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J. E. Day
Division Vice President
Technology Division
U.S. Ecology Inc.
212 South Tyron Street, Suite 300
Charlotte, NC 28281

Dear Mr. Day:

SUBJECT: U.S. ECOLOGY REPORT "STABILITY OF NS-1 SOLIDIFIED WITH HIGH STRENGTH ASPHALT," REPORT NO. USE-61-001-P, REVISION 0; WM-100

The subject report was reviewed by our technical consultants, Brookhaven National Laboratory (BNL) and National Institute of Standards and Technology (NIST), and the review comments were sent to us recently. Because of other high priority work and resource limitations, our staff has not completed the review of either the subject report or the consultant's comments on the report. Therefore, our staff has not yet prepared a formal "Request for Additional Information (RAI) " to be sent to you. It will be prepared after the staff has reviewed both the report and the consultant's comments. However, we are providing you with copies of our consultant's comments. They should be considered as informal comments on your topical report. We hope this will be helpful to you in formulating your response to a formal request by the NRC for additional information on your Topical Report. You may expect to receive this formal request in March 1989. Once again, these are advance copies of preliminary comments on your topical report and should be treated as such.

If you have any questions on this, please call me or Dr. Banad Jagannath of my staff (301- 492 0593).

Original Signed By

Michael Tokar, Section Leader
Technical Branch
Division of Low-Level Waste Management
and Decommissioning, NMSS

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WM-100
NL11

BROOKHAVEN NATIONAL LABORATORY

MEMORANDUM

DATE: December 9, 1988

TO: File #80

FROM: B. S. Bowerman BSB

SUBJECT: Questions and Comments on USE Topical Report #USE-61-001-P

A topical report (TR) describing the solidification of decontamination wastes in bitumen is being reviewed as part of the effort under Task 12, FIN A-3174. The solidification process was originally developed in France and licensed to Associated Technologies, Inc. (ATI). U.S. Ecology, Inc. (USE), who recently bought out ATI, submitted the TR to NRC for approval. The review will evaluate the solidification process in terms of its acceptability under Branch Technical Position (TP) criteria. Additional concerns about long-term stability may also be addressed in the review. The purpose of this memorandum is to discuss the adequacy of the report in providing all necessary information and to provide a basis for a request for additional information to the vendor. A preliminary draft Technical Evaluation Report will be prepared by January 9, using the information identified here.

General Remarks

One waste stream consisting of about 11,000 gallons of decontamination waste is considered in the TR. This is to be solidified in a high-strength asphalt (or bitumen). (The identity of the asphalt is proprietary.) The wastes resulted from the decontamination of the Unit 1 Primary Cooling System at the Dresden Nuclear Generating Station operated by Commonwealth Edison Company. NS-1 solvent (Dow Chemical Co.) was used for the decontamination campaign, and the wastes from the campaign were evaporated to ~1,000 gallons and have been stored since 1983.

This limited application is similar in some respects to the West Valley solidification campaign, where wastes which had been stored for years in a tank are being processed and solidified in cement. ATI presents a radiochemical analysis of the waste to be solidified, but no chemical analysis. The adequacy of the waste stream simulation may be open to question, as discussed in more detail below. The TP states that "waste specimens should be prepared based on the proposed waste streams to be solidified and based on the range of waste stream chemistries expected".

The solidification process concentrates the waste because water is removed as the waste form is made. There is the distinct possibility that the final waste form could be greater than Class C if the waste loading is too high. The TR presents test data for a formulation with 40 weight percent (wt%) waste solids and 60 wt% bitumen. A review of the Process Control Plan (PCP) may be necessary to ensure that the waste loading limits are not exceeded.

There are some questions about the behavior of the waste samples when they are exposed to water and radiation. In several instances, the samples were wrapped before the exposure, then unwrapped and "trimmed" before being tested for compressive strength. The impression given is that the waste forms swell when exposed to water and radiation.

Photographs of test samples before and after testing are mentioned in several places in the report. However, there was only one reproduced in the report. More photographs would be very useful and informative.

It would be convenient if pages in the Appendices were numbered consecutively after the end of the text and referenced by page number where appropriate. This would make it easier to locate the relevant raw data for each TP test.

Specific Comments and Questions

Section 5.0, p. 5, Description of the Waste

What are the chemical characteristics of the decontamination waste? Is the waste homogeneous (all solids are dissolved) or heterogeneous (includes suspended solids and particulate)? Waste stream properties should be identified which could affect the solidification process adversely, for example, total organic carbon, pH, and total dissolved solids. An analysis of the actual waste for chromate may be necessary, to establish whether the waste is mixed waste or not.

