WSRC-TR-2002-00189, Revision 0
April 16, 2002

Key Words: **Zinc Bromide Waste**
Solidification

Retention: **Permanent**

Aqueous Zinc Bromide Waste Solidification (U)

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Report Date: April 16, 2002

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Report Date: April 16, 2002

REVIEWS AND APPROVALS

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C. A. Langton, Savannah River Technology Center   Date

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G. M. Iversen, SCUREF, Savannah River Technology Center   Date

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B. T. Butcher, Level 4 Manager, SRTC   Date

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J. K. Denny, Facility Decontamination and Decommissioning Division   Date

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B. T. Butcher, Technical Review, Savannah River Technology Center   Date

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LIST OF ACRONYMS AND ABBREVIATIONS

CIG	Components in Grout
CIF	Consolidated Incinerator Facility
DOE	Department of Energy
SCUREF	South Carolina University Research and Education Foundation
SRS	Savannah River Site
SRS (E-Area)	Savannah River Site E-Area
SRTC	Savannah River Technology Center

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1.0 INTRODUCTION

Approximately 12,500 gallons of non hazardous, low-level radioactive solution are currently stored in two of three rail tank cars located on a rail spur west of the l05 C reactor building. The solution is neutralized zinc bromide solution that was removed from shielded cell windows. The solution in the two tankers is a low-level radioactive liquid. It is not classified as RCRA hazardous waste. Solidification in the tankers currently used to store this solution is a treatment option for final disposal in E-Area that is currently being considered by FDD. Chemical analyses of the solution and additional background information are provided elsewhere [1].

Treatment and disposal of the zinc bromide solution is a WSRC FY02 performance based initiative (PBI). FDD personnel selected organic polymer sorption as the preferred treatment method for disposal in the existing tankers. The criteria included the following:

- Organic sorbents produce light-weight waste forms which minimize the stresses on the aged tankers during filling and transportation to E-Area. In addition, the weight of the disposal package (two railcar tankers) does not exceed the weight limit for the E-Area crane. Therefore, they can be placed in a trench using existing crane(s) and procedures.
- Organic sorbents provided effective solidification of the waste solution.
    - no free water or drainable water
    - no liquid expression at 50 psi
    - absorption preferred to surface adsorption
    - moderate to rapid solidification rate
- Processing and packaging the final waste form does not require extensive mixing.
    - The solidification process will be engineered and carried out by FDD engineers and operators.
- The organic sorbents are cost effective.

Since the tankers also require disposal, FDD is pursuing using the tankers as disposal containers in keeping with the waste minimization effort at SRS. W. Hinz, NDE/WSRC, performed a nondestructive structural evaluation of the tankers. The results support the use of these rail tankers as disposal containers [2]. The tankers are identified as:

Railcar #1 TVA X 306 (SRO5843) contains about 55 inches of liquid or about 5230 gallons.
Railcar #2 TVA X 310 (SRO 5844) contains about 75 inches of liquid or about 7140 gallons
Railcar #3 TVA X 311 (SRO 5847) empty, contents repackaged in 55 gallon drums and stored in the N- Area Hazardous and Mixed Waste Storage Facility.

The current plan is to pump the zinc bromide solution from railcars 1 and 2 into a tank supplied by FDD then use each of the three rail cars as disposal containers of the solidified waste form. The rail cars will be disposed of as Components In Grout (CIG) in E-Area.

1.1 Objective

The goal of this study was to:
1. Select one or more commercially available aqueous sorbents to solidify the zinc bromide solution stored in C-Area.
2. Identify the polymer to zinc bromide solution ratio (waste loading) for the selected sorbents.
3. Identify processing issues that require further testing in pilot-scale testing that is being conducted by T. M. Jones, IT, and J. R. Gordon, EES.

1.2 Approach

The approach was to acquire several commercially available aqueous sorbents and to evaluate them with water. The results were compared to the vendor claims and recommendations. The most promising polymers were evaluated with the zinc bromide waste solution. The sorbents tested in the bench-scale studies are listed in Table 1-1. The sorbents with the highest waste loading and the best waste form processing and final properties were recommended for scale-up testing which is reported elsewhere [3].

Table 1-1. List of polymer sorbents, vendors and product descriptions.

Vendor	Products	Description	BulkDensity g/cc (lb/ft^3)	Estimated Cost ($/unit)
Aquadox Robert S. Wright 630-964-1300	AquaSorbe 2212 for heavy brines	Organic Polymer, Coarse particles more cross-linked than Aquadox HP	0.5 to 0.8 (31-50)	$4 to $5/lb max no bulk discount
	Aquadox HP	Organic Polymer Fine particles	0.5 to 0.8 (31-50)	$3.50/lb max 50 lb bags $2.75 to $3.00 for bulk discount
Cetco Allen Bullock 800-527-9948	Instasorb	Organic polymer and clay mixtue,.black and white fine particles, pasty, may require high shear mixing	1.04 (65)	$1.05/lb 44lb sacks 500 lb super sacks
	QuickSolid	Organic polymer Fine particles	0.67 (42)	$1.85/lb
M^2 Polymer Technologies Inc. M. Matushek 847-836-1393	Waste Lock 770	Organic polymer, fine particles, few dark particles, Cross linked Na polyacrylate	0.5 to 0.7 (31-44)	$2.35/lb
Water Works America 440-725-5987	Water Works SP 400	Na Polyacrylate	0.62 (40)	$4.80/lb < 10 bags $4.40/lb < 35 bags $2.30/lb truck

1.3 Background Information the Use of Aqueous Sorbents

Super absorbents are currently being used to solidify low-level radioactive and/or hazardous waste solutions in the nuclear industry. For example, a number of DOE sites including Los Alamos, Mound, Oak Ridge Y-12, Paducah, and the Savannah River Site have used organic sorbents for solidifying radioactive aqueous waste streams. Los Alamos used AquaSorbe 2212 to solidify WIPP brines for disposal as TRU waste at WIPP. Nochar and Water Works were used at Mound for solidification of tritiated water. QuikSolid was used for solidification of tritiated heavy water at SRS. The resulting waste form was disposed of in the SRS E-Area low-level waste facility. A summary of several applications involving radioactive wastes is provided in Appendices A and B.

2.0 EXPERIMENTAL APPROACH

2.1 Initial Water-Sorbent Solidification

The initial mixtures were prepared in three different ways:

1. Water added to the sorbent
2. Sorbent added to the water
3. Water added to the sorbent plus mixing with a spatula
4. Sodium chloride solution (2 weight %) added to the AquaSorbe 2212 sorbent.

In the initial testing sorbent to water proportioning was 1:20. 1:30, and 1:40, by weight. The products were evaluated for the presence of free liquid, the overall appearance, i.e., granular versus gel and opaque versus clear/translucent and the compressibility per the EPA SW840 Procedure. In addition, the rate of sorption was qualitatively evaluated.

2.2 Aqueous Zinc Bromide Solution Solidification

A 1:1 mixture (by volume) of the solution collected from Railcar #1 and Railcar #2 was used in the actual radioactive solution testing. The scope of the testing for the actual radioactive zinc bromide solution was significantly reduced based on the results of the water testing and the fact that the higher waste loadings could not be achieved for the polymer sorbents using dilute salt solutions rather than water.

