TREATMENT OF DOE MIXED WASTES USING COMMERCIAL FACILITIES

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ABSTRACT

In a demonstration program, Department of Energy (DOE) solid mixed wastes generated during uranium processing operations are characterized to define the unit operations required for treatment. The objectives included the implementation of these treatment operations utilizing a commercial Treatment, Storage and Disposal Facility (TSDF).

In contracting for commercial hazardous and mixed waste treatment, it is important to characterize the waste beyond the identification of toxicity characteristic (TC) and radiological content. Performing treatability studies and verification of all the unit operations required for treatment is critical.

The stream selected for this program was TC hazardous for barium (D005) and contaminated with both depleted and low enriched uranium. The program resulted in the generation of characterization data and treatment strategies. The characterization and treatability studies indicated that although a common unit operation was required to remove the toxic characteristic, multiple pretreatment operations were needed. Many of these operations do not exist at available TSDF's, rendering some portions of the stream untreatable using existing commercial TSDF's.

For this project the need for pretreatment operations resulted in only a portion of the waste originally targeted for treatment being accepted for treatment at a commercial TSDF. The majority of the targeted stream could not be successfully treated due to lack of an off-site commercial treatment facility having the available equipment and capacity or with the correct combination of RCRA permits and radioactive material handling licenses. This paper presents a case study documenting the results of the project.

INTRODUCTION

The limitations of the licenses and permits at existing Treatment Storage and Disposal Facilities (TSDF's) have severely restricted the type and amount of solid mixed waste which can be treated at commercial facilities. Solid mixed wastes from the many DOE facilities involved in the processing of uranium tend to be well characterized in terms of toxic and radiological content. However, these characterizations often lack the information essential for successful treatment. Even in cases where treatability testing was performed, the tests failed to identify important pretreatment unit operations such as crushing, shredding, and blending. Characterization lacking treatability data combined with the matrix of regulations and regulatory agencies, complicates the process of obtaining commercial off-site processing capacity for these waste streams.

Characterization of solid mixed waste is a basic requirement for regulatory compliance for TSDF's including DOE owned facilities. It is also a critical step in identifying treatment strategies. DOE facilities which can accept and dispose of solid mixed wastes, such as the facility proposed for the Nevada Test Site (NTS) (1), are not yet available. Commercial mixed waste disposal facilities (burial cells) for solid mixed waste cannot be utilized under existing DOE orders. Because of this, treatment remains a key option for the elimination of mixed wastes during site remediation.

Because DOE facilities which can accept low level radioactive waste (LLW) are available, one treatment strategy which can be successful is the removal or elimination of the hazardous constituents from the mixed waste. Waste treated in this way can then be disposed of as radioactive waste at existing DOE LLW sites such as NTS. This strategy is considered to be an attractive route because it can be readily applied for Toxicity Characteristic (TC) Waste using EPA Best Demonstrated Available Technology (BDAT). It also avoids the problems of defining the Below Regulatory Concern (BRC) levels for the alternative strategy of decontamination and disposal as hazardous waste.

This route, however, is not without problems. Even following successful identification of the TC constituents, the BDAT and treatment program, the requirement for radioactive materials management inherent to the DOE system coupled with a severe shortage of properly permitted treatment facilities can result in the inability to locate a TSDF willing or able to accept it for treatment. Most successful demonstrations of processing solid mixed waste have often been limited to on site processing by the generator (2) or on site processing by the site management contractor (3).

For this program, the DOE prime contractor has the responsibility for the safe storage and disposal of a number of 55-gallon drums of barium chloride salts, salt contaminated fire brick and other salt contaminated waste generated from the clean-out of molten salt baths used in the extrusion of low enriched and depleted uranium. The majority of these drums are in storage, while some were located at a subcontractor facility which originally generated the waste under contract to the DOE. Due to the politically volatile nature of the radioactive, hazardous and mixed waste issues, it is anticipated that obtaining permits for on-site treatment of this waste stream will be a lengthy process. For this reason, the Department of Energy has elected to explore the processing of this waste at off-site subcontracted facilities.

