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Technical Bulletins provide information to States, compact regions, and other interested parties on issues related to the development of low–level radioactive waste disposal facilities. The Bulletins distribute information that is either of immediate concern to the States and compact regions or that is not suited to more formal reports. These Bulletins are published on an as–needed basis.

The objective of this particular Technical Bulletin is to provide an understanding of solidification of low–level radioactive waste (LLW) to provide the structural stability required by 10 CFR 61. Regulatory requirements, current and past practices, packaging efficiencies, problem wastes, quality control and solidification systems are discussed.

PORTLAND CEMENT: A SOLIDIFICATION AGENT FOR LOW–LEVEL RADIOACTIVE WASTE

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Executive Summary

The Nuclear Regulatory Commission (NRC) regulation 10 CFR Part 61, "Licensing Requirements for Land Disposal of Radioactive Waste" specifies that all low–level radioactive waste must meet certain minimum requirements to be acceptable for near–surface disposal. All low–level radioactive wastes (LLW) are categorized into Classes A, B, or C, depending on contained radionuclide type and concentration. The higher–concentration Classes B and C must meet the structural stability criteria of Section 61.56 of 10 CFR 61 to prevent subsidence of the disposal trench cover and to limit exposure to an inadvertent intruder. Structural stability can be provided by the waste form itself or by a container in which the waste is placed.

This bulletin discusses the solidification of waste streams using Portland–type cement to provide the structural stability required by 10 CFR 61. Portland cement has been used in this role since early in the commercial nuclear program as a simple and inexpensive solidification medium for immobilization of radioactive wastes. Through the use of additives, most waste streams can be satisfactorily immobilized with Portland cement. However, some problem waste streams can not be solidified with Portland cement at this time, and those are discussed in this document.

Both the Department of Energy (DOE) and the commercial nuclear power industry have developed formulations that include additives such as fly ash, buffers such as calcium hydroxide, trisodium phosphate, and sodium hydroxide, and strengthening pozzolanics (siliceous cements) to improve waste form stability. Both mobile and stationary systems are available to combine the waste and cement into acceptable waste forms. In the commercial sector, NRC guidance prescribes a series of waste form tests including leachability

tests to certify specific formulations to 10 CFR 61 criteria. In response, solidification vendors and waste generators, working in conjunction with disposal site operators, have developed methods to inspect waste packages after mixing to ensure that complete solidification has taken place.

Introduction

Low–level radioactive waste disposal in the United States is regulated by the NRC and Agreement States for commercial sites and by DOE for DOE sites. The NRC regulates the disposal of low–level radioactive waste under 10 CFR Part 61, "Licensing Requirements for Land Disposal of Radioactive Waste," and regulates the waste form with the NRC Branch Technical Position on waste form.[1] Agreement States regulate waste using 10 CFR 61 equivalent regulations. DOE regulates all such activities under DOE Order 5820.2A. In September 1988, DOE embraced the principles employed in the commercial sector under 10 CFR 61, specifically the use of three LLW classifications and the regulation that higher concentration classes be required to maintain structural stability. Stabilization under 10 CFR 61 requires structural stability by the waste itself, by use of high–integrity containers, or by solidification of the waste. This bulletin addresses waste solidification.

The NRC developed a Branch Technical Position on waste form to provide guidance to waste generators on how to perform acceptance tests on solidified waste forms. The series of tests recommended by the TP, when successfully applied to a waste form, demonstrates compliance with 10 CFR 61. Of the TP prescribed tests, the immersion, leach, and compression tests are used most frequently to determine waste form acceptability and to compare waste forms. Revision 1 (TP)[2] became effective January 24, 1991. That revision specifically modifies the requirements cement–solidified waste forms must meet. First, the leach testing period was reduced to 5 days after it was shown that the percentage differences between 5–day and 90–day leach indices were relatively small. A second important change was to increase the minimum acceptable compression strength from 60 psi to 500 psi. These changes and guidance on qualification testing and performance confirmation have been included as Appendix A to TP Revision 1.