The actual zinc bromide waste mixture was added to the polymer sorbents. The waste loading was limited to 1:6, 1:10 and 1:15 (polymer: zinc bromide solution). No mixing was used in the bench-scale testing.

3.0 RESULTS

3.1 Water-Sorbent and Sodium Chloride Solution Sorbent Results

Results of the initial sorbent evaluations are presented in Tables 3-1 to 3-5. The 1:20 sorbent to water loading was used as the starting point for the initial testing. Proportioning was carried out on a weight ratio basis. In general, the sorbents performed according to the vendor claims for solidifying aqueous media (converting water to a solid form). However, at the higher water loadings, these simulated waste forms were wet gels with free water rather than completely solid. If the material remained granular, opaque, and showed no free water at this water loading, the lower loadings were not tested. The appearance was recorded at several time intervals. The volume of the water to resulting sorbed product was also measured and recorded. The volume of the product was measured by applying 50 pounds of force to the sample. All of the samples showed some small amount of rebound after compression.

Addition of the liquid to the polymer sorbent was the preferred method of making the product. When the polymer sorbent was added to the liquid, sorption of the particles first contacting the liquid resulted in rapid swelling that interfered with wetting of the remaining sorbent. Mixing was required when the sorbent was added to the liquid.

All of the sorbents tested showed a significant reduction in the sorption capacity when 2 wt. % sodium chloride solution was used instead of water. AquaSorbe 2212 performed the best with respect to salt solution solidification. Results for AquaSorbe 2212 are shown in Table 3-6.

3.2 Radioactive Aqueous Zinc Bromide Solution-Sorbent Results

Based on the water sorption results and the limited testing with the dilute sodium chloride solution, the waste loadings for the actual zinc bromide solution were limited to 1:6, 1:10 and 1:15 by weight. Results are summarized in Table 3-7. The Instasorb material, which contains both an organic and inorganic sorbent was eliminated from consideration because after 24 hours the $ZnBr_2$ solution was not absorbed. The Instasorb material also had a density about two times greater than the organic polymer sorbents.

After 1 hour the Aquadox HP, QuickSolid, Waste Lock 770 waste forms appeared similar and performed in a similar manner at the 1:10 loading. These waste forms were not homogeneous and consisted of a mixture of clear and opaque grains. The Water Works SP400 and AquaSorbe 2212 waste forms were homogeneous and made up of opaque grains. The AquaSorbe 2212 waste form was coarser grained and reacted slower than the others.

The 1:6 waste forms were similar. The most uniform/satisfactory waste forms were made with Water works SP400 and the AquaSorbe 2212. The coarser grain size of the AquaSorbe 2212 resulted in easier handling of the dry polymer and better permeability of the waste form, which enhanced contact between the waste and sorbent during processing. AquaSorbe 2212 resulted in the most uniform product.

Table 3-1. AquaSorbe 2212 polymer –water sorption evaluation.

Waste Form Preparation Method **AquaSorbe 2212**	Waste Loading Sorbent to Waste by wt.	Polymer Sorbent Weight (grams)	Amount of waste spg ~1.0 (mL)	Volume of Waste Form (mL)	Compressed Vol of Waste Form after 24 hr. (mL)	Waste Form Appearance	Comments on Rate of Absorption
Pour water into sorbent	1:40	1	40	52	42	Large individual clear grains	Slow sorption compared to other polymer products. 10 min until all liquid was sorbed. No free liquid
	1:30	1	30	40	28	Large individual clear grains	Slow sorption compared to other polymer products. 10 min until all liquid was sorbed. No free liquid
	1:20	1	20	30	20	Large individual clear grains	Slow sorption compared to other polymer products. 10 min until all liquid was sorbed. No free liquid
	1:10	5	50	55-3min 56-5min 58-15min 60-30min 64-60min 68-120 hr 70-24hr	56	Fish eggs sink to bottom, water on bottom crystallizing upward, no free water, crystallizes downward reabsorbing clear gel type material	Slow.i.e. 3-4 min to first set up (no free liquid). Considerable volume expansion.
	1:8	5	40	44-2min 56-10min 62-60min 56-24hr	46	Fish eggs sink to bottom, water on bottom crystallizing upward	Moderate. Expansion starts after 5-10 min as it turns granular
	1:6	5	30	32-start 36-3min 46-5min 50-15min 52-30min 56-24hr	36	Fish eggs sink to bottom and gel upwards. Become more granular with time	Initially sorbent grains sink to bottom and gels upward. After 5 min looks granular After 15 min all is granular
Pour sorbent into water	1:8	5	40	42-start 50-3min 60-8min 63-18min 62-24hr	46	Settles from an initial float as it is wetted. Doesn't displace water upward. Still granular from top	Slow. Minutes. Must be wetted before it rains down through water

Table 3-2. QuickSolid- water sorption evaluation.

Waste Form Preparation Method **QuickSolid**	Waste Loading Sorbent to Waste by wt.	Polymer Sorbent Weight (grams)	Amount of waste spg ~1.0 (mL)	Volume of Waste Form (mL)	Compressed Vol of Waste Form after 24 hr. (mL)	Waste Form Appearance	Comments on Rate of Absorption
Pour Water into sorbent	1:40	2	80	80	79	Clear gel, no grain boundaries	Quick to gel, inhomogeneous after 10 minutes
	1:30	2	60	62	59	Clear gel, no grain boundaries	Quick to gel, inhomogeneous after 10 minutes
	1:20	2	30	46	40	Mixture of clear gel and opaque grains. Opaque grains are at the top of the waste form	Quick to gel, inhomogeneous after 10 minutes
	1:10	5	50	55 58-24hr	56	Inhomogeneous, gel for most part	Quick to gel, inhomogeneous after 10 minutes
	1:8	5	40	45 50-24hr	46	Homogeneous Gel in middle portion Dry on top portion and bottom	Quick but not homogeneous even after 10 minutes
	1:6	5	30	35 38-24hr	34	Not homogenous Some areas white crystal Near bottom wet gel like	Quick but not entirely homogenous after 5 minutes After 10 minutes-better distribution
Pour Sorbent into water	1:8	5	40	48 56-24hr	44	Will be rate dependent. Bottom forms gel. Top sits on gel	Quick but limited entry of sorbent into water. Sorbent remains on top after 10 minutes. 0-26 mL- clear gel 26-36 mL-White clear crystals 36-56 slightly reacted sorbent

Table 3-3. WasteLock-water sorption evaluaton.

Waste Form Preparation Method **WasteLock 770**	Waste Loading Sorbent to Waste by wt.	Polymer Sorbent Weight (grams)	Amount of waste spg ~1.0 (mL)	Volume of Waste Form (mL)	Compressed Vol of Waste Form after 24 hr. (mL)	Waste Form Appearance	Comments on Rate of Absorption
Pour water into sorbent	1:40	2	80	81	80	Clear gel, no grain boundaries	Quick sorption. Slightly inhomogeneous after 5 minutes
	1:30	2	60	62	61	Mixture of clear gel and some opaque gel with traces of grain boundaries	Quick sorption. Slightly inhomogeneous after 5 minutes
	1:20	2	40	52	46	Opaque to translucent grains,	Quick sorption. Slightly inhomogeneous after 5 minutes
	1:10	5	50	60 64-24hr	56	Gel-like in bottom 2/3-1/2 White crystals on top. Quickly equalizing	Quick. Seems to homogenize fairly quickly
	1:8	5	40	52 56-24hr	46	Inhomogeneous Dry sorbent on bottom.	Quick sorption except for the driest pockets on the bottom. Seems to homogenize quicker than QuickSolid.
	1:6	5	30	42 42-24hr	36	Fairly homogeneous Quick sorption. Dry packing left in bottom – seems like slight exposure	Quick sorption. Slightly inhomogeneous after 5 minutes
Pour Sorbent into water	1:8	5	40	45 58-24hr	--	Void/gel spaces throughout.	Same effect as QuickSolid, i.e., gel in bottom with unused sorbent sitting on top Homogenizes faster than QuickSolid

Table 3-4. Aquadox HP-water sorption evaluation.

