate. The bases for this selection of the Sr removal technology also considered the following:

- No known sorption processes are effective in removal of Sr from complexed wastes.
- Isotopic dilution meets radionuclide removal requirements.
- Isotopic dilution has demonstrated plant scale application at Hanford’s B-Plant.
- Process does not increase IHLW volume.
- Filtration of all LAW solutions to be performed to remove particulate $^{90}$Sr solids.

Organic destruction processes for decomplexation require the use of equipment that is not well suited for operation in a nuclear environment.
Other chemical additives (Fe$^{+2}$, Fe$^{+3}$, Co$^{+2}$, Mn$^{+2}$, etc.) were less effective in removing TRU elements from the complexants.
The resultant adsorped TRU element on the Mn are separable by filtration.
Final waste form requirements for TRU concentration can be met.
Na is preferred as the cation for the permanaganate to preclude the addition of potassium to the process flowsheet, which would interfere with Cs ion exchange.
The process can be combined with Sr removal and be conduced in a single step.

Removal of Radioactive Cs

The preferred technology for the removal of Cs from the alkaline supernatant is the use of elutable ion-exchange materials using the SuperLig® 644 resin. SuperLig® 644 is an organic ion exchange with a high selectivity and capacity for cesium. Major factors that resulted in the selection of SuperLig® 644 include the projected cesium removal performance, irradiation stability, stability in chemical systems similar to Hanford waste solutions, and compatibility of an elutable resin system with the baseline melter design. The SuperLig® 644 is regenerated using dilute nitric acid, eluting cesium captured by the resin during the loading cycle, followed by returning the resin to the sodium form using dilute caustic.
The bases for this selection also considered the following:
Cs removal requirements (approximately 99 to 99.9% removal) can be met. The Cs eluant from ion-exchange does not increase the volume of IHLW produced. Some Hanford tank wastes have high potassium concentrations (This disfavors the use of sodium tetra-phenylborate, BobCalixC6 extractant, and crystalline silicotitanate methods to remove Cs which have been evaluated by other DOE projects). Hanford tank waste chemistry (i.e., Cs/Na molar ratio, pH, pressure of competing cations) benefits from absorption properties of elutable ion-exchanges.

**Removal of Technetium**

The preferred technology for the removal of Tc from the alkaline supernatant is the use of elutable ion-exchange using the SuperLig® 639 resin. SuperLig® 639 (SL-639) resin is a fairly new ion exchange material developed by IBC, Advanced Technologies, Inc. for the separation of pertechnetate as a salt-pair from acidic or basic solutions. SuperLig® 639 is an organic ion exchange resin that uses polystyrene as the supporting bead structure. The SuperLig® 639 is regenerated using warm water (60 to 70 °C), eluting technetium captured by the resin during the loading cycle, followed by readjustment of the solution pH using dilute caustic. The basis for this selection also considered the following:

- SuperLig® 639 has favorable ion-exchange removal (capacity, selectivity) and elution characteristics when compared to other candidate exchangers.
- The process is capable of meeting the Tc removal requirements as specified in the WTP Contract.
- The Tc eluant does not increase the volume of IHLW produced.

**TECHNOLOGY NEEDS IDENTIFICATION**

The research and development activities that have been identified to support the WTP have benefited from the significant investments that have occurred for High-Level Waste processing in the U.S. and by Foreign Governments. The approach for the establishment of technology development needs for the WTP involves the following elements.

- Utilization of the Technology Roadmap (3), as identified in DOE guidance to define the basic data and technical risk mitigation needs.
- Development and incorporation of technical risk mitigation strategies into the technology plan via Technology Roadmapping.
- Evaluation of the existing research infrastructure to define how to make the best utilization of testing capabilities.
- Use of a disciplined process to review technology testing data and accept results.
- Periodic reviews and reassessments of the technology development needs.

This approach, as defined for the WTP project has been formulated to meet project needs for concurrent design and construction, and to capture the key elements listed above. It also is based on establishing a completion plan that consists of risk analysis, gap analysis, integration of R&T requirements, and work execution, and data acceptance. This approach is summarized in Figure 2. The roadmap depicts identification of open issues, basic data needs, that are captured in an overall Research and Technology Plan (R&T Plan) and the process for work definition (specification), and work plans (test plans). This approach is built around a definition of inputs and requirements from the WTP Project disciplines (e.g. design engineering, permitting, safety and waste form qualification), followed by implementing steps to complete work, and transfer technology results to project users. The major work products from this planning process are a; 1) Risk Register that defines the technical risks and identifies handling strategies, 2) Technology Roadmap that outlines the needed technical activities and demonstrations necessary to
provide to the designers, operators, and to ORP management the information/basic data necessary to proceed through key decision points and design of the project; and 3) R&T Plan that is the strategic document that integrates needs from Technology Road mapping, WTP Contract requirements, lessons learned, peer review comments, emergent technology integration and historical work. The R&T Plan also defines the needs, research strategies, and paths to closure.

