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ABSTRACT

The suitability of selected solidification media for application in the disposal of low-level oil and other organic liquid wastes has been investigated. In the past, these low-level wastes (LLWs) have commonly been immobilized by sorption onto solid absorbents such as vermiculite or diatomaceous earth. Evolving regulations regarding the disposal of these materials encourage solidification.

Solidification media which were studied include Portland type I cement; vermiculite plus Portland type I cement; Nuclear Technology Corporation's Nutek 380-cement process; emulsifier, Portland type I cement-sodium silicate; Delaware Custom Materiel's cement process; and the U.S. Gypsum Company's Envirostone process.

Waste forms have been evaluated as to their ability to reliably produce free standing monolithic solids which are homogeneous (macroscopically), contain < 1% free standing liquid by volume and pass a water immersion test. Solidified waste form specimens were also subjected to vibratory shock testing and flame testing.

Simulated oil wastes can be solidified to acceptable solid specimens having volumetric waste loadings of less than 40 volume-%. However, simulated organic liquid wastes could not be solidified into acceptable waste forms above a volumetric loading factor of about 10 volume-% using the solidification agents studied.

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1. INTRODUCTION

The work reported here represents an effort at the Brookhaven National Laboratory (BNL) to determine the suitability of certain solidification agents for the disposal of radioactively contaminated oils and other organic liquid wastes.

Oils and other organic liquid wastes represent a particularly troublesome radioactive waste category for producers of low-level wastes (LLWs). Typically, these organic wastes are generated in low volume quantities at both government and commercial facilities, and often contain relatively low levels of radioactive contamination. Little success has been reported in the past for the immobilization of these wastes in acceptable waste forms with reasonably high loadings ($\geq$ 20 volume-%. In the past, oils and other organic liquid LLWs have commonly been immobilized by sorption onto solid absorbents such as vermiculite or diatomaceous earth. However, evolving regulations regarding the disposal of these materials encourage solidification. As a result, there is a need to identify appropriate solidification agents and determine how they can be best applied. Alternatively, and where it is available for this application, incineration may be an acceptable treatment option for these wastes.

In the present study, the following solidification agents were investigated:

Portland type I cement, with and without additives and including vermiculite

NUTEK 380-cement[a]

DCM cement shale silicate[b]

Envirostone polymer-modified gypsum cement[c]

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[a] Nuclear Technology Corp., Amston, Connecticut.
[b] Delaware Custom Materiel, Inc., State College, Pennsylvania.
[c] U.S. Gypsum Co., Chicago, Illinois.

The simulated liquid organic wastes which were used to prepare the waste form samples included a lubricating (vacuum pump) oil and an organic solution ("NEN") containing selected alcohols, alkanes, ketones, aldehydes, esters, aromatics, and chlorinated hydrocarbons. The experimental matrix for this study is given in Table 1.1.

The solidified waste forms were evaluated in terms of being free-standing monolithic solids and having no free liquid following solidification. Other testing was applied to selected specimens, viz immersion testing, vibratory shock testing, and flame testing. Immersion testing involved placement of the waste form specimens in water at ambient temperature for periods of 72 hours or longer. If there was no evidence of a loss of sample integrity, the specimens were judged to have passed the immersion test. Vibratory shock testing was intended to simulate transportation conditions which the waste forms might experience when shipped to a burial site. Specimens were considered to have passed this test if they exhibited little in the way of physical breakup or deterioration of sample integrity. Flame testing involved determining the response when the sample was subjected to an open flame propane torch and noting whether any burning of the specimen was sustained when the torch was removed.

This study concentrated on high waste loading formulations which are assumed to be representative of actual practice of LLW generators. At lower waste loadings ($\leq$ 10 volume-%), improved waste form properties should result.

