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DEMONSTRATING THE ADVANTAGES OF SUPER ABSORBENT POLYMERS FOR STABILIZATION OF TRITIUM CONTAMINATED AQUEOUS DECONTAMINATION SOLUTIONS AT THE MOUND D&D LARGE SCALE DEMONSTRATION AND DEPLOYMENT

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ABSTRACT

The Mound Plant in Miamisburg Ohio was constructed just after WW II to continue its role in the development and production of nuclear weapons that began as part of the Manhattan Project in several separate laboratories in Dayton. From 1947 until the end of the Cold War, Mound played a key role in the production of both nuclear and non-nuclear components of the U.S. nuclear weapons arsenal. With the cessation of nuclear weapons production, Mound has been designated as a site to be closed and turned over to the local community for possible commercial reindustrialization. The shutdown involves a massive D&D effort of Mound's nuclear facilities, some of which are being demolished while others are cleaned up to industrial or free release standards.

The major D&D project is focussed on the tritium processing facilities at Mound with the R/SW Building complex slated for demolition and the T Building scheduled for clean up to free release. This effort will generate a low activity tritium contaminated aqueous waste stream requiring immobilization prior to shipment offsite for disposal. This waste stream is a continuation of a historically generated low level "beta" wastewater from both process and cleanup activities. For several years, this stream was solidified with cement; 25 gallons of water in a 55 gallon DOT Spec 17-H open head drum and shipped offsite for disposal. Within the last two years, an improved fixative agent was deployed that was capable of immobilizing 40 gallons of liquid in a 55 gallon drum using four (4) 50 lb. bags of the fixing agent. This paper reviews the investigation of the innovative use of "super absorbents" to fix this waste stream for shipment and disposal. Such materials are capable of absorbing 100 to 150 times their weight of water. Thus one could potentially immobilize 50+ gallons of water with 3-5 lbs. of absorbent involving no mixing or stirring and a negligible increase in volume.

The material of interest is a member of a family of polyacrylates that have seen commercial applications but have not been utilized for the fixation of drum quantities of radioactive liquids. The Large Scale Demonstration and Deployment Project of the DOE EM-50 D&D Focus Area is partnering with the baseline D&D program at Mound to demonstrate and deploy innovative technologies such as this one that will potentially accelerate the cleanup schedule at Mound, result in significant dollar savings and improved worker safety. The paper will examine bench scale testing that was conducted to identify proper ratios of absorbent to water and full scale non-rad tests in which the process for the timed addition of the absorbent material to the aqueous waste stream was optimized. The demonstration also consisted of environmental testing including vibration tests on the immobilized

waste and observations of the effect of pressure on desorption. The influence of co-contaminants and the effects of other parameters such as temperature and pH were also observed. The solidification of actual drums of tritiated aqueous waste was an important phase of this project. During the full scale demonstration, appropriate data was collected and analyzed by the Army Corp of Engineers to allow an objective comparison of the cost per gallon of liquid absorbed for the baseline and innovative technologies.

The paper will detail the adequacy of performance of these absorbent materials and the significant cost advantage realized by deploying this technology at Mound and at other appropriate sites.

INTRODUCTION

The Program

The Mound Plant located in Miamisburg Ohio was built in 1947 and was the first permanent AEC facility constructed after WW II. Several laboratories in or near Dayton had been part of the Manhattan project and the work at these labs was consolidated and located at the Mound Plant named after a nearby prehistoric Indian mound. The original mission of the facility was to manufacture the neutron source for nuclear weapons. Over the next 40+ years this plant was an integral part of the weapons complex, carrying research, development and production of a number of non-nuclear weapons components including timers, detonators, transducers and firing sets. In addition, the plant carried out important work with tritium processing/handling with regard to thermonuclear weapons developed after the War. Multi-kilogram quantities of tritium were handled in glovebox lines, large process equipment, and miles of tubing and piping. With the end of the Cold war, the Mound Site was selected for shutdown and its weapons production skill sets were transferred to other DOE facilities. The primary objective of the DOE is to close down the site as quickly, cheaply and safely as possible. To that end, the D&D of the tritium facilities is on the critical path for shutdown and represents the largest tritium D&D activity attempted in the DOE complex to date. Significant incentives are tied to the effective cleanup of the tritium process buildings.