Waste Form Preparation Method **Aquadox HP**	Waste Loading Sorbent to Waste by wt.	Polymer Sorbent Weight (grams)	Amount of waste spg ~1.0 (mL)	Volume of Waste Form (mL)	Compressed Vol of Waste Form after 24 hr. (mL)	Waste Form Appearance	Comments on Rate of Absorption
Pour Water into Sorbent	1:40	2	80	82	81	Clear to opaque gel, no grain boundaries, Mostly clear gel	Rapid
	1:30	2	60	62	62	Clear to opaque gel, no grain boundaries, About 50 % opaque gel	Rapid
	1:20	2	40	44	42	Clear to opaque gel, no grain boundaries, Mostly clear gel	Rapid
	1:10	5	50	52 54-24hr	52	Strong grading. Gel on top. Almost solid on bottom	Quick set. Very graded
	1:8	5	40	42 44-24hr	NA	Displaced water upward so sorbent is thicker in bottom	Quick. Graded distribution top to bottom (most)
	1:6	5	30	32 34-24hr	34	White fine crystals throughout. Wispy. Some unactivated in bottom. Looks like shaved ice.	Quick. Not graded
Pour Sorbent into Water	1:8	5	40	37/46 (gel/dry) 54-24hr in 2 phases because of unreacted polymer	43	Two phased. Gel on bottom. Crystals on top.	Quick. Gel builds upward until water is gone. The remainder of the sorbent piles up on top. Gross distribution within gel. Crystals and gel do not further homogenize overnight. One shot to mix thoroughly

Table 3-5. Instasorb-water sorption evaluation.

Waste Form Preparation Method **Instasorb**	Waste Loading Sorbent to Waste by wt.	Polymer Sorbent Weight (grams)	Amount of waste spg ~1.0 (mL)	Volume of Waste Form (mL)	Compressed Vol of Waste Form after 24 hr. (mL)	Waste Form Appearance	Comments on Rate of Absorption
Pour Water into Sorbent	1:40	2	80	82	54	Takes 1-2 minutes to get started. Then rises. Separation of polymer on top and clay in bottom. Polymer is granular.	Slow. Water piles on top. Air bubbles. Polymer rises to top in a graded fashion. Sorbent is denser than others tested.
	1:30	2	60	62	50	Takes 1-2 minutes to get started. Then rises. Separation of polymer on top and clay in bottom. Polymer is granular	Slow. Water piles on top. Air bubbles. Polymer rises to top in a graded fashion. Sorbent is denser than other tested
	1:20	2	40	46	40	Takes 1-2 minutes to get started. Then rises. Separation of polymer on top and clay in bottom Polymer is granular.	Slow. Water piles on top. Air bubbles. Polymer rises to top in a graded fashion.
	1:10	5	50	56 56-24hr	55	In the end the top is mostly clear polymer and the bottom is dry.	Similar to 1:30. Water on top until polymer rises to top.
	1:8	5	40	42 51-24hr	40	With different pour still seems to be polymer rich on top with clay on bottom. Much better overall distribution. Some dry remains on top	Sorbent mass floated to top and started to rain down.
	1:6	5	30	41 48-24hr	37	Takes 1-2 minutes to get started. Then rises. Separation of polymer on top and clay in bottom	Slow. Water piles on top. Air bubbles. Polymer rises to top in a graded fashion.
Pour Sorbent into Water	1:8	5	40	42 57-24hr	46	In the end there is some dry polymer on top. The rest is a monolith of clay particles within a clear gel	Polymer sits on top until wetted. Then rains down as a homogeneous mix. This polymer/clay product may segregate during handling.

Table 3-6. AquaSorbe 2212 –sodium chloride salt solution sorption evaluation.

Waste Form Preparation Method **AquaSorbe 2212**	Waste Loading Sorbent to Waste by wt.	Polymer Sorbent Weight (grams)	Amount of waste spg ~1.0 (mL)	Volume of Waste Form (mL)	Compressed Vol of Waste Form after 24 hr. (mL)	Waste Form Appearance	Comments on Rate of Absorption
Salt solution added to Sorbent	1:10	5	49	50-3min 60-24hr	ND	Initially sinks,” fish eggs”.Xtal white mass looks more granular as more water is drawn in. After 24 hours all xtalline. Air drying.	Slow. Xtallization rises from bottom of cylinder. 1 min-1/2 way 3min-3/4 4min-48 out of 50 5min-still tad of free water 8min-Essentially solid
	1:20	5	98	98-3min	ND	Clear gel to 90. Rest is granular on top.(90-100)	Start-grains fall to bottom 3min-40 mL out of 98 xtal 5min-50 mL out of 98 xtal 9 min-64 mL out of 100 xtal, 14 min-78 mL out of 100 xtal. Still freewater 0-70/gel 70-80 opaque gel 80-100 grains
	1:30	5	147	147-3min	ND	Media at 100 out of 150 mL (Had to use beaker due to volume)	START-25 mL 4min-50 mL 9min-2/3 gel,1/3 xtal 0-25 clear 25-135 opaque
Sorbent added to salt solution	1:30	5	147	--	ND	Initially floats then rains down. (Had to use beaker due to volume)	Same as liquid into solid for 1:30 0-25 clear gel 25-135 opaque gel

Table 3-7. Results of zinc bromide solution solidification using polymer sorbents.

Sorbent	Mixture	1 hour	24 hour	Waste form volume (ml)
Aquadox HP	1:15 5 g sorbent : 73 ml waste	Trace free liquid, opaque grains on top, clear grains in bulk	No free liquid, soft, clear gel and clear grains, grains agglomerated	
QuickSolid	1:15	Trace free liquid, opaque grains on top, clear grains in bulk	Trace free liquid, soft, clear gels with no definite grain boundaries	
Instasorb	1:15	Liquid not absorbed	Liquid not absorbed	
Waste Lock 770	1:15	Trace free liquid, opaque grains on top, clear grains in bulk	No free liquid, soft clear gel and grains, unsused material in beaker	
Water Works SP400	1:15	Trace free liquid, grains on top, clear grains in bulk	No free liquid, soft, opaque grains, uniform appearance top to bottom	
Aquadox HP	1:10 5 g sorbent : 49 ml waste	No free liquid, bottom 1/3 clear grains, remainder opaque grains	Same as 1 hr.	~60
QuickSolid	1:10	No free liquid, bottom ¾ clear grains, remainder opaque grains	Same as 1 hr.	~60
Waste Lock 770	1:10	No free liquid, bottom ½ clear grains, remainder opaque grains	Same as 1 hr.	~60
Water Works SP400	1:10	No free liquid, all opaque grains	Same as 1 hr.	~70
AquaSorbe 2212	1:10	Slower to react than other sorbents (free liquid after 5 min.), No free liquid, all opaque grains, coarser grains than other samples	Same as 1 hr.	~60
Aquadox HP	1:6 5 g sorbent : 29 ml waste	No free liquid, firm opaque grains, v. fast sorption	Same as 1 hr.	~40
QuickSolid	1:6	No free liquid, firm opaque grains	Same as 1 hr.	~40
Waste Lock 770	1:6	No free liquid, firm opaque grains	Same as 1 hr.	~40
Water Works SP400	1:6	No free liquid, opaque, v. granular, almost fluffy,	Same as 1 hr.	~50
AquaSorbe 2212	1:6	Slower to react than other sorbents (free liquid after 5 min), No free liquid, large clear to opaque grains	Same as 1 hr.	~50