The detailed technology testing work is defined in test matrixes, included in the R&T Plan that defines the technical issues, WTP Contract requirements, the strategy and pathways to close the issue, and the closure requirements. The strategy includes clearly defined tasks (test specifications) that describe test conditions and needs; and test plans prepared by R&T subcontractors that detail the individual testing activity work plans, and conclude with test reports.

The technology data closure process includes a review of completed test plans and test reports, with a comparison of technology testing results with predetermined test result acceptance criteria. The closure process also includes incorporation of testing results into the design product (i.e., functional specifications, basis of design, systems descriptions, design calculations) flowsheet models (as appropriate) that are used to confirm that the facility design meets plant technical performance and capacity requirements, and environmental permits and operational planning documents.

In addition, the review and evaluation of testing results includes the ability to incorporate new discovery into the technology testing program.

SUMMARY OF MAJOR PRETREATMENT TECHNOLOGY DEVELOPMENT STUDIES AND TESTING PRIORITIES

The major activities and areas of emphasis for the Pretreatment technology program supporting the WTP are described for each major unit operation in the Pretreatment Process flowsheet.

Solids Removal and Sludge Washing

Ultrafiltration using cross flow filters was selected as the most efficient method for removal of entrained solids from LAW feed, concentration of HLW sludge solids and provides for the ability to leach and wash the HLW solids. Additionally, ultrafiltration of entrained solids ensures that downstream equipment in the pretreatment process will not be adversely affected by plugging.

The performance of an ultrafiltration system depends on the properties of the solution to be filtered. Ideally, ultrafiltration tests should be conducted at the pilot scale using samples of the actual LAW and HLW feed solutions. It has proven very difficult to obtain sufficient samples to perform these tests. Therefore, the WTP has adopted an approach of conducting tests of the LAW and HLW feed solutions using a small-scale, single-element ultrafiltration system. In parallel with the radioactive tests, simulant tests will be conducted using a duplicate of the single-element filter system to validate the simulant and provide information for scaling the radioactive test results to a pilot-scale ultrafiltration system. A pilot scale ultrafiltration system will be tested to provide information directly related to the performance of the plant scale system. In this manner, WTP will be able to validate the performance of the selected filter media using a combination of simulants and radioactive waste samples.

The primary objective of the ultrafiltration tests is to provide data for correlating the radioactive, small-scale ultrafiltration and pilot-scale simulant filtration test results to validate the WTP design basis. The small-scale simulant and radioactive ultrafiltration tests are compared in order to validate the simulant and correlate the simulant and radioactive sample test results. Then the small-scale and pilot scale ultrafiltration test results are correlated for the same simulant. Finally, a correlation is made between
Fig. 2. Technology Needs Identification and Development Process
the small-scale radioactive and pilot-scale simulant ultrafiltration test results. Correlating the ultrafiltration tests results in this manner will provide confidence in the design filter flux rate for the entrained solids separation system. An additional objective is to examine the cleaning requirements for the ultrafiltration units.

The general approach for testing will use the following methodology:

- Testing the crossflow ultrafiltration unit operation with actual waste samples is the cornerstone of this program. Because of limited availability of tank waste samples and radiation levels this testing is done on a small, single-tube filter mock-up in a hot cell. These tests give initial information on solids removal, flux rates, and chemical cleaning requirements.
- Where it is deemed necessary to conduct tests at pilot scale, simulants are developed and these are validated first by tests on a single-tube mock-up.
- Pilot scale tests (a seven tube array) give more representative information on flux rates, slurry fouling characteristics and general scale up and process control issues. These tests employ only nonradioactive simulants.

The second aspect of the ultrafiltration work is to demonstrate the filtration performance during the washing and leaching of HLW solids. Tests have been conducted using tank waste samples to assess performance of the ultrafilter and the effects of solids washing and leaching to remove soluble waste components (i.e., Na, Al, Cr) that could increase the volume of IHLW. Future experiments will include prototypic sludge washing to provide both filter flux and to remove glass limiting components. This work will include optimization of the sludge washing and leaching conditions.

In addition, the impact of separable organics present in the tank wastes and the erosion of filter unit components will be evaluated. The separable organics task will use simulants to assess the impact of separable organics on filter performance. The erosion task will use a combination of experimental and computational work to assess the potential for erosion within the filter loop. Initial experimental work will identify the most abrasive slurries for subsequent study. The computational work will identify the most susceptible filter loop elements. Finally, experimental work with a prototypic filter loop will demonstrate the anticipated wear of filter loop elements.

**TRU Removal and Sr Isotopic Dilution**

Removal of $^{90}\text{Sr}$ and transuranic elements (TRU) from WTP process streams is required to produce LAW stream from process feed. Testing has determined that isotopic dilution using nonradioactive Sr(NO$_3$)$_2$ followed by carbonate precipitation was the optimum method for removal of $^{90}\text{Sr}$. Similar work identified permanganate precipitation as the best way to remove TRU from the LAW. Both precipitation processes occur sequentially in the ultrafilter feed vessels. The precipitated $^{90}\text{Sr}$ and TRU are filtered from the LAW and washed to produce a concentrated sludge that is combined with the HLW solids and fed to the HLW melter system.