Using fresh NS-1 and nitrate salts for tracers is not an adequate simulation of the actual waste. The actual waste will include corrosion products and degraded chelating agents, which may or may not have deleterious effects on the final waste form. The negligible effects of the full range of waste components need to be confirmed with test results, before the results obtained using simulated wastes can be considered completely acceptable.

p. 6, last paragraph

"It was desirable that the waste contain no more than 75% of the Class C limit when solidified. ...a volume reduction factor of 1.3 would stay within this limit. A VR of 1.3 corresponds to a 40 weight percent solids and 60 weight percent high-strength asphalt product. Forty/sixty is the solids to asphalt ratio used in making the specimens for stability testing."

Does the PCP assure that the 40/60 composition is adhered to? If the waste includes supended solids, are there procedures to assure that the waste will be homogenized?

Section 6.0, p. 7, 1st paragraph

Clarify whether the simulated waste was prepared by adding the specified quantities of cobaltous nitrate, cesium nitrate, and strontium chloride to 50 gallons of unused NS-1. Later sections refer to nickel analysis. Was nickel another tracer additive? How much nickel and in what chemical form?

Explain the pretreatment of samples made "in accordance with the USE Process Control Program in order to ensure optimum product quality." Has this PCP been approved by NRC?

p. 7, 3rd paragraph

What was the original sample size in the molds before they were trimmed? How were the samples trimmed?

Section 6.2.1, p. 8

Compressive strengths were obtained at 55°F, and not at 77°F as required in ASTM D-1074. USE argues that "55°F is representative of the ground temperature in a near surface burial site." Since raising the temperature for the test will significantly reduce compressive strength, the appropriate test temperature is an important consideration. Although measured compressive strengths were about 700 psi, well above the 60 psi minimum required, the strength after immersion dropped to about 250 psi. At 77°F this may be below 60 psi.

My initial recommendation is that the tests should be repeated at 77°F. The TP was not intended to simulate the burial environment and so the changes in test conditions are not really acceptable. However, the matter is subject to some discussion.

Section 6.2.2, p. 8, 3rd paragraph

The nickel tracer is mentioned here but not in sample preparation section.

Section 6.2.2, p. 8, 4th paragraph

What analytical method was used to determine total solids?

Section 6.2.2, p. 9, 1st paragraph

What size sample was used for the leach tests?

Section 6.2.3, p. 9

Why were samples wrapped as described? Does radiation induced deformation occur? If so, to what extent?

Section 6.2.5, p. 10, 2nd paragraph

What was the size of the samples before the test was conducted? How were the samples "trimmed"? The thermal cycling test does not conform to the ASTM procedure exactly. ASTM B553 specifies that the samples should be maintained at the high and low temperatures for an hour. The vendor should explain why this was not done.

p. 11

Was the 55-gallon drum size sample made in France prepared with the same asphalt as the test samples? Is the Luwa extruder/evaporator identical to that in use at Commonwealth Edison? What was the actual volume of waste in the drum (or amount of void space)?

Section 7.0, Test Results

Average values for measured compressive strengths should be reported as well as standard deviations. The measured strengths exceed the 60 psi minimum, but what is the value at 77°F? USE is to be commended for providing stress-strain curves in Appendix A. Some waste forms fractured before 10% deformation, but this is not important, since the strength is thus a fairly well-defined compressive strength analogous to those determined in cement, which is tested to failure.

Table 7.2.1, p. 12

Show average value for compressive strength.

Section 7.3, pp. 12-13

The leach test specimens were a non-standard geometry, being more disc-shaped than cylindrical. (Specimens were 2.4 inches diameter and 0.7 inch high.) Explain why this geometry was chosen.

Appendix A-3 which presents the raw data mentions that samples 19A and 19B, tested in demineralized water, were "concave on the bottom." Samples tested in synthetic sea water were "almost unchanged in appearance." Measurements of sample dimensions and a picture of each should be provided to show that degradation of the sample did not occur and that swelling was not severe enough to affect the calculation of the leach index.

Section 7.4, p. 14

The compressive strength after 90 days' immersion is 250 psi, which exceeds the TP criterion, but is much lower than the 720 psi found for non-immersed samples. Was the water used in the test discolored after the test was completed? What were the specimen dimensions before and after the test? Did any of these samples exhibit degradation, for example swelling, surface cracking or pitting? Pictures of the specimens before and after the test should be provided.