To assure consistent levels of Quality Assurance (QA) and a common point of responsibility, the DOE prime contractor has issued the mixed waste treatment contract to a management subcontractor. The management subcontractor is the project management company which provides the service of project organization, scheduling and QA. Project logistics as it pertains to the regulations, transportation planning, treatment alternatives, treatability studies, process development, and project process control planning are also provided. In this position it acts as a liaison (or otherwise, a buffer) between the prime and the many other project associated vendors, such as the transportation vendor, laboratory vendor and waste processing facility.

Chronologically, the project is divided into eight activities: 1) Project specific management and QA development; 2) Transportation to the TSDF; 3) Storage; 4) Process verification (treatability study); 5) Process and engineering development; 6) Waste processing; 7) Waste certification; 8) Transportation to Nevada Test Site (burial site).

WASTE DESCRIPTION

As part of the uranium processing operations conducted by the DOE, uranium billets were extruded to attain a desired shape. Prior to extrusion, the billets were heated to approximately 1100°F by immersing them into a molten salt bath. During normal operation, salt adhered to the surfaces of the billet as it was moved between the salt bath and the press. This salt was collected and placed into 55-gallon drums for disposal. Also, during normal maintenance of the baths, the salt was solidified, broken up and placed into 55-gallon drums for disposal.

The eutectic salt mixture used in the baths is primarily composed of barium chloride (55%), potassium chloride (20%), and sodium chloride (25%). Due to contact with the uranium billets, the salt is contaminated with uranium, its related daughters and trace amounts of other radioactive elements. The salt mixture exhibits the toxicity characteristics for Barium, Environmental Protection Agency (EPA), Hazardous Waste No. D005.

The salt contains levels of uranium typically in the range of 0.01 to 0.1% by weight, but the maximum concentration can be as high as 20%. Other metals including chromium, lead and copper are also present. The metal contamination is the result of contact by the salt with other types of metal billets extruded in addition to uranium. The metals exist primarily as oxides, but some, such as copper, are also present as metal shavings. Lead oxide is also present from contamination by lubricants used in the extrusion process. Despite the presence of these metals, they are low in concentration and insoluble. Testing to date has shown the waste salts only fail the EPA TCLP analysis for barium (D005).

Salt contaminated matrix materials (bricks, scrap metal, insulation, etc.) are also present with the process waste stream. Each of these matrix materials poses unique processing problems compared to drums containing primarily salt. These salt contaminated materials contain low levels of salt, generally less than 4% by weight, but sufficient to cause the waste to fail the TCLP for barium. The matrix material tends to fall into three categories: 1) insoluble material in a fine particulate form, such as graphite, oxides, lime based filter cake, and soils; 2) insoluble material in large sections, such as fire brick and metal brackets; and 3) porous materials, work gloves, mineral and fiberglass insulation, and wood. The presence of large quantities of these materials presents significant processing problems by preventing the barium from going into solution and contacting the sulfate ion during treatment.

METHOD OF TREATMENT

The primary method of treatment for barium contaminated waste is to remove the characteristic toxicity by forming an insoluble precipitate of barium with sulfate or carbonate (4). Barium sulfate is not toxic to humans or animals due to its extremely low solubility. The sulfate precipitate is preferred because barium sulfate is more than 10 times less soluble than barium carbonate. Barium sulfate does not undergo photolysis or oxidation. The sulfate reaction is shown below:

$$BaCl_2 + Na_2SO_4 \rightarrow 2NaCl + BaSO_4 \text{ (precipitate)}$$

The process requires that the barium chloride be in solution and contacted with a soluble sulfate salt such as sodium sulfate. For the waste composed primarily of salt, the treatment steps are: 1) Dissolution of the salt in water; 2) Mixing and reacting the salt solution with a sodium sulfate solution; 3) Separation of the sulfate precipitate by sedimentation and filtration.

