ASPHALT SOLIDIFICATION OF MIXED WASTES

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ABSTRACT

Mixed wastes pose a problem to generators since there are no burial sites or treatment facilities currently accepting this waste type. One potential disposal method is treating the waste to render it non-hazardous, and disposing of it in accordance with radioactive waste requirements. A possible means of accomplishing this transformation is solidifying the waste in asphalt (bitumen).

Associated Technologies Incorporated, in cooperation with Oak Ridge National Laboratory, solidified in asphalt a surrogate sodium nitrate-based waste, spiked with EPtoxic metals and non-radioactive cesium and strontium. This paper reports the characteristics of the spiked ORNL solution that was solidified as well as the properties of the solidified end product. The waste samples generated underwent EP toxicity testing as well as ANS 16.1 leach testing for 90 days and the results of those tests are presented. Also, a discussion of the criteria for classifying a waste as hazardous are included in order to demonstrate that the waste, once solidified in asphalt, may no longer be considered hazardous.

BACKGROUND

Oak Ridge National Laboratory currently has eight 190,000 liter (50,000 gallon) tanks full of waste which is both radioactive and hazardous. The waste is produced by the regeneration of ion exchange columns, yielding a nitric acid-based solution. This solution is heated to remove any reclaimable nitric acid, and the remaining slurry is adjusted to a pH of 12 and stored in the "Melton Valley" storage tanks. Oak Ridge has initiated a plan to characterize the waste and determine the best methodology to dispose of this waste due to the fact that these tanks are filling rapidly and a more permanent means of disposal is required.

One of the treatment methods that Oak Ridge is investigating is the solidification of this waste in asphalt. Asphalt solidification may be used to render the waste non-hazardous, allowing it to be "delisted" as a hazardous waste and to be disposed of in accordance with radioactive waste requirements alone. Tests toward this end were conducted using a thin-film evaporator- based asphalt solidification process owned and operated by Associated Technologies, Incorporated (ATI) of Charlotte, North Carolina.

The testing was conducted in March 1986 in a fabrication shop where ATI's Transportable Volume Reduction (TVR III) had just completed preoperational testing. Upon completion of testing, the TVR III traveled to Illinois Power Company's Clinton Power Station to begin a solidification service contract. The TVR station used for the testing is a full-scale unit capable of solidifying up to 1900 liters (500 gallons) of waste in an eight-hour shift.

The Oak Ridge waste, which contains both radioactive and hazardous compounds, was prepared according to a formulation developed at Oak Ridge (Table I). The surrogate waste was a 27 weight percent solution of primarily sodium nitrate with eight heavy metals plus nonradioactive cesium and strontium.

The TVR III System (Fig. 1) which was used in the testing is an over- the-road, self-contained, trailer-mounted system which is centered around a thin-film evaporator. It also contains subsystems for the waste feed tank, distillate collection tank, heating fluid and HVAC system. The asphalt tank is separate from the trailer and is electrically heated.

The waste is transferred from the client via temporary connections to TVR's waste batch tank where it is pretreated for optimum solidified waste properties. The waste is then recirculated through the tank while a smaller side stream is metered from the recirculation line into the evaporator at a rate determined by the solids concentration in the waste. Simultaneously, hot asphalt is pumped into the evaporator at a controlled rate to yield the target solids content in the solidified product. The evaporator is 1.7 m (5.5 ft.) tall, 0.4 m (15 in.) diameter cylinder which is jacketed with heating fluid. The waste and asphalt are supplied to the internal surface of the cylinder where they are mixed by the rotor blades which pass within two millimeters of the evaporative surface. As the waste and the asphalt enter at the top of the evaporator through distributors, they are swept into a thin film which allows rapid evaporation of the waste water leaving the waste solids embedded in asphalt. The asphalt and solids mixture exits through a cone-shaped nozzle at the bottom of the evaporator. The evaporated water (distillate) is pulled up through the evaporator by a

