

TREATABILITY STUDY OF ABSORBENT POLYMER WASTE FORM FOR MIXED WASTE TREATMENT

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ABSTRACT

A treatability study was performed to develop and characterize an absorbent polymer waste form for application to low level (LLW) and mixed low level (MLLW) aqueous wastes at Argonne National Laboratory-West (ANL-W). In this study absorbent polymers proved effective at immobilizing aqueous liquid wastes in order to meet Land Disposal Restrictions for subsurface waste disposal. Treatment of aqueous waste with absorbent polymers provides an alternative to liquid waste solidification via high-shear mixing with clays and cements.

Significant advantages of absorbent polymer use over clays and cements include ease of operations and waste volume minimization. Absorbent polymers do not require high-shear mixing as do clays and cements. Granulated absorbent polymer is poured into aqueous solutions and forms a gel which passes the paint filter test as a non-liquid. Pouring versus mixing of a solidification agent not only eliminates the need for a mixing station, but also lessens exposure to personnel and the potential for spread of contamination from treatment of radioactive wastes. Waste minimization is achieved as significantly less mass addition and volume increase is required of and results from absorbent polymer use than that of clays and cements. Operational ease and waste minimization translate into overall cost savings for LLW and MLLW treatment.

The treatability study of absorbent polymer waste forms involved bench-scale and full-scale treatment of actual and surrogate MLLW streams. Bench-scale test analyses included thermal cycling, free-liquids testing, and metal immobilization via Toxicity Characteristic Leaching Procedure (TCLP) for particular metals. A full-scale test was conducted with surrogate waste in a 55-gallon drum to verify scale-up of the process and to validate operations for large volume waste treatment. Results of the treatability study for absorbent polymer waste forms are compared and contrasted against previous solidification experience at ANL-W with clays and cements and with absorbent polymer experience at another waste treatment facility.

An absorbent polymer waste form was developed for immediate application to treat 2500 gallons of aqueous MLLW stored in 55-gallon drums at the Sodium Component Maintenance Shop (SCMS) at ANL-W, as well as aqueous sodium carbonate solution resulting from sodium deactivation of Experimental Breeder Reactor II systems and components. The SCMS is a Resource Conservation and Recovery Act (RCRA) permitted treatment facility for MLLWs, carrying RCRA codes D001 through D0011. Based on the success of the treatability study, minor facility modifications are underway at the SCMS to implement the use of absorbent polymers for LLW and MLLW treatment.

INTRODUCTION

The purpose of this activity was to develop and characterize an absorbent polymer waste form for potential application to aqueous wastes in the Sodium Components Maintenance Shop (SCMS) at ANL-W, and specifically to a Naval Reactors Facility (NRF) Evaporator Bottoms Tank liquid waste.

ANL-W received approximately 2500 gallons of NRF liquid waste in fifty-six, 55-gallon drums in January 1999. The liquid is a mixed waste — radioactive, corrosive, and toxic with EPA waste codes D002 and D008 — and contains Underlying Hazardous Constituent (UHC) metals. The waste drums will be treated in SCMS, which is a RCRA permitted treatment facility. Treatment of the NRF waste shall produce a final form which is non-hazardous and meets Land Disposal Requirements (LDR) for subsurface disposal at the Idaho National Engineering and Environmental Laboratory (INEEL) Radioactive Waste Management Complex (RWMC). This necessitates a pH in the final waste form of between 2 and 12.5 and immobilization of the liquid and UHC metals to meet free liquid testing requirements and Universal Treatment Standards (UTS), respectively (1).

Prior experience with treatment of a similar mixed waste, i.e. a corrosive and UHC metal-containing aqueous waste from deactivation of the EBR-I NaK, involved lowering the pH of an aqueous alkaline solution to less than 12.5 and solidifying the waste in 55-gallon drums with Aquaset II-H (2). Solidification with Aquaset II-H (a clay and cement composite produced by Fluid Tech, Inc.) was effective at immobilizing the liquid and UHC metals and the final waste form met LDR. However, the solidification process was labor intensive, due largely to the necessity of high-shear mixing of the Aquaset with the waste solution under radiological controls.

