THE SOLIDIFICATION OF LOW LEVEL RADIOACTIVE ORGANIC FLUIDS WITH ENVIROSTONE® GYPSUM CEMENT

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ABSTRACT

The primary method for the management of low level radioactive waste (LLW) has been and continues to be the isolation of the waste in a solid mass. Of the four typical LLW streams, organic fluids pose the most significant waste isolation problem. The organic fluids comprised of lubrication oils, hydraulic fluids, sludges, scintillation fluids, etc., result from the operation and maintenance of nuclear power generating stations, research activities, tooling operations, and diagnostic analyses.

The United States Gypsum Company developed the patented ENVIROSTONE® Gypsum Cement system for the solidification of all types of low level radioactive wastes to facilitate handling and transportation to regulated LLW disposal sites. For the solidification or organic fluids, ENVIROSTONE Gypsum Cement is used in conjunction with ENVIROSTONE® Emulsifier, selected for its ability to emulsify a broad range of organic fluids in aqueous solutions. In the solidification process it is theorized that as the crystalline matrix of the gypsum forms, the micelles of the emulsifier behave as a chemical bridge which draws the organic fluid into the crystalline structure via the hydration water.

Initial testing of physical properties of solidified waste forms, including leachability, per the requirements and the procedures specified for 10 CFR Part 61 as outlined in the Branch Technical Position Report from the United States Nuclear Regulatory Commission were in progress as of the writing of this paper. Upon completion of this testing a Topical Report will be submitted to the USNRC for review and approval.

The presentation reviews field experience in the use of ENVIROSTONE Gypsum Cement for the solidification of low level radioactive organic fluids from nuclear power generating stations and makes an economic comparison between ENVIROSTONE Gypsum Cement and portland cement systems.

INTRODUCTION

Since the inception of the use of ENVIROSTONE Gypsum Cement, this system has been used for the solidification of a wide range of troublesome low level radioactive wastes by production facilities, laboratories, and nuclear power generating stations. The LLW organic fluids resulting from these operations have sparked considerable interest in the product due to its proven performance in the field in handling these waste streams.

The ENVIROSTONE Gypsum Cement system has been successfully used for two years by over twenty utilities, service organizations, and government facilities for the solidification of LLW organic fluids in addition to acidic waste streams, ion exchange resins, and decontamination solutions.

Presented in this paper are the experiences of three nuclear power generating stations with ENVIROSTONE Gypsum Cement. Four examples of solidification projects are presented. Two of the examples represent the use of the product by solidification services organizations under contract to the utilities. The other two examples reflect the experiences of use of the product by the utilities as part of in-house solidification operations. One of the plants is represented under both contracted services and in-house programs. Three different types of solidification equipment are presented to provide a view of the performance of the binder under a variety of use conditions. The experiences described will demonstrate three processes which must be present for the successful management of LLW. These are identification, determination, and communication.

Vermont Yankee Nuclear Station - Vernon, Vermont
Vermont Yankee Nuclear Power Corporation

This site contracted with Numanco, Inc., Pawtucket, Rhode Island, for solidification of approximately 2700 gallons of LLW organic fluids using ENVIROSTONE Gypsum Cement as the waste binder. Included in this lot were lubrication oils, miscellaneous organic fluids, and chelating acids such as EDTA used to decontaminate primary coolant piping. The miscellaneous fluids included engineering solvents, welding release agents, and paint thinners. Also present were residual sludges from freon-based dry cleaning operations.

The solidification equipment consisted of an electrically powered, variable speed mixer. The ENVIROSTONE Gypsum Cement was fed via a screw-type transfer tube from a binder storage hopper. The mixer blade was a cage type arrangement mounted on the mix head. This was raised and lowered using a pneumatic assembly. This set up was scaled for use with 55-gallon drums.

Solidification operations began with bench scale testing of the waste stream. A representative waste sample was drawn for analysis from each of the waste storage containers. These samples were tested for pH, separation, density, light pass, and water content. These results along with ratios developed from prior bench scale solidification tests were then entered into a microcomputer program for scale-up to the 55-gallon mix size. This provided a check for both the plant and Numanco, Inc. support personnel to insure proper proportions were used.

