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Tests of Absorbents and Solidification Techniques for Oil Wastes

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Prepared for
U.S. Nuclear Regulatory
Commission

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ABSTRACT

A representative of each of six classes of commonly used absorbents was chosen for a series of tests. After reviewing ASTM and other related standard tests, uncomplicated procedures were developed for carrying out specific tests to determine absorbency for simulated oil waste and for water, under static and simulated transportation (repetitive shock) conditions. The tests were then applied to the six representative absorbents. Solidification tests were performed using these absorbents saturated with oil and loaded to 50% of saturation. The binders used were Portland I cement and Delaware Custom Material (DCM) cement shale silicate. Samples were checked for proper set, and the amounts of free liquid were measured. Another series of tests was performed on samples of simulated oil waste without absorbent, using Portland cement and DCM cement shale silicate. Samples were checked for proper set, free liquid was measured, and compressive strengths were determined. The state-of-the-art parameters were identified which satisfy NRC disposal criteria for solidified radioactive waste. The literature was reviewed for alternative methods of managing oil wastes. Conclusions are drawn on the relative utility of the various methods.

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TESTS OF ABSORBENTS AND SOLIDIFICATION TECHNIQUES FOR OIL WASTES

1. INTRODUCTION

Some oil waste is generated by every nuclear power plant during its normal operation.(1) Since published information on kinds and amounts of this waste and its properties are not available, a questionnaire was devised and sent to over 50 operating nuclear power plants. Ten of the plants responded with answers to most of the questions. A copy of the questionnaire is reproduced in Appendix A along with a summary in tabular form of the information obtained from the respondents. The main points are given below as background for this report.

The amount of waste oil generated annually at reporting power plants varied from 100 to 1000 gal. The major components of the oil wastes were pump oil, turbine seal oil, and lubricating oil. Minor amounts of other wastes such as grease, snubber oil and sludges may be mixed with the oil. The water content in the oil wastes generated from PWR power plants was normally very small. However, in the waste oils from reporting BWR plants, the water content varied from 0 to 90%. At most of the power plants, the pH values of the water contents in oil wastes have not been measured. However, of the two that were measured, one was reported to be neutral and the other was acidic, with a pH of 3.5.

In general, the level of contamination in the oil wastes was low. Two major components of radioactive contamination (Cs-134,137 and Co-58,60) were found in the range of 10^{-5} to 10^{-6} μCi/mL. Mn-54 has been identified at one plant at a level of 10^{-5} μCi/mL. The other components in lower levels that can be identified were Xe-133, H-3, Zn-65, Np-239, W-187, and Tc-99. The source of oil contamination in BWR plants is considered to be the turbine oil which has been in contact with the primary coolant. In PWR plants, it is the pump oil that has been in contact with a contaminated atmosphere through ventilation. This waste pump oil may initially contain only traces of radioactive contaminants such as Xe-133, but will later be mixed with contaminated oils from other sources or become contaminated by contact with a contaminated environment such as piping.

At the present time, there are a number of methods in use for managing the oil wastes. These include storing the wastes in-plant for future disposal, absorbing the wastes using absorbents accepted by burial sites, filtering through diatomaceous earth and resin, and solidifying the wastes with cement or similar rapid solidification materials [e.g., Delaware Custom Material (DCM) cement shale silicate binder]. For wastes containing water, one treatment method used at a single power plant is to separate the water for liquid radwaste treatment. At another plant, the water-containing waste is loaded on absorbent and shipped to Hanford. For oils slightly contaminated with Xe-133, the oil is stored to allow the activity to decay, then it is treated as clean oil.

BNL has investigated methods of preparing oil wastes for disposal using commercially available absorbents and standard solidification techniques. We have also performed a literature survey to evaluate alternative methods for treating oil wastes. These alternatives include decontamination, incineration, ozonation, and regeneration.

In the experimental program, typical absorbents were evaluated by determining absorption capacity for oil and for water under static conditions and under simulated transportation conditions. The solidification media investigated were Portlant I cement and Delaware Custom Material (DCM) cement shale silicate. Oil wastes were solidified using these media, both with and without absorbents. Degree of setting, amount of free liquid, and compressive strength of the solid forms produced, as well as the proportion of oil incorporated in them, were the properties used to evaluate the solidification techniques. A third solidification medium, Dow vinyl ester-styrene polymer, was used to prepare a few test samples with water containing 0.2% oil, but could not be applied to oil itself.

It is expected that the results of this study will be of use to NRC in providing guidance to licensees and agreement states on the management of oil wastes.

2. ABSORBENCY TESTS

Uncomplicated test procedures for determining both oil and water absorbencies were selected and shown to be satisfactory by carrying out experimental absorbency determinations using six representative absorbents. The determinations were made under both static and simulated transportation conditions.

2.1 Representative Oil Wastes

For testing absorbents, and also solidification techniques, BNL devised a simulated oil waste which was considered representative based on the oils used in PWRs and BWRs according to information obtained from the licensees. The choice and the rationale for it are as follows.

Reactors can use any brand of oil for the coolant pump or turbine which meets the specifications given by the pump or turbine manufacturer.* Differences between brands should be negligible as far as the refined hydrocarbon component is concerned. Any differences in the minor components (rust and oxidation inhibitors) should have an insignificant effect on the absorbency to be determined in laboratory tests.

The waste pump and turbine oils at power plants are usually collected in 55-gallon drums for storage. At this stage, oil waste from other sources and assorted rust, dirt, sludge and grease suspected or known to be contaminated will often be mixed with them.(2) Therefore, the composition and level of contamination of pump and turbine oil wastes varies from batch to batch. They will be largely either pump oil or turbine oil, but not a mixture of these two types. For testing purposes, however, because the oils have quite similar compositions, it was considered reasonable to use a mixture, rather than carry out two series of tests, one with each kind. Because of the variability and small amount of extraneous material encountered in practice, no attempt was made to devise a representative mixture of such material. Thus, the simulated oil waste used was a 1:1 mixture of turbine seal oil (Mobil DTE 797, used in BWR turbines) and PWR coolant pump oil (Mobil DTE medium).

2.2 Selection of Test Procedures for Determining Oil Absorbency

BNL has reviewed available ASTM and other standard procedures for testing the capacity of absorbents and developed from these tests an uncomplicated standard test procedure for use with oil wastes. The procedure chosen for determination of absorption capacity has two parts, the first applying to static conditions, and the second to acceleration and vibration conditions encountered during transportation.

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*According to General Electric Company manual GEI-1563Y on Oil Recommendations for Steam Turbines, cleanliness of the oil and lubricating system is of utmost importance. A reasonable variation in oil properties is allowed, e.g., Saybolt Viscosity range at 100°F is given as 140-170 SSU.

2.2.1 Test of Absorption Capacity Under Static Conditions

A number of ASTM tests for liquid absorption were located and reviewed. The one which appeared most applicable to oil absorption by a variety of absorbents was ASTM D/483-60 (Reapproved 1979), "Oil Absorption of Pigments by Gardner-Coleman Method." It was adopted for our purposes, with slight modifications. These include an eight-fold increase in sample volume and a ten-fold increase in weighing sensitivity to provide higher precision.

The modified procedure is as follows:

a. Measure and record volume of absorbent (10 to 15 mL) in mL and its weight in g (to the nearest 0.01 g) then pour into a small vial.

b. Pour oil waste into a buret and record the initial volume.

c. Slowly titrate the absorbent with liquid waste while stirring the mixture gently with a stainless steel spatula. Several minutes should be taken for the addition when the absorbent contains coarse particles to ensure that the particles have been saturated.

d. Stop adding the liquid waste when a uniform mixture (without a smear of excess liquid) is reached.

e. Record the final volume of liquid in the buret.

f. Subtract the final volume from the initial volume to obtain the volume of liquid added.

g. Calculate the absorbency by the following formulas

$$\text{Absorbency by volume} = \frac{\text{volume of liquid absorbed in mL}}{\text{volume of absorbent in mL}}$$

$$\text{Absorbency by weight} = \frac{\text{volume of liquid absorbed in mL x density (g/mL)}}{\text{weight of absorbent in grams}}$$

2.2.2 Test of Absorption Capacity Under Simulated Transportation Conditions

Reports on shock vibrations encountered in rail and truck transportation(3,4) were reviewed. Among the findings described in these reports was the fact that the vibrations occurring on the road depend on the characteristics of the vehicle used, road conditions, shock absorbers used, geometric position of the sample on the vehicle, and many other factors. The situation is similar for rail transportation. For both rail and truck transportation most of the vibrations with frequency in the 0-10 Hz range show a high proportion of intermittent shock-like inputs from an uneven road surface, having accelerations up to approximately 1 g.(4) Most of the higher frequencies, over 50 Hz, such as those due to motor vibrations, are more nearly continuous but generally produce accelerations up to only 0.1-0.2 g.

Even a very elaborate vibration testing machine with high frequency capabilities cannot simulate exactly actual transportation conditions. In any case, testing with such a machine using such refined methods would not fulfill the requirement of an uncomplicated test. Several vibration tests for simulated transportation conditions are available. Two ASTM procedures, a military test and a DOT test, (the last two reproduced in Appendix B), are:

1. ASTM D3580-77T "Tentative Method of Vibration (Vertical Sinusoidal Motion) Test of Products,"
2. ASTM D999-75, "Standard Methods for Vibration Testing of Shipping Containers,"
3. MIL-STD-810C military standard vibration test, and
4. DOT test for steel drums, from 49CFR178, Section 16-13(a)(2).

The ASTM procedures call for testing over a broad frequency range (0.2 Hz to at least 100 Hz) whereas the military test uses a fixed frequency of 284 rpm or 4.7 Hz. The DOT test does not specify a frequency but requires subjecting the test drums to one hour of vibration at a frequency that causes them to be raised at least 1/16 in. off the test platform. The amplitude required by the military and DOT tests (1 in. peak to peak) causes an acceleration of approximately 1 g at the 284 Hz used in the military test, whereas the ASTM tests call for only 0.1 to 0.5 g.

A test machine was acquired which was capable of providing the vibration conditions specified in the military and DOT procedures and in Method A of ASTM Test D999. This machine, Type 100-SVM manufactured by L.A.B. Corporation, has a vibration amplitude of 1 in. peak to peak and the frequency can be varied continuously from 0 to 5.4 Hz. The platform is driven in sinusoidal motion which provides both vertical and horizontal vibration components.

ASTM Procedure D999, "Method A-Repetitive Shock Test," does not require covering the complete frequency range available as do the other ASTM methods. It specifies starting the frequency at about 2 Hz and steadily increasing it until some portion of the test specimen repeatedly leaves the platform or until the acceleration of the platform is 1.1 g. One hour is the time recommended for maintaining this condition. In the operating instructions for the L.A.B. test machine it is stated that one hour in this repetitive shock condition is roughly equivalent to 1,000 miles of shipping travel.

The test developed and used by BNL, based largely on Method A of ASTM Procedure D999 and the DOT test, is as follows:

a. Place on the vibration platform the sample from the static absorbency test which is held in a sealed container. A fence or barricade must be kept around the container to prevent it from falling off the platform.

b. Starting at zero frequency, gradually increase the frequency until the container bounces on the table and against the fence. Adjust the frequency until a 1/16 in. strip of metal can be slid freely under the container.

c. Shake under these conditions for 1 hour.

d. Stop the shaking, immediately open the container, remove and weigh any free liquid.

e. To determine absorbency under transportation conditions, subtract the amount of liquid measured in d from that originally measured in the static absorbency test and recalculate the absorbency using this corrected amount.

2.3 Experimental Determination of Absorbency

As will be described in the next section (2.3.1), six representative absorbents were chosen for evaluation. Oil absorbencies under static and simulated transportation conditions were determined using the test procedures outlined in sections 2.2.1 and 2.2.2. Water absorbency under the same conditions was determined at a number of pH values according to the procedure given in section 2.3.2.

2.3.1 Choice of Absorbents to be Tested

A list of absorbents and their manufacturers supplied by NRC is given in Appendix C, Table C.1. It contains 22 absorbents and 10 different suppliers. BNL located suppliers for all the products listed and obtained brochures with information on their properties. Table C.2 of Appendix C lists the compositions and the manufacturer's absorbency values for 20 of the absorbents. Based on the vendor's data on the composition of the different absorbents, they can be grouped into six main categories, within which there is usually only a small difference in oil absorbency. Because of the similarity within the category, it was decided that the material within each category having the highest oil absorbency would be tested. The six absorbents chosen and their categories are listed below.

