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ENHANCED CHEMICAL CLEANING: A NEW PROCESS FOR CHEMICALLY CLEANING SAVANNAH RIVER WASTE TANKS

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ABSTRACT

The Savannah River Site (SRS) has 49 high level waste (HLW) tanks that must be emptied, cleaned, and closed as required by the Federal Facilities Agreement. The current method of chemical cleaning uses several hundred thousand gallons per tank of 8 weight percent (wt%) oxalic acid to partially dissolve and suspend residual waste and corrosion products such that the waste can be pumped out of the tank. This adds a significant quantity of sodium oxalate to the tanks and, if multiple tanks are cleaned, renders the waste incompatible with the downstream processing. Tank space is also insufficient to store this stream given the large number of tanks to be cleaned. Therefore, a search for a new cleaning process was initiated utilizing the TRIZ literature search approach, and Chemical Oxidation Reduction Decontamination – Ultraviolet (CORD-UV), a mature technology currently used for decontamination and cleaning of commercial nuclear reactor primary cooling water loops, was identified. CORD-UV utilizes oxalic acid for sludge dissolution, but then decomposes the oxalic acid to carbon dioxide and water by UV treatment outside the system being treated. This allows reprecipitation and subsequent deposition of the sludge into a selected container without adding significant volume to that container, and without adding any new chemicals that would impact downstream treatment processes. Bench top and demonstration loop measurements on SRS tank sludge stimulant demonstrated the feasibility of applying CORD-UV for enhanced chemical cleaning of SRS HLW tanks.

INTRODUCTION

SRS has 49 HLW tanks currently not decommissioned. Approximately one half of these tanks were built in the 1950’s, while the others were built in the 1970’s. The tanks are 75- to 85- feet in diameter, 24- to 33-feet tall, 750,000- to 1,300,000-gallon capacity, made of carbon steel, typically contain miles of carbon steel cooling coils, and are located subsurface. About a sixteen of the older tanks have developed leak sites, adding to the urgency of tank closure [Ref. 1].

SRS prepares tanks for closure in three phases: bulk waste removal, heel removal, and chemical cleaning. SRS HLW tanks must be very clean in order to support closure due to the high specific activity of the residual waste and the close proximity to the water table. For closure, the residual volume of HLW in most tanks must be 50 to 500 gallons (or less), which translates to 0.01 to 0.1 inches of waste if the waste were spread on the tank bottom in an even layer. It is expected that the radioactive source term adsorbed onto corrosion products on the tank internals will, by itself, exceed this allowable residual waste volume.

For chemical cleaning of the tanks, the use of oxalic acid is considered the technical baseline [Ref .2]. Oxalic acid is one of the preferred acids for cleaning metal surfaces because of its combined cleaning and chelating effects. Other common acids used for cleaning include nitric acid and oxalic/citric acid blends. Since the SRS HLW tanks are made from carbon steel and the oxalic acid forms a passivation layer on carbon steel surfaces, oxalic acid is preferred over nitric acid [Ref. 2]. Pure oxalic acid is preferred to oxalic/citric acid mixes because the oxalic acid has been shown to be equally effective in dissolving HLW residuals, and the potential downstream impacts of adding citric acid to the process are undesirable [Ref. 3].

In the mid 1980’s, SRS demonstrated that concentrated oxalic acid can be used to chemically clean residual waste from a HLW tank. Over 99% of the initial activity was removed as the result of an oxalic acid cleaning effort [Ref. 4]. Currently, two other tanks are also scheduled to be cleaned using the same strategy. The baseline process strategy includes:

- addition of concentrated oxalic acid to the tank to be cleaned
- mixing of the acid within the treatment tank
- transferring the spent acid and dissolved sludge to another HLW tank
- restoring the pH of the spent solution to within tank corrosion control limits
- transferring the resultant solids to a pre-qualified Defense Waste Processing Facility (DWPF) feed batch, and
- transferring the resultant liquid to an evaporator drop tank where additional oxalates will precipitate