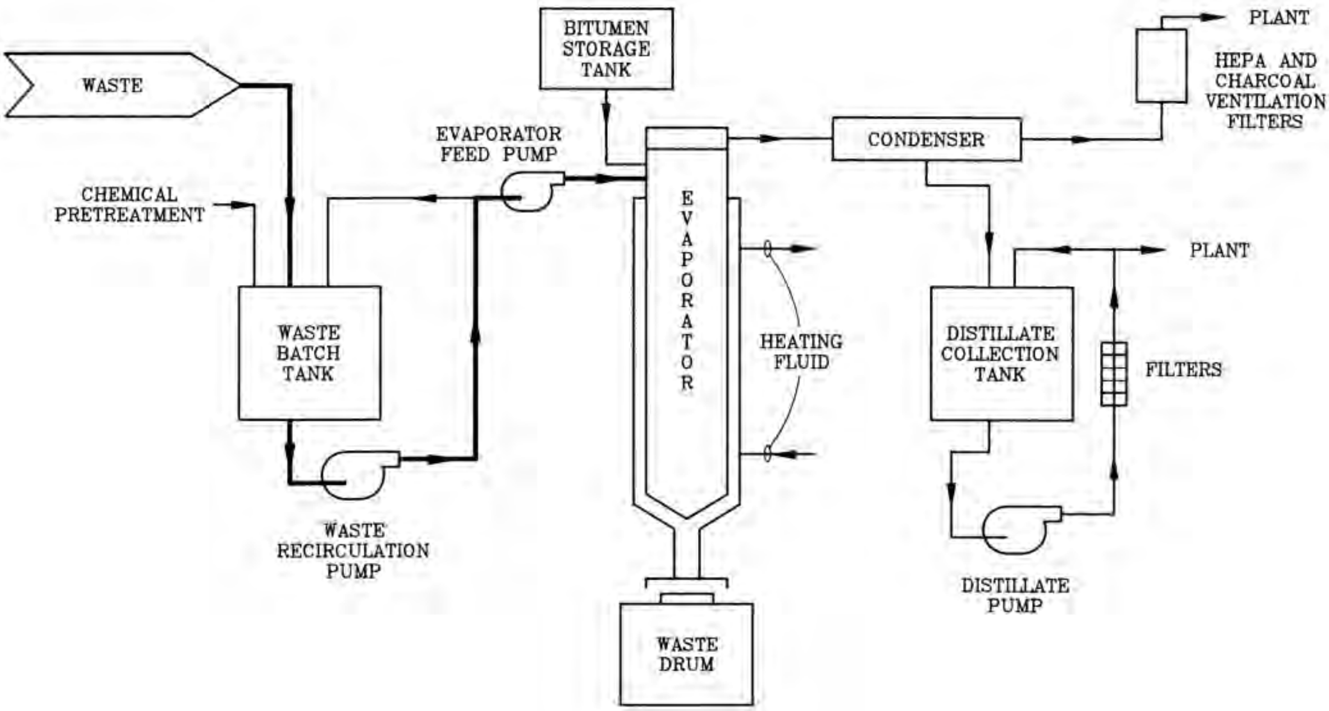

Fig. 1. TVR-III System Flow Diagram.

TABLE I

Melton Valley Storage Tank Surrogate Waste

Species	Concentration (ppm)
Arsenic	43
Barium	47
Cadmium	48
Calcium	13,000
Cesium	46.3
Chloride	2,200
Chromium	49
Lead	50
Magnesium	920
Mercury	31.6
Nitrate	212,000
Selenium	24
Silver	49
Sodium	81,000
Strontium	47
Sulfate	200

fan and through a heat exchanger where the moisture is condensed. The condensate flows to a collection tank for treatment, if necessary, before being returned to the client. The air which was pulled up through the evaporator with the distillate is filtered, monitored for activity and released to the environment or to the client's HVAC system.

THE PRODUCT

The asphalt used in testing is an oxidized asphalt classified by the American society of Testing and Materials as ASTM D312 Type I roofing asphalt. Two waste form loadings were achieved during operation of the system. The waste was solidified into 0.10 m (4 in.) diameter molds to be used for testing and analysis. The waste specimens were cut after cooling to a 0.10 m (4 in.) height. All solidified waste forms were returned to Oak Ridge for analysis and evaluation.

TESTING - LEACHABILITY

In order to delist the solidified product as being nonhazardous, one criterion it must pass is to meet established limits in the performance of an EP (Extraction Procedure) Toxicity test (1). This test was developed by the Environmental Protection Agency (EPA) to determine the quantity of hazardous materials leached in a 24-hour period. EP Toxicity tests were conducted on each of the two waste-loadings, using deionized water as the extracting solvent and maintaining a pH of 5 ± 0.2 with acetic acid, as specified in the procedure.

Both waste loadings were also tested according to the American Nuclear Society's leaching test, ANS 16.1(2). This procedure, performed as a 90-day test, is used in the determination of waste form stability as required by the Nuclear Regulatory Commission's Branch Technical Position (BTP) (3). The BTP specifies the stability requirements which a solidified radwaste product must meet in order to be considered acceptable at a shallow land radwaste burial facility (Consult Ref. 3). The test prescribes sample dimensions, leachate volume, leachate changeout frequency and evaluational mathematical parameters. The test measures the effective diffusivity of radionuclides from the waste form, and the "leach index" is then defined as an arithmetic average of a log function of the effective diffusivity for a given time period. (Consult Ref. 2 for further detail.) The leach index provides a "yardstick" by which waste solidification agents can be measured for their leaching tendencies. The BTP requires that all radionuclides exhibit leach indices of 6 or greater in order for a solidification agent's leachability to be acceptable. In this testing, the leach index for all waste constituents was measured so as to provide general indication of the overall leaching tendency of the asphalt product.