Section 7.5 Irradiation tests, p. 15

The compressive strength drops significantly when the bitumenized waste samples were irradiated. One sample only had 69 psi after the test. There may be a correlation of reduced effect (higher strength) with lower dose rate, but more data would be required to confirm such a conclusion. All samples fractured before 10 % deformation was reached. All samples exceeded the TP's minimum 60 psi criterion.

G21 tests, p. 16, second paragraph

Although no fungal growth was observed on the tops and sides of the specimens, some was observed attached to the bottom and sides of the specimen. The argument about a "leachate" supporting the growth is reasonable, and probably true. The lack of growth at the top and sides is most likely due to the lack of essential salt nutrients which are provided in the agar suspension. However, the TP specifically states that "some visible culture growth from contamination, additives or biodegradable components on the specimen surface which do not relate to overall substrate integrity may be present. FOR THESE CASES, ADDITIONAL TESTING SHOULD BE PERFORMED." [Emphasis added.]

The presence of a "leachate" and fungal growth on the specimen is evidence of failure of the G21 test. Retesting after a rinse procedure is therefore necessary.

G22 tests, p. 16-17

The same conclusion as for G21 test results applies, that further testing is required. The presence of growth in the agar adjacent to the specimens means that the specimen has failed the test. Further testing is required.

Table 7.6.1, p. 17

Table 7.5.1 on page 17 should be numbered correctly as 7.6.1. The compressive strengths after biodegradation testing meet TP criteria by exceeding the minimum 60 psi strength. However, see the two comments previous to this one.

thermal cycle tests, pp. 17-18

The results of the compressive strength tests should be tabulated.

Section 7.8, p. 18

Where are the elemental analysis data from CEA, France?

Section 7.9, pp. 18-19

What recipe was used for preparing the 55-gal drum of simulated waste? How were the 2-inch by 2-inch specimens for compressive strength testing "extracted" from the 55-gal drum and molded?

The correlation between bound water content and compressive strength suggest that the process must minimize bound water to "achieve the maximum practicable compressive strengths" and thus be consistent with the intent of the TP. Is this reflected in the PCP? How does the 7-10% moisture content product behave on immersion? If a corresponding decrease of compressive strength occurs as noted earlier, tests should be conducted to demonstrate that the higher water content product will also pass the immersion test criterion.

Section 7.10, pp. 19-20

The table on page 20 should be numbered correctly as 7.10.1.

Why are solids and bound moisture contents for the Luwa specimens reported as a range of values rather than a specific value?

Appendix A-1, Compressive Strength Data

The compressive strengths are reported in a format different from what I am familiar with. USE should verify that the "Compressive Load" really is the compressive strength for the samples. My understanding is that compressive load normally is reported as pounds and refers to the reading on a pressure gauge. Compressive load must be divided by the sample surface area to obtain compressive strength.

Appendix A-2, Leach Test Data

A-2 is incomplete in that some of the data that belongs in this Appendix is contained in A-3.

With reference to the data sheets describing leach tests (now in A-3), the two samples tested in deionized water were both "concave on the bottom" after the test was completed. USE should provide before and after test sample dimensions and a sketch if pictures are not available.

The leach index calculations are still being checked. One discrepancy found so far is the calculation of S/V for sample 19A. This will not significantly change calculated leach indices, but it does raise questions about the index calculations in general. (The calculations are still being verified at BNL).

Appendix A-3, Immersion Test Data

USE should provide before and after photographs of the immersion test specimens, and the sample dimensions before and after the test as well. The shape of the stress-strain curve is very different for the immersed samples.

Appendix A-4, Irradiation Test Data

USE should verify that the samples which had lower than 60 psi strength were different formulations than NS-1 in bitumen. (All other samples are identified in other test result reports.)

Some data on the amount of swelling observed as a result of radiation damage would be useful, e.g. pictures or measurements.

Appendix A-5, Biodegradation Test Data

The photographs of the biodegradation test samples should be included in the report. It is not clear how the agar medium would support growth when "leachate" from the sample diffuses into it while the sample surface has "no clear indication of bacterial growth." Was there a boundary a small distance from the surface at which growth began to occur?

The change in weight data are most interesting. Were similar data taken during the immersion and leach tests?

What was the shape of the samples? The data sheets suggest cubical samples were used. ASTM D-1074 specifies cylindrical samples be used; otherwise, comparisons with other sample geometry test results are invalid.

Appendix A-6, Thermal Degradation Tests

It is interesting to note that two of the three test samples lost weight and became longer, even though they were wrapped with tape. Also, all three of the pure asphalt samples expanded along the cylindrical axis.