At the TSDF, barium chloride salt can be dissolved with water. Large insoluble pieces of material must be removed, sized reduced and processed separately by water leaching prior to sulfate treatment. Sodium sulfate is added to the barium salt solution, and the precipitated barium sulfate and uranium fines will be recovered by sedimentation and filtration. The filtercake can then be dewatered and packaged for disposal at NTS. Upon completion of this clarification process, the remaining sodium/potassium chloride salt solution is collected and analyzed for radiological content. The radiological analysis determines if the remaining solutions may be discharged under the permit conditions of the TSDF or if they require volume reduction, solidification and disposal as LLW. By maintaining the pH above 7.0, dissolution of the metals is minimized, and the clarified salt solution is free of dissolved metals and uranium.

The processing of the barium chloride salt is controlled by a QA Project Plan, applicable System Operating Procedures and a Process Control Program (PCP). The integration of these programs will insure that the quality level of the barium sulfate product meets or exceeds the applicable transportation and disposal criteria. Any non-conforming product will be reprocessed to insure total compliance. Under the project management Work Plan, all of the waste resulting from the treatment process will be shipped to the Nevada Test Site (NTS) for disposal under a current disposal contract in accordance with the Nevada Test Site Waste Acceptance Criteria, document number NVO-325.

When processing any uranium above the natural enrichment of 0.71% U-235, criticality safety must be addressed. Although very little uranium in the waste is identified as enriched, criticality safety is still maintained throughout processing by limiting the mass of Special Nuclear Material (SNM) on the TSDF's site to 350 grams. This is accomplished by establishing an inventory program to track and account for all enriched uranium in process and shipments to and from the TSDF.

PILOT STUDIES

On-site processing of the barium salt waste was tested at the Feed Materials Production Center (FMPC) in 1984 by the site management contractor. In this test, over nine tons of salt were processed in a pilot-scale facility. The process used ammonium sulfate in a similar process to that described in the previous section.

These pilot-test runs concluded the barium salts could be effectively treated to remove the characteristic toxicity for barium by precipitating the barium as barium sulfate. They also indicated that suspended insoluble material could not be easily recovered without treatment. In the pilot tests, uranium oxide was separated from the salt dissolution prior to sulfate treatment. Removal of these solids for uranium recovery was feasible, but the recovered material required large amount of wash water to lower the barium content to an acceptable level.

With the shutdown of uranium processing facilities, the need to recover and recycle uranium is greatly diminished. This fact combined with the difficulty encountered by the pilot study in treating recovered uranium has eliminated this step from the current treatment operation. Also, the presence of significant amounts of sodium and potassium chlorides reduces the advantages of using an ammonium sulfate salt over a sodium sulfate salt. The presence of significant amounts of copper also discourages the use of ammonia over sodium. For these reasons, sodium sulfate was selected for the current process in preference to the ammonium sulfate used in the pilot study.

With the quantity of salt remaining to be treated estimated to be over 400 tons, the project could have proceeded with on-site treatment of the waste material. However, with the promulgation in 1987 of the DOE "By-Product Material Rulemaking," the regulatory issues which needed to be addressed became more complex. Due to the extreme regulatory pressures at the Feed Materials Production Center (FMPC) site to remove the barium chloride waste, commercial off-site treatment was explored.

WORK PLAN

Due to the source of the material, the destination of the waste, and the various states involved, the work scope associated with the processing of mixed waste at a commercial waste processing facility is more complex than just the process method. The entire project involves several independent companies and regulatory agencies, as well as the disposal site management. The companies would include the DOE prime contractor and/or subcontractor, the project management contractor, the laboratory vendor, the transportation vendor, the TSDF and the radioactive burial site. The regulatory agencies include the Department of Energy, the Environmental Protection Agency, the Department of Transportation, Nuclear Regulatory Commission, and a number of state agencies, including the Ohio Environmental Protection Agency, the Texas Water Commission and the Texas Department of Radiation Safety. The disposal site is governed by the DOE and managed by a second prime contractor.

A well-prepared Work Plan was the first step taken to insure coordination by the organizations involved. The Work Plan dictated the steps necessary to complete the treatment while providing uniform and adaptable methods to insure that regulatory compliance is maintained.