Once the mix ratios were determined, the waste oil was pumped into the 55-gallon drum staged under the mix head. Depending upon the waste composition, the amount varied from 22 to 30 gallons of waste per drum. Next, an addition was made of 2.2 gallons of ENVIROSTONE® Emulsifier followed by sufficient water to bring the total water content in the drum to 12 gallons including the water content of the waste oil.

At this point the mixer was ramped up to about 1600 rpm and operated at this speed for two minutes. When the mixer was stopped, a uniform emulsion was observed.

For the addition of the binder the mixer was initially operated at a low speed up to 50 rpm, which supplied just enough energy to fold the first portions of ENVIROSTONE Gypsum Cement into the liquid. As the binder addition continued the mixer was ramped up in 500 rpm increments. By the time the last of the 300 to 400 lb of binder was loaded, depending upon the composition of the waste, the mixer was operating at approximately 1600 rpm. During the mixing operation the amperage load on the motor was electronically monitored. When the load reached 11 amps the mixer automatically shut down. The mixing unit was then raised, the container was removed, and the next drum was staged.

Concentrations of alcohol solvents exceeding 25% of the waste posed problems in the set or hardening action could be retarded or inhibited. However, the extensive Process Control Procedure (PCP) testing used on this job uncovered these problems during the bench scale testing. Appropriate adjustments and dilutions were made prior to full scale solidifications to prevent difficulties in these operations.

Approximately 110 drums of solidified waste representing 2700 gallons of waste were .ompleted for shipment.

Peach Bottom Nuclear Station - Peach Bottom, PA
Philadelphia Electric Company

Vikem Industries, Inc., Newburyport, Massachusetts, was contracted by this site for the solidification of approximately 17,000 gallons of LLW organic fluids during the period of January to July 1983. Using ENVIROSTONE Gypsum Cement, Vikem was able to solidify waste liquids which included turbine oils, heavy oils (est. 90 wt.), solvents, sludges, and electropolishing solutions. These wastes were generally in the form of mixtures of oil, aqueous fluids, and solids.

The solidification equipment was designed and constructed by Vikem. The mixer was an electrically powered motor which drove a helical auger blade via a hydraulic pump and hose assembly. The blade was designed to fit a 55 gallon drum. Variable speed control was built into the unit. A hydraulic assembly raised and lowered the mixer auger for solidification operations.

Using bench scale testing, mix ratios were verified. For full-scale 55 gallon containers, the ratio was 300 lb ENVIROSTONE Gypsum Cement, 23 gallons waste oil, 2.5 gallons ENVIROSTONE Emulsifier and 12 gallons water.

Operations began with the staging of a 55 gallon drum preloaded with ENVIROSTONE Gypsum Cement under the mixer head and insertion of the auger blade. The mixture of ENVIROSTONE Emulsifier, waste oil, and water was batched in a separate drum.

Once the mixing of the liquids in the separate drum had produced an emulsion, the solution was pumped via the mix head into the drum containing the ENVIROSTONE Gypsum Cement. The auger was turning at slow speed during this addition in order to blend the binder with the waste solution to provide a homogeneous slurry. Once the container was fully loaded, the mixer was ramped up to approximately 60 rpm. This speed was maintained for about 15 minutes for the lighter oils and sludges. The heavier oils required only 4 to 5 minutes of mixing. After the mixing period was completed, the auger was shut down and raised out of the drum, and the next preloaded drum was staged under the mix head. The material generally began hardening within 15 minutes of removal from the mixer.

Miscellaneous liquids such as acetone caused hardening problems when present in sufficient quantities. When this situation occurred the non-set material was diluted into succeeding drums at up to 10% usage.

Approximately 750 drums of solidified waste (17,000 gal of raw waste) were successfully completed for shipment. These included mixtures of acids, water, sludges, and oils as well as pure forms of wastes which were incorporated into the solid casts.

Browns Ferry Nuclear Station - Decatur, Alabama
Tennessee Valley Authority

The job at this site consisted of the solidification of a collection of turbine oils, hydraulic fluids, paint thinners, and miscellaneous liquids. This job served as an evaluation of ENVIROSTONE Gypsum Cement by TVA for the solidification of these wastes. Testing was conducted by plant personnel.

