ALTERNATIVES TO INCINERATION-ONE YEAR LATER
A STATUS REPORT ON DEPARTMENT OF ENERGY SPONSORED DEVELOPMENT AND DEMONSTRATIONS

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ABSTRACT

Over a year and a half has passed since a public stakeholder initiated lawsuit led to the termination of a planned Transuranic (TRU) waste incinerator at the Department of Energy's (DOE) Idaho National Engineering and Environmental Laboratory (INEEL). Concurrent with this event, operation of existing DOE mixed low-level waste incinerators at the INEEL and the Savannah River Site (SRS) were permanently shutdown or suspended. In addition, DOE continues to evaluate the potential FY 2003 closure of DOE's remaining operating incinerator at Oak Ridge. In response to this abrupt loss in DOE waste incineration capacity, review committees were established to provide path forward recommendations as to how DOE will replace the role of a work horse treatment technology that is no longer in vogue with respect to either public sentiment or anticipated emission regulations. Most notable of these review committees was a Blue Ribbon Panel (BRP), formed as a condition of the lawsuit settlement, and tasked to identify and recommend alternatives to the terminated INEEL TRU waste incinerator. The Panel recommended four top tier and four-second tier technological alternatives; and promoted additional funding for their development through DOE's Office of Science and Technology (OST).

In response to these incinerator closures and suspensions, and in accordance with the BRP's recommendations, OST's Transuranic and Mixed Waste Focus Area (TMFA) has initiated a number of technology development and demonstration activities as a first step in replacing the role of incineration with processes that are both stakeholder and environmentally acceptable. This paper provides a brief update and description of those technologies currently placed under development by the TMFA in the past year and a half, and also provides the rationale for their selection. In particular, a summary of the development activities underway to deploy thermal desorption, a top tier BRP recommended technology, as a preliminary alternative for the displaced INEEL TRU waste incinerator is highlighted. The choice of thermal desorption over the other BRP recommended alternatives is made evident by knowledge of the INEEL TRU waste characteristics coupled with an understanding of the requirements that govern its transportation to and disposal at the DOE's Waste Isolation Pilot Plant (WIPP).

To address DOE TRU waste streams requiring more destructive environments beyond that provided exclusively by thermal desorption, the development of additional BRP recommended alternatives has also been initiated. Technologies in this category include super critical water oxidation (SCWO) and mediated electrochemical oxidation (MEO). Likewise development and demonstration activities associated with alternatives specifically applicable to mixed low-level waste are also presented. For this application, technologies placed under OST development include the molten aluminum process, mediated electrochemical oxidation, and a low temperature stabilization method.

INTRODUCTION AND BACKGROUND

Located at the INEEL's Radioactive Waste Management Complex (RWMC) in the Idaho desert, is over 40,000 barrels (i.e., 2 million gallons) of legacy TRU waste sludge. The waste, which originated from glove box clean-up operations at the former DOE plutonium finishing plant near Rocky Flats CO, consists of an organic sludge containing Texaco Regal oil, various chlorinated organic solvents and polychlorinated bi-phenyls (PCBs). To facilitate safe shipping of the waste from Rocky Flats, as well as interim safe storage at the INEEL, the sludge was solidified with calcium silicate and/or calcium sulfate-giving it its current viscous consistency of peanut butter.

Current DOE policy requires that all TRU waste be disposed of at the designated WIPP site in New Mexico. Even though TRU waste is exempt from Resource Conservation and Recovery Act (RCRA) Land Disposal Restrictions (LDRs), treatment of this specific TRU sludge inventory was still anticipated. Potential treatment was needed to ensure adherence to Nuclear Regulatory Commission- (NRC)/ Department of Transportation (DOT) requirements for WIPP shipments and/or meet particular WIPP waste acceptance criteria (WAC) currently in effect for Toxic Substance Control Act (TSCA) regulated chemicals, such as PCBs. More specifically, the presence of organics and alpha emitting actinides in the waste stream may generate enough radiolysis-induced hydrogen and/or other flammable VOCs to exceed container head space gas concentration limits that have been imposed through the NRC/DOT requirements regulating WIPP shipments. Obviously aggressive treatment via incineration would destroy all organics in the TRU waste inventory, thereby mitigating any potential VOC, hydrogen gas, and or PCB issue. Consequently, DOE originally selected the well-developed and robust technology of incineration as the most economical approach for treating the waste prior to WIPP disposal of the residues. However, well-organized regional public opposition to the incinerator resulted in its removal as an option, despite the proposed design of a state-of the-art incinerator and off gas treatment system. The chief stakeholder concern, however remote, revolved around the large volume of emissions inherent with an incinerator; especially under upset conditions