Table 1.1 SOLIDIFICATION MEDIA INVESTIGATED

	Immobilization of Oil	Immobilization of "NEN"
Portland Type I Cement	X	
Vermiculite and Portland Type I Cement	X	
Nutek 380-Cement	X	X
Emulsifier, Portland Type I Cement, and Silicate	X	
DCM Cement	X	
Environstone Cement	X	X

2. SOLIDIFICATION OF SIMULATED OIL WASTES

A representative hydrocarbon lubricating oil was chosen for use as a simulated oil waste in this study (Inland Vacuum Industries #19 Vacuum Pump Oil). This oil is in common use as a vacuum pump oil at BNL and has a density of 0.86 g/mL at ambient temperature. As discussed in the following sections, simulated waste form specimens of this oil and the various solidification media were prepared and evaluated as to their suitability for immobilizing oil wastes.

Samples were prepared on a batch basis and were mixed by hand or by laboratory mixer. A Hobart Model N-50, 3-speed, heavy duty electric mixer was used for many of the preparations. For those preparations in which an emulsifier was used for solublizing the organic waste, a Gast Model 1-AM, 2-inch air-powered mixer was used. This air-powered mixer was capable of delivering a high speed, high shear mixing action.

For each formulation batch, at least two or three specimens in the form of right circular cylinders were prepared in polyethylene containers which were then capped during the period of curing. Two specimen sizes were employed with nominal diameters of approximately 31 and 47 mm, respectively. Typical specimen heights were two or three times the diameters. The resultant solids had nominal volumes in the ranges of 40-60 mL and 140-160 mL, respectively. After curing for at least a two week period, the specimens were removed from the plastic containers and subjected to property testing.

2.1 Portland Type I Cement.

Portland type I cement has been widely used as a solidification agent for LLW. The use of this agent by the nuclear waste industry and its advantages and disadvantages have been discussed recently by Fuhrmann and co-corkers [1].

Formulations of oil, Portland type I cement, and water which were prepared for this study are given in Table 2.1. Samples 11 and 16

Table 2.1 SOLIDIFICATION OF OIL WITH PORTLAND TYPE I CEMENT

Sample I.D.	Formulation Weight Percentage			Volume-% Oil	% Weight Loss on Curing in Air
	Oil	Portland I Cement	Water		
11	10.	30.	60.	(a)	(a)
12	30.	35	35.	45	25
13	30.	50.	20.	50	7
14	20.	50.	30.	34	14
15[b]	5.	75.	20.	12	2
16	50.	30.	20.	(a)	(a)

[a] Not determined.

[b] Formulation judged to yield the most satisfactory solid in this group.

contained relatively large fractions of free liquid, whereas samples 12 and 13 exhibited relatively little free liquid. Only a trace quantity of free oil remained on the surface of sample 14, while sample 15 cured to an essentially dry solid. All of the specimens were wiped dry and allowed to cure in air following the initial 3-day curing period in the containers. The specimens were placed on a paper mat during the subsequent air curing period and it was observed that oil ran out of the specimens and spread along the paper mat.

From the standpoint of general appearance and its lack of free liquid, the best performance rating for these samples was assigned to formulation number 15. This formulation, with a water/cement ratio of 0.27, also exhibited the least weight loss on curing in air. The weight loss includes both water lost through evaporation and oil lost by seepage onto the paper mat, although the relative amounts of each were unassignable. While rated best among the oil/Portland type I cement specimens, sample number 15 represented an oil loading efficiency of only 12 vol%, however, indicating that this solidification media is not very effective for oil wastes.

2.2 Vermiculite and Portland Type I Cement.

Many nuclear facilities routinely dispose of oil and other organic liquid LLWs by sorbing them onto solid sorbents such as vermiculite which are then packaged for burial [2]. These materials may then be further immobilized by incorporating them into cemented solids.