The Department of Energy Office of Science and Technology (OST) among its objectives is tasked with supplying innovative and emerging technologies to the line organizations of the Environmental Management Division. As part of a plan to respond to this objective, a program has been established to demonstrate innovative or improved technologies for the D&D of DOE facilities. Known as the Large Scale Demonstration and Deployment Project (LSDDP), the program seeks to conduct demonstrations in a variety of settings such as reactors, laboratories, and processing facilities. The demonstrations also seek to address a wide range of contaminants including plutonium, uranium, highly enriched uranium and tritium. The concept involves identifying and screening candidate technologies, conducting a "real world" demonstration of the technology and evaluating the cost and performance as it compares to the baseline technology that was planned for the operation. The results of the demos are publicized through reports, videotapes, conferences and web sites among other media. The ultimate objective is the deployment to other sites of successful technologies that provide a more cost effective and efficient and /or safe approach to the D&D of contaminated facilities. In early 1998 four new LSDDPs were announced by DOE that included;

- an HEU Fuel Fabrication Facility at the Savannah River Site

- a TRU waste disposition project at LANL
- a Fuel Storage Canals and Underwater/Underground Facilities project at INEEL
- **a Tritium Decontamination and Decommissioning project at Mound**

There were several precursors to the start of the LSDDP at Mound that provided critical pre-project information. These included a 2.5 day Tritium Forum in Dayton hosted by the Mound Plant and held in July of 1997. DOE contractor personnel from a number of sites involved in tritium processing attended. This conference not only laid out the plans for the Mound tritium D&D project but also provide a forum for the identification of current baselines tritium technologies and practices. Discussion panels were active on the topics of characterization, decontamination, dismantlement and demolition, waste minimization, waste packaging, soils and ground waster contamination, and project/program planning. In December of 1997, a major technology exchange meeting was sponsored by DOE and held in Miami. At this symposium, a workshop was organized by Mound personnel that attempted to identify tritium D&D issues and match those with potential technical solutions from the commercial vendors that were present at the conference. These two meeting and other interactions of a less formal nature served to;

1. allow an evaluation and critique of the Mound baseline D&D plan
2. identify issues needing technical resolution (and possibly the application of innovative technology)
3. identify key personnel in the tritium complex that could play a role in the LSDDP

The last objective was the initial activity of the project and identified the companies, facilities and individuals that would form the primary planning group for this demonstration. The DOE contractor members were solicited from sites with tritium handling/processing and with future D&D projects planned. The sites selected were the Savannah River Site, Los Alamos National Laboratory and the Princeton Plasma Physics Lab. Candidates were chosen by their respective labs based upon qualifications provided by the LSDDP leadership that obviously involved experience with tritium and D&D activities.

Commercial vendors were asked to submit corporate qualifications for the D&D of tritium facilities. These were evaluated and a short list was developed of qualified vendors. They were then required to submit a candidate for the IC Team based upon the same criteria and a final selection was made. The commercial members of the Mound IC Team are IT Corp. Foster-Wheeler, BNFL, and of course the contractor at Mound B&W of Ohio who has overall responsibility for managing the project. In addition, Florida International University and the Corp. of Engineers are a part of the Mound IC Team by virtue of the unique role they play/have played in the LSDDP process. The DOE FETC office has overall responsibility for the program and assistance is also provided by the DOE Ohio Field Office and the DOE Miamisburg Environmental Management Program. Activities for the first several months of the Mound LSDDP involved the identification and screening of candidate technologies. These were gathered from a variety of sources including;

- ICT members
- CBD notices
- Booths knowledge/experience of individual at conferences; Spectrum '98, ANS Winter Meeting, WM'99
- Search of websites

The areas/issues for which candidate technologies were sought lined up with topics identified in the Forum and the Miami conference, that is, characterization, decontamination, dismantlement and demolition, waste minimization, waste packaging, soils and ground waster contamination. The Mound Facility is an ideal candidate for a D&D Focus Area Large Scale Demonstration and Deployment Project since its closure requires the D&D of numerous radioactively contaminated facilities. The tritium operations areas in T Bldg. and the SW/R Bldg. complex are on the critical path for the closure project. This means that the deployment of innovative technologies into this baseline project is not only an attractive idea but something that may be required if the projected cost and scheduled are to be met. A member of innovative technology candidates have been identified for potential demonstration in the Mound project ranging from characterization techniques to decontamination methods to preparation of waste for disposal.