4.0 CONCLUSIONS

Solidification of the low-level radioactive zinc bromide solution with organic polymers appears to be an acceptable treatment for converting this aqueous waste into a solid form suitable for disposal in E-Area. Use of the rail tankers as the disposal containers requires production of a low-density waste form so that the total weight does not exceed the limits of the E-Area cranes and does not over stress the structural integrity of the tankers. Organic polymers meet these requirements.

The sorption capacity of the polymers was significantly reduced for salt solutions. The absorption capacity of all of the sorbents tested was reduced by about 5 times when sodium chloride solution and the zinc bromide solution were used instead of water. The transition from a white, opaque granular waste form to a clear non-granular gel material was gradual for all of the polymer sorbents. The acceptable proportioning (waste loading) for a radioactive waste forms was based on the product appearance using the following criteria:

1. No free liquid
2. Opaque granular waste form.

The most effective way to absorb liquid waste is to add the liquid to the sorbent. Mixing is also effective but requires additional equipment and results in fluffing (bulking up) the product. This is supported by the fact that mixing was required for the solidification effort at SRS in which QuickSolid was added to tritiated heavy water in 55-gallon drums [4].

5.0 RECOMMENDATIONS

The Water Works SP400 and the AquaSorbe 2212 are recommended for additional mock up testing. The AquaSorbe 2212 material is coarser grained and reacts somewhat slower with the ZnBr2 solution that the Water Works SP400 material. Both sorbents produced the most uniform waste forms with no free liquid at the 1:6 to 1:10 waste loadings. The 1:6 waste loading is recommended as the design formulation. The 1:6 waste loading is approximately twice the amount of sorbent necessary to achieve opaque grains.

6.0 QUALITY ASSURANCE

Work was conducted according to the approved Task Plan and QA Plan [5]. Samples were prepared using calibrated balances and standard volumetric cylinders. The error on the proportioning is +/- 0.05g for the solid materials and +/- 1ml for the liquid portion. Data are recorded in WSRC-NB-2002-00013.

7.0 REFERENCES

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8.0 ACKNOWLEDGEMENTS

J. K. Denny, Facility Decontamination and Decommissioning Division, WSRC supported this task. B. T. Butcher processed the Task and QA Plans and facilitated transfer of the radioactive samples into appropriate containers.

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9.0 APPENDIX A. EXAMPLES OF SORBENTS USED FOR SOLIDIFICATION OF RADIOACTIVE WASTES

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Vendor	Aquadox Inc. Robert S, Wright 630 964 1300
Product	**AquaSorbe 2212** Absorbent Recommended for $ZnBR_2$ Solidification based on SRTC study. Uniform and coarse grain size (1-2mm) important for success with salt solutions
Customers/Contact	* Los Alamos/D.R. Yeamans **Puget Sound Naval Base
Disposal Sites	WIPP
Volumes Disposed	*800 gals **190 gal
Containers	NA
Type of waste	* Pu brine solution **Contaminated Sea Water Brine
Reports	"Absorbing WIPP Brines: A TRU Waste Disposal Strategy"
WACS Cleared	Envirocare NTS

Vendor	Aquadox, Inc. Robert S. Wright 630 964 1300
Product	**AquaSorbe HP** Similar to AquaSorbe 2212 but less effective due to finer grain size
Customers	Piketon WIPP Brookhaven Duratek Paducah, KY Hanford Oak Ridge Gaseous Diffusion Plant Wisconsin Power (Point beach) TVA (Watts Bar) M4
Disposal Sites	NTS Envirocare Hanford
Volumes Disposed	NA
Containers	Topped off Gondolas
Type of waste	LLW, Hazardous, Mixed
Reports	NA
WACS Cleared	Envirocare NTS

Vendor	Waterworks America Scott Altmayer 440 209 1440 Cell phone: 440 725 5987
Product	**SP 400**
Customers	Mound (LSDDP)
Disposal Sites	NTS Envirocare Hanford
Volumes Disposed	40-53 gal of waste per 55 gal drum
Containers	55 gal drums B-12 containers B-25 Containers Intermodals (25 cu.yds.) Gondolas (2-3 feet of standing water at top of loaded Gondolas)
Type of waste	Low Level tritium contaminated waste
Type of waste	Aqueous liquids (solutions, slurries) containing radionuclides or heavy metals, and salts but not mixed waste (rad plus hazardous metals)
Reports	"The Use of Innovative Super Absorbents to Economically Stabilize Contaminated Aqueous Decontamination Wastewater for Disposal" "The Mound Tritium D&D Large-Scale Demonstration and Deployment Project – Waterworks Crystals Aqueous Liquid Solidification Agent"
WACS Cleared (Contact)	Nevada Test Site (Mike Nolan) Envirocare Hanford Low –Level Disposal Site

Vendor	CETCO Allen Bullock 800 527 9948
Product	**Quick Solid**
Customers/Contact	1) Savannah River Site 2) Oak Ridge-Y12 3) Fernald, OH 4) Paducah,KY 5) Wayne, NJ 6) Orange, NJ 7) Bruce Nuclear, CAN
Disposal Sites	1) E-Area Trenches 2) Envirocare 3) Envirocare/ NTS 4) NTS 5) Envirocare 6) Envirocare 7) N/A
Volumes Disposed	1) >40 55-gal drums 2) 4.2M kg 3) >1.1Mkg 4) >10K cu.yds. 5) Approx 25cu. yds 6) Approx 11K cu.yds. 7) > 300 55 -gal drums
Containers	1) 55 gallon drums 2) Century Containers 3) B-25 Boxes/Intermodal Containers 4) N/A 5) Intermodal Containers 6) Intermodal Containers 7) N/A
Type of waste	1) LLW 2) LLW/Mixed 3) LLW/Mixed 4) LLW/Mixed 5) LLW 6) LLW 7) LLW
Reports	1) WSRC-RP-98-00073, 1/23/98 1-7) CETCO corporate Literature
WACS Cleared	1) SRS E-Area Trenches Envirocare NTS

Vendor	M2 Polymer Martin Matushek 847 836 1393 Cell phone: 847 226 5295
Product	**Wastelock 770**
Customers	Oak Ridge Brookhaven Paducah Rocky Flats Honeywell (Toby Davis) Los Alamos West Chem Livermore Ashtabula, OH (AEMP) Pantex (Hg related spill) Laboratory for Energy related Health Research (LEHR)
Disposal Sites	Envirocare Hanford
Volumes Disposed	NA
Containers	Roll out boxes 55 gal drums Tanks B-25 containers Gondolas (top off for free liquids)
Type of waste	Aqueous liquids (solutions, slurries) containing radionuclides or heavy metals, and salts but not mixed waste (rad plus hazardous metals)
Reports	NA
WACS Cleared (Contact)	Nevada Test Site (Mike Nolan) Hanford Low Level and Mixed Waste Disposal Facilities