1. Conwed for natural fibers
2. 3M 'LSM' for synthetic fibers
3. Amorphous Silicate for the silicates
4. Super-Fine for diatomaceous earth
5. Vermiculite for mica
6. Instant-Dri for clays.

2.3.2 Procedure for Testing Effect of pH on Water Absorbency

The water absorbencies of the 6 materials listed above were determined using water with pH values 1, 4, 7, 10, and 13. The test procedure was as follows:

a. Adjust the pH of distilled water to the desired value with NaOH and HCl.

b. Record the initial pH and carry out the absorbency test as given in Section 2.2.1, a through g.

c. Calculate absorbency.

d. Add a volume of distilled water equal to that already added during determination of the absorbence. Stir the mixture and measure the pH of the excess water. If the measured value differs from the initial pH value by an amount other than ±0.3 units,* because of reaction between the absorbent and water, remeasure the absorbency by the following procedure:

   (i) Using standard HCl or NaOH solution, back titrate to the initial pH and calculate the equivalents of acid or base used in the back titration.

   (ii) Repeat the absorbency test with a fresh absorbent sample of the same size as previously used. Add the number of equivalents of acid or base determined in (i), before reaching the end point. Include the amount of water in this addition in the total used for calculation of the absorbency.

   (iii) Check the pH as in step d.

2.3.3 Oil Absorbency Test Results

Results for the oil absorbency determinations are recorded in Table 2.1. (Note that the table refers to both static and simulated transportation conditions.) Each value listed is the average of three determinations. Reproducibility from sample to sample was within ±1%. This precision was readily achievable with most of the materials, but with Conwed, stirring had to be very gentle to prevent small variations in the end point. Even without this special precaution the precision obtained was well within ±5%. Values of

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*If there is no interaction between the absorbent-water mixture and the added distilled water, dilution by a factor of 2 with distilled water increases the pH by 0.3 units for acidic solutions and decreases it by 0.3 units for basic solutions.

absorbency are only about half that quoted by the supplier in several cases (LSM, Conwed, and Instant-Dri), but differences are expected since absorbency will vary with the viscosity of the oil used. Some of the absorbent materials are designed for such uses as clean-up after crude oil spills, and apparently they exhibit considerably higher absorbencies with the very viscous oils involved in such spills.

Table 2.1

Oil Absorbency Under Static and Simulated Transportation Conditions

Absorbent	Density (g/mL)	Absorbency g of oil / g of absorbent	Absorbency mL of oil / mL of absorbent
Super-Fine	0.482	1.16	0.646
Conwed	0.062	12.9	0.926
Vermiculite	0.099	3.03	0.347
LSM	0.120	5.72	0.796
Amorphous Silicate	0.046	11.1	0.587
Instant-Dri	0.714	0.645[a]	0.533[a]

[a] Values under static conditions. Under simulated transportation conditions the absorbency values determined were 0.639 and 0.528.

Under conditions of the simulated transportation test, there was no release of oil from any of the absorbents except Instant-Dri and, possibly, vermiculite. With Instant Dri the amount released was barely enough to measure, and with vermiculite, the amount was so small it was not clear whether or not it represented an uncertainty in determining the end point in the static test. Even with Instant-Dri the absorbency determined under simulated transportation conditions was within 1% of that measured under static conditions.

2.3.4 Water Absorbency Test Results

Results of the water absorbency tests under static conditions and a range of pH values are given in Tables 2.2 and 2.3. Each value listed in the tables is the average of five determinations. As with the oil absorbency tests reproducibility from sample to sample was within ±1%. The water absorbency under static conditions for all absorbents was almost constant from pH 1 to pH 10. A small change in absorbency at pH 1 was observed for Super-Fine, and at pH 13 for Super-Fine and Instant-Dri. Conwed, showed a large increase in absorbency at pH 13. According to the information supplied by the manufacturer, the surface of Conwed was treated to repel water in order to make the material effective in dealing with marine oil spills. Apparently in water of pH 13 the surface coating was attacked by the 0.1 M NaOH and either destroyed, or damaged to such an extent, that pores previously not open to water became available.

Table 2.2

Water Absorbency by Weight Under Static Conditions
(g of Water/g of Absorbent)

Absorbent	pH 1	pH 4	pH 7	pH 10	pH 13
Instant-Dri	0.65	0.66	0.65	0.66	0.75
Vermiculite	4.08	3.98	4.00	3.93	3.81
Super-Fine	1.56	1.44	1.40	1.44	1.56
Amorphous Silicate	13.1	13.0	13.0	13.1	13.5
Conwed	5.6	5.7	5.8	6.1	13.9
LSM	6.36	6.26	6.22	6.16	6.10

Table 2.3

Water Absorbency by Volume Under Static Conditions
(mL of Water/mL of Absorbent)

Absorbent	pH 1	pH 4	pH 7	pH 10	pH 13
Instant-Dri	0.46	0.47	0.46	0.47	0.53
Vermiculite	0.40	0.39	0.39	0.39	0.38
Super-Fine	0.75	0.69	0.67	0.69	0.75
Amorphous Silicate	0.60	0.60	0.60	0.60	0.61
Conwed	0.35	0.35	0.36	0.38	0.86
LSM	0.76	0.75	0.75	0.74	0.73

As with the oil absorbencies, variation among the six materials was only about a factor of 2 on a volume basis. Actual values were slightly less than for oil, but paralleled those for oil except for Conwed at pH values from 1 to 10, where its surface coating denies to water some of the potentially available space. At pH 13, Conwed exhibits a water absorbency in line with its oil absorbency, being one of the two top absorbers, for both oil and water, along with LSM.

In Table 2.4, the results of the vibration tests are reported as percent water absorbed under static conditions which was released under simulated transportation conditions, rather than as absorbencies. This method of reporting the results is used since for one material (Amorphous Silicate) almost all absorbency was lost. The samples used were the same ones that had been used for the absorbency determination under static conditions, five for each material at each pH. After storage for a week, they were subjected to the simulated transportation test, and the amounts of free water measured. Vermiculite released no water at any pH, and LSM released none except at pH 13. Instant-Dri also performed quite well, releasing only approximately 0.01 mL per mL of absorbent except at pH 13. Super-Fine and Conwed were intermediate in performance, and Amorphous Silicate lost almost all the water it had absorbed in the static test. The repetitive shock treatment of the simulated vibration test reduced the material to a fine powder and obviously essentially destroyed all its absorbent powers for water. Note that this does not occur with oil (Section 2.3.3).

Table 2.4

Percent Water Released Under Simulated Transportation Conditions

Absorbent	pH 1	pH 4	pH 7	pH 10	pH 13
Instant-Dri	3.76	2.4	1.9	1.7	6.3
Vermiculite	0	0	0	0	0
Super-Fine	12.8	7.0	6.5	8.0	14.7
Amorphous Silicate	86	87	83	97	84
Conwed	32	25	22	18	12
LSM	0	0	0	0	5.4

3. SOLIDIFICATION TESTS

Using the solidification media Portland I cement and Delaware Custom Material (DCM) cement shale silicate, solidification of oil waste was investigated both with and without absorbents. A number of test samples were prepared with varying proportions of oil, or oil-containing absorbents. The amount of free liquid, if any, associated with the samples was measured. In the case of the samples prepared without absorbent, the compressive strength was also measured.

A third commercial solidification medium, Dow vinyl ester-styrene polymer, could not be used for tests with absorbents. As described in Section 3.2.1.3, several samples were prepared without absorbent, using water containing 0.2 weight percent oil.

3.1 Solidification of Oil Waste With Absorbent

These tests involved solidifying simulated oil waste contained in an absorbent medium completely saturated, and loaded to only 50% saturation, with oil. The six absorbents used in the absorbency tests reported in Section 2 were used for the solidification tests.

3.1.1 Solidification Tests With Portland Cement

3.1.1.1 Test Procedure

Portland I Cement was used for the cement solidification tests. Each of the 6 absorbents was treated with simulated oil waste to form a set of samples saturated with the oil, and a second set containing 50% of the amount required to saturate the absorbent. Each set of samples was used to make up a series of solidified samples having 5 or more different absorbent-to-cement ratios. To prepare workable samples, at least 25% water (as weight percent of the cement) was required. Since partially oil saturated absorbents absorb some water, additional water was often required for mixtures containing these materials.

After the absorbent was evenly mixed with cement and water, the mixture was sealed in a cylindrical polyethylene mold 5 cm in diameter x 10 cm high and left undisturbed for 3 days. The samples were then tested by probing with a spatula to determine whether they were fully set. Any free liquid was removed and weighed. In general, when samples were soft, without definite setting, there was no distinct separation of liquid and it was not feasible to make a determination of drainable or unincorporated liquid. Thus, the test for free liquids was considered not applicable in such cases.

3.1.1.2 Results

Results of the tests with Portland cement are summarized in Tables 3.1-3.12. In all the tables, + and - in the column, "Set at 3 days," mean set and not set, respectively. "None" in the column, "Free Oil," means no liquid was observed, other than surface moisture in some cases. A rough measurement of the amount of this surface oil could be made by weighing a Kimwipe before and after wiping the sample cylinder until its surface was "dry." Amounts determined in this way were very low--much below 0.5 volume percent. Whenever free oil could be measured, as in several of the samples using Instant-Dri and Vermiculite, the amount was >0.5% by volume.

(Continued Page 17)

Table 3.1

Solidification of Portland Cement With Instant-Dri Saturated With Simulated Oil Waste

Cement (g)	Absorbent (g)	Water (mL)	Set at 3 days	Free Oil (g)	Density of Solidified Waste (g/mL)
200	53.8	61	+	None	1.85
200	100	71	+	None	1.80
200	200	60	+	1.71[a]	1.70
200	400	60	+	10.7[a]	1.65
200	800	60	+	32[a]	1.48

[a] >0.5% by volume.

Table 3.2

Solidification of Portland Cement With Instant-Dri Half Saturated With Simulated Oil Waste

Cement (g)	Absorbent (g)	Water (mL)	Set at 3 days	Free Oil (g)	Density of Solidified Waste (g/mL)
200	50	60	+	None	1.65
200	100	60	+	None	1.68
200	160	60	+	None	1.69
200	400	60	+	None	1.52
200	800	60	+	None	1.26
200	1200	67	+	None	1.29

Table 3.3

Solidification of Portland Cement With Amorphous Silicate Saturated With Simulated Oil Waste

Cement (g)	Absorbent (g)	Water (mL)	Set at 3 days	Free Oil (g)	Density of Solidified Waste (g/mL)
200	100	51	+	None	1.40
200	120	50	+	None	1.30
200	200	60	-	NA[a]	NA
200	400	65	-	NA	NA
200	600	75	-	NA	NA

[a] Not applicable.

Table 3.4

Solidification of Portland Cement With Amorphous Silicate Half Saturated With Simulated Oil Waste

Cement (g)	Absorbent (g)	Water (mL)	Set at 3 days	Free Oil (g)	Density of Solidified Waste (g/mL)
200	20	55	+	None	1.65
200	50	60	+	None	1.42
200	100	70	+	None	1.24
200	200	90	-	NA[a]	NA
200	400	120	-	NA	NA

[a] Not applicable.

Table 3.5

Solidification of Portland Cement With Vermiculite Saturated With Simulated Oil Waste

Cement (g)	Absorbent (g)	Water (mL)	Set at 3 days	Free Oil (g)	Density of Solidified Waste (g/mL)
200	100	120	+	None	1.09
200	200	170	+	2.21[a]	0.85
200	400	250	+	3.04[a]	0.65
200	500	300	+	4.47[a]	0.67
200	600	366	-	NA[b]	NA

[a] >0.5% by volume.
[b] Not applicable.

Table 3.6

Solidification of Portland Cement With Vermiculite Half Saturated With Simulated Oil Waste

Cement (g)	Absorbent (g)	Water (mL)	Set at 3 days	Free Oil (g)	Density of Solidified Waste (g/mL)
200	8.2	65.5	+	None	1.86
200	12.6	63.2	+	None	1.80
200	58.1	81.4	+	None	1.04
200	116.7	100	+	None	0.90
200	225	135	+	None	0.73A
200	300	160	+	None	0.57
200	400	190	-	NA[a]	NA

[a] Not applicable.