The Need for an Alternative Tank Cleaning Technology

The baseline technology for chemical cleaning uses several hundred thousand gallons of 8 % (wt %) oxalic acid per tank to partially dissolve residual waste and corrosion products such that the waste can be pumped out of the tank. The pH of the spent cleaning solution is restored by adding caustic and then evaporated and stored in the active HLW tanks for eventual feed to downstream waste treatment and disposition facilities [Ref. 5]. However, the addition of oxalic acid with subsequent pH restoration adds a significant quantity of partially soluble sodium oxalate to the tanks. Since oxalate solubility is a function of sodium concentration, and the range of the sodium concentrations within the process varies from less than 1 M during sludge washing to greater than 15 M after evaporation, treating more than three tanks with concentrated oxalic acid using the baseline technology causes significant process incompatibilities. They include:

- Solids begin to form during concentration and overwhelm the evaporator system
- Foaming occurs in the evaporator pot
- A longer feed preparation time is required for DWPF sludge
- A decrease in DWPF canister glass durability occurs
- An increase in the number of DWPF canisters produced is created, and
- There is a decrease in DWPF throughput

In addition to the incompatible downstream processing impacts, there is an immediate issue of available tank space to temporarily store this stream due to the large number of tanks to be cleaned. Therefore, a search for a new cleaning process was initiated.

RESULTS

TRIZ Identification of Candidate Alternative Tank Cleaning Technologies

The search used a modified TRIZ literature review. TRIZ is a Russian acronym for "Teoriya Resheniya Izobretatelskikh Zadatch," which roughly translates as the Theory of Solving Inventive Problems. TRIZ is different from other approaches in that it is based on the underlying principle that "Inventing is the removal of technical contradictions." A key advantage associated with TRIZ is it looks directly for analogous, resolved problems from different industries, and adapts their solution to the current, unresolved problem.

Using the TRIZ approach, the need for an alternative method for chemical cleaning was restated as: "Remove 90% of 5,000 gallons of mostly radioactive metal oxides and hydroxides from HLW tanks, while minimizing the creation of secondary waste, disposing of spent cleaning solution with minimal impacts to tank space, and disposing of spent cleaning solution with minimal impact to downstream facilities."

A review of current industrial practices and capabilities was undertaken to identify an analogous problem with a solution that could be adapted for SRS HLW tank cleaning. Using the TRIZ approach, scale removal from primary coolant loops of nuclear reactors was identified to be analogous to residual tank heel cleaning.

Six primary decontamination technologies (DTs) that are commercially used for scale removal were identified as potentially adaptable. They are:

- Low Oxidation Metal Ion - LOMI
- Canadian Depleted Uranium (reactor) decontamination - Can-Decon
- Citric Acid/Oxalic Acid - CITROX
- Decontamination for Decommissioning - DfD
- Decontamination for Decommissioning Improved - DfDx
- Chemical Oxidation Reduction Decontamination with Ultraviolet light - CORD-UV

The direct addition of strong oxidation agents to clean the treatment tank, such as peroxide or potassium permanganate would have a detrimental impact on the tank components or be incompatible with the HLW process and therefore were not considered in the TRIZ evaluation. Each of the six primary decontamination technologies (DTs) was reviewed for potential issues (contradictions) in their use for cleaning HLW tanks.

LOMI

Chemicals used in LOMI are vanadous ion, V^{+2}, as a reducing agent, and picolinic acid, $C_6H_5NO_2$, as the chelating agent. In LOMI, the oxide film is removed by chelation assisted reductive dissolution. The technology is novel in that it uses the V^{+2} ions to quickly reduce the ferric ion to ferrous ions.

During decontamination, a sodium picolinate solution is prepared in a mix tank. Once the sodium picolinate is well mixed in the decontamination volume, vanadous formate is injected directly into the system to be cleaned. This is done to prevent air oxidation of the vanadous ion. Due to the air sensitivity of the vanadous ion, direct measurement of vanadous concentration is typically performed on-line.

Since this technology cannot be used in open-air systems such as HLW tanks and adds a significant amount of organic chemicals to the HLW tanks, it was quickly deleted from consideration as a possible alternative.

CAN-DECON

The chemicals used for the Can-Decon process are oxalic acid, $H_2C_2O_4$, as the reducing and chelating agent, and ethylene diaminetetracetic acid (EDTA), $C_{10}H_{16}N_2O_8$, as a complexing agent. Citric acid may also be used.

