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PROPOSED WASTE FORM PERFORMANCE CRITERIA AND TESTING METHODS FOR LOW-LEVEL MIXED WASTE*

Eena-Mai Franz, Mark Fuhrmann, and Biays Bowerman, Brookhaven National Laboratory, Upton, New York 11973

ABSTRACT

Proposed waste form performance criteria and testing methods were developed as guidance in judging the suitability of solidified waste as a physico-chemical barrier to releases of radionuclides and RCRA regulated hazardous components. The criteria follow from the assumption that release of contaminants by leaching is the single most important property for judging the effectiveness of a waste form. A two-tier regimen is proposed. The first tier consists of a leach test designed to determine the net forward leach rate of the solidified waste and a leach test required by the Environmental Protection Agency (EPA). The second tier of tests is to determine if a set of stresses (i.e., radiation, freeze-thaw, wet-dry cycling) on the waste form adversely impacts its ability to retain contaminants and remain physically intact. In the absence of site-specific performance assessments (PA), two generic modeling exercises are described which were used to calculate proposed acceptable leach rates.

INTRODUCTION

The U.S. Department of Energy (DOE) is developing processes and systems for the treatment and disposal of radioactive and hazardous mixed wastes accumulated during decades of weapons production and other operations. The treatment and disposal of these wastes has to be performed in a way that minimizes exposure to operational personnel, assures the health and safety of the public, and protects the environment from the risks associated with the release of hazardous chemical and radioactive components from the waste. These wastes must be managed also according to applicable State and Federal regulations, as well as DOE orders.

There is no single set of regulations which governs the treatment and disposal of all of DOE's low-level mixed waste (LLMW), although in 40 CFR Part 268.42 the EPA has identified technology-based treatment standards for a limited number of mixed wastes. Management of the chemically hazardous component of mixed waste must meet EPA regulations in accordance with the requirements of the Solid Waste Disposal Act, as amended by RCRA in 1976, and the Hazardous and Solid Waste Amendments Act of 1984. In cases where the state's regulations are more stringent than EPA's, the state's regulations prevail, according to the Federal Facility Compliance Act of 1992 (FFCA). The management of the radioactive components of the waste is governed by the guidance in DOE Order 5820.2A, Chapter III, Management of Low-Level Waste. If the waste is to be transported, it must meet the Department of Transportation and State transportation requirements.

The first barrier to releases of contaminants after disposal in a multiple barrier system is the solidified waste form. In the past, waste form characteristics were considered to be of secondary importance to the hydrogeochemical characteristics of the disposal site. Experience gained in operating low-level waste (LLW) disposal sites has made it apparent that waste forms play an important role in isolating the radioactive and other toxic components of the waste. Degradation of waste forms in disposal has resulted in releases of the contaminants from the disposal units into the environment. Also, poorly solidified waste forms, due to chemical and mechanical instabilities, have resulted in incompletely solidified waste unsuitable for disposal, thus requiring reprocessing at additional cost.

In order to judge whether or not the waste form will retain the hazardous components, waste form performance criteria are necessary. Such criteria, related specifications and test methods will allow comparison of technologies for treatment systems, demonstrate regulatory compliance, introduce uniformity into waste form comparisons across the DOE complex, improve quality control, help predict long-term waste form performance, and generate data for input to models for site performance assessment. The criteria and testing methods proposed here provide guidance for those developing and testing waste forms.

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WASTE FORM PERFORMANCE CRITERIA AND PERFORMANCE ASSESSMENT MODELS

Waste form performance criteria are meant to provide some level of assurance that the treated waste will perform as expected over a defined period of time. To establish the necessary level of performance the waste form must be viewed as part of the entire waste disposal system; including components such as the engineered structure, the container, the geochemistry of the site and its climate. After estimates have been made quantifying the various components of the disposal facility and its environment, a performance assessment (PA) model can be used to estimate the dose that would be received as a result of disposal under the assumed conditions. By varying the quantities used to describe individual functions or performance, the PA model can be used as a tool that provides, within rather broad ranges, an assessment of how the various components of the disposal system interact to alter the final dose estimate. Waste form performance, in the sense of release rates, is a major factor in the performance of the system. While it is desirable to use PA models developed for site-specific applications to develop criteria for each site, those PAs are several years away. Meanwhile, there is an urgent need within DOE to develop generic criteria so that waste treatment processes and site designs can proceed and be tested against the criteria.