The key documents required by the Work Plan are: 1) Quality Assurance/Quality Control Procedures and QA Project Plan; 2) Characterization Plan and Report; 3) Transportation Procedures; 4) Process Verification/Treatability Study Report; 5) Process Design Report; 6) Process System Operating Procedures; 7) Process Control Procedures; 8) Final Waste Certification Procedure.

The Quality Assurance Program for this project has been developed in accordance with, and meets the intent of, the quality requirements of NQA-1. Since NQA-1, as it is presently written, cannot be fully implemented on this type of environmental mixed waste project, certain modifications and adjustments to the NQA-1 requirements had to be made. Department of Energy (DOE) Certification Plan requirements and the acceptance criteria of NVO-325 for the waste burial at the Nevada Test Site also had an impact on the development of the project quality assurance requirements. All of these requirements and criteria had to be orchestrated into one cohesive Quality Assurance Program. This is done to assure smooth operations and processing, as well as a consistent waste form quality which meets the DOE Certification Plan requirements and the acceptance criteria of the waste burial site.

CHARACTERIZATION

The first step performed in the characterization process is the verification of the waste profile, which is performed by visual inspection. The salt has a unique appearance compared with other waste types. This inspection insures that the contents of a particular waste drum are correctly recorded and further insures that other waste profiles are not inadvertently identified as salts.

Second, inventory records are examined to verify the process of origin for each drum. Process knowledge is relied upon to identify the hazardous characteristics of the waste. If visual inspection indicates that the waste drum contains salt and the inventory records indicate it was generated from the extrusion process, then the waste drum is identified as hazardous due to barium toxicity and tagged for processing.

Additional characterization is performed by sampling and chemical analysis. The purpose of this analysis is an overcheck of process knowledge to characterize the waste as hazardous. Sampling plans are prepared based on the waste profiles. Inventory records and visual inspection records are used to identify individual groups of drums to be sampled and analyzed.

A second reason for sampling and analysis is to fill in any gaps which exist in records designed to provide an accounting for enriched uranium. Due to the requirement for criticality control of enriched uranium at the treatment facility and for shipping documentation, the amount of enriched uranium at the TSDF must be inventoried and controlled.

TREATABILITY AND PROCESS VERIFICATION

Treatability testing was performed on samples taken from four different material profiles contained in the waste stream. These streams were salt, salt sludge, graphite/salt lubricant residue, and salt contaminated firebrick. Three composite samples were formed for the salt, sludge and graphite materials. The composite samples were then dissolved in water, and the water leach solutions were analyzed to determine the presence to significant contaminants. The result of the water dissolutions are presented in Table I. The presence of lead in the graphite waste was traced to the use of lead bearing lubricants during some operations. Barium was present in the anticipated concentrations, and the uranium was insoluble.

The water leach solutions were then mixed with sodium sulfate to precipitate the barium. The precipitate was recovered, and the filter cake and the filtrate were analyzed. The results for the filter cake and filtrate are presented in Tables II and III respectively.

Treatability of the firebrick presented some unique problems. Samples taken from interior and exterior sections of the brick indicated that barium was present in significant concentrations throughout the brick. Any section for brick selected for analysis failed TCLP testing for barium. From the TCLP results, it was evident that the barium was leachable and once leached could be treated. A series of tests were required to determine the minimum size reduction required to successfully leach the barium from the brick. Excessive size reduction would result in additional equipment requirements, while insufficient size reduction would result in brick material which would not pass TCLP testing. The test series determined that the material would need to be size reduced no further than 3/8 inch in diameter. Further, water leach times of three hours or more would be needed. Water volume to crushed brick volume ratios of 2:1 would also be required.

This brick treatability testing was significant because the addition of two stages of crushing and the associated air handling and filtration equipment represented a significant burden on the TSDF anticipated for use.

