Radium/Barium Waste Project – 15043

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ABSTRACT

The treatment, shipping, and disposal of a highly radioactive radium/barium waste stream have presented a complex set of challenges requiring several years of effort. The project illustrates the difficulty and high cost of managing even small quantities of highly radioactive Resource Conservation and Recovery Act (RCRA)-regulated waste. Pacific Northwest National Laboratory (PNNL) research activities produced a Type B quantity of radium chloride low-level mixed waste (LLMW) in a number of small vials in a facility hot cell. The resulting waste management project involved a mock-up RCRA stabilization treatment, a failed in-cell treatment, a second, alternative RCRA treatment approach, coordinated regulatory variances and authorizations, alternative transportation authorizations, additional disposal facility approvals, and a final radiological stabilization process.

INTRODUCTION

PNNL had an inventory of radium chloride (both solid and solutions) that had been used as a source of radon gas (Rn-222) for health effects studies. After completion of these studies, PNNL sought potential future uses of this material. Some of the radium chloride was purified and repackaged for transfer to a private firm, with the remaining material prepared for disposal. Approximately 22,200 MBq (0.6 Ci) of radium chloride was stored in a number of small vials in the Radiochemical Processing Laboratory (RPL) Shielded Analytical Laboratory (SAL) hot cell.

The radium chloride contained a high concentration of barium as a contaminant, along with traces of silver, cadmium, chromium, lead, and thallium. Analysis of the stock solutions found that barium was present in concentrations exceeding the RCRA D005 waste code threshold. Several other metals exceeded Underlying Hazardous Constituent (UHC) limits and also required treatment. Treatment to meet Land Disposal Restrictions (LDR) standards was required to allow Hanford Site disposal. The treatment process selected for the material was to perform in-cell stabilization using blast furnace slag cement grout.

INITIAL RCRA TREATMENT AND PACKAGING

Mock-Up Treatment

A mock up treatment of the process on a non-radioactive barium chloride surrogate was tested. The treatment methodology consisted of dissolution of the solid material in dilute hydrochloric acid, precipitation of the barium as barium sulfate, neutralization, and solidification of the resulting mixture with a mixture of 90% ground granulated blast furnace slag and 10% Type I/II Portland Cement. Test treatments were performed at three different ratios of waste to grout to determine the most effective ratio. All analysis results were well below the LDR treatment standards.

In-Cell Treatment

Treatment of the radioactive waste proceeded in March 2008, and samples were taken to confirm LDR compliance. The treatment was performed in a hot cell due to the high dose rate of the material (up to 120 mSv/hour). The treatment consisted of the following steps:

- The vials were crushed and contents transferred to a beaker. There was more radium/barium residue than expected.
- 500 mL of 0.1 molar hydrogen chloride (HCl) was added to cover the crushed glass/residue.
- A mixer was run for 10 minutes.
- 30 grams (g) of solid ferrous sulfate heptahydrate was added and mixing continued. A milky precipitate formed upon mixing. Mixing continued for an additional seven minutes.
- 20 mL of 10% magnesium hydroxide slurry was added.
- pH was measured with a pH strip and verified to be between pH 6 and pH 7.
- The solution was added to a grout mix and mixed with paddle mixer.
- The mixture was transferred to two metal cans.
- The grout was sampled for toxicity characteristic leaching procedure (TCLP) analysis.

Two samples of approximately 10 mL each were taken while the grout was being mixed. The samples were allowed to cure and then size reduced for TCLP extraction. Reduced-volume TCLP samples were used [1] due to the high dose rate and very high alpha contamination levels.

Analysis Results

For reasons that are not clear, the stabilized waste did not meet the concentration based LDR treatment standard for barium, although it did meet the treatment standards for the other metals of concern. The barium results were 129 milligrams (mg)/L TCLP and 157 mg/L TCLP for the two samples, while the treatment standard was 21 mg/L TCLP.

It is not clear why the treatment did not stabilize the barium as effectively as it did for the nonradioactive surrogate. It is possible that there were differences between the waste and nonradioactive surrogate that were not apparent from the available process knowledge. Operational differences between the treatment of the nonradioactive surrogate and actual waste (e.g., mixing) could have affected the effectiveness of the treatment. It is also possible that the radiation emitted by the radium could have affected the stabilization process, although it is unlikely because grouts have been widely studied [2] and used for the solidification of radioactive waste. Documentation for the treatment process has been reviewed, and there were no apparent mistakes in the reagent quantities or formulations.

Packaging of Grouted Waste Cans

Due to the high dose rates associated with the waste, the cans were removed from the hot cell and packaged into a 208-liter (L) lead shielded steel drum. The gross weight of the packaged drum was recorded at 555 kilograms (Kg), and the dose rates on the drum were noted at 0.70 mSv/hr (70 mR/hr) at contact and 0.15 mSv/hr (15 mR/hr) at 30 cm.