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10.0 APPENDIX B

PUBLICATIONS RELATED TO THE SOLIDIFICATION OF AQUEOUS RADIOACTIVE WASTE STREAMS WITH ORGANIC POLYMER SORBENTS

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WM'02 Conference, February 24-28, 2002, Tucson, AZ

ABSORBING WIPP BRINES: A TRU WASTE DISPOSAL STRATEGY

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ABSTRACT

Los Alamos National Laboratory (LANL) has completed experiments involving 15 each, 250-liter experimental test containers of transuranic (TRU) heterogeneous waste immersed in two types of brine similar to those found in the underground portion of the Waste Isolation Pilot Plant (WIPP). To dispose of the waste without removing the brine from the test containers, LANL added commercially available cross-linked polyacrylate granules to absorb the 190 liters of brine in each container, making the waste compliant for shipping to the WIPP in a Standard Waste Box (SWB). Prior to performing the absorption, LANL and the manufacturer of the absorbent conducted laboratory and field tests to determine the ratio of absorbent to brine that would fully absorb the liquid. Bench scale tests indicated a ratio of 10 parts Castile brine to one part absorbent and 6.25 parts Brine A to one part absorbent. The minimum ratio of absorbent to brine was sought because headspace in the containers was limited. However, full scale testing revealed that the ratio should be adjusted to be about 15% richer in absorbent. Additional testing showed that the absorbent would not apply more than 13.8 kPa pressure on the walls of the vessel and that the absorbent would still function normally at that pressure and would not degrade in the approximately 5e-4 Sv/hr radioactive field produced by the waste. Heat generation from the absorption was minimal. The *in situ* absorption created a single waste stream of 8 SWBs whereas the least complicated alternate method of disposal would have yielded at least an additional 2600 liters of mixed low level liquid waste plus about two cubic meters of mixed low level solid waste, and would have resulted in higher risk of radiation exposure to workers. The *in situ* absorption saved $311k in a combination of waste treatment, disposal, material and personnel costs compared to the least expensive alternative and $984k compared to the original plan.

PURPOSE AND INTRODUCTION

The purpose of this experiment and subsequent process was to remove excess liquids from a transuranic (TRU) waste stream so that the waste could be packaged to meet criteria for disposal at the Waste Isolation Pilot Plant (WIPP). Experimentation showed that brines similar to those found in the underground portion of the WIPP near Carlsbad, New Mexico, can be effectively absorbed to create a liquid free matrix that meets the requirements of the RCRA permit issued for the operation of WIPP, that is, less than 1% liquid in the shipping container, less than one inch liquid in any internal container, and less than 1% liquid in the aggregate of all internal containers within the shipping container. The *in situ* absorption was the safest, fastest, and least costly of the alternatives studied, saving as much as $311k(1) to $984k in the combination of costs for waste treatment and disposal and for material, facilities and personnel(2).

Los Alamos National Laboratory (LANL) had an inventory of waste including about 2800 liters of brine at the completion of the Actinide Source Term Waste Test Project (STTP) in 2000. The waste was 15 each, 250-liter experimental test containers (Fig. 1) of actual TRU heterogeneous waste immersed in two types of brine. LANL explored several alternatives for disposing of this waste.

Fig. 1 250-liter Containers With WIPP-type Brine and Waste

1. Pumping the brine out of the test containers and managing it as Low Level Waste (LLW), leaving the wet heterogeneous waste in the test containers, remediating the liquid condition, and packaging it in Standard Waste Boxes (SWBs). This would have had the following waste streams, costs and risks.
    - 2500 liters of waste water (LLW) to be shipped off site for treatment and shipped again for disposal
    - 8 SWBs (TRU) containing the 15 titanium test vessels with absorbent added to remediate any potential excess liquid condition
    - personnel time ~ $320k
    - disposal costs ~ $111k (LLW) and $553k (TRU)

- risk in shipping and handling liquids; risk in off site treatment and additional shipping from there.

2. (Original Proposal) Pumping the brine out of the test containers and managing it as Low Level Waste (LLW), repackaging the wet heterogeneous waste into 55-gallon shipping containers. This would have had the following waste streams and costs.
    - 2500 liters of waste water (LLW) to be shipped off site for treatment and shipped again for disposal
    - 15 drums of TRU waste
    - 15 titanium vessels to be disposed of as LLW
    - personnel time ~ $640k
    - facility modification and program equipment ~ $750k
    - disposal costs ~ $113k (LLW) and $107k (TRU)
    - risk of worker exposure in handling TRU waste; risk in shipping and handling liquids; risk in off site treatment and additional shipping from there.

3. (Selected Alternative) Absorbing the brine *in situ* in the test containers and packaging them in Standard Waste Boxes (SWBs). This would have had the following waste streams and costs.
    - 8 SWBs (TRU) containing the 15 titanium test vessels with absorbent added to remediate any potential excess liquid condition
    - personnel time ~ $120k
    - disposal costs ~ $553k (TRU)
    - risk of spill during liquid transfers.

On the basis of experiments(3) that showed the absorption process was effective, and also based on a cost saving of over a million dollars (offset by a minor increase in disposal costs) LANL chose option 3, the *in situ* absorption of liquids and subsequent packaging into SWBs. The disposal approach was approved by the Los Alamos Area Office of the Department of Energy with concurrence from the LANL Transuranic Waste Characterization/Certification Project(4). Regulatory experts from LANL agreed that adding absorbent to the containers with liquid met the intent and requirements of the RCRA rules governing treatment, absorption, and packaging(5).

A brief summary of the absorption experiments supporting LANL's decision follows.

- Two types of brine, Brine A and Castile Brine, were used in absorption experiments. These are sodium, magnesium and potassium chloride brines with some lesser salt constituents typical of the WIPP environment. About 50ml of brine was put into a beaker and Aquasorbe-2212® cross-linked polyacrylate polymer was added in an initial ratio of 1 part absorbent to 10 parts brine and the mixture was observed (Fig. 2). More absorbent was added as necessary until full absorption was observed by tipping the beaker and seeing that no brine moved within the interstices of the absorbent matrix. A volumetric ratio of 1 part absorbent to 10 parts Castile Brine and 1 part absorbent to 6.25 parts Brine A was determined. Up to 30% expansion was seen at full absorption.