With the overall goal of easing operations and consequently minimizing radiation exposure to personnel, alternate treatment technologies for aqueous wastes were pursued. Specifically, absorbent polymers exhibited an application for treatment of SCMS aqueous wastes, which does not require mixing. The common component of absorbent polymers from various suppliers is sodium polyacrylate which assimilates water and dissolved ions to form a gel. With adequate absorbent polymer loadings, liquid wastes can be immobilized and meet free liquid test requirements. Furthermore, appropriate control of pH and UHC metals along with adequate addition of absorbent polymers has the potential to convert SCMS aqueous mixed waste into a non-hazardous form and meet LDR.

WASTE CHARACTERIZATION

The NRF evaporator bottoms tank contained a two-phase aqueous matrix — a liquid saturated with dissolved solids and a bottoms sludge of precipitated or insoluble solids. Sampling and analysis was performed on the NRF evaporator tank liquid. During this procedure NRF personnel recirculated the liquid within the tank and acquired representative samples. Sample analyses were performed by a third-party analytical laboratory. The pH of the liquid was

approximately 13.3 and the highest concentrations of UHC metals per the test method for total metals (3,4) are listed in Table I.

The NRF evaporator bottoms tank liquid was loaded into fifty-six, 55-gallon drums containing a rigid poly liner for a nominal liquid loading of 45 gallons per drum. The NRF evaporator tank liquid was recirculated when the drums were loaded. The drums exhibited radiation levels on contact with the drums at 8 to 18 mR/hr. A liquid sample was extracted during the filling operation of the drums and sampled by ANL-W analytical laboratory for independent verification of analyses per TCLP (5). Results of UHC metal concentrations from this verification analysis are also listed in Table I.

Table I. NRF Liquid Waste Sampling and Analyses

Sample source	Recirculated evaporator liquid prior to drum filling	Representative sample of bulk liquid during drum filling
Chemical analysis agency	independent third-party analytical laboratory	ANL-W analytical laboratory
Sample procedure	TM (mg/kg)	TCLP (mg/l)
Antimony (Sb)	4.2	--
Arsenic (As)	4.0	--
Barium (Ba)	0.09	--
Beryllium (Be)	0.04	--
Cadmium (Cd)	0.59	0.18
Chromium (Cr)	1.1	0.40
Lead (Pb)	4.7	8.1
Mercury (Hg)	0.06	0.03
Nickel (Ni)	56.2	53.5
Selenium (Se)	0.30	--
Silver (Ag)	0.60	<0.04
Thallium (Tl)	0.18	--

TM: Total Metals; TCLP: Toxicity Characteristic Leaching Procedure; (--): No Analysis Performed

Assessment of NRF Liquid Waste Treatment with Absorbent Polymers

Immobilization of UHC metals by absorbent polymers may be largely accomplished by merely solidifying the liquid. Significant additional retention of UHC metals by absorbent polymers via chemical binding or encapsulation was not expected. Hence, a simple approach to estimate maximum expected UHC metal concentrations in an absorbent polymer waste form is to apply a

20 to 1 decontamination factor, which accounts for immobilization of the liquid waste and subsequent application of TCLP for determination of UHC concentrations (5). This approach conservatively assumes a specific gravity for an aqueous waste of 1.0 and neglects any mass addition from the solidifying agent. By applying the 20 to 1 decontamination factor to representative NRF metal concentrations and proportioning the results to UTS, constituents of concern may be identified, as shown in Table II. The analysis within Table II suggests that absorbent polymers should be appropriate for the 56 drums of NRF liquid waste with lead as the limiting constituent.