In order to determine some suitable formulations, samples of unloaded (with oil) vermiculite plus water and Portland type I cement were prepared as shown in Tables 2.2 (for untreated vermiculite) and 2.3 (for water-saturated vermiculite). Good solid specimens were obtained with all of the formulations. In the case of untreated vermiculite, an excess of water over that required for cementation was added in order to saturate the vermiculite, since the cement and vermiculite would otherwise compete for the limited water which was present. According to

TABLE 2.2 SOLIDIFICATION OF UNTREATED VERMICULITE WITH PORTLAND TYPE I CEMENT

Sample I.D.	Formulation Weight Percentage: Untreated Vermiculite	Portland I Cement	Water	% Weight Loss on curing in Air
26	5.6	45.	49.	33
27	7.7	39.	54.	38
28	5.5	57.	38.	14
29	7.4	46.	46.	29
30	5.5	50.	45.	30
31	7.7	42.	50.	53

TABLE 2.3 SOLIDIFICATION OF WATER-SATURATED VERMICULITE WITH PORTLAND TYPE I CEMENT

Sample I.D.	Formulation Weight Percentage: Water-Saturated Vermiculite(a)	Portland I Cement	Added Water	% Weight Loss on Curing in Air
20	28.	45.	27.	32
21	39.	39.	23.	37
22	27.	57.	16.	14
23	39.	48.	14.	23
24	27.	50.	23.	25
25	39.	42.	19.	33

(a) ∿80 wt% water

Lin and MacKenzie [2], under near neutral to highly basic conditions, vermiculite will absorb water up to about 4 g per g of absorbent. In terms of the total amount of water added and hence available for cementation (over that required by the vermiculite) in each case, samples 20-25 are thus directly comparable to samples 26-31, respectively. This appears to be reflected in the similar degree of weight loss on curing in air for the comparable samples, suggesting that the manner and order in which the ingredients are added is unimportant in this case. The minimum amount of weight loss for these specimens on curing in air is exhibited for a water/cement ratio of 0.28 by weight.

Samples were prepared using vermiculite which had been partially loaded with oil (50% saturated) plus water and Portland type I cement. The formulations are given in Table 2.4. With these samples, there was insufficient water to both saturate the sorbing capacity of the vermiculite and also provide a water/cement ratio sufficient for a good cement product. For example, only for sample number 47 was there an excess of water over that which would be required to saturate the vermiculite and in this case a water/cement ratio of only 0.10 would result if all of the water so available were to be sorbed onto the vermiculite. Adequate cement hydration occurred, indicating that Portland type I cement is able to compete with vermiculite for the available water. However, due to the relatively small amounts of water available for solidification, samples 6-10 and 41-46 were too dry to give solids. Samples 47-52 did give good solid specimens, however, and the best overall specimen was judged to be number 49. However, the volumetric loading efficiency (11 vol% oil) for this sample is rather low.

Results for samples prepared using oil-saturated vermiculite plus water and Portland type I cement are given in Table 2.5. Oil-saturated vermiculite contains approximately 3 g of oil per g of absorbent (density of untreated vermiculite is 0.099 g/mL) [2]. These samples set up in about three days to give good free-standing monolithic solids, however, all had an initial oily appearance and traces of free liquid were

TABLE 2.4 SOLIDIFICATION OF PARTIALLY (50%) SATURATED (OIL) VERMICULITE WITH PORTLAND TYPE I CEMENT

Sample I.D.	Formulation Weight Percentage: Oil (50% Sat'd.)-Vermiculite[(a)]	Portland I Cement	Water	Volume-% Oil	% Weight Loss on Curing in Air
6	17.	59.	24.	10	9
7	28.	48.	24.	12	13
8	40.	36.	24.	13	18
9	45.	30.	24.	15	20
10	51.	25.	24.	16	20
41	19.	51.	30.	13	12
42	27.	45.	27.	16	19
43	19.	63.	18.	(b)	(b)
44	19.	63.	18.	(b)	(b)
45	19.	56.	25.	13	10
46	27.	50.	23.	14	13
47	17.	45.	38.	10	26
48	23.	38.	38.	13	30
49[(c)]	17.	55.	28.	11	13
50	23.	48.	29.	14	17
51	17.	50.	33.	11	16
52	23.	42.	35.	14	29

(a) ∿37.5 wt% oil.

