Regulatory Support of Treatment of Savannah River Site PUREX Waste - 9369

Luke T. Reid
Savannah River Site
Box A, Aiken, SC 29802

ABSTRACT

This paper describes the support given by federal and state regulatory agencies to Savannah River Site (SRS) during the treatment of an organic liquid mixed waste from the Plutonium Extraction (PUREX) process. The support from these agencies allowed (SRS) to overcome several technical and regulatory barriers and treat the PUREX waste such that it met LDR treatment standards.

BACKGROUND

The Plutonium Uranium Extraction (PUREX) process at Savannah River Site (SRS) was used to separate Plutonium and Uranium isotopes from fission products. This process has generated tens of thousands gallons of liquid waste at SRS since the 1950s. The waste from this process was an organic liquid consisting of tributyl phosphate and n-parrafin, which were used for their extraction properties, and was heavily contaminated with alpha emitting radionuclides. Most of this waste was stored in two sets of underground tanks, Tanks S1-S22 and Tanks S23-S30. Solvent Tanks S1 –S22 were closed under a CERCLA closure action in the late 1990s. The PUREX waste in Solvent Tanks S23 – S30 was a mixed waste due to the presence of Hg, benzene, and TCE and several underlying hazardous constituents (UHCs) such as n-butyl alcohol, ethyl benzene, toluene, and naphthalene. However, these tanks did not meet the requirements of RCRA subpart J for hazardous waste stored in tanks and subsequently underwent a RCRA closure in 1997.

During the RCRA closure of tanks S 23 – S30 approximately 50,000 gallons of legacy PUREX waste was transferred to new Solvent Storage Tanks S33 and S35 located in H-Area at SRS. These tanks were constructed specifically to accept the PUREX legacy waste still residing in Tanks S23-S30 and were located within close proximity to the SRS Consolidated Incineration Facility (CIF) where treatment was initially planned for this waste stream.

Once the waste was transferred to Tanks S33 and S35 efforts began to treat this waste to LDR treatment standards. The remainder of this paper will discuss the technical and regulatory barriers which were encountered and overcome, with the help of the regulatory community, to successfully treat this waste steam

TREATMENT APPROACHES

The most appropriate method of treating this waste stream per 40 CFR was incineration of the hazardous organic constituents followed by stabilization of the hazardous metal constituents remaining in the ash. Therefore, SRS made commitments in the Site Treatment Plan (STP) to the South Carolina Department of Health and Environmental Control (SCDHEC) to have the PUREX waste stream treated by the end of FY 19 through the use of the Consolidated Incineration Facility (CIF) at SRS. CIF was designed to provide both thermal destruction and stabilization by creating ‘ashcrete’ (ash and concrete mixture) as an end product of the incineration process. The prolonged period to treat this waste stream by 2019 was due to the highly contaminated nature of this waste stream (E5 dpm/ml alpha) relative to the allowable

radiological inventory within CIF, i.e. the PUREX waste would have to be metered into CIF in very low quantities to stay within radiological inventory limits as it was processed.

Treatment of the PUREX at CIF began in 1997 and continued through 2000. During that period the inventory of the PUREX was reduced to 27,000 gallons; however, in 2000 the decision was made to discontinue operations at CIF.

Once CIF discontinued operations alternative treatment methods were evaluated. The levels of radioactive contamination were too high for thermal destruction at other commercially available treatment facilities. Therefore, beginning in 2001, SRS invested considerable time and effort to identify immobilization technologies, in lieu of incineration, to treat this waste stream.

Several immobilization technologies (stabilization reagents) were identified and evaluated in "PUREX Waste Stabilization", WSRC-TR-2001-00526.

Six sorbents (four organic polymers and two clay products) were tested for solidification of PUREX waste. Waste forms were evaluated for processing, storage and transportation, leaching and durability. The sorbent materials and the waste forms were characterized by gravimetric, thermal spectroscopic, and X-ray techniques in order to understand the mechanisms of sorption, the PUREX/sorbent interactions, and the long term stability of the solidified PUREX material.

Vibration cycling and thermal stability tests were conducted to demonstrate the treated waste form would withstand cross country travel and long term storage/disposal. Additionally, testing was conducted to prove radiation and pressure stability as well as microbial degradation, and aging effects. Two of the reagents were rejected as result of these tests. One of the polymer reagents was found to be plasticized by the tributyl phosphate, while another of the polymer reagents was found to swell with water contact. This was deemed unacceptable since a portion of the legacy PUREX is an aqueous phase.