Table 3.7

Solidification of Portland Cement With Conwed Saturated With Simulated Oil Waste

Cement (g)	Absorbent (g)	Water (mL)	Set at 3 days	Free Oil (g)	Density of Solidified Waste (g/mL)
200	40	60	+	None	1.80
200	60	60	+	None	1.64
200	80	65	+	None	1.54
200	200	70	+	None	1.26
200	300	70	+	None	1.20A
200	400	75	-	NA[a]	NA
200	500	80	-	NA	NA

[a] Not applicable.

Table 3.8

Solidification of Portland Cement With Conwed Half Saturated With Simulated Oil Waste

Cement (g)	Absorbent (g)	Water (mL)	Set at 3 days	Free Oil (g)	Density of Solidified Waste (g/mL)
200	20	55	+	None	1.92
200	50	62.5	+	None	1.70
200	120	70	+	None	1.40
200	267	80	+	1.23[a]	1.27
200	500	100	-	NA[b]	NA

[a] >0.5% by volume.
[b] Not applicable.

Table 3.9

Solidification of Portland Cement With Super-Fine Saturated With Simulated Oil Waste

Cement (g)	Absorbent (g)	Water (mL)	Set at 3 days	Free Oil (g)	Density of Solidified Waste (g/mL)
200	66.7	59.2	+	None	1.77
200	200	80	+	None	1.40
200	400	114	+	None	1.37
200	600	160	+	None	1.32
200	800	150	-	NA[a]	NA

[a] Not applicable.

Table 3.10

Solidification of Portland Cement With Super-Fine Half Saturated With Simulated Oil Waste

Cement (g)	Absorbent (g)	Water (mL)	Set at 3 days	Free Oil (g)	Density of Solidified Waste (g/mL)
200	50	71.4	+	None	1.79
200	100	100	+	None	1.52
200	200	150	+	None	1.40
200	400	250	+	None	1.26
200	800	425	+	None	1.16

Table 3.11

Solidification of Portland Cement With LSM Saturated With Simulated Oil Waste

Cement (g)	Absorbent (g)	Water (mL)	Set at 3 days	Free Oil (g)	Density of Solidified Waste (g/mL)
200	60	80	+	None	1.54
200	200	120	+	None	0.99
200	260	160	+	None	0.95
200	300	165	+	None	0.79
200	400	200	-	NA[a]	NA

[a] Not applicable.

Table 3.12

Solidification of Portland Cement With LSM Half Saturated With Simulated Oil Waste

Cement (g)	Absorbent (g)	Water (mL)	Set at 3 days	Free Oil (g)	Density of Solidified Waste (g/mL)
200	67	155	+	None	1.17
200	100	167	+	None	0.98
200	133	222	+	None	0.80
200	200	266	+	None	0.78
200	300	320	+	None	0.76
200	400	400	-	NA[a]	NA

[a] Not applicable.

With the exception of one sample, all those producing free liquid were made with saturated absorbent (Tables 3.1 and 3.5). The exception was a sample containing Conwed, a natural fiber, half saturated with oil (Table 3.8). It is expected that oil-saturated absorbents will give rise to free oil when one attempts to solidify too large an amount with a small amount of cement. However, it is not clear why this sample containing half saturated Conwed yielded free oil (Table 3.8) when those containing saturated Conwed did not (Table 3.7). The reason may have to do with the action of the pH 12 aqueous phase in freshly mixed concrete on the water-repellant coating of Conwed (see section 2.3.3).

In samples with oil-saturated absorbent, the oil may protect this coating from the aqueous phase, whereas some of the coating on the half saturated absorbent may be destroyed, allowing water to compete with oil for pore space.

All of the absorbents, whether half or fully saturated, could be incorporated with Portland cement in reasonable proportions to form satisfactory solids with no free oil. Some absorbents gave good solid forms when used in a weight ratio of absorbent to cement of as high as 3 for oil saturated absorbent (Super-Fine, Table 3.9), and 6 for half saturated absorbent (Instant-Dri, Table 3.2). The absorbent which gave the lowest weight ratio, 0.6, was Amorphous Silicate (Table 3.3). It should be kept in mind that, since Amorphous Silicate was the least dense of the absorbents used (0.046 g/mL), this still can be considered a good performance since it represents a high ratio on a volume basis. Thus relatively high proportions of either saturated or half saturated absorbents can be solidified with Portland cement and still meet the criterion of no free oil. It was observed that a number of mixes which did not set in 3 days eventually did set, without liberating oil. (These were, of course, the mixes containing the largest amounts of absorbent.) Quite large amounts of absorbent can satisfactorily be solidified after a 3-day curing time. We see no point in specifying a test procedure employing a long curing time which would achieve only a slight increase in the amount of absorbent incorporated.

3.1.2 Solidification With DCM Cement Shale Silicate

3.1.2.1 Test Procedure

For tests with DCM cement shale silicate, the manufacturer's directions were followed. In addition, samples were prepared in which the amounts of materials were varied somewhat in order to establish the range in which the formulation was satisfactory. The manufacturer's recommended procedure was as follows. Pour absorbent into the container of the Gal-1 kit to 2/3 of the container volume. Add water to a level 1 in. above this, then add the bag of powdered cement provided with the kit and mix thoroughly. Add 312 mL of silicate solution and mix thoroughly for 10 seconds. Leave undisturbed for 5 hours.

For the BNL performance tests, the amounts of materials used were scaled to fit a 5 cm diameter x 10 cm high cylindrical polyethylene mold. The samples were sealed with a tight cap to prevent evaporation. After curing, the samples were evaluated for setting and the presence of free liquid in the same way as for the Portland cement tests. As with the Portland cement tests, 10 samples of each absorbent were prepared, 5 saturated with simulated waste oil and 5 containing 50% of the saturation amount. For both saturated and half-saturated absorbents, specimens were prepared at the composition recommended by the vendor. Additionally, specimens with variations of ± 30% in the amount of absorbent incorporated and ± 30% in the amount of silicate solution used were also prepared.

3.1.2.2 Results

The results of the solidification tests using DCM with absorbents are given in Tables 3.13-3.24.

All of the solidification samples prepared with DCM set satisfactorily in 15 hours. However, mixtures containing several of the absorbents released liquid. This liquid, amounts of which are listed in Tables 3.13-3.24 under "Free Liquid," could arguably be described as surface moisture. It was difficult to tell how much oil it contained because it was found only on the walls of the containers and the outer surfaces of the solid samples, and was too viscous and/or present in too small an amount to collect at the bottoms of the containers. Amounts were determined by wiping with a weighed Kimwipe and reweighing. Unlike the situation with the Portland cement samples, where any liquid present was clearly oil which collected at the bottom of the molds, the liquid associated with DCM solidification samples appeared to be mostly viscous aqueous solution.

Samples with vermiculite and Amorphous Silicate released free liquid whether the absorbent was saturated or only half saturated with simulated oil waste, those containing Conwed (natural fiber) and Super-Fine (granular diatomite material) only when the absorbent was saturated, and those containing LSM (synthetic fiber) and Instant-Dri (clay) not at all. With vermiculite and Super-Fine the amounts released were <0.5% by volume; with Conwed and Amorphous Silicate they were >0.5%, ranging from just over 0.5% to slightly >1%. Within the range of the proportions used, the amount of absorbent had no bearing on whether or not free liquid was released. However, the amount of free liquid increased somewhat with the amount of absorbent. The amount was also inversely proportional to the amount of silicate solution added, although the effect was not large.

(Continued Page 23)

Table 3.13

Solidification of DCM With Vermiculite Saturated With Simulated Oil Waste

DCM Cement (g)	Absorbent (g)	Water (mL)	Silicate (mL)	Set at 15 h	Free Liquid (g)	Density of Solidified Waste(g/mL)
52	33	69	15	+	0.54	0.70
52	45	70	15	+	0.59	0.75
52	22	70	15	+	0.40	1.19
52	34	70	20	+	0.41	1.20
52	33	70	10	+	0.47	0.70

Table 3.14

Solidification of DCM With Vermiculite Half Saturated With Simulated Oil Waste

DCM Cement (g)	Absorbent (g)	Water (mL)	Silicate (mL)	Set at 15 h	Free Liquid (g)	Density of Solidified Waste (g/mL)
52	21.8	50	15	+	0.45	1.13
52	31.2	50	15	+	0.55	1.11
52	14.0	50	15	+	0.41	1.18
52	22	50	20	+	0.39	1.19
52	22	50	10	+	0.43	1.17

Table 3.15

Solidification of DCM With Conwed Saturated With Simulated Oil Waste

DCM Cement (g)	Absorbent (g)	Water (mL)	Silicate (mL)	Set at 15 h	Free Liquid (g)	Density of Solidified Waste (g/mL)
52	62.3	45	15	+	0.83	0.81
52	80.8	45	15	+	1.71	1.02
52	47.0	45	15	+	1.27	0.89
52	61.8	45	20	+	0.79	0.98
52	61.3	45	10	+	0.90	0.91

Table 3.16

Solidification of DCM With Conwed Half Saturated With Simulated Oil Waste

DCM Cement (g)	Absorbent (g)	Water (mL)	Silicate (mL)	Set at 15 h	Free Liquid (g)	Density of Solidified Waste (g/mL)
52	29.4	80	15	+	None	1.27
52	40.0	80	15	+	None	1.22
52	20.1	80	15	+	None	1.21
52	30.0	80	20	+	None	1.26
52	30.0	80	10	+	None	1.23

Table 3.17

Solidification of DCM With Amorphous Silicate Saturated With Simulated Oil Waste

DCM Cement (g)	Absorbent (g)	Water (mL)	Silicate (mL)	Set at 15 h	Free Liquid (g)	Density of Solidified Waste (g/mL)
52	52.0	60	15	+	0.91	0.94
52	62.0	60	15	+	1.88	0.96
52	41.2	60	15	+	1.60	0.93
52	52.0	60	20	+	1.01	1.16
52	52.0	60	10	+	1.38	1.09

Table 3.18

Solidification of DCM With Amorphous Silicate Half Saturated With Simulated Oil Waste

DCM Cement (g)	Absorbent (g)	Water (mL)	Silicate (mL)	Set at 15 h	Free Liquid (g)	Density of Solidified Waste (g/mL)
52	33.4	60	15	+	1.89	1.16
52	46.6	60	15	+	2.12	1.18
52	23.9	60	15	+	1.78	1.15
52	34.0	60	20	+	1.66	1.19
52	34.0	60	10	+	1.85	1.15

Table 3.19

Solidification of DCM With Super-Fine Saturated With Simulated Oil Waste

DCM Cement (g)	Absorbent (g)	Water (mL)	Silicate (mL)	Set at 15 h	Free Liquid (g)	Density of Solidified Waste (g/mL)
52	75.6	60	15	+	0.82	1.10
52	100.0	60	15	+	0.85	1.02
52	51.0	60	15	+	0.80	1.06
52	74.8	60	20	+	0.75	1.10
52	75.0	60	10	+	0.77	1.14

Table 3.20

Solidification of DCM With Super-Fine Half Saturated With Simulated Oil Waste

DCM Cement (g)	Absorbent (g)	Water (mL)	Silicate (mL)	Set at 15 h	Free Liquid (g)	Density of Solidified Waste (g/mL)
52	60.0	70	15	+	None	1.11
52	81.8	70	15	+	None	1.03
52	41.5	70	15	+	None	1.13
52	59.4	70	20	+	None	1.00
52	59.3	70	10	+	None	1.07

Table 3.21

Solidification of DCM With Instant-Dri Saturated With Simulated Oil Waste

DCM Cement (g)	Absorbent (g)	Water (mL)	Silicate (mL)	Set at 15 h	Free Liquid (g)	Density of Solidified Waste (g/mL)
52	72.3	60	15	+	None	1.26
52	101.5	60	15	+	None	1.49
52	50.4	60	15	+	None	1.32
52	73.3	60	20	+	None	1.34
52	72.1	60	10	+	None	1.34

Table 3.22

Solidification of DCM With Instant-Dri Half Saturated With Simulated Oil Waste

DCM Cement (g)	Absorbent (g)	Water (mL)	Silicate (mL)	Set at 15 h	Free Liquid (g)	Density of Solidified Waste (g/mL)
52	73.5	60	15	+	None	1.33
52	95.1	60	15	+	None	1.36
52	53.0	60	15	+	None	1.37
52	73.5	60	20	+	None	1.44
52	74.0	60	10	+	None	1.35

Table 3.23

Solidification of DCM With LSM Saturated With Simulated Oil Waste

DCM Cement (g)	Absorbent (g)	Water (mL)	Silicate (mL)	Set at 15 h	Free Liquid (g)	Density of Solidified Waste (g/mL)
52	34.2	70	15	+	None	1.07
52	42.4	70	15	+	None	1.00
52	21.3	70	15	+	None	1.11
52	34.0	70	20	+	None	1.15
52	34.0	70	10	+	None	1.14

Table 3.24

Solidification of DCM With LSM Half Saturated With Simulated Oil Waste

DCM Cement (g)	Absorbent (g)	Water (mL)	Silicate (mL)	Set at 15 h	Free Liquid (g)	Density of Solidified Waste (g/mL)
52	23.3	70	15	+	None	1.19
52	34.0	70	15	+	None	1.02
52	12.9	70	15	+	None	1.16
52	23.0	70	20	+	None	1.17
52	23.0	70	10	+	None	1.04

3.2 Solidification of Oil Waste Without Absorbent

In the evaluation of solidification techniques for handling oil waste *without* the use of absorbents, the same properties were investigated as in the case of solidification *with* absorbents, namely, setting characteristics and amount of free liquid associated with the solid product. In addition, compressive strengths were determined at all compositions yielding samples which set properly and showed no free liquid.