The Product

The technology being evaluated in this demonstration is an absorbent for aqueous waste that is representative of a number of polymer based materials that may offer benefits over traditional solidification agents such as cement and the baseline for the Mound project, which is a commercial product called Aquaset®. The properties of the radionuclide of interest in this project is such that significant quantities of tritium contaminated aqueous solution can generated during D&D activities. Waste generators are always seeking solidification agents that provide advantages in performance and/or cost

The solidification of aqueous solutions of relatively low specific activity of the common radionuclides generated in the former DOE weapons complex has historically been carried out using cement or other similar materials such as plaster of Paris. The use of absorbent materials such as vermiculite, florco or other clay based absorbents has also seen use although some disposal sites have periodically restricted certain absorbent materials because of the potential for water at the base of the package to be "squeezed out". Polymer absorbents have been on the market for some time but have seen limited use in radwaste applications. This demonstration will examine the potential advantages of a polyacrylate material that is marketed under the name Waterworks crystals. This product is representative of a family of similar absorbents that have the following characteristics

1. High ratios of liquid to absorbent in the range of 100-150 to 1 by weight.
2. No mechanical mixing required promoting the absorption process.
3. Little or no increase in volume of the waste form. "no swelling"
4. Very high retention in the form of a gel-like material (not pourable like vermiculite)
5. Little or no secondary waste generation
6. Lower weight waste packages

Other polyacrylate products on the market that exhibit similar properties include Stergo® manufactured by the Corpex Technologies Inc. and QUIK-Solid® distributed by CETCO Inc.

The demonstration will validate the performance of the polyacrylate in relation to the baseline technology, document the relative cost of the material per unit of water solidified and track the labor costs for the solidification/absorption operation. While to focus of this demonstration is on the solidification of an aqueous waste stream into 55 gallon open head drums, this material can also find use in a D&D project for incidental moisture associated with sludges, soils and other similar waste forms that may have moisture subject to evaporation/condensation processes.

The work plan is designed to demonstrate the absorbent properties of the candidate material in an actual real time process with actual (not simulated) tritium contaminated aqueous liquid waste from tritium processes at the Mound Plant. In addition to using this material in a side-by-side comparison with the baseline technology, the following additional tests will be carried out to support performance.

- Relevant physical and chemical characteristics of the waste stream will be determined by direct measurement and/or historical data
- Bench scale tests with the Waterworks crystals and real waste will be conducted to observe absorbent performance on other than distilled or tap water
- Full-scale tests will be conducted with distilled or tap water with the absorption step followed by vibration tests simulating over-the-road transport. After a 24-hour vibration test, the waste container will be breached at the base to check for desorbed water.
- Document testing that demonstrates the performance of the absorbent in a variety of environmental conditions such as freeze-thaw and a high radiation field.

DATA COLLECTION

Phase 1 Bench Scale Tests

The first phase of the study involved bench scale testing on various ratios of water to absorbent ranging from 175:1 down to 50:1 by weight. In each case, a 500 ml. Beaker was filled with 350 ml of distilled water at a room temperature of 70°F. The water was measured using a standard 100ml graduated cylinder. The appropriate amount of absorbent was then added to the beaker. The absorbent was weighed out using an electronic analytical balance that had been calibrated in accordance with the Mound QA program for metrology. The purpose of this phase was to identify the properties of the absorbent in varying ratios, observing the rate of solidification ("jelling"), the uniformity of the absorbed material and the properties of the final waste form. A variable of some interest is the rate at which the absorbent is added to the water. At a ratio of water to absorbent of 175:1, the 2 grams of absorbent was added essentially all at once. The absorbent settled to the bottom and began to jell from the bottom up. Within 5 minutes, all of the water had been absorbed. At 100:1, the material was added over a 60 second period and the water was totally absorbed in 170 seconds. At a ratio of 50:1, the 7 grams of absorbent was added in two batches with approximately half added during the first minute and the remainder added over a 15 second period after a pause of 30seconds. In this case, an excess of absorbent was visible on the surface of the absorbed liquid that is some of the absorbent did not react.

