DEVELOPMENT OF IMPROVED CRITERIA FOR BITUMINOUS LOW-LEVEL RADIOACTIVE WASTE

Jennifer Davis, Joseph Kane, and Robert Shewmaker
U.S. Nuclear Regulatory Commission

ABSTRACT

In January 1991, the Nuclear Regulatory Commission's (NRC) Low-Level Waste Management Branch, (Office of Nuclear Material Safety and Safeguards), issued Revision 1 to the Technical Position on Waste Form. This technical position provides guidance on waste form test methods and results acceptable to the NRC staff for implementing the 10 CFR Part 61 waste form requirements and includes an appendix specifically regarding cement stabilization of low-level radioactive waste (LLW).

In 1992, the NRC intends to provide a similar appendix regarding bitumen solidification of LLW. The methods and results appropriate to bitumen solidification are significantly different from those applicable to cement stabilization due in part to the differences in the materials (brittle versus elasto-plastic) and the solidification processes (chemical reaction versus encapsulation). To provide a complete and useful document, the NRC staff is studying the available references and seeking input from waste form solidification vendors, professional associations, NRC contractors, States, and other knowledgeable groups relative to bitumen materials.

INTRODUCTION

The United States Nuclear Regulatory Commission's (NRC) requirements for the licensing of facilities for the land disposal of low-level radioactive waste (LLW) are primarily contained in Part 61 to Title 10 of the Code of Federal Regulations (10 CFR Part 61), "Licensing Requirements for Land Disposal of Radioactive Waste" (1). This regulation also contains basic requirements concerning the physical form of low-level waste prior to land disposal. In May 1983, the NRC's Low-Level Waste Management Branch (Office of Nuclear Material Safety and Safeguards) issued a Technical Position (TP) on Waste Form (2). This technical position provided guidance on waste form test methods and test results acceptable to the NRC staff for implementing the 10 CFR Part 61 requirements.

One of the main requirements of 10 CFR Part 61 is that LLW in Classes B and C must be structurally stable. Structural stability may be provided by placing the waste in a high integrity container or acceptable structure, or by solidifying the waste into a monolith. A variety of materials may be used for solidification, provided the finished product can be shown to meet the requirements of 10 CFR Part 61. Some of the more commonly used solidification materials are cements, polymers, and bitumens. The TP provided general criteria applicable to the various solidification media. It was revised in January 1991 to include an appendix specifically regarding cement stabilization of LLW (3).

In 1992, the NRC intends to provide a similar appendix regarding bitumen solidification of LLW. The methods and results appropriate to bitumen solidification are significantly different from those applicable to cement stabilization, due in part to the differences in the materials (brittle versus visco-elastic) and the solidification processes (chemical reaction versus encapsulation). To provide a complete and useful document on bitumen, the NRC staff is studying the available references and seeking input from waste form solidification vendors, professional associations, NRC contractors, States, and other knowledgeable groups.

CHARACTERISTICS OF BITUMENS AND BITUMEN-STABILIZED WASTE FORMS

Bitumens are dark brown to black, solid or semi-solid cementitious materials which occur in nature or as a by-product of petroleum distillation (4). Asphalt is the subclass of bitumen most commonly used to produce waste forms. (The term "asphalt" will be used interchangeably with bitumen for the remainder of this document.) Bituminous materials are commonly used for paving surfaces, roofing, water-proofing, sealing etc. There are three main factors affecting the acceptability of bituminous waste forms: type of bitumen, type of waste, and the ratio of waste to bitumen. The bitumen used for waste stream solidification is a visco-elastic solid and can be characterized as either oxidized or distilled. Distilled asphalt is a direct result of the petroleum refining process and is generally slow-curing and relatively soft. Oxidizing is an additional processing step in which air is blown through the distilled asphalt, making the resultant product harder. In addition, oxidized (or blown) bitumen generally has a higher compressive strength than distilled bitumen, although even the high bitumen compressive strengths are significantly lower than those of cements. Bitumen, however, is more versatile than cement with regard to waste composition. As a thermoplastic material, bitumen will solidify (harden) upon removal of heat. This means that no chemical reaction is required for solidification, and essentially any waste stream mixed with molten bitumen is likely to be solidified. Oils are one exception. In significant amounts, oils will cut back (liquify) the asphalt, preventing effective solidification. Although bitumens do solidify well, leach resistance, immersion resistance, and other properties generally deteriorate with increasing waste to binder ratios.