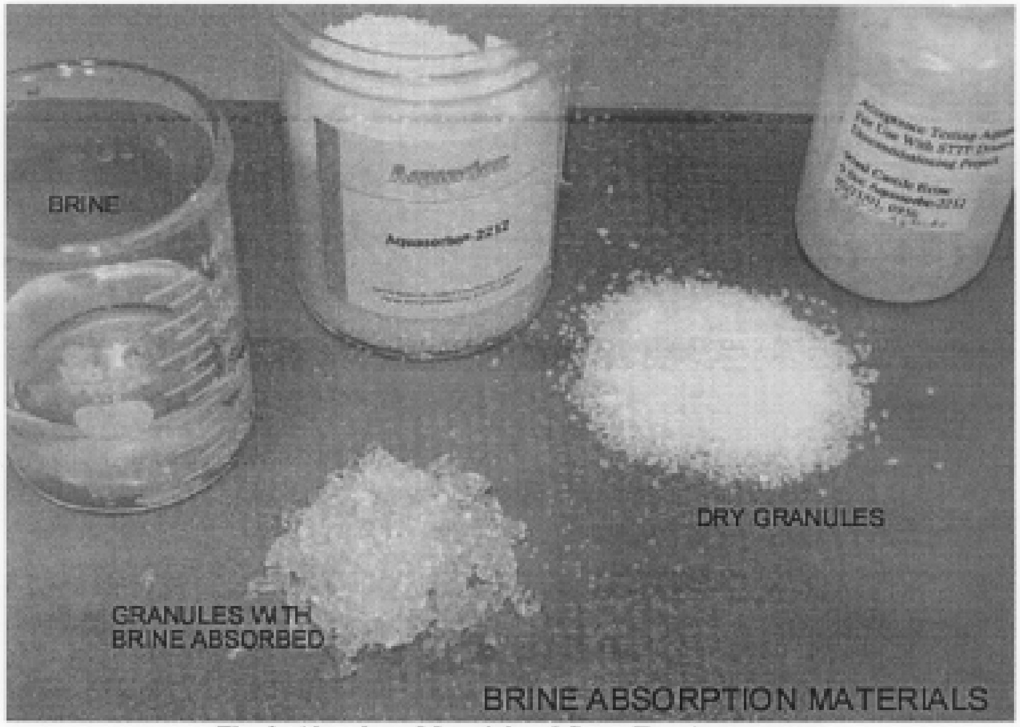

Fig. 2 Absorbent Material and Some Test Apparatus

- The manufacturer of the absorbent performed independent tests that showed the absorbent would not put more than 13.8 kPa pressure on the walls of the container if constrained but that absorption would not be inhibited by the pressure. Additional tests at LANL showed that uncapping the container would not lead to sudden extrusion of the constrained absorbed mass.

- Two bottles packed with waste-like materials were prepared and filled with brine, leaving a small headspace. The correct amount of absorbent was added to each bottle and the caps put on. The bottles were gently rolled on a bench top to simulate agitation of the 250-liter waste containers. The absorbent became evenly distributed throughout the bottles and the brines were completely absorbed.

LANL also absorbed 1-liter samples of actual brine from STTP test containers to verify that the ratios of absorbent to brine were correct.

FULL SCALE MOCKUP TESTING

LANL also had two 250-liter test containers with about 170 liters of non-radioactive brine each. Waste-like material consisting of lab coats, booties, gloves, glassware, cheesecloth, and bags was added and the drums were sealed except for a ¾-inch (about 2.5 cm actual size) pipe threaded hole in the top. Using a HEPA filtered steel funnel, absorbent was added through the hole and then the hole was plugged. The drum was set horizontally on a roller and rotated about its long axis for 15 minutes to agitate the mixture and assure complete mixing. A thermocouple attached to the outside of the container showed a temperature rise of about 2°C for less than a minute immediately after the rotation. A slight pressure build up was observed during the agitation.

Then the drum was opened and the matrix inspected (Fig. 3). Even though the material passed the paint filter test(6), when a container was placed on its side and a valve at the bottom was opened for two months, about 200cc of sticky syrup leaked from the valve. The test material met the criteria for no excess liquids, but LANL increased the ratio of absorbent 15% for added assurance. All the tests clearly showed that the absorbent would be effective at remediating the excess liquid condition.

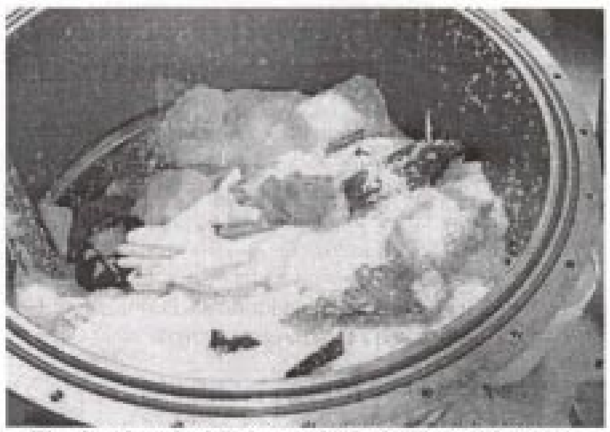

Fig. 3 Absorbed Brine and Mock Waste Materials

One of the major concerns for waste handlers was whether the full amount of absorbent would fit in the test containers. LANL performed a $P_1V_1=P_2V_2$ measurement of the headspace of each container and found a barely sufficient space to add absorbent given that the absorbent packing fraction was about 0.5, that is the absorbent would displace 5 liters of liquid for 10 liters added. To deliver all the absorbent would require enough free space in the container to allow the free flowing granules to sink. This was a condition not achieved in the actual drums.

About 2 ½ inches below the lid of each container there was a coarse screen to hold waste away from the sampling ports of the containers. In order to allow freer flow of absorbent into the brine, LANL cut a 2.2 cm diameter hole in the screen using a hole saw. However, the plastic waste materials were lighter than the brine and floated up to the screen and stopped, thus blocking the newly formed hole as well as most of the mesh. To solve the blockage LANL pumped about 120 liters of brine from the container into a temporary storage tank so that there would be a large headspace into which to pour the absorbent, after which the liquid would be pumped back into the container. The containers were agitated by rolling them gently about their long axis for 15 minutes, after which the lids were fitted with a WIPP certified filter vent. In some containers not all the brine could be returned to the original vessel so it was absorbed separately in a plastic bag (Fig. 4).

Fig. 4 Bag of Absorbed Extra Waste

SWB PACKAGING

After absorption the containers were set two at a time into SWBs along with associated experimental piping and the extra absorbed brine, and a valve on each was locked open, further assuring that the containers were not pressurized. The fit was quite precise but to assuage fears that the contents would move, vermiculite was added to the SWBs. The vermiculite also created an additional measure of safety should liquid ooze from the containers. LANL TWCP visual examination experts assisted in the packaging to give the highest probability that this waste stream can be disposed at WIPP.

Safety Concerns

One reason that alternative #3 was chosen was that it would expose workers to less radiation and potential contamination than either of the other two. No contamination was detected during the month required to complete the operation.

CONCLUSIONS

Excess liquid conditions can be safely and inexpensively eliminated by adding a cross-linked polyacrylate polymer absorbent to a container holding WIPP-type brines. However, the reader is cautioned that in order to maintain RCRA compliance the absorbent should be added at the first time the shipping package is prepared or should be added to the waste prior to packaging. Adding absorbent to the shipping container after initial packaging should be addressed as a regulatory issue separate from the process described here.

SIGNIFICANCE OF THE PAPER

This research shows that a cross-linked polyacrylate polymer can be used to absorb chloride brines. This paper shows that significant cost savings can be realized from absorbing liquids in waste containers at the time of packaging as opposed to opening a container, separating the components and treating or packaging them separately. The cost savings and risk avoidance this method provides could save generators of aqueous TRU waste products a great deal of money as well as making it safer to dispose of the waste.