A caption and better copy of the photograph would be useful.

The results of compressive strength testing (since they aren't tabulated in the main section of the report) are:

Sample	Strength (psi)	Average
1	570	
2	380	490 ± 98
3	520	
1A	800	
2A	900	867 ± 58
3A	900	

The solidified waste meets the TP criterion.

Appendix A-7, Solids Content and Tracer Content Data

No comments.

Appendix A-8, Free Liquids/Homogeneity Data

Notes on the testing lab's summary report state that the "samples were melted and remolded from submitted specimens." What did the samples look like? What were their dimensions? The actual geometry used for the test was apparently a 2-inch cube. ASTM D-1074 calls for cylindrical specimens. The shape of the stress-strain curve is very different from that for cylindrical specimens, and exhibits no fracture.

Appendix A-9, Correlation of Luwa and Guedu Specimens Data

Again, samples were "melted and remolded" into cubes. However, these did exhibit fracture.

Appendix B-1, Waste Analysis

Was the sample filtered before analysis?

cc: B. Siskind

REVIEW OF USE/ATI TOPICAL REPORT "STABILITY OF NS-1 SOLIDIFIED WITH HIGH STRENGTH ASPHALT"

by

James R. Clifton
and
Robert G. Mathey
National Institute of Standards and Technology

We have several comments and questions arising from our review. Many of the questions seek further information on the production process, nature of the materials, and testing practices. We have reservations regarding the temperature at which the compressive strength measurements were carried out (comment no. 9) and the results of the fungus test (comment no. 17). Both of which could result in the need for further testing by USE. We feel that all of the following items need to be addressed by USE.

COMMENTS AND QUESTIONS

1. Used NS-1 cleaning solution is being solidified with bitumen by USE. It is stated in their topical report that NS-1 is patented by the Dow Chemical Company. Because of the pertinence to the review of the topical report, the chemical composition and physical properties of NS-1 should be given. Providing this data will not disclose proprietary information (because of the patent). This information will facilitate interpreting the test data.

2. A complete description of the solids in the waste should be given, including the non-radioactive materials. This information will be useful in interpreting the test data and in analyzing the potential durability of the bituminous solidified LLW.

3. Page 4, Section 4.0, what is meant by "high-strength asphalt"? Is this a generic classification for the asphalt?

4. The identification of the material used to solidify LLW is vital because each formulation needs to be qualified. Changes in the solidification material can necessitate requalification. It is not easy to "finger-printing" bituminous materials. Often certain physical properties are determined, which even collectively do not uniquely identify a material but identifies a class of materials. On page 4 of the topical report, three properties of the asphalt were listed, softening point, penetration, and flash point. They will not uniquely identify the asphalt, but they are important properties. Four ASTM

Specifications for asphalt requires the determination of at least two other properties. In addition to the above three properties, ASTM D449 (Asphalt Used in Dampproofing and Waterproofing) and D312 (Asphalt Used in Roofing) require the determination of i) ductility at 25°C and ii) solubility in trichloroethylene. ASTM D946 (Penetration-Graded Asphalt Cement Used in Pavement Construction) and D3381 (Viscosity-Graded Asphalt Cement for Use in Pavement Construction), both covering asphalt for pavement, in addition, require the thin film oven test and the rolling thin-film oven test.

We suggest that the proper characterization of the asphalt should include:

*softening point
*penetration
*flash point
*ductility
*solubility in trichlorethylene

Often, the infrared (IR) spectrum is used to finger-print organic materials. The usefulness of IR spectroscopy for finger-printing asphalt mixtures for solidifying LLW's can be determined by comparing the spectra of the asphalts. We recommend that vendors or developers of asphalt and bituminous solidified LLW's be requested to submit an IR of the bituminous materials.

5. Pg. 6, last paragraph: the calculation of the volume reduction factor needs to be clearly explained.

6. Pg 7, Section 6.1, 2nd paragraph: the two ways of processing the wastes are not clearly explained. A brief description of the Luwa thin-film evaporator and the Guedu evaporator/mixer is requested, including their operational principles and operating temperatures. What type of processor will be used in full scale production?

7. Pg. 7, 3rd paragraph: the method of combining NS-1 and the high strength asphalt should be briefly described. Also, what was the temperature of the "hot bitumenized product"?