The cans were topped off with activated charcoal and tightly sealed to limit the release of radon gas and prevent spread of alpha contamination. The drum itself was not vented to prevent radon release. However, calculations indicated that the radiolytic hydrogen production from the waste could exceed the lower flammability limit for hydrogen gas (4% hydrogen by volume), so the drum required periodic venting.

ALTERNATIVE RCRA TREATMENT

Evaluating Retreatment

Retreatment inside the hot cell was considered after the analysis results showed that the first treatment had failed. One possible approach was to repulverize the immobilized waste and reattempt to immobilize the barium content. This approach was not advised to limit the release of radon gas during material pulverization. Additional highly contaminated waste would also result. For example, the manipulators used in the hot cell are incapable of performing manual crushing activities. Introduction of equipment into the hot cells large enough to crush the monolithic grout would be difficult at best and possibly infeasible.

Macroencapsulation Variance

After reviewing alternatives, a site-specific petition for a one-time LDR variance was prepared and submitted to the Washington State Department of Ecology (Ecology). The variance request proposed that the lead-shielded 208 L drum in which the waste was packaged be macroencapsulated in a heat-sealed high density polyethylene (HDPE)-lined 416 L drum. After providing the required public notice and comment period, Ecology approved the variance request.

Macroencapsulation Treatment

The macroencapsulation process performed in August 2014 involved the use of an Ultratech manufactured macro container equipped with an internal HDPE liner with embedded wires that enable the lid to be heat sealed. In the presence of Hanford Site verification staff, the 208 L drum was overpacked (Figure 1) into the macro container and an inorganic void filler added to the annulus space. The drum lid was then closed and the embedded wires on the container connected to the electrical controller unit (Figure 2). A weight distribution device was placed (Figure 3) on the lid, and approximately 400 Kg of lead bricks was used to maintain weight on the lid during the process. When all preparations were complete, the electrical current was turned on and heated the embedded wires to melt the HDPE on the inner lid such that it fused with the containment unit.

Fig. 1. Overpacking   Fig. 2. Electrical controller   Fig. 3. Lid prep with lead bricks

TRANSPORTATION AND DISPOSAL CHALLENGES

The initial shipping and disposal plan for the macroencapslated radium drum was to overpack it into a Standard Waste Box (SWB) and ship under road closure conditions using an existing on-site transportation safety analysis (Safety Analysis Report for Packaging [SARP]) to the Hanford Site Low-Level Burial Grounds (LLBG). The LLBG was then expected to perform in-trench radiological stabilization to meet structural strength and Hanford Greater-than-Category-3 requirements. As time passed, however, several conditions changed, necessitating a new shipping and disposal approach. The SARP intended for use expired, and the Hanford Site Waste Acceptance Criteria (WAC) was revised to require that all waste be received in disposal-ready condition, thus eliminating the in-trench stabilization approach. With an uncertain future for disposal, further activities were placed on hold until a formal project plan could be developed to determine the steps appropriate to make the project successful. In early 2014, a refocused effort was made to encompass the critical transportation and disposal pieces.

Transportation

The shipment of the macroencapsulated waste requires that specific shipping authorization documents be prepared and approved by the U.S. Department of Energy (DOE) because the material exceeds the U.S. Department of Transportation (DOT) Type A limits and is not being shipped in a Type B container.

The Hanford Site Transportation Safety Document governs the review of and approval for such road closure shipments on the Hanford Site. In consultation with CH2M Hill Plateau Remediation Contractor (CHPRC) Transportation Safety organization, possible shipping configurations were considered. The selected packaging authorization needed not only to meet transportation needs but also to ensure that the package arrived at the burial site ready for direct disposal. The Monolith Special Packaging Authorization (M-SPA) document was selected as the technical basis for shipment.

The M-SPA authorizes the use of a risk-based packaging system composed of a containment boundary, a confinement boundary, and associated administrative controls. A key component of the M-SPA is the use of an approved immobilization media. In the case of the radium waste, the macroencapsulated 416 L drum required further encapsulation inside a Type A box using an approximately 20,000 kPa (3000 pounds per square inch) grout mixture. PNNL worked with the CHPRC Transportation Safety organization to develop a payload evaluation, M-SPA requirements compliance matrix, and tiedown analysis that could meet the criteria of the M-SPA. The appropriate reviews were obtained from DOE Richland (RL) and CHPRC. Included in the approval was a specified 90-day shipping window that will expire on December 23, 2014.

Disposal

The final obstacle for disposal was the fact that the concentration of radium in the waste exceeded the Hanford LLBG Category 3 limits. These concentration-based limits are defined in the Hanford WAC and are based on the Hanford LLBG Performance Assessment.