To establish leach rate guidelines for use in the waste form performance criteria (Tables I and II), two sets of PA modeling exercises were used. Each set included two generic sites, humid and arid. One set was conducted for radionuclides by IT Corp.[1] for the DOE Mixed Waste Treatment Project and the other for RCRA metals by Brookhaven National Laboratory.[2] Similar methods and assumptions were used. However, the regulatory criteria for the two are different. For the radiological modeling an effective dose equivalent of 25 mRem/year (DOE Order 5820.2A) is used as the pass/fail limit. For RCRA metals the limit that was chosen is a metal concentration that is 100 times the EPA drinking water standard in ground water at the bottom of the disposal trench.[3]

Results from the radiological assessment indicate that the major contributors to the dose at a generic site are ^{238}U and its daughters, ^{228}Ra, and ^{99}Tc. The generic PA model for a humid site uses a release rate for the waste form of 8.12×10^{-6} per year (8 parts per million per year), which yields an effective dose equivalent greater than the DOE limit. For an arid site, the same waste form release rate results in an annual effective dose equivalent that is below the DOE limit. It is the inventory, the geochemistry and the hydrology of the site that control doses over long times (> 1000 years). Considering the large uncertainties of the estimated doses, and the fact that release rates measured in the laboratory test procedures are conservative since the tests expose the waste form to far more water than a disposal environment, we have chosen a maximum leach rate of 10^{-5} per year as a reasonable generic value for wastes containing long-lived or high toxicity radionuclides. This value is subject to change if site-specific PAs show that site characteristics will accommodate higher (or require lower) leach rates.

These results, as well as those from work at Savannah River Site (SRS)[4], indicate that the radionuclides that have the greatest impact are those with long half-lives and some of the daughters that are generated by their decay. It is evident that large quantities of U/Th wastes will result in significant long-term doses at humid sites, even for a waste form with a very low release rate. This is the result of the extremely long half-lives and the limited credit that can be claimed for the long-term performance of waste forms and engineered structures. Thus, for some radionuclides limits on inventory in the disposal facility are necessary.

The presence of long-lived radionuclides makes it clear that there needs to be an approach by which doses are attenuated, if not reduced in total, for the long-lived radionuclides. This can be achieved by requiring very low releases from the waste form. Radionuclides with shorter half-lives can be sequestered sufficiently long by the disposal facility to allow them to decay to levels at which there is little concern, assuming other features of the disposal facility perform as expected. As a result, very low leach rates only need to be required for long-lived (or high hazard) radionuclides, while short-lived radionuclides can be released at higher rates without increasing risk. This concept places emphasis on waste form quality (regarding release) where it is needed, while accepting a lower quality and, therefore, usually lower cost waste form when appropriate. This is reflected in the three levels of waste form performance in Table I. These three categories were determined by a method which includes calculation of a figure of merit (FOM) based on allowable limits of intake (ALI)[5], the half-life and a generic inventory of DOE LLW. This method is described in reference 2.

DISCLAIMER

A similar argument can be made for non-radioactive hazardous constituents of the waste. Materials regulated under RCRA are found in an estimated 70,000 cubic meters of stored low-level mixed waste and in currently generated waste streams that have an annual generation rate of about 7700 cubic meters per year[6]. From a preliminary review of the gross composition of mixed wastes (personal communication with Wayne Ross, Pacific Northwest Laboratory) approximately 2 weight % of the waste consists of lead, 1.9 weight % is chromium, 1.5 weight % is nickel, 0.02 weight % is mercury (all in one waste stream), 0.02 weight % cadmium (two waste streams) and 0.02 weight % beryllium (two waste streams). Releases of these materials must also be considered with respect to requirements in the DOE order regarding protection of public health and groundwater resources.

Unlike assessment of doses resulting from radionuclides, a PA is not required for RCRA constituents. However, to calculate what the guidelines should be for the limit on the release rate of RCRA constituents from the waste form, a PA method similar to the one described above for radionuclides was employed.[2]

Assessments of releases from an underground disposal unit using the Disposal Unit Source Term (DUST) Code[7] were made for lead (Pb), chromium (Cr), and mercury (Hg). This was one of the codes which was used by IT Corp in the PA modeling discussed above. The DUST Code is a one-dimensional code that models the transport of contaminants from waste containers to the disposal unit boundary. The parameters were chosen to match as closely as possible the conditions used in the IT Corp. PA.

The effects of several parameters were examined. Of greatest interest was the effect of a waste form's fractional release rate on contaminant concentration at the base of the disposal unit and how these concentrations differed at humid and arid disposal sites. Although it is certain that the water infiltration rate affects the fractional release rate, the intent was to examine the effects of varying conditions on contaminant transport by varying one parameter at a time. A second reason for the DUST modeling exercise was to see how concentrations of Pb, Cr, and Hg (which correspond roughly to potential dose exposures for radionuclides) changed as a function of time. A value one hundred times the EPA drinking water standard for the specific RCRA metals was used as a target (at the bottom of the disposal unit) concentration.

Waste form fractional release rates from 10^{-8} to 10^{-2} were used in the calculations. From this exercise release rate targets for waste form performance were developed that are not based on regulations, but on performance needed under a set of disposal conditions. While actual allowable release rates should be determined on a site-specific basis, this process allowed the setting of an annual release rate of 10^{-5}/yr as a numerical guideline. The modeling indicates that at this release rate the groundwater concentrations below the trench slightly exceed the target concentration. However, the modeling is highly conservative, since it did not consider factors such as sorption by the soil and solubility limits of contaminants.