Leachability testing was performed on all six waste forms using the Toxicity Characteristic Leaching Procedure (TCLP) and all six met LDR treatment standards for the known metal hazardous constituents. Organic treatment standards are typically expressed as numerical standards and not as leachate concentrations; therefore, a major concern associated with stabilization of any organic hazardous constituent is to ensure it is not being diluted below the numerical treatment standard, i.e. it is important to ensure the treatment approach is not impermissible dilution. In other words, the organic constituents must be chemically bound within the treatment matrix and not diluted to get below the treatment standard. Post solidification testing demonstrated that two of the reagents (1 polymer based and 1 clay based) produced results where chemical bonding/interaction was taking place between the solidification reagent and the waste form. For example, the use of Fourier Transform Infrared (FTIR) Spectroscopy indicated a change in the molecular structure of the clay based reagent demonstrating that the waste is chemically interacting with the solidification reagent.

Since immobilization of hazardous organics is somewhat irregular, the results of the study discussed above were presented to both South Carolina Department of Health and Environmental Control and EPA Region 4. Both agencies agreed that stabilization of the PUREX was an appropriate treatment, even for the organic hazardous constituents since analytical data indicated that the hazardous organic concentrations were reduced below the numerical universal treatment standards (UTS) due to immobilization by chemical bonding, and not due to dilution by addition of the stabilization reagent, i.e. this approach was not impermissible dilution.

Once it became apparent that stabilization of the PUREX waste was a viable treatment approach a new STP commitment was made to SCDHEC to have the waste treated by the end of FY 07 (Sept. 2007).

COMMERCIAL TREATMENT ISSUES

Once regulator agreement was reached concerning the treatment approach, SRS entered into a commercial contract to have this waste treated using stabilization/immobilization. The vendor selected used a proprietary stabilization reagent somewhat similar to the clay based reagent which was successfully demonstrated in the study discussed above.

The vendor initially intended to use air sparging to attempt to remove the organic hazardous constituents prior to treating with a stabilization reagent which would only be used to treat the hazardous metals. Lab tests indicated that air sparging removed certain RCRA organic hazardous constituents and underlying hazardous constituents (benzene, ethyl benzene, and toluene), but certain other underlying hazardous constituents (UHCs), primarily naphthalene and n-butyl were not removed via air sparging below the Universal Treatment Standards (UTS).

The vendor had conducted testing to evaluate the potential to destroy the tri-butyl phosphate in the mixed waste, so the resulting inorganic phosphate could be removed by a liquid-liquid extraction process. This investigation did not identify any selective means of destroying the tri-butyl phosphate in the organic matrix of the PUREX waste. Additionally, the vendor was unable to identify an incinerator which could burn an organic liquid with as much phosphorus content and radioactivity as this waste stream contained.

Therefore, the use of stabilization techniques as previously discussed with EPA and SCDHEC were pursued for both the hazardous metals and organics in the PUREX waste. Analytical results from lab testing indicated that the naphthalene, once stabilized, was reduced below the UTS, and that reduction could be attributed to immobilization and not dilution. Lab testing indicated naphthalene concentrations were reduced by 14X to 2.4 ppm (vs. a UTS of 5.6ppm) with a 2.5X dilution factor attributed to the stabilization reagent.

However, the n-butyl could not be demonstrated to be below the treatment standard using stabilization. The typical result for naphthalene post stabilization would indicate that it was not detected, but the lower limit of detection (LLD) was typically an order of magnitude above the treatment standard of 2.6 ppm. This inability to establish an LLD below the treatment standard was due the highly complex chemical nature of the legacy PUREX which had been co-mingled with Laboratory waste. Attempts to lower the LLD via sample dilution only served to drive to final result of the naphthalene above the treatment standard once dilution multiplication factors were applied to the lab result.

Fortunately, it had been anticipated that stabilization of some of the organics might be problematic and a Treatability Variance had been submitted by the vendor to EPA-IV in June 2007 to address this concern. The Treatability Variance (TV) was requested based on the unique and complex nature of this PUREX solvent that made it difficult to treat the waste to established LDR standards. It was noted that several treatment approaches had been evaluated and none were successful in treating all the hazardous constituents in the waste to meet LDR treatment standards.