Two solidification media, Portland I cement and DCM cement shale silicate, were used to investigate the range of oil concentrations over which suitable solidification samples could be prepared. A few tests were done with a third medium, Dow vinyl ester-styrene polymer, but it was not feasible to use it for the same type of tests as carried out with the other two media. Its nuclear reactor waste applications have been to aqueous wastes, including *oily* wastes, but not to *oil* wastes. Mr. B. Owens of the Dow Chemical Company informed us that the company could not recommend formulations for oil waste within the time frame of this task.* It was suggested that BNL follow the procedure published in the Dow Topical Report DNS-RSS-001P(5) on solidification of simulated BWR aqueous waste containing a small amount of oil. The simulated waste, containing 0.2% motor oil, was prepared according to the procedure given in the Dow report, and was solidified in accordance with their proprietary process.

3.2.1 Preparation of Solidification Samples

3.2.1.1 Portland Cement

Samples were prepared by varying each of the three components--oil, water, and cement--by 10% increments from 10% to 80%, so that the extreme compositions contained 10% of two of the components and 80% of the third. One sample was prepared at each composition. A number of extra samples with changes smaller than 10% in the amount of each component were prepared in the composition region where no free liquid was observed. The reason for preparing these samples was to obtain more compressive strength data. The procedure used for sample preparation was to stir the oil and water to form an emulsion and, while still stirring, to add the cement gradually. The mixture was stirred until homogeneous, then poured into a standard 5 cm diameter x 10 cm high polyethylene mold. It was sealed to prevent evaporation and left undisturbed for 3 days at room temperature (about 72°F).

3.2.1.2 DCM Cement Shale Silicates

For this medium, the preparation method was based on the manufacturer's recommended procedure. This called for a 6:14:1 ratio by volume of oil:water:detergent (Nutek 316) to be emulsified by stirring for 5 minutes. To this emulsion was to be added 0.49 g of DCM cement and 0.178 mL of silicate solution for every mL of emulsion. As in the tests with absorbents, the amounts were scaled to fit the 5 cm diameter x 10 cm high mold. The actual amounts for this sized product were 84 mL emulsion, 40 g DCM cement and 14 mL silicate solution. The DCM has to be mixed in first and the silicate solution added last with rapid stirring, since the mixture sets in 10 seconds after addition of silicate. For curing, the mixture was sealed in its mold and left undisturbed overnight at room temperature.

The proportions of materials used in the standard procedure were varied in order to investigate the effects of compositional variation. First the proportions of oil, water and detergent in the emulsion were varied, keeping the amounts of emulsion, DCM cement and silicate solution constant. Five samples were prepared with the volume fraction of oil ranging from 0.211 to 0.348 (25% on each side of the recommended amount), while the ratio of water to detergent was kept constant. Similarly, 5 samples were prepared where the

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*Telephone communication between R. E. Davis of Brookhaven National Laboratory and B. Owens of Dow Chemical Company, March 31, 1981.

fraction of detergent varied from 0 to 0.090, keeping the oil:water ratio constant, and 5 with the water fraction varying from 0.600 to 0.714 while the oil:detergent ratio remained constant. In the second series of experiments, the amounts of silicate solution and emmulsion were independently varied while the amount of cement was kept constant at 40 g and the oil:water:detergent ratio of the emulsion at 6:14:1. Five sets of samples were prepared, one each using 60, 70, 80, 90, and 100 mL of emulsion. In each set 5 samples were prepared, with the amount of silicate solution varying from 6 to 22 mL in increments of 4 mL.

3.2.1.3 Dow Vinyl Ester-Styrene Polymer

In Dow's proprietary topical report(5) a formulation is given for treating a representative BWR aqueous waste containing up to 0.2% motor oil by weight. A simulated waste was made up containing the same proportions as in the BWR waste, which were 93.4% H_2O, 5.5% Na_2SO_4, 0.9% Na_3PO_4 and 0.2% oil. The materials used for the solidification process were a binder of vinyl ester-styrene monomer, a promoter and a catalyst, all in liquid form. The method of mixing with the waste is proprietary, but obviously requires mixing the liquid aqueous and organic phases. These were mixed in an appropriate manner, poured into 5 cm dia x 10 cm high polyethylene molds and allowed to cure for 2 days.

Since the amount of oil in the simulated waste was so small, there was presumably no point in preparing samples with amounts varying by the normal 25-50% used in tests with the other solidification media. However, several different samples were prepared in which the waste:binder ratio was varied from 1.25 to 2.25, while the proportion of binder, promoter and catalyst was kept constant.

3.2.2 Results of Tests for Free Liquid

All the mixtures tested with the DCM cement shale silicate solidified at the expected time of 10 seconds after addition of silicate solution. The vinyl ester-styrene polymer samples with simulated aqueous waste containing 0.2% oil, prepared by Dow's proprietary method, also solidified well. In no case with either medium was there any free liquid.

3.2.2.1 Portland Cement

Results of the solidification tests with Portland cement are given in Table 3.25 and Figures 3.1 and 3.2. In Table 3.25 as in previous tables, the + and - signify set and not set, respectively. NA (not applicable) is entered several places in the final column and also in the figures. It indicates that there was no free liquid but the sample was otherwise unsuitable, namely because it did not set.

The compositions of all samples are plotted on the ternary diagram of Figure 3.1 with an indication as to whether they did or did not set. The amounts of free liquid for the same samples are shown in Figure 3.2. These results include those listed in Table 3.25 and those from the extra samples, described in Section 3.2.1.1, which were prepared in the composition region where no free liquid was observed. The boundary lines drawn in Figure 3.1 and 3.2 are not meant to indicate a sharp division between regions, but rather represent compositions which are on the borderline of giving unsatisfactory performance and where small changes in procedure can tip the balance in either direction.

There is a considerable composition range over which good solidified samples were prepared, including a number with 30% or more oil. These are of particular interest for an oil waste disposal method. The region of no free liquid is nearly the same as, but slightly smaller than, the region in which samples set properly. A few samples inside but around the edge of the region of proper setting released liquid, both on the oil-rich and the water-rich side, but in general samples either set without releasing liquid, or else did not set. In general, also, the free liquids were oil for samples containing a high proportion of oil, water for those containing a high proportion of water, and mixtures of oil and water for those with intermediate amounts. Within this region, when free liquid formed at all, it was always considerably >0.5% by volume.

Table 3.25

Solidification of Oil Wastes by Portland Cement

Cement (g)	Oil Waste (g)	Water (g)	Set at 3 days[a]	Free Liquid (g)
10	10	80	-	63.2
10	20	70	-	50.7
10	30	60	-	38.9
10	40	50	-	17.0
10	50	40	-	21.0
10	60	30	-	32.2
10	70	20	-	51.0
10	80	10	-	55.0
20	10	70	-	40.3
20	20	60	-	37.8
20	30	50	-	31.6
20	40	40	-	32.1
20	50	30	-	NA[b]
20	60	20	-	39.9
20	70	10	-	61.0
30	10	60	-	24.3
30	20	50	-	15.9
30	30	40	-	6.36
30	40	30	-	NA
30	50	20	-	NA
30	60	10	-	21.4
40	10	50	+	11.5
40	20	40	-	None
40	30	30	+	None
40	40	20	-	1.18
40	50	10	-	4.30
50	10	40	+	None
50	20	30	+	None
50	30	20	+	10.8
50	40	10	-	None
60	10	30	+	None
60	20	20	+	None
60	30	10	+	None
70	10	20	+	None
70	20	10	+	None
80	10	10	-	NA

[a] + = set achieved; - = no set.
[b] Not applicable.

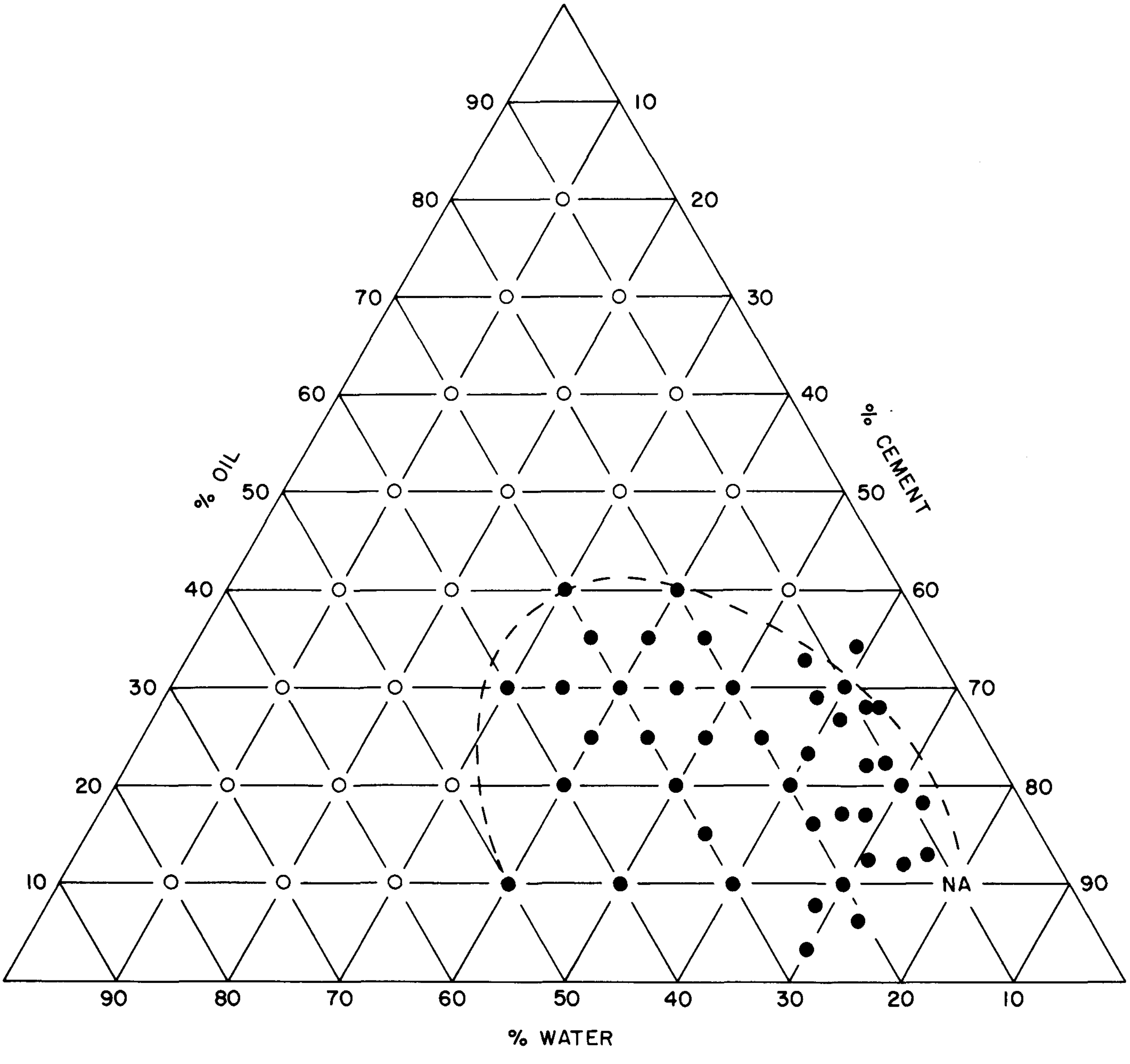

Figure 3.1 Setting of oil-water samples mixed With Portland I cement.
● Set after 3 days
o Soft or unsolidified after 3 days