In this technology, mixed bed ion exchange resins are utilized to remove the chemical cleaning agents from the product stream. However, the large amount of organic chemicals is not acceptable for the HLW tank project due to the downstream processing requirements.

CITROX

The chemicals used in the Citrox process are citric acid, $C_6H_8O_7$, and oxalic acid, $H_2C_2O_4$, as a reducing and chelating agents.

The cleaning solution is made from organic acids added in a dry powder form. Typically, the dry acid is dissolved in a mixing tank, heated, and injected into the preheated system to be decontaminated. The dissolution occurs rapidly even at room temperatures. Being a regenerative process, the solvent is continuously circulated through a cation exchange resin bed to remove dissolved metals including radionuclides and return the organic acids to their original acidic forms. Citric acid is used to complex the metal ions maintaining their solubility in the solution until the metals are removed via ion exchange. CITROX minimizes iron oxalate precipitation in the primary loop. When the scale is dissolved, the cleaning solution and remaining dissolved metals are removed in a mixed cation and anion resin column. However, a significant problem with the technology is the quantity of spent ion exchange resin that will be created.

Although the use of citric acid and oxalic acid have been shown to work well in scale removal in nuclear power plants under specific applications, the use of oxalic acid alone has been determined to be just as effective in dissolving HLW sludge.

DfD

The primary chemical used for DfD is, fluoroboric acid (HBF_4), which serves as both a reducing and a chelating agent.

This process has been applied to a wide range of components such as operating nuclear power plants and DOE facilities and recycling of components. When the decontamination process is complete, several options are available for disposal of the cleaning solution. The limitation of the process is the cleaning solution is passed through a cation exchange resin, neutralized, and discharged creating large quantities of resin waste.

DfDx

The primary chemical used is fluoroboric acid (HBF_4), which serves as both a reducing and a chelating agent. The DfD process generates problematic ion exchange resin waste. This enhancement, termed DfDx, has been developed to overcome this waste issue. The result is a factor of ten reduction in volume and a metallic waste form.

The downstream process impacts to the Saltstone Facility, the Salt Waste Processing Facility, and DWPF associated with fluoroboric acid are not well understood. Additionally, to date, the technology's use has been restricted to the decontamination of single components (e.g., pumps); therefore, the throughput capability has not been demonstrated to meet the requirements of SRS HLW tank cleaning.

CORD-UV

The chemical used for dissolution is oxalic acid, $H_2C_2O_4$, which serves as a reductant. The CORD-UV family of technologies has been most widely applied in the commercial nuclear power industry for removing highly radioactive deposits and scale from the internals of reactor coolant systems in nuclear power plants.

CORD-UV treatment steps typically include:

- A series of customized chemical oxidation and/or reduction steps optimized for the unique surface of the contaminant to be removed,

- On-line removal of dissolved and mobilized contaminants coupled with regeneration of the dissolution solution, and

- Decomposition of the solvent (in this case oxalic acid) to carbon dioxide and water utilizing a patented UV light treatment process, such that all chemicals used for cleaning the system are removed.

Normally within a reactor, the whole process is performed with only one system full of demineralized water. Exposure to oxalic acid results in dissolution of metal hydroxides and oxides to give soluble metal oxalates. The oxalates are then decomposed with a patented UV light technology coupled with a strong oxidant.

A primary goal of the SRS HLW tank project is to minimize the volume of material returned for storage in the tanks. CORD-UV minimizes volume by delivering the removed sludge and/or saltcake as a precipitate after oxalic acid decomposition. In addition, it continually regenerates and reuses the solvent, thereby minimizing total water added. That is, the volume of liquid required initially for pumping is all the water required for the full treatment.

Other advantages include that no new chemical additions occur to disposition the final waste. The oxalic acid used for dissolution and mobilization is decomposed by UV treatment such that no new chemicals are introduced into the HLW process. As for flammability concerns or downstream process impacts, no compounds likely to generate volatile organics are used. The use of oxalic acid for sludge dissolution has been successful in the past so consistency with this baseline minimizes the need for operational modifications and the risk associated with them.