A solidification medium must exhibit long–term structural stability and provide retention of radionuclides present in order to be considered a suitable immobilization medium for LLW. Historically, all types of low–level radioactive wastes have been solidified with Portland cement. The first waste stabilized in cement mixtures were aqueous based, such as evaporator concentrates, which used the water fraction for hydration of the cement. With the implementation of 10 CFR 61, commercial ion–exchange resins were included in the category as wastes being solidified with cement. Preparations to treat processing wastes containing elements such as sodium salts, process and filter sludges, and incinerator ash were made. Generally, the cement mixtures solidified well and the resulting waste forms performed well in the TP testing.

Although Portland cement is widely used in the nuclear industry as a solidification agent that can be applied to stabilize wastes for disposal in low–level radioactive waste disposal facilities, failures to solidify have been encountered in laboratory testing of the simulated and real waste forms as well as in the field with real wastes. There have been instances where solidifications in drums and liners failed to completely harden and test samples taken during the mixing failed to pass leaching, immersion, and compression tests. It was found that some wastes required chemical additives prior to solidification in order to be chemically and physically compatible with the cement and to improve resistance to leaching of radionuclides. Also, some waste such as decontamination ion–exchange resins that contain chelating agents and organic materials require such complex treatment that acceptable methods are just being developed.

The NRC convened a workshop on Cement Stabilization of Low–Level Radioactive Waste[3] in 1989 to discuss difficulties and develop suitable regulatory guidance to help resolve outstanding issues. Some of the key subjects addressed at the workshop were waste streams that are incompatible with cement, generators' characterization of waste prior to processing, waste stream pretreatment, suggested changes to the 1983 Technical Position on Waste Form, process control plan requirements, and post solidification testing of full–scale cement waste forms. The workshop proceedings include lists of chemical constituents of waste streams that require pretreatment prior to cement solidification. Those lists, provided by solidification system vendors, are too extensive to present here but can be found in Reference 3, pages 213 and 214. The NRC workshop clearly established that cement is a viable stabilization medium, from a technical standpoint, for low–level radioactive waste. Almost all waste streams can be incorporated into a stable cement waste form if the waste concentrations are low enough. The issue is one of commercial, rather than technical, viability.

The workshop participants agreed that generators can do a better job of characterizing their wastes prior to processing through improvements in knowledge of process and improved methodologies. The solidification vendors provided lists of chemicals that can adversely affect the solidification process. Using these lists, potential problem waste streams can be identified and appropriate mitigation applied. The results of this workshop are extensive and would not be appropriately reported in this bulletin. Revision 1 of the TP and research conducted at several DOE laboratories under direction of the NRC [4,5,6,7] are results of the workshop findings. The reader is encouraged to review the proceedings from this workshop and Revision 1 of the TP for more details and listings of appropriate NRC and other reports.

Using Portland Cement as a Solidification Agent

Regulatory Requirements

Portland cement has been used to dependably produce acceptable waste forms in many applications within the nuclear industry. Radionuclides in the waste are either trapped in the cement matrix or react chemically with the cement. A large amount of the waste produced by nuclear power stations is liquid process waste, such as evaporator concentrates, or damp material with residual water such as bead resins from ion–exchange columns and powdered resins from precoat filters. The wet wastes must have the liquid removed, absorbed, or solidified in order to meet the requirement of 10 CFR 61 for less than 0.5 percent free liquids. If the wastes are Class B or C, they also must be solidified or placed in a high–integrity container and be dewatered or have the water absorbed. It becomes apparent why solidification has been attractive to radioactive waste managers. The waste can be placed in a drum or liner, pretreatment and cement added, and a mixing/stirring device can easily be attached to the top of the container. After a brief mix the head is removed, leaving behind the expendable mixing blades. A cover is installed, and the waste is ready for disposal.

This simple solidification procedure is somewhat complicated by 10 CFR 20, "Standards for Protection against Radiation," Paragraph 20.311, which requires waste generators and processors to conduct a quality control program to certify that the waste forms are in compliance with the requirements of 10 CFR 61, including structural stability. That program includes a process control program (PCP) in which PCP samples are cast and then examined to determine batch quality. The TP provides recommendations on acceptable methods to obtain that certification. Information and guidance for cement waste form surveillance, PCP specimen preparation, specimen examination, statistical sampling of the cemented waste, and reporting of mishaps are included in TP, Appendix A, for cement solidification.