(b) Not determined

(c) Formulation judged to yield the most satisfactory solid in this group.

TABLE 2.5 SOLIDIFICATION OF OIL-SATURATED VERMICULITE WITH PORTLAND TYPE I CEMENT

Sample I.D.	Formulation Weight Percentage: Oil-Saturated Vermiculite[(a)]	Formulation Weight Percentage: Portland I Cement	Formulation Weight Percentage: Water	Volume-% Oil	% Weight Loss on Curing in air
1	24.	48.	29.	27	11
2	35.	35.	30.	34	22
3	47.	24.	29.	40	29
4	50.	20.	30.	45	30
5	51.	17.	31.	43	33
32	20.	50.	30.	26	17
33	27.	45.	27.	35	15
34	33.	42.	25.	40	18
35	20.	63.	18.	24	7
36	27.	57.	16.	29	7
37	33.	52.	15.	34	8
38[(b)]	20.	55.	25.	30	10
39	27.	50	23.	36	12
40	33.	46.	21.	39	14

(a) ∿75 wt% oil.

(b) Formulation judged to yield the most satisfactory solid in this group.

observed with all samples. Sample 38 was judged to be the best overall specimen, with a volumetric loading efficiency of 30% and only a 10% weight loss on curing in air.

If oil wastes are to be disposed of by first sorbing on vermiculite and then solidifying with Portland type I cement, it appears that best results are obtained by saturating the vermiculite with oil prior to solidification. With unsaturated oil-vermiculite, lower volumetric efficiencies for waste loading are obtained and poorer solids result due to competition for the water between cement and the absorbent.

2.3 Nutek 380-Cement.

The Nuclear Technology Corporation (NUTEK) has developed a proprietary chemical process to solidify radioactive waste oils [3]. Ingredients and details concerning waste formulations were obtained from NUTEK. Samples prepared for this study are listed in Table 2.6. The ingredient Nutek 380A serves as an emulsifying agent; Nutek 380B serves to accelerate the set time.

In this procedure, oil and Nutek 380A are mixed to a creamy emulsion consistency, then added to a mixture of Portland cement and slaked lime and stirred until homogeneous. (The amount of lime added to the cement is less than that which yields a masonry cement.) The Nutek 380B is then slowly added and the composition is stirred slowly for a short period and allowed to set (48 hours).

Good solid monoliths were obtained with this procedure and there were no instances of free liquid formation with these compositions. Samples 78 and 80 were judged to be best in appearance and apparent strength, followed by 79 (which was somewhat softer) and 81 (which was softest). It appears that this process yields good solid waste forms at volumetric oil loadings of about 30%.

TABLE 2.6 SOLIDIFICATION OF OIL WITH NUTEK 380-CEMENT

Sample I.D.	Formulation Weight Percentage: Oil	Portland I Cement	Lime	Nutek 380A	Nutek 380B	Water	Volume-% Oil
77	21.	48.	6.6	21.	3.2	0.0	29
78[a]	19.	44.	6.0	19.	2.9	8.8	29
79	24.	38.	5.2	24.	3.6	5.5	32
80[a]	20.	53.	0.0	20.	3.0	4.6	30
81	27.	31.	4.5	27.	4.1	6.3	43

[a] Formulations judged to yield the most satisfactory solids in this group.

2.4 Emulsifier, Portland Type I Cement, and Sodium Silicate.

Simulated waste specimens were prepared from batch mixtures of oil, emulsifier (Nutek 316, also available from Nuclear Technology Corporation), Portland type I cement, and sodium silicate. An aqueous solution of sodium silicate (weight ratio of 3.22; 41.0°Be) was used in these preparations. The formulations used for this study are given in Table 2.7. No free standing liquid was observed with any of these specimens.