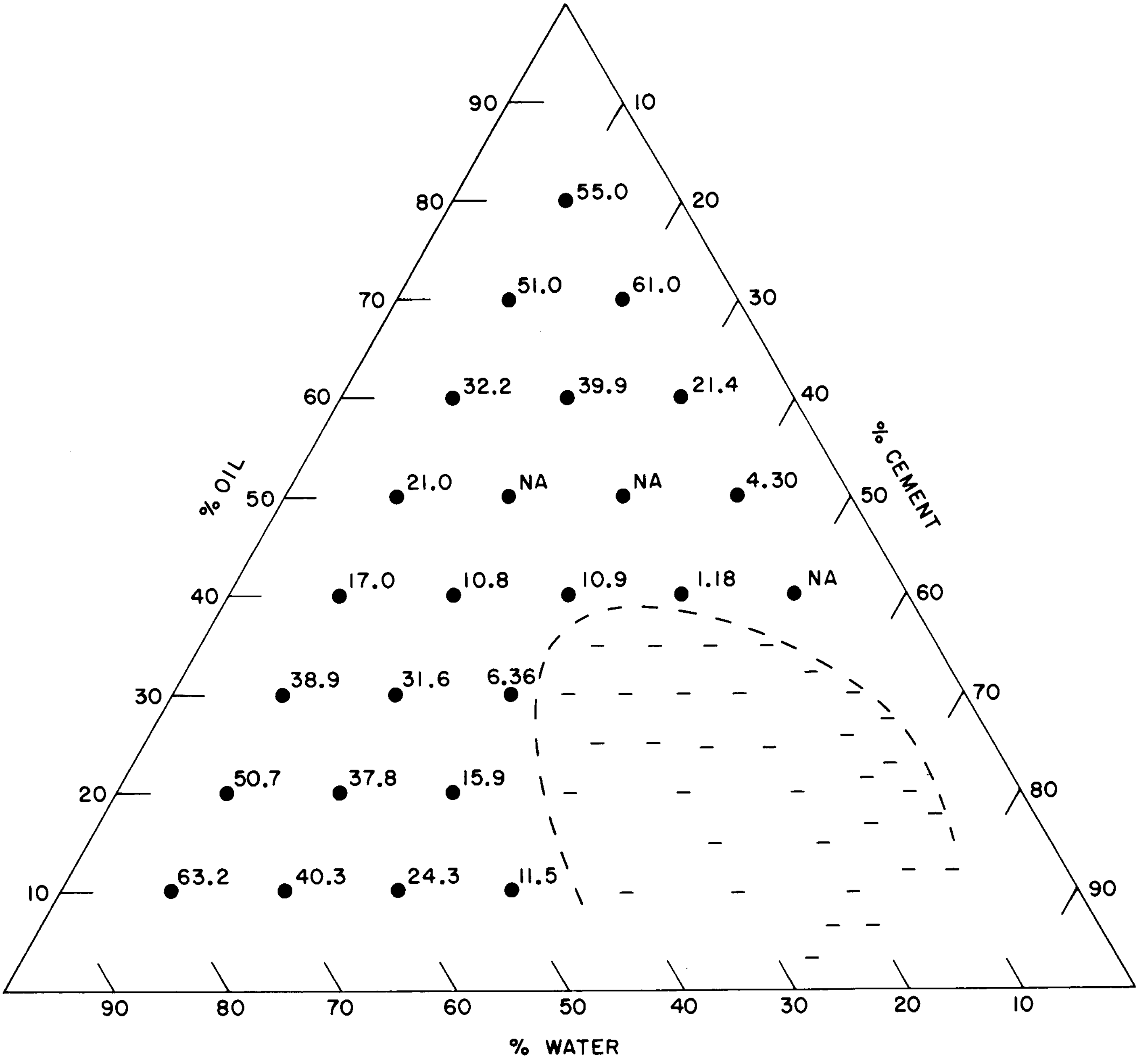

Figure 3.2 Free liquid released from oil-water samples mixed with Portland I cement.
- Compositions releasing no liquids.
Numbers are weight percent amounts of free liquid for the compositions shown.

3.2.3 Results of Compressive Strength Tests

Compressive strengths were determined in accordance with the ASTM method C39-72, "Test for the Compression Strength of Cylindrical Concrete Specimens."

3.2.3.1 Portland Cement

The results of the compressive strength measurements are given in Figure 3.3. Each value is the average of measurements made on several replicate samples, usually 5, but as few as 2 for some of the specimens which showed high strength.

Not surprisingly, the samples with the highest compressive strength contained the least oil. However, very good strengths were obtained for samples with relatively high proportions of oil as long as they contained in the neighborhood of 30% water. The compressive strength values dropped off relatively rapidly near the boundary of the region in which proper setting occurred. Thus, even if compositions near the boundary give solids which are satisfactory in terms of set and absence of free liquid, they are likely to have poor mechanical strength.

It was observed that addition of a small amount of detergent to mixtures containing relatively large proportions of oil facilitated solidification and increased strength. For example, a mixture of 50% cement, 35% oil, and 15% water did not set after 3 days and showed free oil. However, on addition of 10 mL detergent (Nutek 316, as used in the DCM procedure) to the formulation, solidification occurred within 3 days with no free liquid. Four replicate samples were prepared for compressive strength tests and gave an average strength of 632 psi, considerably higher than samples with compositions in the same region prepared without detergent.

The strength of oil-rich samples also increased with time of curing. Samples containing 68% cement, 22% oil, and 10% water cured for 3 days had an average compressive strength of 173 psi. Other samples of the same composition cured for 14 days yielded an average value of 372 psi. Similar results were obtained with samples having still higher oil contents.

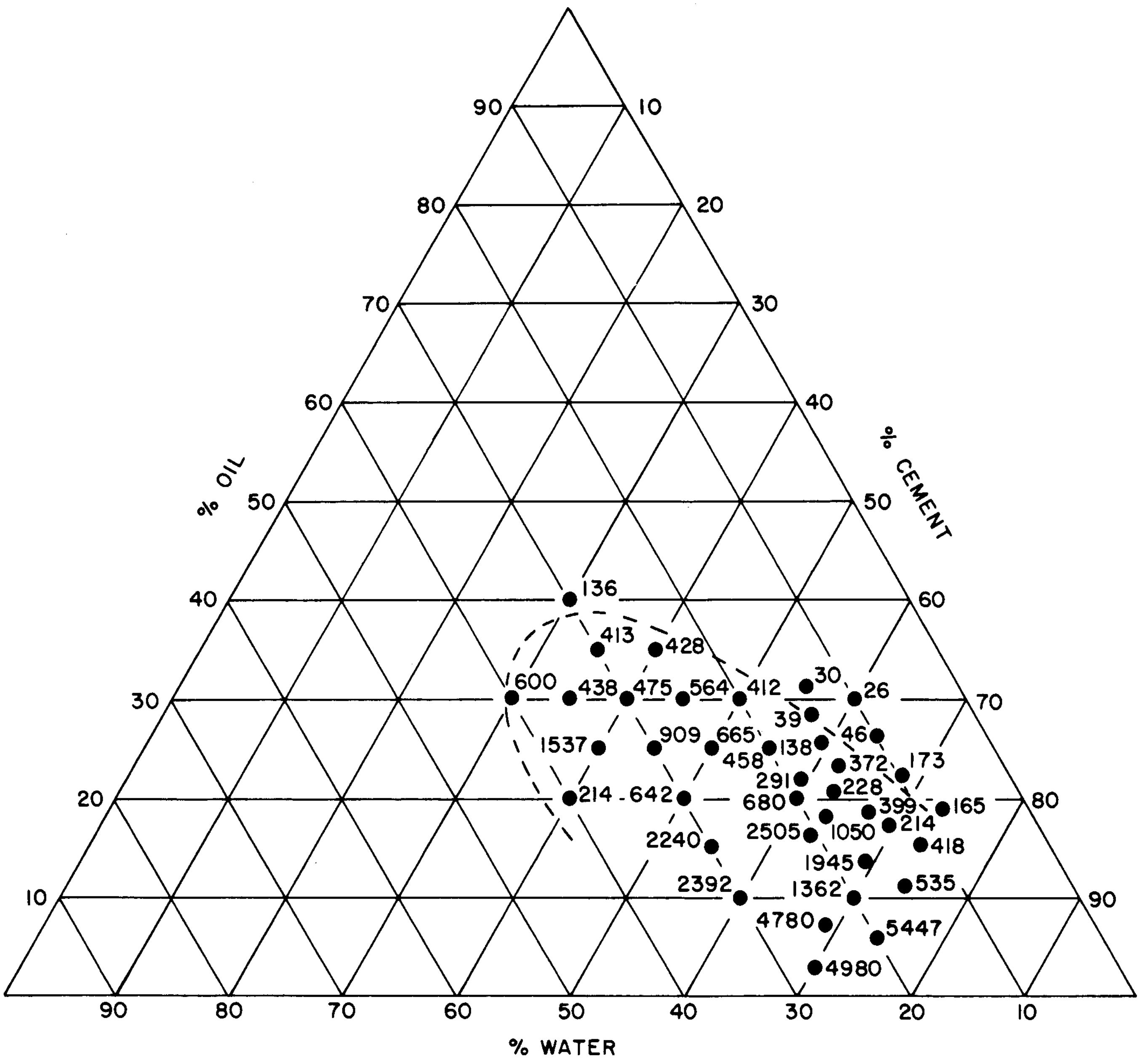

Figure 3.3 Compressive strength of samples prepared by solidification of oil-water mixtures with Portland I cement. Numbers are compressive strengths in psi for the compositions shown.

3.2.3.2 DCM Cement Shale Silicate

Within the range of compositions used in preparing the test samples (described in Section 3.2.1.2), there was no apparent change in compressive strength with composition. One specimen for each of 20 representative compositions was tested, and all the strength measurements yielded values around 300 psi. Five replicate specimens of the composition specified by DCM's formulation were tested using equipment in BNL's metallurgy division which provides high precision in the low strength range. The average strength determined for the five samples was 287 psi with a standard deviation of ± 19 psi.

3.2.3.3 Dow Vinyl Ester-Styrene Polymer

Five samples of the solid polymer formed by the Dow process were tested. All of them withstood stresses of 10^5 psi without cracking, but showed deformation of 15-20%. The average value of the stress at 10% deformation was 3000 ± 50 psi. In this case the ±50 psi represents the smallest scale division on the test apparatus used.

3.3 State-of-the-Art Test Parameters to Satisfy the Minimum Acceptance Criteria

An acceptable waste form is a freestanding, monolithic solid which is homogeneous and contains no free liquid.(6) Free liquid is operationally defined here as "any drainable liquids not bound by the solidified matrix." The June 29, 1981, draft of 10CFR61 requires no free liquid upon solidification, but permits a maximum of 1% free, noncorrosive liquid at the disposal site. However, individual disposal sites can have more stringent requirements, and in fact at Beatty, Nevada, no free liquid is allowed. Another proposed requirement which must be met by a waste form is the ability to withstand the pressure caused by overburden at the burial site and to maintain its freestanding monolithic condition. NRC in the June 29, 1981, draft of 10CFR61 is currently considering a minimum compressive strength of 50 psi for this criterion. The three solidification techniques which we have examined are considered for their suitability in terms of the above criteria.

3.3.1 Portland Cement

The composition region in which satisfactory solid waste forms can be made is clearly indicated in the ternary diagrams of Figures 3.1, 3.2, and 3.3, discussed in Sections 3.2.2.1 and 3.2.3.1. Up to 35% oil (by weight) can be incorporated as long as the water content is in the range of 25-35%. For example, for oil:water:cement ratios of 35:30:35 and 35:25:40 the compressive strengths were over 400 psi, well over the 50 psi required, and no free liquid was observed. For compositions with 40% oil, those with 20% and 30% water set properly, but released liquid while all the other compositions failed to set. Thus, 40% oil is too high a proportion for preparing acceptable waste forms.