TRIZ Results

All of the technologies were considered to have an acceptable impact on tank space. When performing the TRIZ operation of "trading the contradictions", LOMI was the only technology that could not be applied in the air atmosphere, and therefore, could not obtain the 90% dissolution. Most of the technologies were based on ion exchange, and as such, resulted in Secondary Waste Contradictions (see Table 1), with the exception of CORD-UV. Potential Contradictions occurred to Downstream Impacts with the addition of new chemicals to the process. All of the technologies were considered to have a well proven throughput with the exception of DfDx.

The results of the TRIZ evaluation of DTs are shown in Table 1.

Table 1. Technologies and Associated Contradictions

Tech	90% Dissolution	Secondary Waste	Downstream Impacts	Throughput
LOMI	**Contradiction** - will not work in air (eliminated)	**Contradiction**- creates used ion exchange resin	Acceptable	Proven
Can-Decon	Proven	**Contradiction**- creates used ion exchange resin	**Potential Contradiction** - uses EDTA; downstream impacts on DWPF are not well understood	Proven
CITROX	Proven	**Contradiction**- creates used ion exchange resin	**Potential Contradiction** - uses citric acid; downstream impacts on DWPF are not well understood	Proven
DfD	Proven	**Contradiction**- creates used ion exchange resin	Uses only fluoroboric acid and its impact on DWPF is not understood	Proven
DfDx	Proven	**Contradiction**– does not use resin, smaller volume of carbon media used to collect metal	**Potential Contradiction** – adds fluoroboric acid; downstream impacts are not well known	**Potential Contradiction** – not well proven
CORD-UV	Proven	Does not create additional waste	Uses oxalic acid	Proven

Of the six DTs, only the CORD-UV technology did not result in any Contradictions or Potential Contradictions. As such, the CORD-UV technology did not require any contradiction trading and was considered the TRIZ identified alternative.

Process Strategy and Technology Gaps

After accepting the CORD-UV technology as the TRIZ identified solution, an effort to identify the technology gaps was initiated. Before identifying the technology gaps, however, a simplified process strategy and flow sheet had to be developed.

Using the CORD-UV process it is expected that the only cleaning agent required will be oxalic acid at a concentration $\leq$ 8%. To show continuity with the current plans for cleaning tanks, but an improvement to the technology, the improved process being developed was termed Enhanced Chemical Cleaning (ECC).

For a process strategy, after sludge removal from the tank by internal spraying with the oxalic acid solution, the dissolved solids will be precipitated and the oxalic acid solution refreshed using on-line CORD-UV decomposition and reagent addition systems. The solid product will be separated from the waste stream and the liquids will be recycled. Dry oxalic acid is added back to the UV treated stream to return it to the required oxalic acid concentration, and the stream is recirculated back to the treatment tank for further removal of the residual material.

The front-end segment focuses on the interaction of the residual material with dilute acid. The tail-end segment focuses on oxalate destruction and metal oxide deposition. Based on the simplified process flow diagram, twelve potential TD gaps were identified, of which, six were applicable to the front end of the process and ten were applicable to the tail end. A testing matrix was developed to identify which of the technology gaps could be evaluated with simulated waste testing and which would be most effectively addressed with actual sludge waste testing. The testing matrix is shown in Table 2.

Table 2. Testing Matrix

	Technology Gap	Process Segment	
		Front End	Tail End
1	Dissolution	Simulant	NA
2	Oxalate Destruction	NA	Simulant
3	Water Addition	Simulant	NA
4	Corrosion	Simulant	Simulant
5	Temperature	Simulant	Simulant
6	Gas Generation, Overpressurization & Flammability	Real Waste	Real Waste
7	Criticality Safety	Real Waste	Real Waste
8	Evaporator	NA	Real Waste
9	Glass Quality	NA	Real Waste
10	DWPF Throughput	NA	Real Waste
11	Intermediate Precipitate	NA	Real Waste
12	Solids Separation Tech	NA	Simulant

Demonstration of the CORD UV process for SRS HLW Simulant

Three key performance indicators were selected to demonstrate the potential effectiveness of the CORD UV process for cleaning of the SRS HLW tanks:

1. Dissolution of greater than 90% of the sludge simulant
2. Destruction of greater than 90% of the dissolution organics (i.e., the oxalic acid)
3. Solids resulting from oxalic acid decomposition contain less than 10% organics.