In this procedure, oil was first added to water and mixed with high speed mixer for 4 minutes. Cement was then added and the mixture was mixed for 2 minutes. Emulsifier was added and mixing was maintained until a good homogeneous mix was obtained. Then, sodium silicate was added. The specimens cured to firm, monolithic solids in about 24 hours.

Sample 83, with a volumetric loading of 39% oil, was judged to be the best composition of this set, followed by 84. Samples 85 and 86 were soft, and 87 was very soft and crumbly.

2.5 DCM Cement Shale Silicate.

DCM cement shale silicate, a proprietary process, is available in kit form from the manufacturer, Delaware Custom Materiel, Inc., State College, Pennsylvania. For the tests done for this study, the manufacturer's directions were followed. Oil and then cement was added to water and mixed for 4-5 minutes. The emulsifier was then added and the composite mixture was mixed for 4 minutes. Then, sodium silicate was added while the mixing was continued until a creamy composition was obtained (in less than one minute).

Sample compositions made up with the DCM cement are given in Table 2.8. In this set, sample 88 was judged to be best with a 30 vol% loading of oil; specimens of this composition exhibited dry hard surfaces. Sample 89 had firm surfaces but evidenced some oily appearance. Sample 90 produced specimens with soft and oily surfaces, while those of 91 were

TABLE 2.7 SOLIDIFICATION OF OIL PLUS EMULSIFIER (NUTEK 316) WITH PORTLAND TYPE I CEMENT - SODIUM SILICATE

Sample I.D.	Formulation Weight Percentage					Volume-% Oil
	Oil	Portland Cement	Emulsifier	Sodium Silicate	Water	
82	18.	51.	0.0	2.5	28.	30
83[a]	23.	46.	2.0	3.8	25.	39
84	29.	41.	2.9	4.6	23.	45
85	33.	38.	3.5	5.3	21.	49
86	36.	35.	3.8	5.9	19.	44
87	38.	34.	4.0	6.1	19.	(b)

[a]Formulation judged to yield the most satisfactory solid in this group.

[b]Not determined.

TABLE 2.8 SOLIDIFICATION OF OIL PLUS EMULSIFIER WITH DCM CEMENT - SODIUM SILICATE

Sample I.D.	Formulation Weight Percentage					Volume-% Oil	Oil Loss on Immersion mL Oil/mL Specimen
	Oil	DCM Cement	Emulsifier	Sodium Silicate	Water		
88[a]	17.	51.	1.6	2.8	27.	30	9/199
89	24.	46.	2.0	3.8	25.	38	16/210
90	29.	41.	2.9	4.6	23.	44	22/198
91	33.	38.	3.3	5.3	21.	48	30/190
92	37.	36.	3.1	5.0	20.	(b)	19/(b)
93	38.	34.	3.8	6.1	19.	(b)	(b)

[a]Formulation judged to yield the most satisfactory solid in this group.

[b]Not determined.

very soft and oily. Specimens from sample 92 were soft and could be crushed easily by hand, while those of number 93 were too soft to handle.

2.6 Envirostone Cement.

Envirostone polymer-modified gypsum cement is manufactured and marketed by the U.S. Gypsum Company, Chicago, Illinois. The manufacturer's directions were used in preparing the formulations in this study. Liquid emulsifier, water, and oil were added to the Envirostone cement in that order and mixed at high speed with the air-powered mixer for 2 minutes. All samples set within about 10 minutes without any evidence of free liquid remaining on any of the specimens.

Sample compositions of oil and Envirostone cement are given in Table 2.9. The specimens for formulations 53 and 54 produced firm solids, while those for 55 through 58 progressively ranged from soft to very soft. Overall, sample 54 was judged to have best performance characteristics of this set (this represents a volumetric loading efficiency of 36%).