Past Practices

In the early 1950s it was reported that drummed waste was solidified with cement for disposal at sea.[8] DOE facilities used Portland cement in the late 1960s to stabilize process sludges before subsurface disposal. Commercial efforts were begun in the early 1970s to immobilize sodium sulfate and boric acid concentrates in cement. It was found that cement additives were required to solidify boric acid. Sodium silicate was determined to be effective in raising the pH and promoting waste form solidification (see Reference 4). Ion–exchange resin solidification studies were begun with several early efforts under NRC funding (see References 4, 5, and 6). Sodium hydroxide was used as an additive in resin studies performed at Brookhaven National Laboratory in an attempt to improve solidification (see References 4 and 5). The Idaho National Engineering Laboratory work for the NRC, using ion–exchange resin expended at the Three Mile Island Unit 2 cleanup, produced waste form specimens that passed all TP tests (see Reference 6). Those waste forms contained no additives, but used a lower waste–to–cement ratio than standard commercial formulations.

Many of the early waste forms developed were not tested for stability or leachability. However, when leachability was measured, it was done by using modified International Atomic Energy Agency long–term test procedures in which leachant was completely replaced, or by equilibrium test procedures where leachant remained unchanged. Not until 1981 was a standardized short–term leach test procedure available with the release of the draft American Nuclear Society Standard 16.1,[9] which was later issued as the American National Standards Institute/American Nuclear Society Standard 16.1.[10]

Past solidification work provided a basis for the techniques in use today to immobilize low–level radioactive waste. It was found that a number of waste streams could be easily treated, while others required special processing. A standard for conducting leach testing, one of the more important performance tests used to ascertain waste form stability, was developed.

Current Industry Practices

By the late 1970s, commercial vendors were marketing cement solidification systems for installation as integral parts of nuclear power plant radioactive waste systems. Mobile services also were made available to plant operators on a lease basis. The ease with which a mobile system could be moved into a waste management system, compared to construction of a permanent solidification system, caused the commercial nuclear power industry to rely heavily on the mobile systems providers. As operating experience was gained with the leased systems, the NRC began tightening disposal requirements with 10 CFR 61 and the TP.

Wastes were initially solidified in 55–gal drums prior to disposal at the commercial disposal sites. Larger containers called cask liners, fabricated from carbon steel with integral lifting eyes, drum cover manways, and fill and drain ports on the top cover, are also employed. They are sized to fit efficiently within shielded transport casks and have volumes of 50 to 322 ft^3. The mixing is usually accomplished in containers after the waste, cement, and additives have been slurried into it, but several in–line systems are available that mix the waste and solidification agent before transferring them to the disposal container. Most nuclear power stations use either drums or cask liners; however, there are cases where both systems are in use in one plant.[11] The use of cask liners has reduced the amount of handling of the waste package because the empty liner is first placed in the shielded transport cask, then filled with waste. This procedure has reduced operating personnel radiation exposure, but has also resulted in less on–site inspection of the solidified package. Waste streams that have normally been treated in the past include evaporation concentrates, ion–exchange resins, and decontamination waste.

Current DOE Practices

DOE began moving in a different direction from the NRC–regulated commercial industry. With locally controlled disposal facilities it was possible to approach the solidification problem differently. First, DOE orders did not require solidification, and NRC requirements did not (and still do not) apply to DOE–owned disposal sites. Second, large quantities of DOE waste are located at several facilities. Third, disposal sites could be located adjacent to waste storage facilities. These factors resulted in decisions to construct solidification plants adjacent to the stored waste and co–locate the disposal facilities there also. Two DOE plants, Savannah River Site, South Carolina, and Hanford Reservation, Washington, are disposing of decontamination salt solutions containing nitrates, phosphates, and sulfates in that manner. The salt solutions at Savannah River and Hanford are being solidified with Portland cement/fly ash mixtures. Both mixes are then conveyed to large vaults where the mixes harden into large monoliths. All DOE sites have solidified problem wastes, such as uranium–contaminated sludge, transuranic (TRU) slurries, and nitrate salts, in drums with Portland and other cements. Those drums are now safely stored as TRU or mixed wastes. The Idaho National Engineering Laboratory (INEL) has been solidifying incinerator ash from the Waste Experimental Reduction Facility (WERF) with cement in drums and disposing of the containers as LLW since 1986.

