LIQUID LOW-LEVEL WASTE SOLIDIFICATION OPERATING EXPERIENCE AND LESSONS LEARNED

S. A. Coleman, CEM, PMP
Brookhaven National Laboratory

D. S. Hodge, CHMM
Argonne National Laboratory

ABSTRACT

The purpose of this abstract is to summarize the activities associated with the solidification of liquid low-level radioactive waste (LLLRW) by Brookhaven National Laboratory’s Waste Management Program (WM), problems with, recommendations and lessons learned from this activity. The goal of this treatment process was to create a solid waste matrix that would not only pass the Environmental Protection Agency (EPA 9095) paint filter test, but also result in the least handling of the waste (e.g. no mixing) and the lowest possible waste volume increase (bulking factor). In November 2001, Brookhaven National Laboratory’s (BNL’s) Waste Management program conducted a pilot test to determine if the solidification of LLLRW was a viable option, both technically and economically. The test determined that it would take approximately 0.18 pounds of solidification agent for every gallon of LLLRW. The solidification of LLLRW using the piloted process resulted in a waste matrix that passed the EPA 9095 paint filter test with no mixing or increase in waste volume. The Treatment, Storage and Disposal Facility (TSDF) waste acceptance criteria (WAC) required that twice the amount of the manufacture’s recommendation, or the amount determined by testing of solidification agent, be used. In order to satisfy this requirement, WM designed the process to use 0.5 pounds of solidification agent per gallon of LLLRW (approximately three times the recommended amount), which provided more than adequate safety margin for the intended solidification process.

Based on the results from the pilot test and detailed review of the WACs, WM began solidifying LLLRW in steel B-25 containers lined with fabricated 10-mil watertight liners. The waste solidification process waste profile was submitted to Envirocare of Utah, Inc. and the Hanford Facility for disposal acceptance. Once approval from the TSDFs was obtained, WM initiated the solidification activities and began successfully shipping solidified LLLRW to the TSDFs.

In June of 2004, the WM program solidified seven B-25 containers of LLLRW for shipment and final disposal at Envirocare. However, the candidate LLLRW for this campaign was slightly different than what was usually solidified and shipped offsite for disposal. This candidate LLLRW was comprised of approximately 300 gallons of geothermal brine waste that contained twenty-five percent (25%) of sodium chloride (NaCl) with a pH of approximately 3.0. WM personnel attempted to solidify this unique LLLRW using the process developed from the pilot test. A batch test was not performed to evaluate the adequacy of the pilot test process on this solution. The pilot test was based on a LLLRW stream with a pH of approximately 6.0 to 7.0 and less than one percent NaCl. For this brine waste, WM personnel observed that the solidification process did not with the same efficiency as the previous waste batches of LLLRW.
that contained less than one percent NaCl. WM personnel stopped solidification activities and informed the Waste Supervisor of the failed solidification. The geothermal NaCl LLLRW remained in the watertight 10-mil liner within the B-25 container for four days as a liquid before it was determined that a batch test should be performed to determine the proper of solidification agent required to successfully solidify the geothermal NaCl LLLRW. The results of the batch test indicated that ten times the amount of solidification agent used in the pilot test would be required to successfully solidify the waste batch. The Operations Manager directed that one hundred and fifty gallons of geothermal LLLRW be pumped into an additional B-25 container equipped with a watertight 10-mil liner and diluted with another aqueous, non-saline LLLRW waste stream with a pH of approximately 7.0. The two B-25 containers were solidified using 5 pounds of solidification/stabilization agent per gallon of geothermal LLLRW.

In July 2004, the subject B-25 containers of solidified geothermal LLLRW were shipped to Envirocare for final disposal. Enroute to Envirocare, while performing an inspection of the transport load at a Wyoming truck rest stop, the driver noticed that a B-25 container had a hairline crack at the weld and was leaking radioactive liquid onto the truck bed.