TESTING - PHYSICAL PROPERTY REQUIREMENTS

In order to evaluate the physical integrity of the waste forms, unconfined compressive strength and homogeneity were measured. Since asphalt is a substance which flows under applied force, a widely recognized criterion for asphalt is that it exhibit a compressive strength of 3.45×10^5 Pa (50 psi) or greater at 10% vertical deformation. Testing was performed in accordance with the ASTM test for the Compressive Strength of Bituminous Mixtures (D 1074-83) (4).

Homogeneity in the waste form is also of interest in determining its stability. Settling of the waste salts could lead to higher concentrations in the product bottom, potentially resulting in higher leachabilities. Waste homogeneity is a requirement of the BTP. Samples taken from the top and the bottom of waste forms of each salt loading were analyzed for salt content in order to determine the degree of settling that the asphalt allowed.

TESTING RESULTS - LEACHABILITY

The results of the EP Toxicity test for the eight hazardous metals in the waste are presented in Table II. As can be seen from the table, the concentration in the leachate of each of the metals is far less than the allowable concentration; thereby, meeting one criterion for delisting of the waste.

A far more stringent requirement on waste form leachability is the ANS 16.1 leach test, the results of which are presented in Table III. Three waste forms at each of the two waste loadings (40.9 and 43.3 weight percent solids in

TABLE II

EP Toxicity Results for Heavy Metals, ppm

	Salt Loading, %			
Species	40.9	43.3	(Pure Asphalt)	Limit
Arsenic	<0.005	0.010	<0.005	5
Barium	0.120	0.140	<0.0010	100
Cadmium	0.010	0.022	<0.0030	1
Chromium	<0.010	<0.010	<0.010	5
Lead	0.010	0.022	0.005	5
Mercury	<0.0002	<0.0002	<0.0002	0.2
Selenium	0.009	0.008	<0.005	1
Silver	<0.0060	<0.0060	<0.0060	5

product) were tested in order to provide an indication of consistency in the data. Some of the tabulated leach indices are reported as "greater than" values which correspond to an analysis which is less than the limit of detection. Leach indices for all of the waste constituents were evaluated using chemical analysis techniques. As the data show from the table, all of the leach indices were above 6.0, and reasonably consistent indices were achieved for all three replicates. No appreciable difference can be seen due to the difference in waste loadings, but since the weight percentages are close to one another, this is not unexpected..

TESTING RESULTS - PHYSICAL PROPERTIES

The results of the unconfined compressive strength tests are tabulated in Table IV. The compressive strengths of the two waste loadings exceeded the 3.45×10^5 Pa (50 psi) requirement at 10 percent vertical deflection. Higher compressive strengths would normally be expected at higher waste loadings since the addition of waste salts has been seen previously to strengthen the solidified product (5). However, since the two weight percentages are relatively close to one another, this overall trend is not readily observable.

A sample from the top and the bottom of each waste loading was analyzed for percentage waste solids to determine product homogeneity, the results of which are tabulated in Table V. The higher salt loading, which increases the strength of the product in most cases, also produced a product less likely to settle. The 40.9 weight percent solids product concentration varied by 5.6 percent from the average concentration; whereas the 43.3 weight percent solids product varied 2.8 percent from the average. Previous testing using 0.21 m^3 (55 gal.) drums showed that there was no appreciable settling and that the solids remained evenly distributed within the asphalt matrix.

HAZARDOUS WASTE CHARACTERISTICS

According to Volume 40 Part 261 of the Code of Federal Regulations (1), a hazardous waste is a waste which exhibits the characteristics of ignitablility, corrosivity, reactivity, EP toxicity or has been assigned an EPA Hazardous Waste Number. A solid waste generated from the treatment of a hazardous waste, classified according to Subpart C, can be classified as non- hazardous if it does not exhibit the characteristics of Subpart C, namely ignitability, corrosivity, reactivity and EP Toxicity (40 CFR 261.3 b(3)(d)(1)). The Oak Ridge waste is considered hazardous because it EP toxic heavy metals - a hazardous waste characteristic according to Subpart C. If the asphalt product generated from the solidification of this waste is no longer EP toxic, and is not corrosive, ignitable or reactive due to the addition of asphalt to the waste, then the EPA can be petitioned to delist the waste. The concern, then, is whether the asphalt solidification process creates a solidified product which is hazardous under the characteristics of Subpart C.