Demonstration that these indicators were met was performed using a two-part demonstration test that included separate dissolution and decomposition process loops. The dissolution loop is shown in Figure 1. It includes a pump, a heating chamber and a sludge dissolution chamber, and holds 18 liters of solution. The flow rate through the dissolution loop is a constant 1.0 gallon per minute with a resulting velocity in the dissolution chamber of 0.02 feet per minute.

Figure 1. Dissolution demonstration loop.

The recirculating pump is in the lower right corner. The dissolution screen rack, on which the sludge is loaded for dissolution testing, is loaded into the stainless steel vessel on the left-center of the figure. The inset shows the dissolution loop screen rack loaded with wet sludge simulant, although both wet and dried simulant runs were performed. The center vessel covered with insulation is the heating vessel. The recirculation flow path is from the pump to the dissolution vessel, then into the heating chamber, then back to the pump.

A sludge simulant was obtained from Savannah River National Laboratory (SRNL) [Ref. 5]. The composition of this simulant was verified by the AREVA laboratory prior to demonstration loop runs.

Extent of dissolution was determined by measuring the level of dissolved iron and aluminum in samples of the circulating fluid at various time points after the pump was engaged. Dissolved iron and aluminum were analyzed by atomic absorption spectroscopy utilizing standard methods. The sampling point was on the discharge side of the recirculation pump. The dependence of dissolution extent and rate on temperature was determined by conducting runs at 25°C, 50°C and 70°C.

To determine whether the key performance indicator for dissolution had been met, mass balance calculations were performed based upon the known composition of the sludge simulant compared to the levels of dissolved iron and aluminum in the process fluid. Additionally, the dissolution loop screens were weighed and the entire loop visually inspected before and after the dissolution runs. Figure 2A shows the dissolution screens after a typical run, while Figure 2B shows the interior of the dissolution loop screen chamber. The dissolution screens (Figure 2A) contain a light film of less than 1 mm in thickness which is likely a metallic oxide or hydroxide. The film on the screen chamber wall (Figure 2B) is less than 1 mm thick, is easily mobilized by scraping and spalls when air dried. However, both weighing and visual inspection clearly show that all sludge simulant has been dissolved or mobilized in the process. Taken together, these results demonstrated that the dissolution process had met the key performance indicator of dissolution of greater than 90% of the sludge simulant.