For solidification with absorbents, at least 30 weight percent oil could be contained in the final mixtures with all the absorbents to give solid waste forms which set properly and released no liquid. With Conwed, 50% oil could be incorporated, and with the others, between 30 and 40%. Compressive strength tests were not carried out on these specimens to determine whether the 50 psi criterion could be met.

3.3.2 DCM Cement Shale Silicate

Using the manufacturer's directions, completely satisfactory waste forms are obtained; although the approximately 300 psi compressive strength is not high, it is well above 50 psi. The amount of oil incorporated in the solid of this standard composition (84 mL emulsion, 40 g cement and 14 mL silicate solution) is 14.7% by weight. The proportion of emulsion was varied by ±25%, and the proportion of silicate solution by ±60%, keeping the amount of cement constant at 40 g and the oil:water:detergent ratio of the emulsion constant at 6:14:1. The proportion of oil and detergent in the emulsion were likewise varied, the oil by ±20% and the detergent by ±100%, keeping the amount of cement and silicate constant. Every sample prepared solidified properly without free liquid and had a compressive strength of approximately 300 psi. The maximum amount of oil incorporated in any of these different compositions was 19.5% by weight. Thus, within these limits, the manufacturer's procedure can be varied, including increasing the proportion of oil to almost 20%, without affecting the quality of the waste form, including its compressive strength.

When used with absorbents, there was a tendency to form free liquid. In most cases it was difficult to distinguish between surface moisture and free liquid because of the high viscosity of the surface liquid and its poor drainage characteristics. We have chosen the conservative approach of considering these "moist" samples to contain free liquid.

Using the manufacturer's procedure, as detailed in Section 3.1.2.1, and within ±33% of the standard proportions, no acceptable solid waste forms could be prepared with vermiculite and Amorphous Silicate, since they released free liquid. With Super-Fine and Conwed, acceptable forms were prepared only when the absorbents were half saturated with oil. With Instant-Dri and LSM, all samples were acceptable, whether the absorbent was half saturated or fully saturated with oil. For Instant-Dri and LSM, the proportions of oil in the final waste form, using the manufacturer's procedure, were 14 and 17%, respectively. The maximum proportions incorporated in these tests were 17 and 20%, respectively. Thus, using DCM cement shale silicate and suitable absorbents, the same proportion of oil can be incorporated in the final waste form as when no absorbent is used.

3.3.3 Dow Vinyl Ester-Styrene Polymer

As discussed in Sections 3.2, this medium could not be tested for a realistic simulated oil waste because the manufacturer could not provide a formulation within the time frame of this investigation. Satisfactory waste forms were prepared with simulated BWR aqueous waste containing 0.2% oil by weight.

4. ALTERNATIVE METHODS FOR TREATING OIL WASTES

BNL has performed a literature survey to evaluate alternative methods for treating oil wastes. The survey was based on a computerized search (RECON program) available at the BNL Research Library. It covered the topics oil waste, decontamination, incineration, ozonation, and regeneration.

Besides incineration and ozonation, which are disposal methods, BNL identified two methods for cleaning the oil so that it could be handled as nonradioactive material. These decontamination methods are extraction with water and filtration. A storage procedure to allow for radionuclide decay was employed at one of the power plants answering BNL's survey. This method is applicable only to contaminants of short-half life. The power plant at Beaver Valley (see Table in Appendix A) generates waste oil from the reactor coolant pump which is contaminated with Xe-133. The oil is stored until the Xe-133 decays (5.27 day half-life) and is then combined with nonradioactive waste oil.

4.1 Regeneration Methods

4.1.1 Decontamination by Extraction With Water

The oil wastes generated at the Kewaunee Nuclear Plant are stored to allow the separation of oil and water (<10%) (refer to Table in Appendix A). The separated water is then treated as aqeuous radwaste. Extraction of oil with water could be a general method of decontaminating oil wastes. Isotopes of Cs and Co are the most common radioactive contaminants of oil wastes, and inorganic salts of these elements would be expected to partition preferentially into an aqueous phase (if no complexing agents were present) when oil and the aqueous phase were contacted. Since information on the partitioning of Cs and Co salts between oil and water was not available, it was decided to carry out an experimental determination. This was done by adding their chlorides to a mixture of water and simulated oil waste and measuring the element concentration in both phases under eqilibirium conditions. The results were as follows:

$$D_{Cs} = \frac{[Cs]_{oil}}{[Cs^{+}]_{water}} = 1.7 \times 10^{-5}$$

and

$$D_{Co} = \frac{[Co]_{oil}}{[Co^{+2}]_{water}} = 3.9 \times 10^{-5}$$

where square brackets represent concentrations. The concentrations in oil are given for the elements simply because it is not known whether the species involved are ionic or molecular.

These results show that is it important to remove the water in oil wastes since Cs and Co salts partition predominantly into the water phase. Also, if no water occurs with the oil waste it can be added to extract the ionic contaminants (Cs^+ and Co^{+2}) from oil wastes. The decontamination factor (DF) is really limited by the efficiency of separation of oil and water phases. As observed, DF's of 5.9×10^4 for Cs and 2.5×10^4 for Co may be achieved.

4.1.2 Filtration

Much of the radioactive material in oil waste will be in the form of particulates, especially Co, Fe, Ni, and Mn which originate in corrosion products in the various reactor systems exposed to neutrons. Some particulate matter may settle out in an aqueous phase if one is present, but filtration will be a more efficient way to remove it.

A filtration process was patented for removing uranium-containing solid particles from oil wastes.(7) This process may also be used to remove other radioactive solid particles from oil wastes. Another process was patented for oil waste regeneration.(8) The process was a combination of water washing (extraction) and filtration through activated alumina. The results (Table 4.1) show a DF of more than 5 was achieved for most nuclides. The DF for Cs was not measured; however, the process may still be useful in treating oil wastes. In fact, the oil wastes collected at Vermont Yankee power station have been decontaminated by filtering the oil through diatomaceous earth and resin, and Nine Mile Point also plans filtration (see Table in Appendix A).

Table 4.1

Regeneration of Oil Wastes by Filtration(9)

Element	New Oil[a]	Oil Wastes Before Filtration[a]	Oil Wastes After Filtration[a]
Ag	<1	5	<1
Al	<1	80	10
B	<1	3	<1
Cd	<1	<1	<1
Co	<10	50	<10
Cr	<1	30	<1
Cu	1	50	10
Fe	<1	>200	5
Mg	<1	30	1
Mn	<1	60	<1
Ni	<1	50	<1
Si	<1	40	5
V	<1	<1	<1
Zn	<10	30	<10
Sn	<1	30	1
Mo	<1	10	<1
U	<100	1037	241

[a] Amounts in μg/mL

4.2 Disposal Methods

4.2.1 Incineration

Incineration treatment of radioactive material can be dated back to 1952 in Los Alamos Scientific Laboratory where an electrically heated single basket incinerator was used for Pu recovery. Since then, many types of incinerators have been designed and tested on the pilot plant or demonstration unit scale. Most of the units were built to treat dry combustible TRU wastes. The wastes were sorted and shredded, then placed in a feeder to be introduced into the incinerator. The feeders of some incinerators are capable of accepting both solid and liquid wastes for continuous burning. Successful demonstrations of liquid feeding systems have been in operation at Savannah River, Rocky Flats, Mound Laboratories, and Penberthy Electromelt. Although off-gas systems have yet to be tested on actual oil wastes, incinerators are currently capable of burning aromatic organics (e.g., toluene) at a rate of 180 kg/hr. The others should be able to handle liquid wastes with some modification to the waste intake system. Alternatively, waste oil could be encapsulated and introduced as solid waste to the feeder. This treatment was demonstrated in the cyclone incinerator at the Mound Facility where smooth burning of scintillation cocktail vials was achieved by hand feeding vials into the pneumatic injection system at a rate of 100 vials in 8 minutes.

One forseeable modification which must be made is with the off-gas treatment systems. Most of the incinerators were designed for TRU wastes. Upon combustion, the heavy metals in TRU wastes form nonvolatile oxides that can be collected as ashes. The currently available incinerators are all equipped with off-gas treatment systems to process TRU wastes, and modification of the off-gas treatment systems for processing beta-gamma radwastes are under way. A few incinerators are at a stage, or nearly so, where they could be used for tests on oil wastes. They include the following.

- It is planned to modify the feeding system of the excess-air cyclone incinerator at the Mound Facility to permit continuous burning of either solid or liquid wastes. For decontamination studies of off-gases from burning low-level beta-gamma wastes, a bench-scale cyclone incinerator has been constructed.(9)

- At the Savannah River Plant, a 180 kg/h prototype beta-gamma incinerator was scheduled to begin test operation on non-radioactive waste at the end of 1980.(1)

- At Rocky Flats, the Rotary-kiln incinerator is equipped with a liquid waste burner to handle liquids and other wet wastes such as resins and filter sludges. The fluidized bed incinerator has been tested for burning liquid including naphtha, hydrazine, tributyl phosphate, oil, methylene chloride, and other liquid chemical wastes.(10)

- The Penberthy Electromelt International, Inc., has tested small-scale burning of toluene in a molten-salt incinerator,(11) and an electromelt incinerator capable of burning 100 kg of toluene per hour is under construction.(11)

- The fluidized-bed dryer/incinerator of Aerojet Energy Conversion Company is able to burn contaminated oil directly in a separate fluidized bed incinerator instead of having to reduce its volume first in a fluidized bed dryer as is usually done with aqueous wastes.(1) The DF for I-131 across the dryer and off-gas cleanup system has been determined to be 10^5 for chemicals containing iodine.(12) The fluidized bed calciner/incinerator develped by Newport News Industrial Company is able to handle both liquid (aqueous and organic) and dry combustible solid wastes.(12) The DF for I-131 is 1×10^5 and for particulates is 7×10^6.

4.2.2 Acid Digestion

Acid digestion of combustible organics for treatment of TRU waste was apparently first suggested by Swedish workers. In this country the method has been developed at Hanford Engineering Development Laboratory to the point where a demonstration scale process is being operated, called the Radioactive Acid Digestion Test Unit or RADTU.(13) The process uses boiling concentrated H_2SO_4 with HNO_3 oxidant to convert organic compounds to CO_2 and H_2O. The main purpose of RADTU is to recover transuranic elements, particularly plutonium, from TRU waste. The method is designed for treatment of solids, although liquids can be digested if they are non-volatile.(14) For example, in treating Purex waste solvent, TBP (tributyl phosphate) itself is digested almost completely but the kerosene diluent only partially. Oil wastes from power reactors may be sufficiently nonvolatile that they could be digested essentially completely.

One of the main reasons for developing the acid digestion process is its capability of handling certain unique wastes which cannot be handled easily or at all by most incinerators. This, of course, does not apply to reactor oil wastes, which can readily be incinerated. The acid digestion process is probably more expensive to operate than incineration, and is technically very demanding. Equipment to withstand the extremely corrosive conditions is very expensive. It seems therefore that as a process for treating oil wastes from power reactors it would be far more sophisticated than required and too costly.

4.2.3 Ozonation of Oil Wastes

Ozonation as a purification process is designed for decomposition of small amounts of organic impurities in water, rather than for destruction of massive amounts of organic waste. Although ozonation has been used to decompose organic complexing agents (EDTA, HEDTA, NTA, and DTPA) in radioactive wastes,(6,15,16) no information was available on the treatment of oil wastes specifically. As the molecular structure of these chelating agents is different from that of the waste oils, prediction of the products of ozonation of oil wastes from the studies on chelating agents is not feasible. Ozonation of structurally related paraffins has been studied in carbon tetrachloride solution.(17) In this study, the major product of the ozonation of pentane was identified as pentanol. From this it can be assumed that the normal ozonation products of oil wastes (saturated hydrocarbons) will be the corresponding saturated alcohols. Such a reaction, if indeed it occurred with high molecular weight aliphatic hydrocarbons, would convert the oils to alcohols which themselves might be oils, or possibly solids. No volume reduction would be accomplished, and presumably nothing useful would be gained by such a step. Also, efficiency appears to be low, even for low molecular weight hydrocarbons, and the cost of such treatment therefore would likely be prohibitive.

5. CONCLUSIONS

In this section, conclusions are drawn from the results of the tests performed. Evaluations are made regarding various methods of managing oil wastes, both those covered in the experimental work, and other possible methods suggested by information obtained from the literature and the survey of power plant experience.