To assist in identifying a publicly acceptable alternative for the INEEL TRU waste incinerator**,** DOE committed to appointing a panel of independent experts to explore technological alternatives to incineration. Specifically, the panel was to recommend acceptable alternatives for the specific class of TRU waste sludges existing at the INEEL. As previously indicated, the sludges, in addition to containing PCBs also have the potential of generating hydrogen gas through radiolysis- a major WIPP transportation issue.

The Blue Ribbon Panel on Emerging Technological Alternatives to Incineration issued its report and associated recommendations in late 2000 (USDOE SEAB 2000, Report of the Secretary of Energy Advisory Board's Blue Ribbon Panel on Emerging Technological Alternatives to Incineration. Washington, DC: USDOE). Among their recommendations, the Panel found that there are 4 top tier and 4-second tier promising technological alternatives to TRU waste incineration. However, the Panel concluded that none are ready for immediate implementation and all need to be further developed and demonstrated with actual waste prior to deployment. As such, the panel also suggested out-year DOE development funding, and recommended that OST's TMFA take the lead in initiating an alternative's development program for the INEEL TRU waste. OST's TMFA was the logical choice since it was already engaged in a similar program as a result of the complex-wide mixed waste incinerator closures. The fact that the TMFA is also involved in developing non-incineration options for TRU wastes located at other DOE sites adds further credence to the BRP recommendation that they initiate the specific alternatives development for the INEEL inventory.

Summarized below is an update on the TMFA sponsored development activities that have been recently initiated in response to: 1. The terminated INEEL TRU waste incinerator and subsequent BRP recommendations, 2. DOE complex wide needs related to other TRU waste treatment issues involving the presence of organics, and 3. The reduction in mixed low-level waste incineration capacity.

SELECTING A BRP ALTERNATIVE FOR THE INEEL TRU WASTE SLUDGES

According to the BRP report, the TMFA is to foremost consider the development of one or more of the top four BRP recommended alternatives. Eventhough the top four BRP recommended technologies of DC arc melting, plasma melting, steam reforming, and thermal desorption are thermal, in that they technically function above 400 degrees C, they differ from incineration in two distinct attributes. They generate less turbulent and lower volumetric off-gas flows and they do not operate exclusively under the oxidizing conditions that lead to potentially toxic off-gas products of incomplete combustion (PICs). Consequently, theTMFA would be initiating development in a technical direction favorable to concerned public stakeholders by staying with in this list of choices. However, the TMFA is challenged in selecting among and developing one or more of these four options considering the limited development resources actually provided, despite the generous BRP recommendations made in regard to funding.

However, in light of certain activities recently initiated in regard to the potential disposal of PCBs at the WIPP site, the TMFA can make a strong argument for throwing all of its current BRP recommended resources at the thermal desorption option. Elements of that argument are as follows:

1. Unlike the other three technologies, thermal desorption is fundamentally designed to be primarily operated in a non-organic destructive mode. It is a separation process, where the desired hazardous gases, VOCs, and other organics are transferred from the liquid/solid state to the gas state and condensed from the waste matrix. They are not initially destroyed. Operating under this condition eliminates the production of PICs and other gas-phase pollutants that may cause stakeholder concerns. The non-TRU but radioactive organics that are removed and condensed can be treated for destruction, if need be, at a remote location and/or at a later time. TRU actinides are not desorbed but are retained in the remaining residues. What is important is that thermal desorption may make the INEEL waste drums shippable to WIPP by simply removing certain constituents-not destroying them.
2. Thermal desorption can be designed as a full-scale in-drum process, eliminating the need for drum content removal.
3. No organic destruction may be required at all in that the waste drums may be made shippable just by mitigating the potential hydrogen gas and VOC issues. The PCB issues will more than likely go away with a regulatory based paper solution that results in the WIPP site obtaining a TSCA permit.