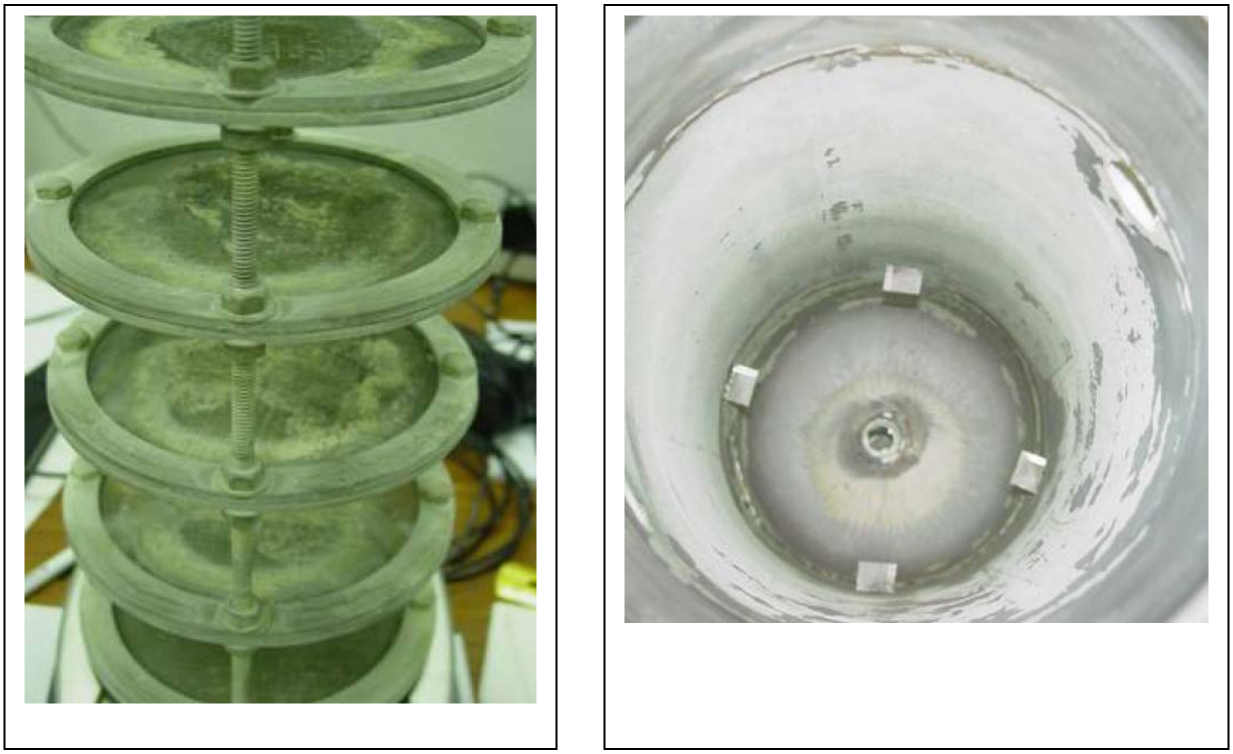

Figure 2. Demonstration loop screens (A) and screen chamber interior (B) after process loop demonstration run.

As the next step, the extent of UV-induced decomposition of the oxalate was observed utilizing the decomposition loop of the system (Figure 3). When the color of the dissolved sludge simulant solution allowed satisfactory colorimetric analysis, decomposition of oxalic acid was monitored by titration with permanganate. However, when the dissolved sludge solution was too opaque for colorimetry and filtration did not allow for sufficient reduction in turbidity, oxalic acid concentration was measured by ion chromatography.

After the dissolution loop was operated for at least 4 hours, cross-flow was initiated between the dissolution and decomposition loops, and the UV source was activated. Decomposition of oxalate, as well as iron concentrations and pH, were monitored from sampling ports at the inlet to the UV treatment module and at the outlet where the UV-irradiated solution is recirculated to the dissolution loop. Metallic precipitates in the decomposition loop were collected on an in-line one-micron filter (cyclone or centrifuge separators will be used for the actual full scale application to the SRS HLW tanks). Aluminum and iron concentrations could be reduced to below detectable levels in the decomposition loop (due to precipitation on the filter) when the oxalic acid concentration was decomposed to less than 100 ppm. These results demonstrated that the dissolution process had met the key performance indicator of decomposition of greater than 90% of the oxalic acid.

Figure 3. Decomposition demonstration loop.

Solids collected on the in-line filters were then digested in a hydrochloric acid solution and analyzed for total organic carbon (TOC). Typical TOCs were in the range of 0.83% (w/w) TOC, confirming that the key performance indicator of less than 10% residual organics (i.e., oxalate) in the precipitated solids was met.

It was important to show that conditions which meet these key performance indicators are unlikely to damage the integrity of the SRS HLW tanks themselves during application of the CORD UV process. Galvanically coupled coupons representative of tank composition at SRS were supplied by SRNL. They were loaded into a dissolution loop and exposed to 10,000 ppm oxalic acid for 53 hours at 70^{o}C and the extent of visible corrosion was examined. The coupons showed a light oxalate coating that generally functions as a passive layer. Coupons were then lightly brushed in soapy water, rinsed, dried and weighed, and compared to their pre-treatment weight. The weight differences extrapolated to a corrosion rate of 36 to 52 mm per year of continuous process treatment. This was well within the SRS-required corrosion allowance of 50 mm per 6 months. Treatment of each HLW tank is expected to occur over time frames significantly less than 6 months.

CONCLUSIONS

After a TRIZ search for an alternative technology for cleaning of the SRS HLW tanks, the CORD-UV process for was selection for further evaluation. A CORD-UV demonstration loop containing dissolution and decomposition loops was constructed. The process met the three key performance indicators selected to demonstrate its potential effectiveness. In demonstration loop studies performed on a sludge simulant provided by SRNL, CORD-UV dissolved greater than 90% of the sludge simulant, destroyed greater than 90% of the dissolution organics (i.e., the oxalic acid), and generated solids which contained less than 10% organics. Additionally, the process did not result in appreciable corrosion of test coupons representative of SRS HLW tank walls.

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