In addition to the wide range of waste streams that can be solidified, other aspects that make bitumen an appealing solidification agent are its water resistance, low leachability, and processing. Bituminous waste forms can be created using a variety of processes, most commonly evaporation, extrusion, or mixing, which may be used separately or in various combinations. Other technologies are available, but are utilized sparingly or are only in the experimental stage. Choice of method is generally based on the binder material's viscosity.

Bitumen solidification results in volume reduction and most of the operations can be performed remotely, which will help keep personnel exposures low. In addition, the process is "operator friendly", meaning that small variations in waste chemistry or mechanical control settings have little effect on the end product.

Notwithstanding bitumen's attributes, there are some difficulties associated with bitumen solidification. Bituminous materials are not noted for high compressive strengths, and as a visco-elastic material, they are subject to creep and tend to slump when exposed to high temperatures from thermal cycling or irradiation. Irradiation at high dose rates (on the order of 3 Gy/s), can cause hydrogen gas generation, which may result in swelling and decreased compressive strength. In addition, although bitumen-solidified waste forms exhibit low leachability during standard testing, they may swell or disintegrate when immersed in water for long periods of time, resulting in increased leachability. Finally, as organic materials, they may be susceptible to some biodegradation.

DEVELOPMENT OF "APPENDIX B"

These and other issues require resolution before Revision 2 to the Technical Position on Waste Form, concerning bitumen solidification, can be completed. To provide the most effective document possible, even the most basic elements of the testing methods and acceptance criteria must be evaluated. For example, the Technical Position on Waste Form describes a series of compressive strength tests on each as-cured formulation and further compressive strength tests following a variety of environmental tests (thermal cycling, immersion, biodegradation, etc.). These tests provide base and comparative measures. The compressive strength of bitumen is usually relatively low, as noted previously, and is difficult to measure accurately. Therefore, leachability, creep, impact testing, or some other test might be more appropriate as the base measure for bitumen.

Once the decision is made regarding the base test for bituminous waste forms, the minimum value for the base test, the specific test to be used, and any variations or limitations on that test method must also be determined. All of the tests (irradiation, biodegradation, immersion, etc.) listed in the Technical Position should be analyzed in this manner to ensure that the testing is necessary, and that the tests recommended are applicable to bitumen. Tests in the area of bitumen characterization, not currently referenced in the TP, are also being considered for inclusion in the new appendix.

To resolve the issues related to bitumen solidification, the NRC has performed a literature search and is reviewing those publications that appear to be most appropriate. Most of the documents are from the United States or Finland, although there are some from Canada, Sweden, and the International Atomic Energy Commission (IAEA). As might be expected, other countries' waste composition and repositories tend to differ from those of interest to the NRC. However, there is an abundance of available and useful information. In addition, the NRC staff held a meeting to discuss the project at NRC headquarters in August 1991, which was attended by waste solidification vendors, national lab personnel, representatives from utility associations, and other interested groups (5). The NRC staff then visited the Atomic Energy of Canada Limited (AECL) Research's Chalk River Laboratories to benefit from Canadian experience.

Current Technical Position Test Methods and Recommended Results

An important initial question to be answered is "what baseline test should be used to evaluate acceptable bitumen solidification?" Traditionally, waste form compressive strengths have been measured before and after environmental testing. This is appropriate for cement waste forms, which are required to have compressive strengths of 3.45 MPa or greater. Bitumen compressive strengths tend to be much lower, and there is a large degree of variability in test results. The test procedure, ASTM D1074, "Standard Test Method for Compressive Strength of Bituminous Mixtures", is intended for bitumens used in pavement surfaces, which usually contain aggregates and fillers (6). The single operator precision of the test is 407 kPa (6), which is approximately equal to the current guidance criteria of 414 kPa. This high variability has been attributed to the visco-elastic nature of the material, the difficulty of achieving flat and parallel ends on test specimens (use of epoxy end-caps might reduce this problem), and sample preparation techniques.