5.1 Testing of Absorbents

ASTM and other standard test procedures were reviewed. On the basis of that review, uncomplicated tests were derived for determining absorbencies of oil and water in absorbent materials under static conditions and under simulated transportation conditions. It is not feasible to simulate transportation conditions exactly in an uncomplicated test with equipment of reasonable cost, but the repetitive shock vibration test described in Section 2.2.2 reproduces the vibration frequencies encountered most often in actual transportation, and with an amplitude and duration comparable to what would be expected in normal road or railroad transportation.

Conclusions which can be drawn from the tests carried out on six representative absorbents are:

- All the absorbents except Conwed, a natural fiber, whose surface has been treated to repel water, exhibit similar absorbencies for oil and for water. With water at pH 13 (0.1M NaOH), the surface coating on Conwed apparently is attacked and the absorbency increases to roughly the same value as for oil. Aside from this there is almost no effect of pH on water absorbency in the pH range 1-13.

- With one exception, Instant Dri, oil absorbencies are not changed when samples are subjected to the simulated transportation conditions; i.e., no oil is released during the 1-hour repetitive shock test. For Instant-Dri, a reduction of <1% by volume is observed.

- When the absorbents saturated with water are subjected to the repetitive shock test, only vermiculite and LSM are unaffected. Instant-Dri loses about 0.01 mL per mL of absorbent. Super-Fine and Conwed are intermediate in performance, while Amorphous Silicate is reduced to a fine powder and releases almost all its absorbed water.

5.2 Solidification of Oil Waste With Absorbent

The principal conclusions from the testing done with absorbents are:

- With Portland I cement, all of the absorbents, whether half or fully saturated with oil, can be incorporated in reasonable proportions to form satisfactory solids with no free liquid.

- At least 30 weight percent simulated oil waste can be contained in the final mixtures, with all the absorbents, to give satisfactory cement waste forms. With Conwed, 50% oil can be incorporated.

- With the DCM cement shale silicate, all samples set satisfactorily, but, with several of the absorbents, free liquid prevents some of the specimens from being considered satisfactory. This is the situation for vermiculite and Amorphous Silicate for both saturation and half saturation with oil, and for oil-saturated Conwed and Super-Fine. All samples prepared with Instant-Dri and LSM have shown no free liquid.

- Using the proportions called for in DCM's procedure, approximately 15 weight percent oil is contained in the mixtures with Instant-Dri and LSM, the best performers. By varying the manufacturer's procedure, up to 20 weight percent can be incorporated using LSM.

5.3 Solidification of Oil Waste Without Absorbents

For the reasons given in section 3.2, simulated oil wastes were not tested with the Dow vinyl ester-styrene polymerization process. A simulated BWR aqueous waste containing 0.2% oil was tested with the Dow process and gave acceptable waste forms. Conclusions for tests done with Portland I cement and DCM cement shale silicate follow.

- Using Portland I cement, there is a considerable composition range over which acceptable waste forms can be prepared. Up to 35 weight percent oil can be incorporated in acceptable waste forms (i.e., with compressive strength >50 psi and releasing no free liquid) as long as the water content is in the range 25-35 weight percent.

- Compressive strengths of the concrete samples are many times greater than the proposed 50 psi NRC requirement, almost to the boundary of the composition region in which acceptable forms are obtained, and then the strength drops off rapidly.

- Addition of a small amount of detergent to mixtures containing relatively high proportions of oil facilitates solidification and increases strength. Increasing time of curing also gives increased strength. Acceptable samples can be prepared with proportions of oil >35 weight percent by these means.

- All the mixtures used with DCM cement shale silicate solidify within 10 seconds and show no free liquid. Variations of at least ±20% can be made in the proportions recommended by the manufacturer.

- Compressive strength changed hardly at all over the range of compositions tested for the DCM cement shale silicate process. The measured value was always close to 300 psi, which is not high, but well above the proposed 50 psi criterion.

- The proportion of oil incorporated in DCM cement using the manufacturer's procedure is 14.7 weight percent. Within the range of compositions covered in the variations, 19.5 weight percent was the maximum oil loading. This amount yields an acceptable waste form.

5.4 Comparison of Methods

- Thirty-five weight percent oil can readily be incorporated into concrete without the use of absorbents. Somewhat more than 35% can be incorporated when a small amount of detergent is included, and when the mixture is allowed to cure for longer than 10 days. Solids prepared with these compositions easily surpass the 50 psi compressive strength criterion. The amount of oil in the standard DCM formulation is 14.7 weight percent and the greatest amount in the variations tested is 19.5%. Thus without changing the DCM formulation and carrying out more tests, it must be concluded that Portland I cement can incorporate almost twice as great a weight percent oil as can DCM.

- When absorbents containing oil are solidified in concrete, at least 30 weight percent oil can be contained in a waste form which sets properly and contains no free liquid, using all the absorbents tested. With Conwed, 50 weight percent oil can be incorporated. This is an even greater proportion of oil than can be held in concrete without absorbent.

- Using absorbents with the DCM procedure does not increase the amount of oil which can be satisfactorily solidified. Following the manufacturer's procedure with LSM, the absorbent permitting incorporation of the highest proportion of oil, a solid with 17 weight percent oil is obtained. By varying proportions within the range used in this study, a maximum of 20 weight percent oil can be incorporated. This is essentially the amount of oil that can be solidified without absorbents, and the maximum weight percent is less than half that obtainable with Portland I cement and the absorbent Conwed.

- The use of absorbents alone for disposal of oil waste should probably not be abandoned. Three power plants answering our questionnaire use absorbent to contain their waste oils, and one (James A. Fitzpatrick) ships the waste to Hanford. Conwed and Amorphous Silicate each can hold over 90 weight percent oil, or >45% even when only half saturated. Neither release any oil when the saturated absorbent undergoes the simulated transportation test. Thus, for oil waste containing no water, or only small amounts, use of absorbent alone for disposal in suitable metal containers seems feasible.

- Simulated transportation tests (repetitive shock) will have to be carried out on waste forms made from Portland cement and DCM cement shale silicate with and without absorbent in order to permit proper comparison of their use with the use of absorbents alone.

5.5 Alternative Methods

- Regeneration is worthwhile to consider as a method for treating oil wastes, whether or not the recovered oil can be re-used. Washing with water and filtration are useful procedures. If used in series, they can remove almost all the radioactivity. Since the water would go to liquid radwaste, the only new secondary waste stream created would be the filters. Because of the very low activity level of the oil wastes, filters could be expected to handle large quantities of waste oil before they would have to be disposed of.

- Of the management methods considered, incineration appears to be the only practical one at present. A number of different types have been developed for use with TRU waste, and several have been adapted for handling liquids. No major problems are anticipated with the off-gas treatment, but this point should be verified.

- Acid digestion, while feasible, is a relatively sophisticated method and would be very expensive.

- Ozonation as a purification process is designed to decompose small amounts of organic impurities in water. Applying it to destruction of hundreds of gallons of oil, assuming chemical attack could lead to such destruction, would be prohibitively expensive.

- Vermont Yankee presently uses filtration and it is planned for use at Nine Mile Point. None of the plants answering our questionnaire have used incineration, but it seems to be completly suitable as a disposal method.

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APPENDIX A

OIL WASTE QUESTIONNAIRE

Copy of questionnaire sent to 37 utilities operating over 50 nuclear power plants, and tabular summary of information contained in returned questionnaires.

QUESTIONNAIRE

Name of Power Station ____________________________________

(A) Volume of radioactive waste oil generated per year (gal/yr)

1. lubrication oil
2. turbine oil
3. pump oil
4. grease
5. sludge
6. others (please specify)

(B) Radioisotopes and level of radioactivity in each waste

1. lubrication oil
2. turbine oil
3. pump oil
4. grease
5. sludge
6. others (please specify)

(C) pH and amount of water in each waste

1. lubrication oil
2. turbine oil
3. pump oil
4. grease
5. sludge
6. others (please specify)

Questionnaire (Cont'd)

(D) Source of contamination (i.e., contact with primary coolant, breath in open handling, etc.)

1. lubrication oil
2. turbine oil
3. pump oil
4. grease
5. sludge
6. others (please specify)

(E) What brand oil or material in each category

1. lubrication oil
2. turbine oil
3. pump oil
4. grease
5. sludge
6. others (please specify)

(F) What is the present waste treatment method employed?

Table A.1

Results of Questionnaire on Oil Wastes From Operating Nuclear Power Plants

	Annual Oil Waste Generation (gal/yr)			Radioactive Contamination				
Power Station	Pump Oil and/or Lubricating oil	Turbine Oil	Sludge and Grease	Isotopes	Amount	Water Content and pH	Source of Contamination	Present Waste Treatment Method
PWR (B&W)								
Crystal River Unit 3	75		NA[a]	Cs-137, Co-58,60		<0.1%, pH not measured	pump oil contaminated from ventilation	storage in plant
Rancho Seco	400		NA	H-3, Cs-137, Co-58,60	10^{-6} - 10^{-7} µCi/mL	nil	pump oil contaminated from ventilation	absorption in sorbents
PWR (Westinghouse)								
Beaver Valley	500		nil	Xe-133		nil	pump oil contaminated from ventilation	kept till radioactivity decays
Connecticut Yankee	>275		NA	Cs-134,137 Co-60	10^{-5} µCi/mL 10^{-5} µCi/mL	nil	not known	NA
Kewaunee	50-100		nil	Cs-137 Co-60	10^{-5} µCi/mL 10^{-5} µCi/mL	<10% pH neutral	indirect contamination from primary coolant	water to radwaste, oil stored on site
Trojan	100			Co-60, Cs-137 I-131	$<10^{-5}$ µCi/mL	NA	radwaste pump, reactor coolant pumps	absorbed in Speedi-Dri in 55-gal drum
BWR(GE)								
Peach Bottom	100	900	NA	Cs-134,137, Co-60, Zn-65	10^{-5} - 10^{-6} µCi/mL	0-90%, pH not measured	contact with primary coolant via steam seal	water to radwaste, oil solidified in DCM Cement
Vermont Yankee	100	100	NA	varies, low activity		varies, pH not measured	contact with primary coolant	filtered through diatomaceous earth and resin
Nine Mile Point	110	330	NA	Cs-134, Co-60	2.4×10^{-5} µCi/mL 9.9×10^{-5} µCi/mL	NA	contact with primary coolant	plans are for filtration and vacuum coalescence
James A. Fitzpatrick	220	500	275 (sludge)	Co-60 Cs-137 Mn-54	1.8×10^{-4} µCi/mL 2.75×10^{-5} µCi/mL 9.3×10^{-6} µCi/mL	<1% in oils pH 3.5-4.0 20-30% in sludge pH 4.0-5.5	contact with primary coolant	absorbed with absorbent and shipped to Hanford

[a] NA - not answered.

APPENDIX B

STANDARD VIBRATION TEST METHODS FOR SIMULATION OF TRANSPORTATION CONDITIONS

1. Military Standard Environmental Test Methods, MIL-STD-810 C, Method 514, Vibration.

2. DOT test for steel drums, 49 CFR 178, Section 16-13(a)(2).

1. Military Standard Environmental Test Methods, MIL-STD-810 C, Method 514, Vibration

4.6.12.1 Part 1 (Former 4.16.1) DISCONTINUED

4.6.12.2 Part 2, bounce, loose cargo

4.6.12.2.1 Purpose. To determine that the equipment, as prepared for field use, shall be capable of withstanding the vibrations normally induced during combat transportation as loose cargo. Equipment in this class is normally transported in a transit case, combination case, or special container from which it is removed just prior to use, e.g., ammunition or missiles.

4.6.12.2.2 Apparatus. A package tester capable of 1 inch (double amplitude) displacement and of suitable capacity for testing military equipment.

4.6.12.2.3 Test conditions. The test bed of the package tester shall be covered with a panel of 1/2-inch plywood, with the grain parallel to the drive chain. The plywood shall be secured with six-penny nails, with top of heads flush with or slightly below the surface. Nails shall be spaced at 6-inch intervals around all four edges. If the distance between either pair of fences is greater than 24 inches, the plywood shall also be nailed at 3-inch intervals in a 6-inch square at the center of the test area. Using suitable wooden fences, constrain the test item to a horizontal motion of not more than 2 inches in a direction parallel to the axes of the axes of the shafts, a distance more than sufficient to insure the test item will not rebound from fence to fence. For large items, care should be taken to avoid potential air-cushioning effects which may exist between the surface of the package tester and the test item.