Ignitability is defined, for substances other than a liquid, as capable of causing fire through friction, moisture absorption, or spontaneous chemical changes under standard temperature and pressure. Asphalt is not capable of causing fire under any of these circumstances and therefore would not be considered ignitable.

Corrosivity is not well-defined for solids under Subpart C so it is not readily refutable when discussing asphalt. However, asphalt is generally not considered a corrosive material as evidenced by the use of asphalt as a corrosion protective coating on underground tanks.

Reactivity, under Subpart C, is defined at length in terms of instability; violent reactivity with water to form explosive mixtures or toxic fumes; capable of detonation at standard temperature and pressure; etc. The fact that asphalt is used in the paving of roads and roofing of buildings verifies the assertion that it cannot be considered a reactive substance.

As proven in the testing at the Oak Ridge National Laboratory, the stabilization of EP Toxic compounds in asphalt results in a solids waste which does not exhibit the characteristic of EP Toxicity. This rounds out the requirements needed to delist a hazardous waste, allowing its treatment as solely a radioactive waste.

TABLE III

Average Leach Indices[a] for All Surrogate Constituents After 90-Day ANS 16.1 Leach Test

Waste Loading:	40.9%		43.3%	
Species	Avg. LI	Std. Dev.[b]	Avg. LI	Std. Dev.[b]
Arsenic	<10.7	0.8	>10.8	0.8
Barium	8.4	0.1	8.9	0.3
Cadmium	>10.5	0.5	>10.7	0.5
Calcium	8.3	0.1	8.7	0.3
Cesium	> 7.8	0.2	> 7.8	0.3
Chloride	> 5.4	1.1	> 5.8	0.9
Chromium	10.1	0.8	>10.2	0.8
Lead	9.5	1.0	9.6	0.9
Magnesium	9.3	0.2	9.5	0.3
Mercury	>13.6	0.8	>13.6	0.8
Nitrate[c]	8.3	0.3	9.0	0.5
Selenium	>10.3	0.4	>10.6	0.6
Silver	>10.6	0.8	>10.6	0.8
Sodium	8.2	0.2	8.7	0.4
Strontium	8.3	0.1	8.7	0.9

a. Average of three replicate leach indices
b. Average of the three standard deviations of the incremental leach indicies
c. Analyses available for only two replicate

TABLE IV

Unconfined Compressive Strength at 10% Vertical Deflection, psi

Salt Loading	Compressive Strength, Pa
40.9	1.93 (10^6) (280 psi)
43.3	1.83 (10^6) (265 psi)
0.0 (Pure asphalt)	3.24 (10^5) (47 psi)

TABLE V

Salt Loading Homogeneity

Specimen Waste Loading wt. % Solids	Top wt. % Solids	Bottom wt. % Solids
40.9	38.6	43.1
43.3	42.1	44.4

RADIOACTIVE WASTE REQUIREMENTS

In order for a Class B or C radioactive waste to be considered stable and suitable for shallow land burial, according to the BTP, it must meet specified criteria in the areas of leachability, thermal cycling, biodegradation, compressive strength, radiation stability, and immersion in water. Testing in all of these areas has been completed for nonradioactive waste surrogates solidified over a range of waste loadings by the TVR III system. A topical report on the results of this testing is currently under review by the Nuclear Regulatory Commission. However, the solidified product presently generated under contract at Palo Verde

Nuclear Generating Station and Clinton Power Station has been accepted at the Hanford burial facility and deemed acceptable at the Barnwell facility. To date, over 567,750 liters (150,000 gallons) of radioactive waste has been processed at the two facilities and solidified in asphalt.

SUMMARY

It is evident, from the testing performed in conjunction with Oak Ridge, that the solidification of certain mixed wastes in asphalt can result in a waste no longer considered hazardous. This "delisting" can permit the disposal of the waste in accordance with regulations for radioactive wastes alone. Primarily, it permits the final disposal of the waste rather than requiring its indefinite storage.

REFERENCES

1. Environmental Protection Agency, "Identification and Listing of Hazardous Waste, "Code of Federal Regulations," 40 CFR 261.

2. American Nuclear Society Standards Committee, "Measurement of the Leachability of Solidified Low-Level Radioactive Wastes by a Short-Term Procedure," ANS 16.1, Final Draft (1986).

3. Nuclear Regulatory Commission, "Branch Technical Position on Waste Form," Rev. 0, (May 1983).

4. American Society of Testing and Materials, "Compressive Strength of Bituminous Mixtures," Annual Book of ASTM Standards, ASTM D 1074-83 (1983).

5. Associated Technologies Incorporated, "Bitumen as a Radwaste Solidification Agent", Topical Report NO. ATI-VR-001-P-A, 1987.