Therefore based on the above three arguments, DC Arc, plasma arc, and steam reforming methods are overkill in that they are all organic destructive processes. Obviously then, thermal desorption is the best and most benign method for the specific INEEL TRU waste if all that is required is the removal of hydrogen and VOCs. Consequently, its development should and is being considered foremost by OST as a replacement for the INEEL TRU waste incinerator.

The Thermal Desorption Approach

In anticipation that PCBs will not pose a barrier for INEEL TRU waste disposal at WIPP, thermal desorption was chosen over the three other top rated BRP technologies as the preferred and primary technology to test as an alternative to incineration. As detailed earlier, thermal desorption is the most benign method to remove the troublesome hydrogen and VOCs from the TRU organic sludge waste and therefore should be favored to stakeholders. However, the potentially complex and unknown diffusive transport behavior and solubility of the hydrogen in the Regal oil justifies a layered thermal desorption testing program. A TMFA sponsored mufti-tier development program is required to fully understand what phenomena are causing the production, storage and subsequent desorption of this potentially explosive gas.

The first level development activity consists of various TMFA sponsored bench scale experiments to determine the behavior of actual INEEL TRU organic sludge waste under thermal desorption conditions. Actual gram scale waste samples will be tested in hot cells and the desorption kinetics for hydrogen and other volatiles absorbed with in the waste matrix will be determined. The determinations will be made through the use of state-of- the-art off-gas analytical equipment; inclusive of thermal gravimetric analyzers (TGA) and mass spectrometry/gas chromatography (MS/GC).

Based on previous, but limited, sampling and characterization of the waste and its corresponding gas generation rate, it was postulated that the hydrogen being generated by radiolysis is possibly being absorbed by oil in the waste matrix. If the hypothesis is not proven, the excessive hydrogen observed during the earlier test may instead be a result of real-time oil cracking and/or radiolysis under conditions of moderately elevated temperatures. Regardless, the specific waste inventory may not pass the required elevated temperature tests to determine if the gas generation from a specific TRU waste drum is of an acceptable concentration to validate transportation to the WIPP.

To date, the investigators responsible for this first level task have completed upgrades to existing glove boxes needed to accommodate the tests, have initiated the procurement of the necessary off-gas analytical monitors and detectors, and have started testing. Preliminary test results indicate that thermal desorption, as a minimum, will mitigate the VOC issue. To support scale –up, testing at gram scale will be followed with actual waste testing at kilogram scale. Testing is scheduled to be complete in FY-02. If the testing gives successful results, a simple thermal desorption method performed under operationally acceptable temperatures and times will be available for advancement to deployment. In relation to this project, a FY-2001 independent review of the experimental approach for the above-described tests was conducted with the assistance of the American Society of Mechanical Engineers (ASME). The reviewers recommended that, among other issues, the TMFA and their project team seek a better understanding of the hydrogen solubility behavior in the oil of the INEEL sludge waste.

A second layer of development is being performed in conjunction with the above activity and this effort involves larger scale development of the in-drum thermal desorption method using surrogate waste. This testing at near drum scale will also occur at in FY 2002 and is supported with both FY-2001 and FY-2002 resources. Similar to the first level study, the activity has been initially funded with FY-2001 plus-up resources as recommended by the BRP. One objective of the testing is to determine the proper drum heating method to ensure that sufficient hydrogen removal is achieved at full-scale. Another purpose is to determine the amount and type of emissions that may occur with the fully scaled thermal desorption process to ensure adequate off-gas treatment designs and therefore gain stakeholder acceptance.

RELATED DOE COMPLEX WIDE DEVELOPMENT ACTIVITIES FOR TRANSURANIC WASTE REQUIRING ALTERNATIVES TO INCINERATION

To support similar TRU waste issues existing elsewhere in the DOE complex, the TMFA has leveraged some of the BRP second tier recommendations. In particular, the TMFA is sponsoring efforts that involve surrogate and actual TRU waste testing of two BRP recommended technologies chosen for development at the Savannah River Site (SRS).