Further progress was made in identifying and treating problem wastes. New processes have been placed into operation on such wastes as salt solutions. Improved containers are now available that have simplified waste solidification, handling, and shipping. Commercial disposal requirements have continued to become more restrictive as the NRC has provided more regulations. That increased regulation has resulted in more structurally stable waste forms.

Packaging Efficiency

One of the objectives in waste immobilization is to obtain a high packaging efficiency, that is, to pack as much solidified waste into a container as possible, where packaging efficiency is defined as the ratio of waste slurry volume to volume of solid product. However, it has been shown that the ratio of waste to cement must be held low enough to allow for stability and leach resistance.

Nielson and McConnell's study (Reference 6) determined that a packaging efficiency of about 40% produced the most acceptable waste form composed of untreated, decanted ion–exchange resins in Portland cement. Efficiency for a specific waste stream will vary from one vendor to another and is dependent on formulation, additives, and mixing characteristics of each system. Moghissi, Gobdee and Hobart[11] list packaging efficiencies as follows:

25 wt/% sodium sulfate slurry	54 to 77%
50 wt/% sodium sulfate slurry	61 to 83%
12 wt/% boric acid slurry	55 to 83%
bead resin slurry	70 to 89%
powdered resin slurry	60 to 87%.

Problem Wastes

It is interesting to note that both commercial and DOE formulations have incorporated the use of buffers such as calcium hydroxide (slake lime), trisodium phosphate, or sodium hydroxide and additives for strength enhancement such as fly ash and other pozzolanic cements, to improve waste form integrity. Pozzolans also improve retention of certain radionuclides. Through the use of additives, nearly any waste stream can be satisfactorily solidified with Portland cement. However, some wastes have proven to be inherently difficult and are not being solidified with Portland cement at this time. Commercial spent decontamination ion–exchange resins and spent demineralizer resins fall into that category. Resins can be easily dewatered and disposed of in high–integrity containers. It is possible that resins will again be solidified in cement, using the findings of recent NRC/DOE research (see Reference 8). On the other hand, evaporator concentrates and filter sludges are being solidified because they normally cannot be conveniently dewatered, but do solidify well.

As noted, some waste streams can be considered hard to solidify with cement, but the incorporation of additives, buffers, or pretreatment can correct the situation. While many of the formulations are proprietary to the solidification service vendors, examples of the use of additives in several waste forms are noted. Bishop[12] describes the use of both sodium hydroxide and sodium bicarbonate to successfully buffer picolinic acid contained on commercial mixed–bed ion–exchange resins and to prevent the formation of calcium picolinate, which has been found to be deleterious to waste form stability. A DOE site is using a formulation containing fly ash and clay to solidify phosphate and sulfate solutions with Portland cement. Another DOE facility is adding vermiculite and sodium silicate to Portland cement to immobilize a slurry containing 75% iron hydroxide.

Most immobilization projects begin by considering Portland cement and alternate materials. Cement has been selected most often because it is a well–known structural material, inexpensive and available, able to easily handle constituents, relatively simple to mix, employs common equipment, results in a dependable product, and retains most LLW radionuclides. Test results show that radionuclides are satisfactorily retained by a Portland cement matrix (see Reference 4, 5, 6, and 7) and the requirement of the TP that a leachability index of greater than 6 is generally accomplished with reasonable waste–to–cement ratio. It has been determined that careful formulation studies employing simulated and actual wastes must be conducted to ensure that the final product will be acceptable under the requirements of 10 CFR 61 and the TP–recommended tests (see Reference 2).