8. Pg. 7, last paragraph: Why was the water content on specimens measured?

9. Compressive Strength Testing: Page 8, Section 6.2.1 and other tests involving compressive strength measurements. The tests were carried out at 55°F whereas ASTM D1074 (Compressive Strength of Bituminous Mixtures) requires the test to be carried out at 77°F±1.8°. The reason that USE carried out the test at the 55°F was that "55°F is representative of the ground temperature." It is our opinion that either ASTM D1074 be strictly adhered to or the NRC TP be changed to indicate that the strength testing be performed at 55°F. Uniformity in testing is important in making decisions on the qualification of solidified LLW forms. Also, the temperature at the burial site may vary, e.g., what will be

the effect of the absorption of radioactivity by the bituminous material on the temperature of solidified LLW? Because of the visco-elastic behavior of bituminous materials their compressive strengths at 55°F may be considerably higher than at 77°F. Therefore, we recommend that USE be required to submit compressive strength data obtained at 77°F for all tests in which the qualification criteria specifies strength values.

10. Pg. 10 and 11, Section 6.2.7: The test for free liquids and homogeneity were made on a 55 gallon drum of NS-1/high strength asphalt product produced at the Cadarache Research Center in France. Were the conditions and procedures for making the specimen identical to those used in the U.S.?

11. Pg. 12, Section 7.2: USE should give the averages and standard deviations of the compressive strength results. In general, statistical data should be provided when more than one test result for a particular test is being reported. Statistical data are important in deciding if a process is well-controlled.

12. Section 7.2: what is the justification for excluding the compressive strength result for specimen No. 13? It had a strength at 10% deflection of less than 82 psi. Data cannot be rejected just because they are low, a reasonable justification is needed.

13. Section 7.2: the reason for the brittle behavior (failing at 8.7% deflection) of specimen should be discussed as it indicates an abnormal behavior.

14. Pg. 14, Section 7.2, Table 7.4.1: Unfortunately the number of specimens for which data are reported is too small to make any definitive conclusions. Based on the data, it seems that the compressive strength of the specimens decreased with length of immersion. If the decrease is valid, it suggests that a soluble material is being leached from the specimens. However, the difference in strength with immersion may reflect the statistical variation of the production and testing of specimens. Regardless of the reason for the apparent trend, the compressive strengths after 90 days of immersion were in excess of 60 psi and possibly represent the highest possible strengths for the immersion test.

15. Pg. 14 and 15, Section 7.5: Data for specimens Nos. 12, 13, 17, and 18 are reported. However, in addition to these specimens, data for specimens Nos. 4, 11, 14, 15, 16, and 19 are given in Appendix A-4, "Radiation Testing Data." The reason for not including in Table 7.5.1 the data for all the specimens should be explained.

16. Pg 15, Section 7.5: It is stated that specimen No. 12 did not swelled as much as specimen no. 13. The amount or percentage of swelling for both specimens should be given. This data will give an indication of the effects of radiation on the dimensional properties of the bituminous solidified LLW. (The effect of

radiation on other properties of asphalt should be understood. Hoiberg reported ("Bituminous Materials, Asphalts, Tars, and Pitches," Volume 1, Interscience Publishers, 1964) changes that occurred to asphalt due to radiation included hardening, decrease in ductility, changes in composition, lower flash point, and increase in volume. The effect of these changes on long-term service should be investigated).

17. Section 7.6: The test result for the ASTM G21 test indicate that fungus growth occurring on the agar was fed by a species diffusion out of the test specimens. The evaluation procedure given in ASTM G21 does not address such exterior growth. USE states that "It was not actually the product which was supporting the fungal growth." However, if the leached material originated from the bitumen solidified LLW then it should be considered as a component of the product. Photographs of the specimens after completion of the test which show the fungal growth in the agar and the condition of the test specimens may help in resolving this issue. If the issue cannot be resolved, then testing based on the Bartha-Pramer Method, as described in the NRC Technical Position, should be required.

18. Pg. 17, Table 7.5.1: The averages and standard deviations should be given.

18. Section 7.7: The table with compressive strength data was not included in report. Also, statistical data should be included.

19. Pg. 19, Table 7.9.1: The bound moisture contents seem to be high and somewhat variable, which needs explanation. What is the source of the moisture?

20. Table 7.9.1: The compressive strength increased with depth of sample location. This trend could be caused by creep of the bituminous material, segregation of the materials of the asphalt solidified LLW, or by variations of the water content, or reflect the variation in the production process. Again, insufficient data was reported to make any definitive conclusions regarding the cause of the trend. What does USE consider to be the cause of the trend? Data on the density of the product at the three sampling locations could be very informative. Was such density data collected?