SRS requires the development of an alternative to thermal treatment for a portion of their Pu-238 contaminated TRU job control debris waste. As detailed for the INEEL TRU waste inventory, waste drums being transported to WIPP have limits on the flammable gases allowed in their headspace. Consequently, treatment of the SRS TRU debris is also required to eliminate the pertinent organics in the waste stream that may lead to hydrogen gas production as a result of radiolysis by the high concentration of Pu-238 existing in the waste. Since the high energy Pu-238 in the waste gets imbedded in the organic matrix of the debris, treatment is especially challenging. As a consequence the BRP recommended alternatives that provide for destruction of the organic phase were desired as long as the emissions are minimized. At this point in the technology selection process, SRS desires to test at least two non-thermal options, before selecting one for deployment.

The two technologies that were selected through a competitive bid process consist of the silver II MEO method, as detailed below, and a supercritical water oxidation (SCWO) process. Both technologies were included in the second-tier of BRP recommendations and produce relatively fewer emissions than any of the 4 top tier recommendations. The MEO method will require considerable pre-treatment to ensure that the solid debris will not plug the membranes of this electrochemical process. However, the silver II MEO method will also decontaminate the more recalcitrant organics, separating the plutonium from the bulk of the matrix. In contrast, the SCWO process may not require pre-sizing, since the proposed method involves a front-end thermal desorption step to extract and transfer the organics in the waste drum to the supercritical reactor. In the reactor water at super critical conditions is a strong oxidizer that is highly soluble of organics and insoluble to inorganics. Additionally, supercritical water has the density of a liquid with the flow properties of a gas; thereby making it an ideal media for effectively mixing and contacting with the organic species- of- concern within the mixed waste matrix. However relative to incineration, SCWO has the disadvantages of requiring longer residence times, special materials to resist their corrosive environments, and considerable residue stabilization.

Based on an RFP solicitation package submitted by NETL in FY-1999, the technologies were selected for award in June of 2001 and final contracts and scopes –of –work (SOW) for each vendor was finalized in the fall of 2001. Contracts require the vendors to test their selected technologies under cold-pilot plant conditions at their respective commercial sites. If these tests are successful, additional hot testing using samples of actual TRU waste debris will be initiated at glove box scale at SRS using a test system designed by the technology vendor. Deployment is planned for the FY 2004-2005 time frame

MLLW ALTERNATIVES TO INCINERATION AS A RESULT OF CIF/WERF SHUTDOWNS

In addition to TRU waste issues, the TMFA is advancing alternatives to resolve mixed low-level waste issues that have surfaced due to DOE incineration closures and the private sector's inability to replace that role. A sample of three of these development efforts is provided below. Even though two of the technologies were not recommended by the BRP, they were requested by the DOE sites possessing the waste issue and constitute low-emission, publicly friendly alternatives nonetheless.

Molten Aluminum for classified and other mixed wastes at Sandia National Laboratories

This activity involved the demonstration and deployment of Clean International Technology Corporation's (CITC) molten aluminum process for treating a variety of organic containing mixed waste (classified and un classified) at Sandia National Laboratory. The molten aluminum process is a low off gas waste treatment method that takes advantage of molten aluminum's high reductive potential at its relatively low melting temperature of 900 degrees C. Sandia has chosen to advance this method to treat classified waste on site because the reduction method is as potentially robust as incineration while producing much lower emissions. In addition, the SNL waste streams could not be declassified for treatment off–site.

Over the past year, Sandia engineers have procured, under TMFA sponsorship, the CITC system through a sole-source contract, prepared procedures and test plans for the treatbility studies, and have received the necessary approvals including those required for permit modifications. Installation of the CITC molten aluminum 50-lb treatability study unit is complete and testing was initiated the first week in December 2001. Test data will include collecting information on particular emissions of public concern, including dioxins and furans.