The TV specifically proposed that the PUEX be stabilized into a solid form, containerized into conventional metal containers, and then macro-encapsulated into welded stainless steel containers. The resulting package would meet the regulatory definition of macro-encapsulation using a “jacket of inert inorganic material”. The TV acknowledged that some of the organic UHCs would remain untreated in the stabilized waste form; however, they were not easily removed from the waste matrix as indicated by the measures taken to remove them using air sparging during bench scale testing. Additionally, stabilization converts the liquids into a solid waste free of releasable liquids, and moreover the use of macro-

encapsulation in stainless steel would provide a no migration solution in lieu of stabilization. The TV was approved by the EPA in February 2008.
Due to the treatment issues described above, SRS requested, from SCDHEC, an extension to the previously agreed upon date of September 07 to have the PUREX treated. SRS invoked the use of 'clean-up credits' from a 2003 agreement established with SCDHEC. Under this agreement SRS earned 'credits' for early completion of specific agreed upon milestones. These credits could then be used to 'buy' additional time for milestones which had fallen behind schedule. For the milestone associated with the PUREX, SRS 'bought' an additional 15 months until December 2008 to have the waste shipped offsite for treatment and disposal.

Once the TV was approved the SRS vendor was ready to begin treatment in April 2008, but as discussed below, issues related to disposal began to emerge in December 2007.

DISPOSAL ISSUES

The PUREX treated waste stream was originally planned for disposal at the Nevada Test Site as a mixed waste. However, during the waste profile review and treatability variance public notice period, the Nevada Attorney General issued a written objection (dated 12/20/07), addressed to the EPA and Secretary of Energy, to the disposal of SRS legacy PUREX at Nevada Test Site.

The letter from the Nevada Attorney General (AG) did NOT object to the treatment method or the treatability variance, but rather based its objections on disposal at NTS to:

1) the belief that this waste is not covered in the 1996 EIS for waste disposal at NTS and
2) the belief that DOE has not complied with certain land withdrawal requirements related to the use of NTS as a waste disposal facility.

At this point, SRS had no viable path to disposal for this waste stream even though it had committed to remove this waste from SRS by December 31, 2008 for treatment and disposal. Several alternative disposal Sites were evaluated such as:
-Clive,Utah (radiological content of the waste exceeded that disposal site's permit)
-Waste Control Specialist (disposal license pending)
-Barnwell (no subtitle D equivalency for de-characterized wastes such as the treated PUREX and no Subtitle C landfill for mixed waste)
-Hanford (cannot accept out of state waste)

The possibility of off Site storage was investigated but proved to be too costly relative to current budgets.

Due to SRS not having a viable disposal or storage outlet, the treatment vendor was reluctant to accept the waste for treatment. As a result of this predicament, SRS met with South Carolina Department of Health and Environmental Control (SCDHEC) in February 2008 to discuss the possibility of returning the treated PUREX to SRS for interim storage until disposal issues could be resolved with NTS. SCDHEC agreed to allow the return of the treated waste for interim storage; however, in return SRS committed to shipping all the un-treated PUREX offsite for treatment by December 2008, and after receiving the treated waste back, agreed to remove all the treated waste from the state of South Carolina by December 31, 2009.

This new agreement with SCDHEC allowed treatment to proceed beginning in April 2008. The last shipment of untreated PUREX left SRS in August 2008 and the last of the treated waste was received back at SRS in January 2009.

Efforts continue to resolve disposal issues at NTS through the DOE-HQ sponsored Mixed/Low Level Corporate Board.

CONCLUSION

Successful treatment of this waste stream would not have been possible without several key regulatory interfaces and concessions.

The first being the agreement from SCDHEC and EPA Region 4 that RCRA hazardous and underlying hazardous organics can be treated using stabilization as long as analytical results demonstrate that the numerical treatment standards are met as a result of stabilization. This ruling by SCDHEC and EPA in 2003 allowed the concept of stabilizing this waste stream, in lieu of thermal treatment, to get off the ground and break the paradigm that incineration was the only approach to effectively treat an organic waste stream.

The second key regulatory concession came in the form of a treatability variance which recognized the unique characteristics and difficulties of treating the PUREX waste stream and went on to conclude that it had been adequately demonstrated that the PUREX waste satisfies the requirements for a treatment variance under 40CFR268.44. As noted earlier, this treatability variance allowed the treatment vendor to overcome issues surrounding the proof of treatment of certain organic UHCs. Without the treatment variance, successful treatment of this waste stream would have been unlikely.

The final key regulator concession was realized when SCDHEC agreed to allow the treated PUREX waste to be shipped back into the state of South Carolina after treatment once the Nevada Attorney General blocked the shipment of treated SRS PUREX to NTS. Without this concession, the initiation of vendor treatment would not have begun since there would not have been a viable storage or treatment outlet.

In conclusion, without the key support of state and federal regulators this complex and difficult to treat PUREX waste stream would have never been successfully treated.

REFERENCES

1. PUREX Waste Stabilization, WSRC-TR-2001-00526