4.6.12.2.4 Performance of test. The test item, as secured in its transit case, or combination case, or as otherwise prepared for field transportation, shall be placed on the package tester within the constraints outlined above. The test item will not be operated during vibration. The package tester shall be operated in the synchronous mode with the shafts in phase. (In this mode any point on the bed of the package tester will move in a circular path in a vertical plane perpendicular to the axes of the shafts.) The package tester shall be operated at 1-inch double amplitude and 284 rpm ±2 rpm for a total of 3 hours. At the end of each 1/2-hour period, turn the test item to rest on a different face, so that at the end of the 3-hour period the test item will have rested on each of its six faces (top, bottom, sides, and ends). At the end of the 3-hour period, the test item shall be operated and inspected and results obtained in accordance with General Requirements, 3.2. The package tester shall be operated in the vertical linear mode (straight up and down in the vertical plane) instead of in the synchronous mode when one of the following conditions occurs:

a. Bouncing of the test item is very severe and presents a hazard to personnel.

b. Forward and rear oscillations cannot be reduced. When operated in the vertical linear mode, wooden fences shall be placed on all four sides of the test item to constrain its motion to not more than 2 inches in either direction.

2. DOT Test for Steel Drums

tive mechanical locking and sealing devices to prevent leakage during normal conditions incident to transportation.

[Amdt. 178-60, 37 FR 2888, Feb. 9, 1972]

§ 178.252-3 Testing.

(a) *Design qualification testing.* In addition to the testing prescribed in § 178.252-5(a), a vibration and a drop test are also required on each design. For these tests, the tank must be filled with a fine, dry powdered material having a density that results in the tank having a gross weight not less than the rated gross weight of the tank.

(1) *Vibration test.* This test must be performed for 1 hour using a minimum double amplitude of 1 inch at a frequency that causes the test tank to be raised from the floor of the testing table so a piece of flat steel strap may be passed between the tank and the table. The tank must be restrained so that all horizontal motion is restricted and only vertical motion is permitted.

(2) *Drop test.* The tank must be capable of withstanding without leakage of contents of 2-foot free drop onto a flat unyielding horizontal surface, striking the target surface in the position and attitude from which maximum damage to the tank (including closures) is expected.

(b) *Production quality control, testing, and inspection*—(1) *Leakage test.* Each tank must be tested by a minimum air or hydrostatic pressure of at least 2 pounds per square inch gage applied to the entire tank. If the air pressure is used, the entire surface of all joints under pressure must be coated with, or immersed in, a solution of soap and water, or other material suitable for the purpose of detecting leaks. If the hydrostatic pressure test is used it must be carried out by using water or other liquid having a similar viscosity, the temperature of which may not exceed 100° F. and all joints under pressure must be inspected for leaks. For either test, the pressure must be held for a period of time sufficiently long to assure detection of leaks. All closures must be in place during the test. Any tank that has detectable leakage or significant permanent deformation does not meet the requirements of this specification.

[Amdt. 178-60, 37 FR 2888, Feb. 9, 1972]

§ 178.253 Specification 57; metal portable tank.

§ 178.253-1 General requirements.

(a) Each tank must be in compliance with the general design and construction requirements in § 178.251 in addition to the specific requirements of this section.

(b) Each tank must have a capacity of at least 110 gallons but not more than 660 gallons.

[Amdt. 178-60, 37 FR 2888, Feb. 9, 1972]

§ 178.253-2 Openings.

(a) Each fill and discharge opening must be equipped with a closure device that meets the following requirements:

(1) Any closure for a fill opening in excess of 20 square inches must be equipped with a device to prevent the closure from fully opening without first relieving internal pressure.

(2) Any product discharge valve, if used, must be provided with a leak tight device, such as a cap or plug.

(3) Each closure must be vapor tight.

(b) A drum-type locking ring closure is authorized for any opening less than 23 inches in diameter. A drum-type locking ring closure must be at least a 12-gage bolted ring with forged lugs having at least a ⅝-inch steel bolt tapped into one of the lugs. The locking ring must be equipped with a lock nut or equivalent device.

[Amdt. 178-60, 37 FR 2888, Feb. 9, 1972]

§ 178.253-3 Protection of fittings.

Each fitting which could be damaged sufficiently to result in leakage of tank contents must be protected by suitable guards or protective housings. The term "fitting" includes valves, closure devices, safety relief devices, and other accessories through which contents could leak from the tank. Each fitting or fitting protection device must be capable of withstanding the fitting protection test specified in § 178.251-5.

[Amdt. 178-60, 31 FR 2888, Feb. 9, 1972]

§ 178.253-4 Vents.

(a) Each tank must be equipped with at least one pressure relief device such as a spring-loaded valve, frangible disc or fusible plug.

(b) Each pressure relief device must communicate with the vapor space of the tank when the tank is in a normal transportation attitude. Shutoff valves must not be installed between the tank opening and any pressure relief device. Pressure relief devices must be mounted, shielded, or drained to prevent the accumulation of any material that could impair the operation or discharge capability of the device.

(c) The total emergency venting capacity (cu. ft./hr.) of each portable tank must be at least that determined from the following table.

Total surface area square feet[1] [2]	*Cubic feet free air per hour*
20	15,800
30	23,700
40	31,600
50	39,500
60	47,400
70	55,300
80	63,300
90	71,200
100	79,100
120	94,900
140	110,700
160	126,500

[1] Interpolate for intermediate sizes.

[2] Surface area excludes area of legs.

(1) The pressure operated relief device must open at not less than 3 pounds per square inch gage and at not over the design test pressure of the tank. The minimum venting capacity for pressure activated vents must be 6,000 cubic feet of free air per hour (measured at 14.7 p.s.i.a. and 60° F.) at not more than 5 pounds per square inch gage.

(2) If a frangible device is used for relieving pressure, the device must have a minimum area of 1.25 square inches and must be rated at less than the design test pressure of the tank.

(3) If a fusible device is used for relieving pressure, the device must have a minimum area of 1.25 square inches. The device must function at a temperature between 220° F. and 300° F. and at a pressure less than the design test pressure of the tank, unless this latter function is accomplished by a separate device.

(d) No relief device may be used which would release flammable vapors under normal conditions of transportation (temperature up to and including 130° F.).

[Amdt. 178-60, 37 FR 2888, Feb. 9, 1972]

§ 178.253-5 Testing.

(a) *Design qualification testing.* In addition to the testing prescribed in § 178.251-5, a vibration test, a drop test, and a pressure test are also required on each design. For the vibration and drop tests, the tank must be filled with a liquid to not less than the rated gross weight.

(1) *Vibration test.* This test must be performed for 1 hour using a minimum double amplitude of 1 inch at a frequency that causes the test tank to be raised from the floor of the testing table so a piece of flat steel strap may be passed between the tank and the table. The tank must be restrained so that all horizontal motion is restricted and only vertical motion is permitted.

(2) *Drop test.* The tank must be capable of withstanding without leakage of contents a 2-foot free drop onto a flat unyielding horizontal surface, striking the target surface in the position and attitude from which maximum damage to the tank (including piping and fittings) is expected.

(3) *Pressure test.* The tank must be capable of maintaining, under hydrostatic test for at least 5 minutes, at least one and one-half times the design pressure prescribed in this paragraph, without detectable leakage or significant permanent deformation. The pressure must be measured at the top of the tank. Each closure must be in place and blocked if necessary as for shipment. Each closure must be standard, except that tapping for pressurizing and gaging is permitted. Design pressure must be determined as follows:

$$P=(hd/115)+3$$

Where:

P=Design pressure in p.s.i.g.;
h=Inside height of tank in inches;
d=Maximum allowable density in pounds per gallon;
115=Number of cubic inches in 1 gallon (231) divided by a safety factor of two.

APPENDIX C

CANDIDATE ABSORBENTS

Table C.1 reproduces the list of absorbents and suppliers as received from NRC, and Table C.2 gives information on composition and properties as obtained from the suppliers for 20 of the absorbents.

Table C.1

LIST OF ABSORBENTS

Information Supplied by NRC

The following is a list of absorbents to be used in this subtask.

ABSORBENTS	POSSIBLE SOURCE
1. Floor Dry 85 Super-Fine	Eagle Piecher Industries 580 Walnut St. Mrs. Tava Witschy Cincinnati, Ohio (513) 721-7010
2. Florco X	Floridin Company Jack Obara Three Pen Center Pittsburgh, Pa.
3. Instant-Dri	Meridian Petroleum Company 330 S. Wells Street Chicago, Illinois (312) 939-2693
4. Hi-Dri grades #40 grades #50 "Dri-Zit" Petro-sorb Zip-Zorb #40	S. Lee Coogan Marketing Manager Waverly Mineral Products Philadelphia, PA (215) 243-1760
5. "LSM" "Oil Sorbent"	Hy-Grade Distributors, Inc. 574 Main Street Tonawanda, New York (716) 695-3960
6. Clean-Dri Super-sorb Safety-Sorb	Excel Mineral Company 1288 Coast Village Road Santa Barbara, CA (805) 969-5811
7. Diatomaceous Earth Celatom M-P 78	
8. Vermiculites (Uncoated) grades: #1, #2, #3, #4	W. R. Grace Company Trenton, New Jersey (609) 587-2570

9. Speed Dry	Fluoridium Co.
10. Super Fine	
11. Perlite fine and medium grades	
12. Oil-dry	Wilson Paper Company 160 S. Seminary Street Galesburg, IL (309) 342-0168
13. Amorphous Silicate	Science Related Materials, Inc.
14. Fiberperl	
15. Petro-Grab	
16. Conwed	
17. 3M Sorbent	
18. Sawdust fine, medium and coarse grades	

Table C.2

Properties of Absorbents as Given by Suppliers

Absorbent	Composition	Combustible	Chemically Inert	Absorbency by Weight For Oil	Absorbency by Weight For Water
Conwed	natural fiber	yes, with <4% residual ash	yes[a]	26	0.02
Sawdust	natural fiber	yes	yes[a]	---	---
Fiberperl	mixture of inert perlite and cellulose fiber	---	yes[a]	4-7	Nil
3M "Oil Sorbent"	polypropylene synthetic fiber	yes	yes	13-25	Nil
3M "LSM"	synthetic fiber	yes	yes	12	10
Celatom MP-78	amorphous silica	no	yes	1.02	---
Super-Fine Floor-Dry 85	granular diatomite material[b]	no	yes	1.02	---
Perlite	earth mineral[b]	no	yes	---	---
Amorphous Silicate	silicate	no	yes	10	10
Safe-t-Sorb	aluminosilicates	no	yes	0.75	0.80
Clean-Dri	aluminosilicates	no	yes	1.0	1.20
Super-Sorb	aluminosilicates and silica	no	yes	1.25	1.35
Vermiculite	mica $(MgCa)_{0.7}(MgFe_3Al)_6(AlSi)_8O_{20}(OH)_4 8H_2O$	no	yes	---	---
Oil Dry	clay	no	yes	0.7-0.8	---
Speedi-Dri	mineral	no	yes	---	---
Florco X	clay	no	yes	1.0	1.20-1.25
Hi-Dri	clay	no	yes	1.0	1.55
Dri-Zit	clay	no	yes	0.90	1.45
Zip-Zorb	clay	no	yes	0.85	1.35
Instant-Dri	clay	no	yes	1.20	1.45

[a] Strong acid and base attack natural fibers, but they are essentially inert to 0.1M solutions.
[b] Mixture of silicates.

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14 ABSTRACT *(200 words or less)*

A representative of each of six classes of commonly used absorbents was chosen for a series of tests. After reviewing ASTM and other related standard tests, uncomplicated procedures were developed for carrying out specific tests to determine absorbency for simulated oil waste and for water, under static and simulated transportation (repetitive shock) conditions. The tests were then applied to the six representative absorbents. Solidification tests were performed using these absorbents saturated with oil and loaded to 50% of saturation. The binders used were Portland I cement and Delaware Custom Material (DCM) cement shale silicate. Samples were checked for proper set, and the amounts of free liquid were measured. Another series of tests was performed on samples of simulated oil waste without absorbent, using Portland cement and DCM cement shale silicate. Samples were checked for proper set, free liquid was measured, and compressive strengths were determined. The state-of-the-art parameters were identified which satisfy NRC disposal criteria for solidified radioactive waste. The literature was reviewed for alternative methods of managing oil wastes. Conclusions are drawn on the relative utility of the various methods.

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