REFERENCES

[1] All disposal costs are derived from the rates listed on the LANL web site http://wm99.lanl.gov/recharge/owa/Rates. The rate for TRU waste storage/certification/disposal in August 2000was $34,550 per cubic meter and the cost for mixed low level waste was $44,200 per cubic meter.
[2] From LANL staff rates for the year 2000 and estimates of fabricating, installing and operating a glovebox.
[3] Yeamans, David R., Absorbing WIPP Brines With a Cross-Linked Polyacrylate Absorbent, LA-UR-00-5211, Los Alamos National Laboratory, 2000.
[4] Meeting with DOE, LANL TWCP and NMT-11, 11/21/2000.
[5] e-mail from Edward L. Horst, LANL, NMT-7, 10/25/2000.
[6] EPA method SWA-846-9095, Paint Filter Liquids Test.

THE USE OF INNOVATIVE SUPER ABSORBENTS TO ECONOMICALLY STABILIZE CONTAMINATED AQUEOUS DECONTAMINATION WASTEWATER FOR DISPOSAL

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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 immobilize 55 gallons of water with 3-5 lbs. of absorbent.

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 perhaps improve 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 fixated 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.

I. INTRODUCTION

A. 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.

B. 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.

II. DATA COLLECTION

A. 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.

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

TABLE 1-Results of paint filter test for Phase 1.

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.

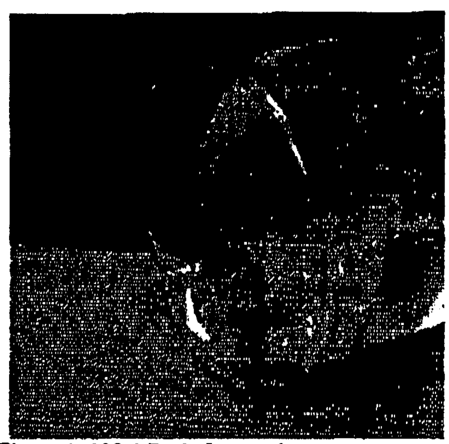


Figure 1 100:1 Ratio Inverted

B. 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

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

Table 2- Results of Paint Filter Test Full Size

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.

Phase C- 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.

III. 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.

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**

Table 4 Cost comparison of the absorbents

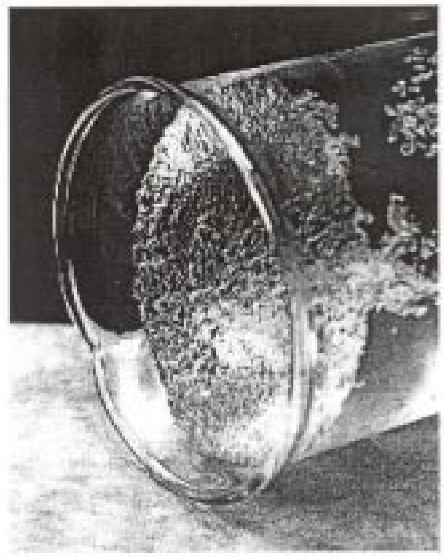
In campaigning a 3000 gallon storage tank, the material savings alone would amount to $8250. In addition, there will be some time (labor) savings in the operation of adding 8+ lb. of a polymer absorbent versus adding four 55 lb. bags of Aquaset®. There is also an advantage with respect to the generation 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, the existing baseline technology will be replaced with the polymer absorbent process

U.S. Department of Energy

The MOUND Tritium D&D Large-Scale Demonstration and Deployment Project

WATERWORKS CRYSTALS® AQUEOUS LIQUID SOLIDIFICATION AGENT



THE NEED

During fiscal year 1999, the U.S. Department of Energy Mound Environmental Management Project (DOE-MEMP) Office and BWXT of Ohio conducted a demonstration utilizing WaterWorks Crystals aqueous liquid absorbent. The intent of the demonstration was to compare this organic polyacrylate super absorber material against the baseline immobilization agents which include Aquaset® and cement. The baseline D&D program has generated and will continue to generate large quantities of low level tritium contaminated aqueous waste. The stabilization of this waste for shipments and disposal results in a weight and in some cases volume increase of the final waste form as compared to the liquid waste itself. More effective stabilizing agents can translate directly into a larger per drum waste loading with a corresponding reduction in the cost of stabilization, transportation and disposal.

THE TECHNOLOGY

The innovative technology that was demonstrated in the Mould LSDDP is a organic polyacrylate that has very high absorbent capabilities for aqueous liquids with weight ratios of up to 200:1 water to absorbent achievable under specific conditions. The absorbent utilized in the demonstration was WaterWorks Crystals® marketed by WaterWorks America, Inc. Other similar products in the polyacrylate family include Stergo® and Aquadox® which have the same basic capabilities and limitations. These products work very well with aqueous solutions and can tolerate some salt content along with the presence of inorganic sludges. They do not work for organic liquids. They do not require mixing when added to the liquid and there is no increase in volume. The product is non-toxic and non-biodegradable. It has been shown to be highly resistant to the effects of radiation and has withstood standard freeze/thaw test environments.

THE DEMONSTRATION

The demonstration involved several phases including bench scale tests with 350 ml. Volumes of water to determine the properties of a variety of ratios . A standard paint filter test was used as an indicator of appropriate immobilization. The results of this phase were applied to 55 gallon drums containing 53 gallons of water. In addition, samples were collected from the bottom of stabilized drums to determine if the absorbent properties were uniform along the vertical axis of the waste container. Finally, a drum absorbed with the preferred ratio was subjected to over-the-road vibration and impact tests.

RESULTS

The bench scale test provided data that indicted the upper bounds of the water to absorbent ratios. Subsequent testing with full-size drums containing 53 gallons of water demonstrated that ratios of up 100:1 would be possible. The Mound preferred ratio of 50:1was primarily chosen to provide a significant level of conservatism to the final waste form and to meet some burial site criteria that specified the use of twice the amount of absorbent needed. Drilling holes at the base of the drum indicated that the performance of the absorbent is consistent throughout the vertical axis. The waste form at a 50:1 ratio also passed the vibration and impact tests. Since the amount of absorbent used at 50:1 is about 8.8 lbs. as compared to 200 lbs. of the baseline absorbent, the costs of the material alone favor the polyacrylate by a 4:1 ratio per gallon of water absorbed.

BWXT of Ohio, Inc.

NETL

University of California
Lawrence Livermore National Laboratory

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Scott Altmayer, Technical Manager, Water Works America, Inc. (440) 209-1440

WaterWorks Crystals Superabsorbent Polymer

An innovative waste water disposal process by WaterWorks America, Inc

The purpose of this absorbing agent is to perform safe, efficient solidification of radioactive / contaminated waste water and provide an acceptable means of transportation and disposal

BENEFITS

- A single step process, and does not require mixing
- Minimizes processing times by reducing handling, and having minimal setup times
- Reduced worker exposure
- Increased productivity
- Provide an overall price reduction for treatment and disposal of tritiated water

MATERIAL

- High technology polymer
- Crystals are white, odorless, granules approximately 400 microns in size
- Non-toxic and non-biodegradable
- Absorbent capacity of up to 200:1 $^{w}/_{o}$ depending on material, pressure/stress conditions
- Absorbs quickly and with a minimal increase in volume

BASELINE TECHNOLOGY

- Solidification with Aquaset®, concrete and/or plaster

Scott Altmayer
<waterworks@ncweb.com>

To: Gary Iversen <gary.iversen@srs.gov>
cc:
Subject: WaterWorks Crystals (WWC): Applications, Photos, and Void Fillers

01/23/02 11:55 PM

Info as requested (view letter frst for void-filler info and pricing): WWC applications charts, WWC fact sheet, photos of process water sludge and sanitary sludge, voids letter, foam site.