The mixer assembly consisted of a hydraulically driven, electrically powered sweep cage-type mixer blade mounted on a pneumatic arm. The electric motor powered the mix head via a pump and hose assembly.

Each mix began with the pumping off of the water layer in the waste container. This water layer would be used as part of the mix water. After the water layer was removed, approximately 23 gallons of waste oil was pumped into a 55-gallon drum. To this was added 2.5 gallons of ENVIROSTONE Emulsifier and 12 gallons of mix water. The drum was then staged under the mix head, the blade was lowered into the drum, and the solution was mixed for 2 to 3 minutes until a uniform emulsion was observed.

With the mixer turning at low speed, the ENVIROSTONE Gypsum Cement was manually added to the drum. The binder requirement for each 55 gallon mix was 300 lb of ENVIROSTONE Gypsum Cement which was sifted into the drum in 100 lb bag portions. The mixer blade was turning at sufficient speed to maintain a slight vortex during the addition stage. After the binder was fully loaded, the mixer was ramped up to maximum rpm which was maintained for 15 minutes. The mixer was then shut down, the blade was raised, and the drum was removed. Solidification began within 10 minutes of removal from the mixer.

Cleaning of the blade was accomplished by either turning the blade in a drum of water between solidification operations or allowing the blade to clean itself while mixing the emulsion for succeeding drums.

To date, approximately 75 drums of solidified waste have been shipped. Waste streams containing a high percentage of paint thinners caused set problems which was solved by dilution of the slurry into succedding drums at up to 20% usage. The plant has put in place a system which requires analysis of waste organic fluids prior to entry into the storage area for LLW radwaste prior to solidification. This analysis gives personnel a better grasp of the characteristics of the waste stream prior to the actual solidification, thus allowing the appropriate segregation and dilution measures to be taken.

Peach Bottom Nuclear Station - Peach Bottom, PA
Philadelphia Electric Company

Following the completion of the oil solidification conducted by Vikem Industries for the Peach Bottom job site, the mix unit was purchased by the utility for future solidification of LLW organic wastes which are to be handled by the plant radwaste department. The second job entailed in excess of 11,000 gallons of waste which included electrohydraulic control oil, snubber oil, lubrication oils, (44 wt. and 32 wt.), solvents (acetone, carbon tetrachloride, trichloroethane), and miscellaneous liquids such as transmission fluids, kerosene, and gasoline. Sludges from pumping down of sumps and concentrated mixtures of 85% phosphoric and 15% sulfuric acid were also present.

As previously stated, the equipment used was the same equipment used by Vikem. The electric motor drove a hydraulic mix head turning a helical auger blade, sized for 55-gallon drums.

The same binder to waste ratios were also used by plant personnel. For a 55 gallon drum the ratio used was 300 lb ENVIROSTONE Gypsum Cement, 23 gallons of waste oil, 12 gallons of water and 2.5 gallons of ENVIROSTONE Emulsifier.

The mix drum was staged under the mix head after being preloaded with ENVIROSTONE Gypsum Cement. The mixture of waste oil, water and ENVIROSTONE Emulsifier were batched and emulsified in a separate drum. The emulsion was then pumped into the mix drum while the auger was turning at sufficient speed to uniformly disperse the binder. Once fully loaded, the auger was then ramped up to approximately 60 rpm. Depending on the waste, the speed was maintained for 15 to 30 minutes. Initial hardening occurred within 30 to 45 minutes with hard dry casts observed within 24 hours.

Acetone which was detected in some of the waste streams presented set inhibition effects in this operation which resulted in the presence of liquid on top of a hard cast. Sectioning of eight drums revealed this to be a top surface phenomena. The problem was overcome by decanting off the layer of liquid and dilution in subsequent drums. When acetone presence was determined in Process Control Procedure testing prior to full scale solidification, the waste was either diluted with other waste streams or evaporated to sludge in a monitored process. The sludge was then solidified with the other wastes. There was only one drum which gelled and did not solidify. The gel was diluted in subsequent drums to complete solidification.