A waste profile was prepared, including an exception request regarding the Greater-than-Category-3 waste. The burial grounds engineering department prepared a LLBG performance assessment evaluation and a notification to DOE to approve the exception request. After review of the evaluation by DOE, the profile was approved.

FINAL STABILIZATION PROCESS

The strategy selected for meeting both the shipping authorization process and the burial grounds radiological and structural stability requirements was to overpack the macroencapsulated 416 L drum into a metal waste box with a prepoured grout floor and then flood grout to fill. Prior to these steps, however, some RCRA permitting changes occurred, and an operational readiness review had to be conducted.

Permitting Changes

PNNL needed to expand its RCRA permitted Treatment, Storage, and Disposal (TSD) footprint in order to grout the waste in a large box, as existing permitted spaces did not have the space or materials handling capability to stage, prepare and store a large, heavy box. The Cask Handling Area and Truck Lock, part of the High Level Radiochemistry Facility (HLRF) in the 325 Building, have the necessary capabilities for managing a heavy box process, and the 3714 pad (an outdoor concrete pad) can also be used for storage of boxes. In order to add these spaces to the RCRA Permit, PNNL and DOE prepared and submitted a Class 3 permit modification and requested a temporary authorization to allow the radium drum to be grouted while the permit modification was in process. Ecology granted a temporary authorization of 180 days on September 2, 2014. The Class 3 permit modification process is ongoing.

Readiness Review

Prior to the initiation of work with the radium waste in the newly authorized TSD spaces, a facility readiness review was conducted by PNNL Operations and RPL facility management. Multiple actions such as procedure revisions, reposting of areas, and spill kit placement were performed on an accelerated schedule to gain facility- and laboratory-level approval prior to proceeding. The readiness review is expected to be completed by early November 2014, with final stabilization operations commencing immediately thereafter.

Stabilization Operation

A mock-up of the container grouting process was performed using a non-RCRA low-level waste drum. After a grout floor was poured in a waste box and allowed to cure, the drum was lifted by overhead crane and placed inside the box. Cargo bar locking mechanisms were used to prevent the container from shifting significantly from side to side or floating to the top during the grout pour. The pour was conducted inside the HLRF truck lock area (Figure 4). Concrete test cylinders were collected and analyzed to validate that the selected grout mix would meet the necessary approximately 20,000 kPa (3000 pounds per square inch) strength requirement.

One lesson learned during the activity was that the grout holdup inside the mixer truck needed to be accounted for in ordering grout for future pours. In the case of the mockup, there was not enough grout procured to fill the box completely, resulting in a partial pour (Figure 5). Additional grout was procured, and the box was filled. After a period of time, the lid was removed (Figure 6) and the container inspected to ensure that the grout had adequately cured. The grouted box was then shipped to disposal on the Hanford Site.

Fig. 4. Mock up pour in HLRF

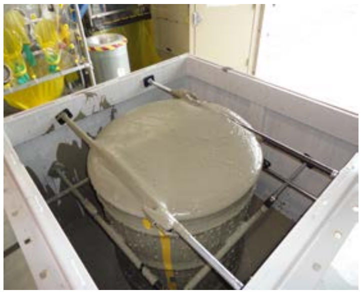

Fig. 5. Partial pour

Fig. 6. Grouted container

Having successfully mocked up the box grouting process, actual radium waste stabilization is scheduled to begin as soon as the facility readiness review is completed.

Shipment

Box grouting is scheduled to begin by mid-November and requires a minimum 20-day cure time as required by the M-SPA compliance matrix. An off-hours road closure will be scheduled to ship the box from the PNNL location to the Hanford Site disposal site under a 16 kilometers (km)/hr speed limit restriction and with temperature limited conditions. Shipment to the disposal site is planned by December 23, 2014.

CONCLUSIONS

This project was important to remove a problematic legacy waste item from the RPL. In doing so, the project will enhance PNNL's capability for dealing with difficult LLMW in the future. The expanded TSD footprint will enable a waste box grouting process that can synchronize shipping authorization and disposal facility requirements. The application or benefit of this project to others is in the operational experience gained. The lessons learned include treatment does not always go as planned, alternative regulatory approvals are possible, and project management tools can help significantly, even for a small volume waste stream.

REFERENCES

1. 62 FR 62079-62094, "Joint NRC/EPA Guidance on Testing Requirements for Mixed Radioactive and Hazardous Waste" (1997).

2. SPENCE, R.D.; BURGESS, M.W.; FEDOROV, V.V.; DOWNING, D.J., "Cementious Stabilization of Mixed Waste with High Salt Loadings", ORNL/TM-13725, (1999).