If you don't get the bag of SP-400 by Thursday (as sent 1/18)...call me to confirm the name and address so I can send more for arrival Friday/Monday.

Scott Altmayer
Technical Manager
WaterWorks America, Inc.
Phone: 440-209-1440
Fax: 440-209-1441

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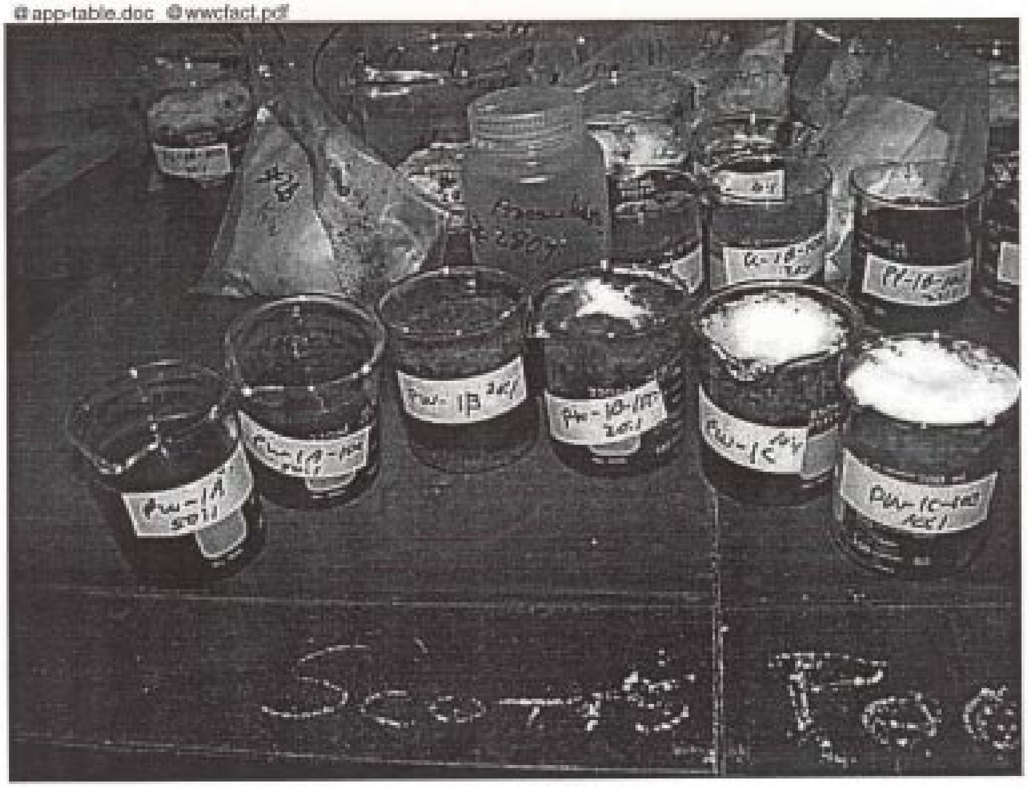

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SP-400 WaterWorks Crystals®
Typical Application Methods
(for reference only)

Wasteform	***Relative Water (%)***	***Absorbent Placement***	***Absorbent Mixing/Blending***
Contaminated Water	High (>95%)	Bulk Additive	None (mixing optional)
Slurry/Sludge	High (>60%)	Layered	Vertical and horizontal probe, or Pugmill/paddle mixer
Wet Debris, Bagged Asbestos	Average (>20%)	Layered, Top and Bottom of Waste	Broadcast
Damp Soil (near optimum moisture)	Low (<20%)	Layered, Top and Bottom of Waste	Broadcast
Condensation (all wastes)	Low (<1%)	Top, bottom, and perimeter of waste container and liner	Broadcast

SP-400 WaterWorks Crystals®
Typical Application Rates
(for reference only)

Container Type	*Typical Max "Soil" Weight (lbs.)*	*Maximum Volume*	*SP-400 Crystals Needed (lbs)*	
			** Soil w/ 10% extra water*	*** Watery Sludge*
Drum	800 lb	7.3 cf	1	9
Supersack	3,000 lb	27 cf	3	33
B12 Box	4,000 lb	44 cf	4	55
B25 Box	8,000 lb	90 cf	8	113
Liftliner$_{TM}$	24,000 lb	260 cf	24	322
Intermodal	42,000 lb	675 cf (= 25 cy)	42	844
Gondola	200,000 lb	1,890 cf (= 70 cy)	200	2,344

Notes:

* *Soil water @ 100:1 ratio (2/3 design capacity)*

** *Typical D&D Contaminated Water @ 50:1 ratio (1/3 design capacity)*

SP-400 WaterWorks Crystals® Absorption/Solidification of Brackish "Salty" Wastewater

(for reference only)

Total "Salts" Concentration	Contaminated Aqueous Liquid (lbs)	SP-400 Absorbent (lbs)	SP-400 Wt %
2,000 ppm (= 0.2 wt%)	90	1	1.1 wt%
10,000 ppm (= 1.0 wt%)	50	1	2.0 wt%
15,000 ppm (= 1.5 wt%)	30	1	3.3 wt%
30,000 ppm (= 3.0 wt%)	20	1	5.0 wt%
65,000 ppm (= 6.5 wt%)	10	1	10.0 wt%

Notes:

1. Approximate minmum application ratios to pass USEPA Paint Filter Test. Use of additional absorbent will increase the safety margin by making a firmer final waste form.

2. Brackish inland coastal waterways and the Great Salt Lake are approximately 6 wt% Total Dissolved Solids (TDS) as "salts" based on empirical field testing and validation. Since results will vary based on actual type of salt and waste form, a simple treatability study is always required to confirm waste-specific performance.

EXAMPLE TECHNICAL REFERENCES ON WASTE FORM DURABILITY

REGULATIONS 10 CFR 61 49 CFR 173 DOE Order 435.1 ANS/ANSI N16.1, Leaching ANS/ANSI N55.1, LLW Process	**SOIL TESTS** ASTM D698-91, Proctor Density ASTM D2850-95, Compression ASTM D2166-91, Compression ASTM D4253-93(96), Vibration Density
MOISTURE ASTM D2216-92 ASTM D2974-87(95)	**FREEZE-THAW RESISTANCE** ASTM D590-96, Soil/Cement Resistance ASTM D4842-90, Resistance ASTM D590-96, Waste Freeze/Thaw EDF WGS-005 (INEEL-specific)
FREE-LIQUIDS EPA Method 9095, PFT @ 0 psig EPA Method 9096, LRT @ 50 psig ASTM D4359-90, Liquid/Solid Pourability EPA Series 600, Method 160.3	**INCINERATION** ASTM D240, BTU ASTM D482, Ash Content
VIBRATIONS ASTM D999-96, Shipping ASTM D4728-95, Random Burrell Wrist-Shaker @ 3cps	**BIODEGRADEABILITY** 40 CFR 264.314(e) (non-biodegradable) ASTM G21-70, Fungi ASTM G22-76, Bacteria

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