TABLE 2.9 SOLIDIFICATION OF OIL WITH ENVIROSTONE CEMENT

Sample	Formulation Weight Percentage					
I.D.	Oil	Envirostone Cement	Liquid Additive	Water	Volume-% Oil	% Weight Loss on Curing in Air
53	18.	52.	2.2	28.	28	21
54[(a)]	24.	47.	3.0	26.	36	21
55	30.	43.	3.7	24.	43	16
56	34.	40.	4.3	22.	48	13
57	38.	37.	4.8	20.	50	12
58	40.	36.	5.0	20	50	12

[(a)] Formulation judged to yield the most satisfactory solid in this group.

3. SOLIDIFICATION OF SIMULATED ORGANIC LIQUID WASTES

Candidate solidification media for organic liquid wastes were surveyed and two were chosen for further study: Nutek-380 cement and DCM cement shale silicate. A simulated organic liquid waste, "NEN" solution, was prepared for this study. This solution, intended to simulate as closely as possible the organic liquid waste stream produced at a typical radiopharmaceutical/labeled compound manufacturing facility, was prepared according to a compositional recipe suggested by a representative of New England Nuclear, Boston, Massachusetts. The composition of "NEN" solution is given in Table 3.1. The density of this solution is 0.81 g/mL at ambient temperature.

3.1 Nutek 380-Cement.

Samples were prepared using "NEN" solution and the Nutek process described in Section 2.3. The sample compositions which were used for this study are given in Table 3.2

Samples 96-98 were unacceptable in that specimens contained considerable quantities of free liquid (ranging to 30% of the specimen volume for number 98). Specimens from samples 101-103 eventually set up and gave dry monolithic solids after curing for several days in closed containers. An acceptable solid was obtained with sample 102 which contained 6 weight percent "NEN" (about 10 vol%). Sample 101 gave softer, more crumbly specimens, while number 103 was intermediate between the two (101 and 102). In all cases, the odor of organic vapors, particularly that of diethyl either, was quite strong.

3.2 Envirostone Cement.

Samples were prepared using "NEN" solution and the Envirostone process described in Section 2.6. Sample compositions are given in Table 3.3.

TABLE 3.1 COMPOSITION OF "NEN" SIMULATED ORGANIC LIQUID WASTE STREAM

Simulated Organic Liquid Waste Stream Composition		
Component	Vol%	Component Formula
Methanol	22	CH_3OH
Ethanol	22	C_2H_5OH
Acetone	9	CH_3COCH_3
Isopropanol	5	$CH_3CHOHCH_3$
Diethyl ether	9	$C_2H_5OC_2H_5$
Ethyl acetate	4	$C_2H_5COOCH_3$
n-Hexane	9	$CH_3(CH_2)_4CH_3$
Benzene	4	C_6H_6
Toluene	4	$C_6H_5CH_3$
Acetonitrile	4	CH_3CN
1,2-Ethylene dichloride	4	$C_2H_4Cl_2$
Chloroform	4	$CHCl_3$
	100	

TABLE 3.2 SOLIDIFICATION OF SIMULATED ORGANIC LIQUID WASTE ("NEN") WITH NUTEK 380-CEMENT

Sample I.D.	Formulation Weight Percentage					
	"NEN"	Portland Cement	Lime	Nutek 380A	Nutek 380B	Water
96	20.	49.	6.7	21.	2.5	0.0
97	18.	45.	6.1	19.	2.9	8.9
98	23.	39.	5.3	24.	3.6	5.6
101	13.	63.	8.5	14.	2.3	0.0
102	6.1	58.	7.9	6.3	1.1	21.
103	10.	59.	8.0	11.	1.6	11.