Silver II Mediated Chemical Oxidation (MEO) testing on SRS surrogate PUREX Solvent

This activity involves the demonstration of the silver II MEO technology as an alternative to incineration in treating spent PUREX solvent. The activity makes use of one of two existing MEO pilot plants at the Department of Defense's test facility near its munitions proving ground at Aberdeen, Maryland. The Army established the test facility as part of its alternatives to incineration program initiated to find alternatives to the incineration of assembled chemical weapons. Therefore, the DOE is saved development expenses by leveraging the Army's test bed for the waste PUREX tests. Since MEO was one of the top eight BRP recommended technologies, the TMFA decided it was prudent to immediately leverage the Army pilot plant in FY 2001 since a window of opportunity presented itself during the scheduled downtime between those tests pertinent to the Army's assembled chemicals weapon's program. Testing of the PUREX simulate at the pilot plant in Aberdeen was successfully completed during the third week in August 2001 and a final report is expected the first quarter of FY-2002

In summary the MEO process makes use of silver's large low-temperature organic oxidation potential when it is at a valance of two. By deploying an electrochemical cell, an acidic silver solution is oxidized to its silver II condition which in –turn will mineralize organics at room temperatures, thereby greatly reducing emissions. PUREX solvent containing a normal paraffin and tri-butyl phosphate (TBP) contaminated with trace actinides and RCRA heavy metals, is a classic fuel reprocessing solvent in relatively substantial quantities at former reprocessing facilities, like those at the Savannah River site. SRS was planning to use its on-site Consolidated Incineration Facility to destroy the PUREX solvent, but operation of that incinerator has been suspended. Even though SRS is testing more favorable alternatives for their spent solvent, inexpensive testing of the PUREX stimulant in the AEA pilot plant was justified in that it validated the performance of this BRP recommended alternative on a simple liquid organic waste stream. In addition SRS plans to test the process's applicability for more recalcitrant TRU waste debris as previously mentioned, and the PUREX test runs provided a preliminary evaluation of the MEO's capability.

Low temperature stabilization as a replacement for the incineration of waste PUREX solvent at SRS

This activity involves testing a polymer based low temperature stabilization process as an alternative method for the SRS PUREX solvent that was to be destroyed in the now idle SRS Consolidated Incineration Facility (CIF). Because the PUREX solvent consists of the non-hazardous organics of (TBP) and dodecane, it does not require destruction. However, the hazardous metals in the waste stream must be stabilized to meet RCRA Land Disposal Restrictions. The TMFA sponsored tests involved preparing various PUREX-polymer based waste forms over a range of waste loadings and then subjecting the waste forms to various leachability tests. In addition to the standard leach tests involving the TCLP protocol, additional testing will involve determining the long-term durability of this new waste form material. Preliminary testing has been completed and the waste form appears promising at most waste loadings.

This TMFA sponsored development effort also involved the testing of an actinide separation process for the PUREX solvent, since the solvent could be treated at a commercial facility if its activity is significantly reduced. To date several solvents and sorbents have been tested and early results indicate that neither will provide sufficient decontamination factors for the actinides present. Stabilization is the preferred choice for replacing the CIF in regard to treatment of the SRS PUREX solvent. Since a low –temperature process produces fewer emissions; the increase in waste volume becomes justifiable for the particular application.

CONCLUSIONS

Through its TMFA, DOE's OST has responded to the closures and terminations of various mixed low-level and TRU waste incinerators by sponsoring technology development efforts that are consistent with the BRP recommendations. Most notable of these efforts involves the advancement of thermal desorption for the INEEL TRU organic sludges. A non-destructive approach involving thermal desorption, as opposed to the other recommended BRP technologies, is appropriate in light of the INEEL waste characteristics that are limiting its shipment to the WIPP disposal site. More destructive BRP recommended alternatives are not required since the PCB issue may be resolved with a WIPP permit change. Consequently a thermal separation process that removes the VOC s and hydrogen from the waste matrix may well be sufficient.

In the past year and a half DOE has responded to the BRP recommendations by initiating the INEEL applicable thermal desorption development effort, as well other similar activities for both TRU and mixed low-level waste. This initiation validates that DOE is committed in advancing alternatives to the publicly unfavorable process of incineration.