In all, 1,408 drums of solidified waste, including those from the Vikem operation were shipped to the Washington disposal site.

ECONOMIC COMPARISONS

In order to discuss the economics of selected waste management processes, several factors must be considered in addition to the cost of the material (i.e. solidification media). Labor charges, manhour requirements, freight rates, burial charges, and state fees must all be brought into the cost evaluation. The impact of any one of these factors will vary depending on the location of the waste generator, the type of waste under consideration, and the location of the disposal site.

Table I was assembled as being representative of these costs as they pertain to solidification of low level radioactive waste oil in 55-gallon drums using either portland cement or ENVIROSTONE Gypsum Cement. Based on previous experience the situation presented is the shipment of one 80-drum truckload of solidified waste oils from Illinois to the Washington disposal site. The comparison was made between the costs per gallon of liquid waste solidification using portland cement (at 12 gallons of waste oil per 55-gallon drum) and solidification using ENVIROSTONE Gypsum Cement (at 23 gallons of waste oil per 55-gallon drum). In summary, the use of ENVIROSTONE Gypsum Cement as the solidification media results in an overall cost savings of $4.09 per gallon of waste solidified and shipped.

TABLE I

Economic Comparison Data - Waste Oil Solidification

	Portland Cement	ENVIROSTONE Gypsum Cement
Fixed Costs		
Transportation	$ 3,377.50	$ 3,377.50
Burial Fee	$10,320.00	$10,320.00
Drums-80 drums @ $30	$ 2,400.00	$ 2,400.00
Labor	$ 2,000.00	$ 2,000.00
Total Fixed Cost/Truckload	$18,097.50	$18,097.50
Total Fixed Cost/Drum	$ 226.22	$ 226.22
Gallons Waste/Drum	12	23
Total Fixed Costs/ Gallon Waste	$ 18.85	$ 9.83
Variable Costs		
Binder (freight, binder, emulsifier, etc.)	$ 12.00	$ 136.00
Miscellaneous	$ 2.00	$ 4.00
Total Variable Costs	$ 14.00	$ 140.00
Gallons Waste/Drum	12	23
Total Variable Cost/ Gallon Waste	$ 1.16	$ 6.09

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TABLE I
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Economic Comparison Data - Waste Oil Solidification

	Portland Cement	ENVIROSTONE Gypsum Cement
Totals		
Total Fixed Cost/ Gallon Waste	$ 18.85	$ 9.83
Total Variable Cost/ Gallon Waste	$ 1.16	$ 6.09
Total Cost/Gallon Waste	$ 20.01	$ 15.92
Results		
Gallons Waste/Truckload	960	1,840
Savings/Gallon Waste	--	$ 4.09

October, 1983 Costs

CONCLUSION

In summation, the field experiences in waste organic fluids solidification presented here have demonstrated three processes which must be present for the successful management of these wastes, indeed of all low level radioactive wastes. The processes are identification, determination, and communication.

Identification of the characteristics and composition of the waste is essential. Due to the increasing complexity of chemical systems, the days of simply throwing the binder into the waste and mixing are long gone. This function can be aided by documentation by the waste generator of the source of the waste in the storage containers. This serves as a guide for the solidification personnel as to the types of tests to be run on the waste. In this way any potential problems can be identified in the Process Control Procedure testing, thus allowing for adjustments prior to the actual full scale solidification runs.

The second factor is determination of mix parameters. In the field this has best been accomplished by bench scale testing of the waste stream using waste/binder ratios representative of the full scale operation. Again the objective is to sort out any potential problems before dealing with the larger volumes associated with the full scale mixes.

Finally, communication among all of the parties involved in the operation must be open and timely. Each of the parties involved has experience and expertise within its sphere of operation which must be recognized and utilized. Information such as the sources of waste, special solidification requirements, segregational needs, and operations support requirements must be shared in order to fully assess the situation and develop a proper manner of solidification. The waste generator, the solidification organization, and the manufacturers of the solidification media must all cooperate in this process. In this way a working environment is created which fosters the open generation of alternate solutions, thereby presenting the best available method for the safe and effective management of low level radioactive wastes.