If it is determined that ASTM D1074 is an appropriate test method, the temperature at which samples are tested must be determined. Bitumen compressive strengths increase with decreasing test temperature. Temperatures of about 13°C (286 K) were used during compressive tests in one bitumen solidification topical report submitted to the NRC (7) and recommended for general use. A second waste vendor supported this recommendation (8). This temperature is thought to approximate that of near-surface disposal sites, and therefore reflects the long-term disposal conditions. ASTM D1074 requires 25 ± 0.5°C (298 ± 0.5 K).

Criteria on the minimum compressive strength must also be selected. Currently 414 kPa, a value closer to the nominal 2 MPa (9), might be more appropriate. However, because bitumens are visco-elastic materials, structural stability may not be the best control on bituminous waste form integrity, and the value of 414 kPa to withstand overburden pressure is likely to be sufficient.

A more appropriate baseline test might be leachability. Bituminous waste forms generally exhibit the high leachability indices one might expect in view of their water-resistance and ability to "self-heal" (meaning that the material's flow characteristics, especially in the softer types, allow it to gradually fill in any discontinuities on the surface). Unfortunately, sample immersion in water can result in large dimensional changes or deterioration, especially after long periods of time (>200 days). Bulk release of radionuclides may result. This is especially likely for hydrophilic waste streams such as salts (sodium sulfate for example) and ion-exchange resins. When a portion of this type of waste is exposed at the surface of the waste form, it can absorb water and swell to up to several times its original size. This then allows water to reach the next layer and continue on, until the sample is greatly swollen or has completely disintegrated. There are ways to alleviate this problem, including lowering waste loading, or coating the outside of the waste form in a thin layer of pure bitumen.

A determination must be made regarding the length of time a sample should be subjected to immersion and/or leach testing. Currently, the immersion and leach tests for bituminous materials specify 90-day durations. It may be appropriate to perform longer leach testing for problem waste streams, such as those containing sodium sulfate, chelating agents, or decontamination agent loaded ion-exchange resins.

Leachability and immersion testing are clearly appropriate for gauging the performance of actual waste forms. Whether the leachability index is used as a baseline test, or not, the minimum value should be determined. In the most recent revision to the TP, the minimum compressive strength value for cementitious waste forms was raised from 414 kPa to 3.45 MPa, because "for solidification agents that are easily capable of meeting the [414 kPa] minimum compressive strength, the waste forms should achieve 'maximum practical compressive strengths,' not just the 'minimum acceptable compressive strength.'" Similarly, bituminous waste forms appear to be able to consistently achieve leachability indices greater than or equal to 8 (9), which is much higher than the current minimum of 6. (Leachability index is a logarithmic function.) The minimum leachability index for bitumen solidified waste forms may be raised in the revised TP, especially if leachability is to be used as the baseline test. Whichever test method is chosen for the baseline, the maximum decline permitted in test results following environmental testing should be determined.

Instructions for measurement of volume and dimensional changes are also needed for sample examination following immersion and leach testing. Samples exposed to thermal cycling or irradiation testing should be examined as well. The high temperatures associated with these tests can cause the samples to slump, swell, or otherwise change shape. In addition, radiation exposure at a high dose rate causes hydrogen gas generation at a rate higher than the gas can diffuse from the sample, which will also cause swelling. It is likely that a maximum dose rate will be recommended for radiation exposure testing. Although it is less expensive to irradiate samples to the full 1 MGy recommended in short time periods, the high dose rate can cause anomalous results as noted above, and furthermore, is not representative of actual conditions.

It is possible that physical confinement of waste form samples during thermal cycling and irradiation testing will be recommended to help prevent slumping or shape change. The compressive testing standard requires that test specimens be right circular cylinders with a length to diameter ratio of about one (6), while the leach test leaves the actual sample shape to the discretion of the testing agency, but does say that "the specimen must have a well-defined shape, mass, and volume" (10). Clearly, extreme changes in shape or size would have a deleterious effect on either test. Thus, confinement during environmental testing would be appropriate, as well as emulating actual conditions, in which bituminous waste forms are generally contained in metal drums, or in the long-term field conditions, are confined by some type of backfill material.