Table II. Assessment of NRF Liquid Waste Treatment with Absorbent Polymers

Source term	UTS (mg/ℓ TCLP)	Bulk liquid waste — represented by highest observed UHC metal concentration in liquid waste from third-party and ANL-W analyses		
Sample form	NA	Maximum observed UHC metal concentration in <i>pre-treated liquid</i>	Maximum expected UHC metal concentration in <i>post-treated gel</i> with 20:1 DF	% of UTS*
Sb (mg/kg)	1.15	4.2	0.21	18%
As (mg/kg)	5.0	4.0	0.20	4.0%
Ba (mg/kg)	21	0.43	0.022	<1%
Be (mg/kg)	1.22	0.04	0.002	<1%
Cd (mg/kg)	0.11	0.59	0.030	27%
Cr (mg/kg)	0.60	1.1	0.055	9.2%
Pb (mg/ℓ)	0.75	8.1	.41	54%
Hg (mg/kg)	0.025	0.06	.003	12%
Ni (mg/kg)	11.0	56.2	2.81	25.5%
Se (mg/kg)	5.7	0.30	0.015	<1%
Ag (mg/kg)	0.14	0.60	0.030	21%
Tl (mg/kg)	0.20	0.18	0.0090	4.5%

NA: Not Applicable; TCLP: Toxicity Characteristic Leaching Procedure; DF: Decontamination Factor;
 *assumes a liquid waste specific gravity of 1.0 and neglects any mass addition from the absorbent polymer

In order to remove the corrosive characteristic the pH would need to be adjusted from 13.3 in the liquid waste to between 2 and 12.5 as measured by a pH meter in the treated waste. This could be accomplished in two ways — by acid addition to lower pH within the appropriate range prior to absorbent polymer addition, or by absorbent polymer addition alone. Thus, in order to address the mode of pH adjustment as well as UHC metal immobilization, bench-scale testing was performed with the NRF liquid waste.

BENCH-SCALE TESTING

Samples were taken randomly from 5 of the 56 drums, as well as drum 56, thus representing approximately 10% of the waste containers. Bench-scale waste forms were prepared from each of the 6 samples of NRF liquid. Waste form preparation involved adding 200 ml of NRF liquid to each of 250 ml clear glass jars. In the first 3 samples approximately 14 ml of 3N nitric acid was added to each jar, in order to lower pH to ≤ 11.5 . In the latter 3 samples no acid addition was performed. The liquid waste samples were a transparent brown and no precipitate or suspended solids were observed. To each of the 6 solutions, 15 g of absorbent polymer (sodium polyacrylate produced by Stockhausen) were added and allowed to stand for 7 days. Each sample gelled quickly after absorbent polymer addition, i.e. within 10 minutes of the polymer addition no free liquid was observed and each jar was inverted and no movement of the gel occurred. The appearance of each of the sample waste forms was indistinguishable.

Sample analysis included free liquid testing and determination of pH and lead concentrations from each of the samples. Free liquid testing subjected the sample to 7 thermal cycles of reduced temperature at -50°F and elevated temperature at 110°F followed by paint filter testing in accordance with RWMC procedures. Lead concentrations were determined by TCLP and pH by a calibrated meter. The results of bench-scale testing with the actual NRF liquid waste are shown in Table III.

Table III. Results of Bench-Scale Testing with NRF Liquid Waste

Drum sampled	Vol. of 3N HNO ₃ added (ml)	pH of gel	paint filter test (pass/fail)	TCLP for Pb (mg/l)
2	14	9.34	pass	0.35
12	14	9.04	pass	0.34
34	14	9.31	pass	0.36
38	0	10.43	pass	0.67
25	0	10.43	pass	0.39
56	0	10.45	pass	0.39

This bench-scale testing characterized the ability of absorbent polymers to adequately treat the NRF liquid waste to meet LDR. Absorbent polymer addition alone was sufficient to lower pH to less than 12.5. After 7 thermal cycles the waste forms exhibited no free liquid and lead concentrations met UTS. Absorbent polymers were added to these bench-scale test samples in a loading ratio equivalent to 30 lbs of polymer per NRF waste drum with a maximum loading of 47 gallons. Thus, the next step in developing the application of this waste form to the NRF liquid was to verify the prescribed loading ratio at full scale with a surrogate waste solution.