What happened? How can there be a leak when the liquid waste in question was solidified and placed in a watertight liner. Or was it? What are the recommendations to preclude recurrence? What are the lessons learned?
INTRODUCTION TO SOLIDIFICATION

The Waste Management Program (WMP), a division of the Environmental and Waste Management Services (EWMS) department of Brookhaven National Laboratory (BNL), in January of 2001, was charged with evaluating solidification of Liquid Low Level Radioactive Waste (LLLRW)\(^1\) as a disposal option. During that period waste generators had become concerned about the costs associated with the LLLRW disposal. As a result of the concerns, senior management charged the waste management program staff with evaluating alternative methods for disposing of laboratory aqueous waste. The waste management program staff, with input from waste generators from the laboratory complex, identified three alternatives:

1. Tanker shipments to approved Treatment, Storage and Disposal Facility’s (TSDFs)
2. Evaporation of LLLRW through the tritiated water evaporator system
3. Solidification of LLLRW

Through brainstorming sessions, waste management staff identified three objectives and that must be considered in the decision to choose a cost effective method for the disposal of LLLRW. The objectives were:

- **Disposal Risks and Liabilities** → the waste management program protects the Laboratory from financial, environmental and operational risks. In this case the transportation of solid vs. liquid waste heavily favored solidification of LLLRW.

- **Economies of Scale and Waste Minimization** → use of solidified LLLRW as void fill allowed for cost-saving activities such as maximizing packaging efficiencies, and the ability to achieve lower cost per unit opportunities offered by TSDFs.

- **Waste Disposal Costs** → the objective waste disposal cost savings are the expenditures associated with each of the disposal option alternatives. Although costs savings was the major reason for undertaking this evaluation, the risk and liabilities, and economies of scale played a much larger role in the selection of the LLLRW disposal alternative.

Based on the evaluation with the objectives above in mind, the most favorable alternative identified was the solidification of LLLRW.

**Discussion of Solidification Activities**

In March of 2001, the WMP began developing a solidification process for LLLRW received. The first step performed was to determine or identify specific requirements for acceptance at an approved TSDF; in this case Fluor Hanford was the facility of choice. Hanford’s Waste Acceptance Criteria (WAC) required the following:

1. Product selected for solidification must be on the Hanford site solid waste acceptance material list.
2. Twice the minimum amount of material must be used. Based on the data from the manufacturer or testing.
3. Waste for disposal must not release liquid under 20 pounds per square inch of pressure.
4. All sorbents and stabilizing material must be nonhazardous, compatible with waste, and nonbiodegradeable as defined in 40 CFR 264.314(e).

After identifying and understanding Hanford’s WAC, waste management personnel conducted a pilot test to ascertain the amount of material required for solidification/stabilization of LLLRW activities. The manufacturer recommended adding approximately 0.18 pounds of solidification/stabilization material per gallon of LLLRW. The test consisted of filling two five-gallon screw top buckets with domestic water and adding 0.4 pounds of solidification/stabilization material (more than twice the amount recommended by the manufacturer) to each five-gallon bucket (see Figure 1). One bucket was for mixing and the other would be for non-mixing. The two buckets of solidified water was then sent to an analytical laboratory for testing and to determine if liquid would release under 20 pounds per square inch of pressure.

The results of the analytical laboratory tests led the WMP to the following conclusions:

- 0.4 pounds per gallon of solidification/stabilization material meets the Hanford WAC and provides more than adequate safety margin for solidification of LLLRW.
- Non-mixed and mixed processes provided similar results. Both five-gallon samples were completely free of liquids

![Fig. 1. Five-gallon Bucket Pilot Study](image)

In November of 2001, the WMP staff began the process of developing a waste profile and procedure for solidification activities. The waste profile was to be submitted to Hanford for review and approval, and the procedure was to be used to conduct solidification of LLLRW in a
B-25 container (see Figure 1), which would be subjected to a transportation shake test (driven across the site for an hour to simulate road conditions) and subsequent test at an analytical laboratory to verify no free liquids and compliance with Hanford’s WAC.