TABLE 3.3 SOLIDIFICATION OF SIMULATED ORGANIC LIQUID WASTE ("NEN") WITH ENVIROSTONE

Sample I.D.	Formulation Weight Percentage				Volume-% "NEN"
	"NEN"	Envirostone Cement	Liquid Additive	Water	
59	17.	52.	2.2	29.	26
60	23.	48.	3.1	26.	36
61	28.	44.	3.8	24.	43
62	33.	41.	4.4	22.	50
63	37.	38.	4.9	21.	(a)
64	38.	36.	5.1	20.	(a)
T1	18.	57.	2.5	23.	28
T2	14.	66.	1.9	18.	25
T3	0.0	55.	7.1	38.	0.0
T4	8.1	50.	6.5	35.	11

(a) not determined

Eventually, all of the "NEN"-Envirostone specimens soldified, although free liquid persisted in some cases. Sample T4 was judged to give the best overall product (at 11 vol% "NEN") on the basis of general appearance and the firmness of the solid which was formed. Number 59 (26 vol% "NEN") was judged to be much less acceptable due to its soft nature, followed by number T1 (28 vol% "NEN"). With samples 60 and 61, the top portions of the specimens were cracked and tended to flake off. Samples 62, 63 and 64 retained substantial portions of free liquid and were considered to be unacceptable. All of the "NEN" - Envirostone specimens initially had a free liquid layer but samples 59-62 and T1-T4 eventually cured to form solids without any free liquid.

As with samples of "NEN" plus Nutek 380-cement, the Envirostone samples exhibited strong odor of the organic mixture when kept in closed containers. However, this diminished on standing for specimens which were removed from their containers due to evaporation of volatile organic constituents in the simulated waste.

4. TESTING OF SOLIDIFIED WASTE FORMS

Selected solidified waste form specimens were subjected to immersion testing in water, vibratory shock testing, and flame testing. Discussion of the performance of these specimens under various testing conditions is described.

4.1 Immersion Testing.

Specimens representing all of the solidified oil formulations were subjected to immersion testing for periods ranging from 72 hours to more than 1 week. The test consisted of immersing each of the solid specimens (which were cylindrical and typically 47 mm in diameter and approximately 100 mm long) in 1750 mL of tap water at ambient temperature. All of the specimens tested passed the immersion test in that there was little if any loss of sample integrity over the period they were immersed. However, in most cases some oil was released from the solids as evidenced by a film on top of the immersion solution. This amount of released oil was determined in a few cases, such as shown in Table 2.8 for samples of oil plus emulsifier, DCM cement shale, and sodium silicate.

The loss of oil from solidified waste forms, whether on draining out of the specimens when removed from containers and placed on paper mats, or on being immersed in water, may bear little or no relation to the containment of radioactivity by actual solidified LLW forms. Actual LLW specimens will contain various radioactive elements in a multitude of chemical states and physical forms. These radionuclides may be activation products, fission products, or natural radioactive isotopes and transuranics (if present at less than 10 nanocuries/g). These radioactive elements may be present as particulates, or as dissolved species, or as sorbed species. In order to ascertain the effectiveness of the various solidification media in containing such materials and to predict the releases of radioactivity under various scenarios, extensive leach testing of the solidified products would be essential. The observations noted here simply relate to the release of fluids (water, oil, etc.) from the waste form specimens.

4.2 Vibratory Shock Testing.

Selected waste specimens were subjected to vibratory shock testing in order to simulate transportation conditions which might be experienced by LLW forms when shipped to burial sites. For this test, an electromagnetic vibrating table (FMC Corporation Model J-50-B) was modified by construction of a metal fence around the outer edge of the platform. The vibrating frequency of this table was 236 revolutions per minute (3.9 Hz).

The vibratory table top was loaded with formulations representing a wide range of oil content and solidification media as follows:

1 to 58	Free-standing solids, had undergone immersion testing.
1 to 58	Free-standing solids, not subjected to prior immersion testing.
65 to 70	Solids contained in closed vials.
82 to 87	Solids contained in closed vials.