FULL-SCALE SURROGATE TESTING

In order to qualify the operations and performance of NRF liquid waste treatment with absorbent polymers, a surrogate solution was prepared in an actual 55-gallon drum and liner. This full-scale test incorporated a drum vibrator to ensure adequate wetting of the absorbent polymer upon addition. The prescribed absorbent polymer loading was a minimum of 30 lbs per drum of surrogate solution, but allowed for up to 50 lbs. The purpose of the test was to verify the adequacy of drummed waste treatment operations and ensure that the final waste form would be consistent throughout the drum and absent of free liquid.

The NRF surrogate solution was prepared with constituent concentrations representative of the significant dissolved solid ion concentrations (i.e. relative concentrations >1%) in the NRF liquid waste, as characterized by the third-party analytical laboratory. To prototype the concentrations for the significant constituents of concern in the NRF liquid waste, the following chemicals were added to raw water (for a total solution weight of 368 lbs.) within a 55-gallon drum and liner and mixed with a drum vibrator: 1) 172 g of CaO; 2) 940g of K₂SO₄; 3) 29 g of KOH; 4) 508 g of NaCl; 5) 7960 g of Na₂CO₃; and 6) 1070 g of NaOH.

The pH of the surrogate solution prior to absorbent polymer addition was 12.9 with a pH meter. Absorbent polymer was added to the vibrating surrogate solution through the large (2 in.) bung hole. The drum vibration precluded the polymer from "gel-blocking," i.e. dry polymer floating on top of a gelled underlayment at the liquid surface. Over 30 lbs. of polymer were added through the large bung, after which dry polymer filled to the bottom of the bung hole. A smaller quantity of polymer was subsequently added through the small bung hole until the polymer likewise filled to the bottom of the small hole. In all, 34.9 lbs. of absorbent polymer were poured into the surrogate solution within a 15 minute period while the drum was vibrating. No free liquid was observed through the bung holes after the addition was complete. The drum was allowed to vibrate for an additional 15 minutes, after which the drum vibrator was stopped and a core sample was taken. The pH of the sample was measured at 9.1 with a pH meter. The drum was sealed and allowed to stand for 7 days, after which the drum liner was removed and inverted, i.e. top down. The bottom of the drum liner was cut and removed. No free liquid was observed at the bottom of the drum and the product was observed to be consistent throughout the drum.

DISCUSSION

For treatment of the particular aqueous mixed wastes at ANL-W a satisfactory absorbent polymer waste form requires the following functions — appropriate adjustment of pH, adequate retention of UHC metals, and immobilization of the bulk free liquid. The following discusses each of these functions, including absorbent polymer performance in relation to clays and cements and another facility's experience with the polymer waste form, as applicable.

Corrosive Characteristic

Although waste treatment with absorbent polymers result in waste forms absent of free liquid per paint filter testing, the resultant gel remains an aqueous matrix and is, consequently, subject to D002 pH determination and restrictions, i.e. via pH meter to between 2 and 12.5. Bench-scale and full-scale tests identified the ability of absorbent polymer addition alone to lower pH. This is based on two possible contributing factors. First, absorbent polymers are formed from sodium polyacrylate, which is a derivative of acrylic acid. Absorbent polymer product information from manufacturers identifies a potential residual of acid in the polymer and a slightly acidic condition of absorbent polymer when wetted with an initially neutral solution. Thus, absorbent polymers may provide some neutralizing effect for basic solutions to lower the pH. Second, absorption of aqueous liquid by absorbent polymers to form a gel can suppress the ionic activity of the waste matrix, resulting in a lower pH reading with a pH meter. Regardless of the mechanism, the pH of test solutions was lowered to non-hazardous levels following absorbent polymer addition, i.e. actual NRF liquid waste at a pH of 13.3 was lowered to approximately 10.5 and the full-scale surrogate solution was lowered from 12.9 to 9.1 as indicated by pH meters.