Fig. 2. Solidified LLLRW after Shake Test

In February of 2002, Hanford accepted the waste profile for the solidification of LLLRW with one stipulation. The solidification of LLLRW in B-25 waste containers shall include a watertight 10-mil Griffolyn liner (See Figure 2).

In May of 2002, the WMP began the arduous task of solidifying LLLRW; refer to the following for an overview of the solidification process (See Figures 3 and 4).

1. Conduct a pre-job briefing to discuss engineering controls, Radiological Work Permit (RWP) and procedural requirements
2. Obtained/staged the following:
   a. B-25 container
   b. Four-hundred (400) pounds of M2 Polymer Waste Lock 770 Super polymer (increased safety margin to 0.57 pounds per gallon)
   c. 10 mil reinforced Griffolyn water tight liner
3. Install/Place the 10 mil Griffolyn liner in the B-25 container
4. Add one hundred (100) pounds of waste lock 770 polymer to the B-25 container
5. Commence filling the B-25 container at a fill rate of five (5) to twenty (20) gallons per minute. While filling add an additional fifty (50) pounds of waste lock 770 polymer to the B-25 container.

6. When the container is half full or approximately 350 gallons has been added, secure filling and add an additional one hundred and fifty (150) pounds of waste lock 770 to the B-25 container. Continue filling the container until three–quarters full and add an additional fifty (50) pounds waste lock 770 polymer.

7. Fill the container until six (6) inches from the top, carefully add an additional fifty pounds, fold the 10 mil Griffolyn liner into the B-25 container, and place the lid/cover onto the container and clip all ends.

Fig. 3. LLLRW Solidification Activities
PROBLEM DISCOVERY AND CAUSAL ANALYSIS

Problem Discovery – Leaking Container

On July 22, 2004, a shipment carrying eight B-25 boxes of solid low-level radioactive waste left BNL for Envirocare. On Monday morning, July 26, 2004 the driver of a truck carrying a radioactive waste shipment from Brookhaven National Laboratory (BNL) to a disposal facility in Utah (Envirocare Utah) noticed that liquid had seeped from one of eight waste containers on the truck during a required inspection. The driver was at a truck stop on Interstate 80 near Green River, Wyoming, approximately 240 miles from the Envirocare facility. The driver immediately contacted BNL response personnel as specified in the shipping manifest. BNL and DOE management were immediately informed of the incident and actions being taken. At the direction of Brookhaven management, the driver notified local authorities. The driver had last refueled and inspected the truck/load on July 25, 2004 in Cheyenne, Wyoming and observed no leak.

The Wyoming State Police radiological incident responder arrived at the scene, inspected the truck, took radiation measurements, and determined that no active leak was occurring at that time. It appeared that liquid had leaked from the corner of one package onto the truck bed and made a 6 to 8-inch spot on the asphalt beneath the truck. The package in question was determined to contain solidified low-level radioactive brine from a geothermal well experiment at Brookhaven and other radioactive wastewater that had been solidified for "transportation. Based on Brookhaven's knowledge of the low radioactivity concentration of waste in this container from review of the manifest, shipping papers and characterization data, it was believed that there was no hazard to human health or the environment.

At BNL's request, the U.S. DOE Radiological Assistance Program (RAP) team responded from Idaho National Engineering & Environmental Laboratory (INEEL), took radiological surveys at approximately 6 PM, Monday, July 26, 2004. An initial large area wipe survey recorded 30,000 disintegrations per minute (dpm) indicating low-level radiological contamination. It began to rain
during the RAP team's survey. A tarp was placed over the waste load and a berm, approximately 6 to 8 feet in diameter, was built around the spill area on the asphalt.

On Monday evening, July 26, 2004, BNL dispatched a three person team to the scene, including a waste operations supervisor, a transportation specialist, and a health physics technician. Upon arrival at approximately 2:00 PM, Tuesday, July 27, 2004, the BNL team began an assessment and coordinated with the onsite RAP team and Wyoming State Department of Environmental Protection staff. The BNL team had prearranged the delivery of a forklift and "Supersacks" to the scene with the intention of overpacking the container.