There are indications that thermal cycling and biodegradation testing, currently in the Technical Position, may not be necessary for bituminous waste forms. Thermal cycling is appropriate for cement-solidified waste, as the various temperatures that waste forms are exposed to could cause related cracking and eventual deterioration. In addition, thermal cycling is one of the few tests which parallels actual environmental conditions. However, bitumens which might crack at extremely low temperatures, can "heal" themselves at the higher temperatures, thereby showing little overall change following the test period (other than possible slumping). Biodegradation, on the other hand, seems at first to be a very necessary test. As an organic material, bitumens naturally offer sustenance for a wide variety of microbials. However, a number of studies performed on biodegradation of bituminous waste forms suggest that marked biodegradation is unlikely (9, 11, 12, 13). If biodegradation tests are included in the projected revision to the TP, there are some related issues which must be resolved. Currently, testing in accordance with ASTM G21 and G22 (14, 15) is recommended by the Technical Position, to be followed by the Bartha-Pramer test (16) if the ASTM tests show positive results. The Bartha-Pramer test recommends that microbials and soil specific to the eventual disposal site be used. This is appropriate for the ASTM tests as well, as soil properties and specific microbials can have significant effects on growth. This could present a real problem during qualification of generic waste forms with the establishment of new facilities reflecting a range of site soil conditions. One possibility is to attempt to identify the most stringent soil parameters and microbial types, and specify those for use in the test procedure.

Once again, the most appropriate biodegradation test method for bitumens is an issue, and if this type of test is performed, which types of formulations should be tested or not. For example, irradiated resins are more susceptible to microbial growth than new resins (an important consideration during qualification testing with simulated waste forms), while boric acid formulations are unlikely to be susceptible to fungal attack at all. One waste solidification vendor is experimenting with biocide additives; unfortunately, most biocides are hazardous materials, and as such, could create a mixed waste if used.

Additional Test Methods and Suggested Results

An important factor in bitumen solidification of actual waste streams is ensuring that the bitumen used has the same characteristics as that used to produce the qualification samples. There are any number of test methods which can be used to measure various bitumen properties. These include tests for penetration, solubility in trichloroethylene, ductility, flash point, softening point, etc. It would be impractical to require performance of all of these tests on every batch of bitumen to be used for solidification. Instead, one or more representative tests could be chosen, for example, viscosity measurements at two discrete temperatures, or the bitumen used could be required to meet a standard specification like ASTM D312, "Standard Specification for Asphalt Used in Roofing" (17).

Other additional tests may be necessary for ensuring process control. Appendix A (Cement Stabilization) currently provides guidelines for preparation of process *control program* (PCP) test specimens. For cement, a sample of the proposed waste formulation is made 24 hours before the planned full-scale solidification. This practice is not amenable to a continuous flow system, which most bitumen processes are. There are a number of variables in process control (e.g., waste stream composition, additives, bitumen type, waste loading, feed rate, and temperature control) which should be verified with some sort of in-process sample. The cement PCP samples are subjected to a compressive strength or penetrometer test; bound moisture content, creep, or impact testing may be more appropriate for bituminous waste forms.

CONCLUSIONS

Mother Nature has been using bituminous materials for millions of years to encapsulate everything from fossil bones to natural reactor fission products. These composites have been exposed to thermal gradients, water, biodegradation, radiation, weathering, oxidation, etc. Although natural bitumens and manmade bitumens are not the same, the range of bitumen properties is such that it makes little difference (18). These natural analogues indicate that the rate of degradation in a "near surface repository" is such that time required to significantly destroy the bitumen matrix far exceeds the time necessary for most radionuclides in low-level waste to decay (18). Study of natural analogues indicates that bitumen is suitable for solidification of low-level waste for ultimate disposal in near-surface disposal sites. Although the bitumens that waste solidification vendors tend to use do vary in chemical and physical form from natural solidification media, the guidelines in the new appendix to the Technical Position will be designed to show that bituminous waste forms can meet the requirements of 10 CFR Part 61 if properly controlled, and are a means of demonstrating that manmade waste forms will perform in a manner approaching that of the natural analogues. Before the Technical Position is revised to provide guidance specifically regarding bitumen solidification, there are a number of important issues to be addressed and resolved. These include choice of test methods, selection of appropriate and technically sound guidelines and acceptance criteria, and modifications necessary to make each test method most suitable for examining the long-term stability of bituminous waste forms.

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