Work completed to date on radioactive waste samples has demonstrated the process and provided a good understanding of mechanism for $^{90}\text{Sr}$ precipitation. Experiments conducted with actual samples showed that the required decontamination factors can be achieved. The mechanism of TRU removal by added permanganate is not as well understood, but the TRU elements as well as other soluble metal ions in solution precipitate on the reduction of Mn$^{7+}$ to Mn$^{4+}$ and Mn$^{4+}$ precipitation as hydrated manganese dioxide. The Mn$^{7+}$ is a strong enough oxidant to react with the various complexing agents known or suspect in the waste. The addition of non-radioactive Sr before permanganate addition is beneficial to TRU removal.
The high TRU solubility in the complexed waste appears to be the result of sodium gluconate in the tank waste. Gluconate is effective at complexing/solubilizing higher valence metal ion in solution, such as Fe$^{3+}$ and Mn$^{7+}$. The Mn$^{7+}$ will oxidize gluconate resulting in precipitation of the complexed metal. Manganese also has a strong interaction with gluconate and may effectively compete for the ligand relative to the TRU elements. Currently, additional thermodynamic data is needed on the Mn-gluconate complexes to determine the importance of TRU removal by ligand displacement versus ligand oxidation.

The planned work includes additional testing to characterize the reaction mechanism and kinetics for the Sr and TRU precipitation processes to enable scale-up of the process. Additional testing is required to verify the performance of pilot-scale, plant-scale precipitation process and to provide operability information for the full-scale plant. Because of the difficulty of obtaining and working with actual waste samples, the testing will be performed primarily with simulants. Scale-up tests and modeling will be used to verify the performance of the precipitation process for the full-scale plant. The general approach for testing will use the following methodology:

- Testing of process variability and reaction mechanisms (kinetics) under different physical and chemical conditions on simulants and actual waste samples
- Testing of process optimization and abnormalities on simulants and actual waste samples
- Piloting of process integration on simulants which mimic the actual process
- Testing of throughput on simulants and actual waste under various process conditions
- Perform peer and high level technical reviews to validate process and to ensure program completeness

Cs and Tc Ion-Exchange

Removal of $^{137}$Cs and $^{99}$Tc from WTP process streams is required to produce a LAW stream for process feed to LAW immobilization. Extensive testing has identified ion exchange as the optimum method for removal of $^{137}$Cs and $^{99}$Tc from LAW process solution using the ion exchange resins from IBC, SuperLig® 644 and SuperLig® 639. The separated $^{137}$Cs and $^{99}$Tc are eluted from the resins to produce a concentrated stream suitable for incorporation as feed to the HLW melter system.

Previous small-scale (5 - 100 ml) tests using radioactive feeds have focused on establishing the decontamination factors produced by the resins, the stability of the resins in simulated chemical and radiation environments, the effect of tank waste organics on resin performance, resin preconditioning requirements, effect of column dimensions and superficial velocity and removal efficiency, and development of models for predicting the operation of plant-scale columns. Additional testing is required to verify the performance of pilot-scale and plant-scale ion exchange columns and to provide operability information for the full-scale plant. Because of the difficulty of obtaining and working with actual waste samples, testing will be performed primarily with simulants. Scale-up tests and modeling will be used to verify performance of the ion exchange process for the full-scale plant. Finally, the resin manufacturing process must be capable of producing the desired quantity and quality of the resins. The general approach for testing will use the following methodology:

- Resin system performance testing on actual supernates is the basis for verifying the process will perform as designed. Systematically designed simulat tests will also be conducted to provide additional information.
- The resin system must be proven stable under operating conditions including: high radiation dose (100 rad/hr), highly alkaline conditions (pH > 14), and cesium elution, which occurs in acidic conditions. The wide envelope of operating conditions will be screened under normal and accelerated-aging conditions using simulants. Use of actual supernates will be use to confirm simulat test results.
Testing will be done to manufacture large batches (100 liters) of resin to demonstrate scale-up of resin production processes. Variability in resin batch chemical and physical properties, combined with expected ranges of supernate feed envelopes will be evaluated to predict plant performance. Scale-up issues related to column performance will be tested with pilot-scale tests. These tests will employ non-radioactive simulants.

**SUMMARY**

The Office of River Protection (ORP) located at Hanford, Washington has established a contract to design, construction, and commission a new Waste Treatment and Immobilization Plant that will treat and immobilize the Hanford tank wastes for ultimate disposal. The WTP is comprised of four major elements, pretreatment, LAW immobilization, HLW immobilization, and balance of plant facilities. This paper describes:

- The pretreatment technologies specified by ORP to be incorporated into the design of the WTP to prepare LAW and HLW process streams for immobilization.
- The technology alternatives considered for specific pretreatment separations and the basis for the selection of the preferred technologies, and
- Identifies the major technology testing activities being conducted to resolve remaining technology needs to finalize the design of the WTP.

**REFERENCES**