By 8:30 PM on Tuesday July 27, 2004 the situation had been resolved. The corner of the package was patched; the package was double overpacked and placed on a second truck en route to Envirocare. The original truck was decontaminated to DOT free release standards and also proceeded to Envirocare. There was no detectable contamination found on the pavement.

**Solidification Container Leak Investigation and Causal Analysis**

On August 24 through 25, 2004, a team consisting of BNL and offsite personnel investigated the contributing and root causes of the leaking container in order to prevent recurrence by providing opportunities to improve existing procedures and processes. The investigation team conducted interviews of affected personnel, reviewed pertinent documentation, conducted bench scale testing, and observed equipment utilized during the solidification operation, including the actual container in question.

The document package review and interviews were conducted to determine the documented facts and establish a timeline of events leading up to the occurrence. The purpose of the bench scale testing and equipment inspection was to clarify the conditions contributing to the leaking container and the failure of the solidification process.

This incident was characterized by tracking the flow of the liquid waste from its entry point into BNL’s Waste Management function, through the solidification process, through its transportation leg, and finally to the discovery of the waste material leaking from the truck.

As the liquid waste material migrated, it had to pass through several barriers before reaching the external environment. The first barrier to fail was the solidification process itself. Then the fluid had to pass through second barrier, which was the liner, into the B-25 box and finally, the fluid exited the B-25 through a corroded weld.

The root causes discovered in the investigation and analysis revolved around problems with materials selection, communications and waste solidification processes.

It is significant to note that the root causes did not represent a breakdown in existing control. Instead, the event and this issue came to light through having to deal with a non-standard waste stream. There was a breakdown in work controls and procurement controls. It was ultimately determined that the geothermal brine waste did not solidify as planned. The waste contained an exceptionally high concentration of salt, which greatly reduces the effectiveness of the solidification agent. This produced a situation in which the waste was left in the liner / container for four days in fluid form. Investigation discovered that the liner, which was previously believed to be water-proof, leaked easily through its seams when holding liquid instead of solidified waste. This allowed the waste fluid to get between the liner and the container.
Later the waste fluid material that was still inside the liner was successfully solidified, but the waste fluid that had already leaked out remained in a liquid state between the liner and the container. The container was stored and eventually shipped. This allowed a low pH / high salt fluid to come and remain in contact with a weld on the container for approximately 37 days. This combined to corrode a hole through a weld on the container and the surface paint, which permitted the leak to occur.

The root and contributing causes discovered were as follows:

1. There was a lack of clear written step by step instructions with sufficient detail to convey the need and responsibility to solidify the brine waste directly in the drums. The actual practice was to discharge the waste drums into the lined b-25 container then solidifying it.
2. During development of the solidification process, BNL Waste Management failed to specify the need for performance testing of the 10 mil griffolyn liner.
3. There was a lack of clear written step by step instructions with sufficient detail to convey the need and responsibility to conduct a bench test prior to solidification of LLLRW.
4. The solidification procedure did not address handling of non-routine liquid waste streams (i.e., require a bench test to determine optimum ratio of waste to absorbent material or neutralization).
5. Although the procurement process did specify water-tight seams, it did not convey the intended use of the liner to the vendor.
6. The solidification procedure did not anticipate batch processing, but rather assumed a homogenous waste stream from large holding tanks.
7. BNL Waste Management did not anticipate the need for a third barrier if the solidification process and liner failed, and therefore did not specify a watertight outer package.

RECOMMENDED ACTIONS/OPPORTUNITIES FOR IMPROVEMENT

Each root and contributing cause was reviewed in a broader sense to gain the most prevention benefit. Suggested opportunities for improvement are summarized below. The causes and deficiencies that led to this event and their corresponding corrective actions can be grouped into three categories.