These samples were tested simultaneously for a one-hour period after which only a very small amount of loose material (vermiculite and cement dust) was observed to be present on the vibratory table top. No free liquid was observed. Thus, all samples appeared to perform adequately in this simulated transportation mode.

Another smaller group of waste specimens was likewise tested. These included solids contained in closed vials (the specimens from formulations 82 to 93). After one hour of testing, two specimens (87 and 93, each containing 223 g oil to 200 g cement) did exhibit a very thin layer of free liquid on the top.

4.3 Flame Testing.

An open flame test was applied to selected waste specimens. In this test, the specimens were contacted with an open flame from a propane torch. In most cases, it was observed that vapors above the samples would ignite and burn as long as contact was maintained with the open flame. With the exception of two specimens, as discussed below, the flames were extinguished as soon as the propane torch was removed. The samples which were tested are listed in Table 4.1

Two specimens, samples number 12 and 32, were observed to continue to sustain combustion after the propane torch was removed. Sample 12 was a oil/cement composition. Sample 32 was a oil-saturated vermiculite/-cement composition. With both of these specimens, as well as one from sample number 77 (oil/Nutek 380-cement), oil was observed to flow out of the solid when heated. These results are not definitive since several weeks had passed since the specimens had been prepared and varying amounts of oil had already been released from these waste forms. However, it appeared that the Envirostone specimens showed the least tendency to lose oil or sustain a flame under these conditions.

TABLE 4.1 FLAME TESTING OF SELECTED SIMULATED WASTE SPECIMENS

Sample I.D.	Flame Test Result: Flame Extinguished When Propane Torch Removed		
	YES	NO	COMMENTS
3	X		
12		X	When heated, oil flowed out of the solid.
21	X		
25	X		
32		X	When heated, oil flowed out of the solid.
36	X		
47	X		
51	X		
54	X		
58	X		
77	X		When heated, oil flowed out of the solid.
81	X		
82	X		
83	X		
84	X		
85	X		
86	X		
94	X		

5. CONCLUSIONS

The results obtained in this study indicate that there are several options available for the solidification of oil or organic liquid LLWs at low waste loadings (≤ 10 volume-%). For higher waste loadings, the choices are more limited and there is greater probability of obtaining unsatisfactory solids. This study concentrated on high waste loading formulations which are assumed to be more representative of actual LLW generators' practices. Based on the criteria applied in this study, acceptable solids were obtained (i.e., selected formulations yielded free-standing monolithic solids with < 1 vol-% free liquid, which passed a water immersion test). However, there are indications that these formulations may not be completely satisfactory on the basis of other or evolving LLW acceptance criteria. Further work would be required in order to more fully characterize these various waste forms including leach testing of selected radionuclides.

Formulations judged to yield the most satisfactory solids for each soldification media with oil and "NEN" solution are summarized in Table 5.1. In the case of oil, volumetric waste loadings of the order of 30-40 volume-% may be realized with specimens of reasonable physical integrity. For "NEN", however, acceptable formulations are generally below about 10 volume-%. Especially for organic liquid wastes, alternative treatments such as incineration may be preferable to direct immobilization.

TABLE 5.1 FORMULATIONS JUDGED TO YIELD THE MOST SATISFACTORY SOLIDS

Immobilization Media	Oil Waste	Simulated Organic Liquid Waste ("NEN")
Portland Type I Cement	#15 (12 vol%)	
Vermiculite plus Portland Type I Cement	#38 (30 vol%), sat'd. #49 (11 vol%), 50% sat'd.	
Nutek 380-Cement	#78 (29 vol%) #80 (30 vol%)	#102 (6 wt%)
Emulsifier, Portland Type I Cement, and Sodium Silicate	#83 (39 vol%)	
DCM Cement	#88 (30 vol%)	
Envirostone Cement	#54 (36 vol%)	#T4 (11 vol%)

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