After a period of at least 30 minutes, a sample of at least 100 grams was taken from each beaker and a paint filter test was performed looking for the presence of free liquid. EPA test method 9095 was utilized which calls for at least a 100 gram sample placed on 60 mesh filter paper. Any evidence of free liquid in a beaker placed under the glass funnel containing the filter paper and sample is deemed a failed sample. This test method was modified to represent a more severe test by introduced a receptive vertical force vector upon the sample, i.e. the funnel was tapped on the ring stand several times. The results of the paint filter test are shown in table 1.

TABLE 1-Results of paint filter test for Phase 1

Ratio	ml. Liquid	Result
175:1	16	Fail
150:1	8	Fail
125:1	0	Pass

After the first passed test, subsequent samples that contained larger quantities of absorbent were not tested. A final measure of the properties of the bench scale absorbed liquid involved the inversion of the test sample beakers on their sides to observe the "pourability" of the absorbed material. Figure 1 is a photograph of the 100:1 sample and shows a slight deformation of the surface of the material but no flow.

The bench scale tests conducted in phase one of this project provided information regarding which ratios of water to absorbent should be considered for the full scale tests. Furthermore, the experimenter gathered important information about the appropriate addition rate of the absorbent to the liquid.

Figure 1 100:1 Ratio Inverted

Phase 2-Full Scale Tests

Based upon the results of the bench scale testing, the experimenter determined that ratios ranging from 150:1 down to 75:1 would be appropriate for full scale testing. The container size now becomes a DOT 17H 55 gallon open head steel drum. One of the anticipated advantages of the polymer absorbent was the ability to stabilize a larger quantity of water in the waste package. The baseline technology could handle 40 gallons of liquid per 55 gallon drum using Aquaset® as the absorbent material. This was, in fact, a significant improvement over the previous process that used cement to solidify 25 gallons of wastewater per drum. With the polymer, since there was no stirring and no swelling, 53 gallons of liquid per drum was selected as the batch size. The appropriate amount of water and absorbent were measured out on calibrated scales and as with the bench scale tests, the absorbent was distributed over he surface of the water evenly during a time period from 1 to 2 minutes. After a period of at least one hour, a 100+ gram sample was removed from the top of the drum and a paint filter test was conducted. The results of the test are shown in Table 2

Table 2- Results of Paint Filter Test Full Size

Ratio	ml Liquid	Result
150:1	19	Fail
125:1	7	Fail
100:1	0	Pass

No further tests were run after the first pass.
The surface of the absorbed liquid at a ratio of 100:1 is shown in figure 2 for the 55gallon drum. It can be seen that there is little if any flow of material after the sample for the paint filter test has been removed.

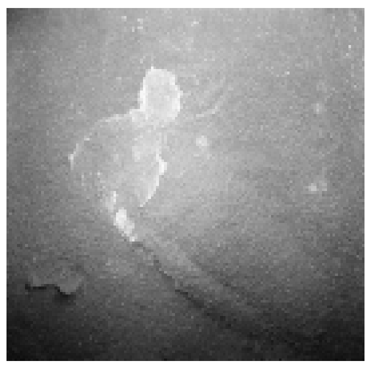

Figure 2 Surface of 100:1 Ratio

In the next part of the full scale test program, the experimenter selected a subset of the five formulations tested and drilled a ¼ inch hole at the base of each drum. Drums containing ratios of 125:1, 100:1 and 75:1 were selected for this test. In each case, a portion of the absorbed liquid was extruded from the hole. Samples of the extruded material were collected for a paint filter test and in each case the sample passed the test. The fact that the sample for the 125:1 passed the test while failing for the sample taken at the top of the same drum demonstrates that there is a variation in the "degree of absorbency" that is a function of the vertical distance from the bottom of the drum since that is where the absorbent material collects and begins to react after addition. Figure 3 shows the extruded material for the 75:1 ratio. This picture was taken approximately 24 hours after the drilling of the hole. Note that there has been no separation of liquid from the absorbent.