First, root causes #1, 3, 4, and 6 were all related to deficiencies in the initial solidification procedures or in the implementation of the procedure.

**Root cause #1** dealt with the informality of work instructions delivered during the plan of the day (POD) meeting. Suggestions included that BNL Waste Management could look for areas like this where more formal instructions (i.e. conduct of operations, which include operator turnovers, log keeping practices, communication protocols) could be left by individuals familiar with the proper steps who are not going to be present or available when the steps are carried out.

**Root cause #3** identified a lack of clear, written step-by-step instructions to conduct a bench test prior to waste solidification. Suggestions include revisions to solidification standard operating
procedures to include requirements for bench testing to determine the ratio of absorbent to liquid waste.

**Root causes #4 and 6** indicated deficiencies in the solidification procedure in that the procedure did not 1) address handling of non-routine liquid waste streams (i.e., require a bench test to determine optimum ratio of waste to absorbent material) and 2) the solidification procedure did not anticipate batch processing, as opposed to processing a homogenous waste stream from larger storage tanks. It is important not to assume that waste is always consistent and variable waste constituents or parameters may be present. Again, formally requiring bench-scale testing to determine the appropriate treatment process would be beneficial.

**Root causes #2, 5, and 7** all related to deficiencies in the equipment procurement process and the need for procured equipment to provide a better barrier and include performance testing.

Root cause #2 involved the failure, during development of the solidification process, of BNL Waste Management to specify the need for performance testing of the liner. BNL Waste Management should evaluate all of the materials and equipment in current use for waste processing, identify the necessary functional characteristics of each, and test to ensure that they function as expected. This is related to root cause #5 in that if the procurement process specifies the intended use of the liner and water-tight seams as conveyed to the vendor and performance testing is performed, recurrence should be prevented.

Root cause #7 involved the need for a third watertight barrier incorporated into the outer package or an evaluation of the need for and the appropriateness of container welds. If outer containers also had a coating that would keep fluids from reaching the welds this could prevent recurrence by not allowing the waste fluids to react with and weaken the container / welds.
Opportunities for Improvement
To prevent recurrence and insure that similar events do not occur, BNL waste management program has committed to the following corrective actions and opportunities for improvement:

- Revise solidification and water processing procedures to include bulking of all LLLRW into D-Tanks to obtain a homogeneous mixture, sample and bench testing (determine ratio of absorbent to waste) prior to solidifying LLLRW, Packaging requirements for disposal of solidified LLLRW.
- Develop inspection and acceptance procedure to include inspection criteria guidelines; this includes intended use requirements flow down to suppliers, performance testing of procured items or materials.
- Revise Laboratory Evaluation of Seller QA programs to provide more definitive criteria concerning suppliers of critical off the shelf items
- Develop, document and implement a new packaging system for solidification of LLLRW (include laboratory subject matter experts).
- Establish criteria for LLLRW that does not meet Radioactive Liquid Waste Solidification acceptance criteria’s.
- Provide and document formal conduct of operations refresher training. Training shall include operator turnovers, timely orders, log keeping practices, procedure compliance and communication protocols
- BNL Quality Management office will review all critical off the shelf purchases received over the last two years, and take or recommend actions required to correct deficiencies.

CONCLUSION
The failure to conduct a bench test prior to attempting solidification of LLLRW was the primary root cause in this incident. Waste Management staff did recognize the need for a bench test because the brine was a non-standard wastewater. However, it was not done due to the lack of clear written instructions. The solidification procedure was also developed using routine neutral radioactive waste water, but was applied to a non-standard waste stream in this case. The bottom line is waste generators that intend to or are already solidifying aqueous waste streams for disposal should insure that they have a full understanding of the liquid waste to be solidified, and a packaging system that is approved for the intended solidification operation.

REFERENCES

FOOTNOTES

i See appendix A for LLLRW Solidification waste acceptance criteria
ii Technical Work Document, Liquid Low-Level Radioactive Waste Solidification