Leaching of Underlying Hazardous Constituent Metals

The initial assessment of absorbent polymer application to the NRF liquid waste conservatively assumed that the polymer gel would immobilize UHC metals merely by immobilization of the aqueous liquid. Bench-scale testing suggests that such an assumption is consistent with the observed leaching of lead. Specifically, the maximum expected concentration of lead per TCLP in the bench-scale waste forms given conservative physical properties was 0.41 mg/l. The actual test results ranged from 0.34 to 0.39 mg/l. However, the outlier concentration of 0.67 mg/l questions the validity of either the 8.1 mg/l lead concentration as representative of the bulk liquid, or the analytical technique. In contrast, substantially higher retention of UHC metals have been observed with Aquaset II-H addition to aqueous wastes. For comparison, a basic solution with lead at 114 mg/l was solidified at ANL-W with Aquaset II-H and leached at 0.37 mg/l per TCLP (2). Thus, in relation to other solidifying agents, absorbent polymers are less capable of binding UHC metals.

Liquid Immobilization

Since the absorbent polymer forms a pliable gel as opposed to a rigid monolith such as clays or cements, its appearance may be better described as a semi-solid rather than a solid. Nevertheless, LDR for waste disposal at RWMC define the acceptance of the waste form not as a rigid solid, but rather that from which no free liquid is released via paint filter testing following thermal cycling. The qualified absorbent polymer waste form for treatment of NRF liquid has demonstrated the ability to meet disposal requirements. However, the non-rigid waste form of an absorbent polymer gel has raised skepticism about its ability to retain moisture, particularly under stressed conditions. Specifically, a Fernald study involved extensive experimentation of performance with various absorbents including clay, lime, diatomaceous earth, and absorbent polymers (6). The study identified limitations in the performance of absorbents with a particular Fernald waste package, based on subjection of the waste forms to freeze/thaw cycling, thermal degradation, and vibration. Since the study did not include the particular absorbent polymer proposed for treatment of the NRF liquid and since waste solution to polymer loading ratios differed, additional experiments were conducted at ANL-W to address disparate conclusions.

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A review of the Fernald study and results of additional testing at ANL-W identified a fundamental difference in the waste matrix and consequent solution to polymer loading ratios between the particular Fernald waste package and the proposed NRF liquid waste treatment. The Fernald waste package involved a heterogeneous matrix of discrete absorbent layers and water-laden sludge. This configuration entailed experimentation of absorbents which were saturated with aqueous test solutions, i.e. solution to polymer loading ratios ranged from 20:1 to over 250:1. In contrast, the proposed treatment of NRF waste would yield a homogeneous matrix which is subsaturated, i.e. solution to polymer loading ratios would range from 7:1 to 12:1.

Portions of the Fernald experiments were duplicated at ANL-W to include the proposed absorbent polymer and the prescribed loading ratio for NRF liquid waste treatment (7). The results of the tests with the prescribed subsaturated loadings met performance criteria, i.e. no free liquid was observed.

CONCLUSIONS

From the bench-scale testing with actual NRF liquid waste and from the full-scale testing with a surrogate solution, it was concluded that the absorbent polymer can effectively treat the 56 drums of NRF liquid waste into a non-hazardous, low-level waste form that will meet LDR and will, therefore, be compliant with RWMC waste acceptance criteria. The absorbent polymer was observed to produce a lower pH in the final gelled waste form, as compared to the initial pH of the liquid waste. Thus, the absorbent polymer can be applied to the NRF liquid waste without prior pH adjustment with acid. In particular contrast to Aquaset II-H, absorbent polymers are less capable of immobilizing UHC metals. Nevertheless, the UHC metal concentrations in the NRF liquid waste are low enough that absorbent polymers can adequately immobilize these constituents to below UTS. Vibration of the liquid waste during treatment in 55-gallon drums displayed a significant advantage in wetting the absorbent polymers upon addition and producing a waste matrix that was consistent throughout the drum and absent of free liquids.

Since the absorbent polymer waste form has met performance criteria as identified in this treatability study, its application for treatment of the NRF liquid at ANL-W is being pursued. Minor facility modifications are underway at the SCMS to provide a drum vibrating station and an absorbent polymer delivery system to implement the use of absorbent polymers for LLW and MLLW treatment.

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