Figure 3   75:1 Ratio Extruded Material

The results of the phase 2 study were used to select the final formulation to be used for subsequent environmental tests and in the "real waste" hot operations. While the studies indicated that 75:1 and even 100:1 ratios would probably be satisfactory, waste management personnel wanted an added safety factor. Therefore a ratio of 50:1 was selected for the final testing and full-scale demonstration. This is also consistent with some burial site criteria for absorbed liquids, which require use of 2x the amount of absorbent needed.

Environmental Tests

The vendor for this organic polymer provided documentation on tests that had been previously performed which included a) a freeze-thaw test and b) radiolysis testing. The freeze-thaw tests were conducted by an independent laboratory in accordance with ASTM test method D590-96. Samples were passed through a full ten cycles and then subjected to the paint filter test which they passed. The radiolysis test involved the use of a 7000 Ci Co-60 source that resulted in a total dose of 5.0 megaRads without a significant loss of the ability of the polymer to retain moisture.

Mound personnel contracted with an outside laboratory to subject the preferred formulation of 50:1 with 53 gallons of water in a 55 gallon drum to a series of vibration tests to simulate over-the-road transport to the disposal facility in Clive Ut from Miamisburg OH and to simulate the conditions of repetitive impact from off-normal incidents. The testing protocol used included ASTM test method D999-96 Standard Methods for Vibration Testing of Shipping Containers and ASTM test method D4728-95 Standard Test Method for Random Vibration Testing of Shipping Containers. After the 2 hours of random vibration and vertical impact testing, the lid was removed. There was **no** sign of any water separation as depicted in Figure 4. What the figure does show is a breaking away of clumps of absorbed material from the main body of the absorbed liquid.

Figure 4 Material after vibration tests

A ¼ inch hole was drilled in the base of the drum and a very mall amount of absorbed material was extruded. Again, there was no evidence of free liquid. The top sample easily passed the paint filter test. Insufficient material was available from the bottom, but it is clear that this material was fully absorbed.

CONCLUSIONS

The overall objective of this demonstration was to evaluate the performance of the polymer absorbent and, if its performance were satisfactory, to examine the economics of this material as compared to the baseline. The tests conducted indicated that a 50:1 ratio of water to absorbent provided a waste form that met or exceeded all disposal site waste acceptance criteria. It is able to effectively handle the tritium contaminated waste water at Mound and is also able to handle and immobilize any sludge material that may be found in the bottom of the storage tanks for this waste.

The economics are very favorably as compared to the baseline technology. The cost of Aquaset® is $37.50 per 50 lb. bag in quantities of 720 bags or more. This amounts to a cost of $.75 per lb. The polymer absorbent has an average cost of $6 per lb. in 2000 lb. quantities. Table 3 shows the relative cost of the absorbents for a 55 gallon drum of waste.

Table 3 Cost comparison of the absorbents

Aquaset®	Polymer
40 gallons water	53 gallons water
200 lb. absorbent	8.83 lb. absorbent
$150 of absorbent	$52.98 of absorbent
$3.75 per gallon	**$1.00 per gallon**

In campaigning a 3000 gallon storage tank, the material savings alone would amount to $8250. In addition, there will be some time (labor) savings in the operation of adding 8+ lb. of a polymer absorbent versus adding four 55 lb. bags of Aquaset®. There is also an advantage with respect to the generation of dust fines. Adding the Aquaset® is a fairly dusty process while the polymer material is more granular. The current requirement allows for a 24 hour wait time at the end of which a small amount of absorbent id added to the top of the drum to capture any unabsorbed water. With the polymer process the drum can be sealed after 1 hour.

As a result of this study, Mound is giving serious consideration to replacing the existing baseline technology with the polymer absorbent process