PROCESS DESIGN

To initiate the actual treatment of the waste a package of documents was prepared for the TSDF to be used within the operating guidelines of their facility. This package includes: 1) Process Design Package; 2) Process System and General Operating Procedures; 3) Process Control Plan

This package is designed to provide the TSDF with the information needed to process the barium chloride waste. The design package includes equipment specifications, process and instrumentation diagrams (P&ID's), cost estimates, manpower estimates, and operating cost estimates. It is intended to coordinate the specific requirements of the DOE and the barium chloride waste treatment process with the capabilities and facilities available at the TSDF.

The operating procedures provided to the TSDF are general in nature and are intended to support the needs of the

TABLE I

Analysis of Water Leach Solutions (ppm)

	GRAPHITE	TOP SALTS	SALT SLUDGE
Sample (gm)	50	153	76
Water (ml)	500	550	275
Soln. (gm/ml)	0.100	0.278	0.276
Arsenic	<0.0320	<0.0320	<0.0320
Barium	5427	75600	61790
Cadmium	<0.002	1.365	0.2925
Chromium	<0.0050	<0.0050	0.0345
Lead	26.15	0.3153	0.8313
Selenium	<0.0520	<0.0520	0.1683
Silver	<0.0060	<0.0060	0.1400
Copper	31.0	1.794	12.013
Nickel	<0.0080	0.1952	0.5210
Zinc	8.05	0.0552	0.1333
Aluminum	<0.0380	<0.0380	3.0925
Iron	3.51	0.0115	0.2148
Sodium	1859	16360	18660
Potassium	2708	16060	27710
Uranium	<1.00	<1.00	<1.91

TABLE II

TCLP Results for Barium Sulfate Filter Cakes

ANALYTE	GRAPHITE	TOP SALTS	SALT SLUDGE	REG. THRESHOLD
Arsenic (ppm)	<0.0320	<0.0320	<0.0320	5.0
Barium (ppm)	7.743	0.0790	0.0977	100.0
Cadmium (ppm)	0.0034	0.4580	0.0247	1.0
Chromium (ppm)	0.1093	<0.0050	0.0683	5.0
Lead (ppm)	2.124	<0.0280	<0.280	5.0
Selenium (ppm)	0.0520	<0.0520	<0.0520	1.0
Silver (ppm)	<0.0060	0.0068	<0.0060	5.0

TABLE III

Filtrate Results

ANALYTE	GRAPHITE	TOP SALTS	SALT SLUDGE
Arsenic	<0.0320	<0.0320	<0.0320
Barium	0.0494	0.0899	0.0335
Cadmium	<0.0020	0.0410	<0.0020
Chromium	<0.0050	<0.0050	<0.0050
Lead	<0.0280	<0.0280	<0.0280
Selenium	<0.0520	<0.0520	<0.0520
Silver	<0.0060	<0.0060	<0.9028
Copper	0.0127	0.3257	<0.0050
Nickel	<0.0080	<0.0080	<0.0080
Zinc	0.0082	<0.0010	<0.0010
Aluminum	0.5181	<0.0380	0.3813
Iron	<0.0040	<0.0040	<0.0040
Sodium	Not Analyzed	Not Analyzed	29925
Potassium	Not Analyzed	Not Analyzed	8638
Uranium	<2.65	<1.25	<2.50
Gross α (pCi/g)	<1.14	1.90	<1.14
Gross β (pCi/g)	1.64	1.60	4.30

DOE. These procedures control the operation of the processing system and will serve as a vehicle for the delineation of safety and quality control instructions to operations personnel.

The Process Control Plan (PCP) governs the operation of the treatment system and establishes acceptance criteria for *each batch* of waste salts processed. The program will include all procedures and data sheets to be used in process quality control. The requirements for waste certification, per the requirements of the DOE burial site, are integral to the PCP.

SUMMARY

This project has demonstrated the problems which can result from waste characterization data which is designed to meet regulatory requirements, but fails to fully address the treatability of the waste. Using commercial TSDF's for mixed waste treatment must take into account the identification of all unit operations required. Commercial TSDF's may not be prepared to make a significant equipment additions into their treatment operations. Also, most commercial TSDF's cannot add new treatment operations without a permit modification. For this project, the completion of treatability testing prevented the shipment of significant amounts of material to a TSDF which did not have the immediate capacity to treat it.

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