Cement Solidification Systems

Several solidification systems are available commercially, and many have been installed as permanent parts of nuclear power plant waste management facilities. There are also vendors who provide solidification services using mobile systems that may be attached to the plant waste systems. Many waste generators in the DOE system have also developed simple mixing systems that are suitable for single drum–sized batches. The WERF ash at INEL is immobilized in such a system.[13] Three basic mixing methods are used to combine the waste and the cement in the disposable container: (a) tumbling or rolling the waste container with a disposable mixing device inside, (b) mixing with a disposable device that is shaft–driven by an external motor (usually hydraulic), and (c) mixing with a removable reusable mixer. The latter method is not often applied because removal of the mixer tends to spread contaminated material outside the waste container, complicating the cleanup process. These methods are used in both mobile and permanent installations. The disposable containers most often used commercially are 55–gal DOT–7H drums and 170– and 200–ft^3 carbon steel cask liners. DOE uses 55–gal DOT–7H and 71–gal[2] DOT–7H drums.

Plant installations normally include all necessary waste and solidification material–handling and control systems and procedures. These include in–line systems that mix the solidification agent and waste before loading into the disposable container and in–container systems that mix in the container. Also normally included is a container–handling system to move drums through the solidification and inspection cycle where drums are used. There are vendors that provide this permanent type of cement solidification system.

Mobile solidification systems are available from several vendors. These systems include the container, all solidification material–handling equipment, mixing head, and plant hookup lines. Trained operating technicians work with NRC–approved procedures and formulations based on specified waste streams. All solidification agents and additives are also furnished. Most of this work is done under renewable contract between the vendor and the waste generator.

Quality Control

A number of quality controls are in place to ensure that each commercial waste package meets the stability and leachability requirements of 10 CFR 61. The formulation, procedures, and system are qualified under the 10 CFR 20 Paragraph 20.311 process control program. PCP samples are mixed, cast, and examined using the certified formulation, procedures, waste and solidification agents, and additives. The same formulation used on the PCPs must be used during full–scale solidification that is verified by a check of procedures. Once the waste is solidified in the container it can be examined physically for hardness. Further examination might include measurement of radiation dose on the outside of the container or shipping cask. A well–mixed batch will exhibit a uniform dose over the entire surface of the container. Acoustical methods, such as tapping the side of a liner and listening for variation in sound that would dicate voids or density differences, have proven useful in determining the condition of the waste form. However, these out–of–cask tests may result in excessive radiation exposure to personnel from unshielded containers. Ultrasonic techniques have been suggested as promising methods to examine the consistency of the mix. DOE has applied real–time radiography to drum–sized waste packages. This technique is adaptable to commercial operations to certify maximum liquid content. A plan that has attracted recent interest is the dipping of samples during mixing and prior to setup of the cement (see Reference 3). Those samples would then be archived and tested if a problem was suspected with a package, or the information could be used to develop a data base for that formulation. Once it has been concluded that the waste/cement mixture has formed an acceptable product, the container is shipped to a LLW disposal site.

The LLW disposal site will normally conduct a sampling of waste packages upon receipt depending on contents listed on the waste manifest. The Barnwell Site in South Carolina performs puncture tests on certain liners (e.g., those which list over 7% by weight chelating agents on the shipping manifest). Liners could be equipped with inspection ports, which would facilitate puncture testing or core drilling. Disposal sites can also perform acoustic tap testing and dose measurement of container waste form uniformity. Radiography of drums is a feasible examination method for site use. Packages that fail any site tests may be returned to the generator, where they are reprocessed or repackaged to comply with disposal requirements.

Conclusions

Portland cement has been used to solidify low–level radioactive waste for many years. The commercial nuclear power plants rely on plant integrated systems to produce waste forms acceptable under the requirements of 10 CFR 61. DOE facilities have developed both single–drum low–production systems and large through–put systems co–located with the disposal site. Nearly any waste stream can be, and has been, successfully immobilized with Portland cement. In many cases additives and buffers are included to ensure a stable waste form. In some cases, such as decontamination ion–exchange resins, successful, cost–effective solutions to these difficult solidifications are just being provided by commercial vendors. A number of methods exist to ensure that the waste form exhibits suitable stability and leach resistance both at the generator location and at the disposal site.

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