PROPOSED CRITERIA AND TESTS

The modeling results show that the fractional release rate is a prime consideration in assessing long-term performance of and subsequently developing criteria for mixed waste forms. The approach to developing the criteria presented in this paper is based on the following:

- Release of contaminants by leaching is the single most important parameter by which the effectiveness of a waste form is judged.
- The waste form should retain the original desirable qualities of the solidification agent.
- Acceptable release rates of contaminants from waste forms are defined by analysis of releases from disposal facilities through Performance Assessment modeling.
- Solidified LLMW contains <100 nCi/gm of TRU
- Only inorganic RCRA hazardous components are addressed here. It is assumed that organics have been removed or destroyed in a pretreatment step or are below regulatory limits.
- The waste form is a monolith.

Since we believe that the rate of release of contaminants from a waste form is the single most important parameter exhibited by the solidified waste, then leachability is the primary property against which a waste form is judged and, as such, is also used to assess the impact that several types of stress can have on the solidified product. Consequently, the first tier of tests includes a leach test required by EPA and a leach test designed to determine the net forward leach rate of the solidified waste. The first tier tests should be performed first to determine acceptability. Only on passing the given specifications for the leach tests should other tests be performed. The second tier of tests is designed to determine if a set of "assaults" on the solidified waste adversely impact its ability to retain contaminants and to remain physically intact. They are meant to be representative of potentially detrimental factors (either external to the waste form or as a result of internal processes such as irradiation). Some second tier tests are not appropriate for all materials and can be omitted for certain solidified wastes. This is left to the judgment of those doing the testing. However, it is important that all materials should be tested at least once with all of the second tier tests because the history of solidification processes is replete with surprise failures. In the case where standard tests are not available, the following is suggested. For radiation stability, if a waste form is expected to be exposed to greater than 10^6 R over a period of 300 years, then it should be tested by irradiation with a source of high energy gamma rays. The total exposure should be equivalent to the total exposure that the waste form will accumulate over 300 years. For testing the stability in water, the samples should be immersed in distilled water for 90 days. In the case of testing for freeze/thaw stability, the apparatus and cycling schedule of ASTM B-553[8] should be used at temperature ranges of 60°C (±3°C) to -20°C (±3°C). It is recommended that once nondestructive testing (NDT) has been developed for examining waste form integrity, it should be used to supplement or replace compressive strength methods in order to reduce the time and cost involved. A compilation of the proposed criteria and tests is presented in Table II and a more detailed discussion is presented in reference 2.

Table I Waste Form Release Guidelines

Waste Form Quality	Release Rate Fraction/Year (full-scale)	Examples of Radionuclides	Waste Categories	Figure of Merit (FOM)
Level 1	10^{-5} or less	Th-232, Tc-99, I-129, C-14, U-235, U-238, Am-241, Pu, Np-237	Long Half-Life (> 100 yrs) with High Toxicity and/or Large Inventory	Radionuclide with FOM > 1000 at 500 years
Level 2	5×10^{-3}	Cs-137, Sr-90	Intermediate Half-Life (> 10; < 100 yrs) with Low Toxicity, Large Inventory or High Toxicity, Low Inventory, etc.	Radionuclides not in level 1, but with FOM > 1000 at 100 years
Level 3	10^{-2}	Co-60, Cs-134, Fe-55	Short-lived < 10 yrs or Low Toxicity or Low Inventory	All others

Table II Summary of Performance Criteria and Tests for Short Term Behavior of Waste Forms

	TITLE	CRITERION	SPECIFICATION	TEST METHOD
TIER I	Release of Radionuclides	Release rate to provide dose no greater than 25 mRem/Yr in context of the disposal system	Fractional Release Rate $<10^{-5}$/Yr, $5x10^{-3}$, 10^{-2} (See Table I)	Accelerated Leach Test[9,10]
	Release of RCRA Constituents	EPA Regulatory Limits • Concentrations in TCLP Leachate • 100 times drinking water limits	• Limits for each material and for listed wastes • Fractional Release Rate 10^{-5}/Yr	TCLP[9] Accelerated Leach Test[9,10]
TIER II	Compressive Strength	Maintain desirable properties of solidification agent	Compressive strength: • Hydraulic Cement: 500 PSI • Thermoplastic Organic Binders: 750 PSI • Thermosetting Organic Binders: 1000 PSI • Sulfur Cement: 500 PSI • Glass/crystalline: 5000 PSI	ASTM C-39[12] (Brittle) ASTM D-695[13] (Plastic) (Replace by Non-Destructive Testing (NDT) Method)
	Stability in Water	Maintain dimensional stability and physical integrity or strength after exposure to moisture	• Dimensional changes <3%, no significant cracking or spalling • <25% reduction in integrity or strength	No Standard Method*, Follow by Compressive Strength test or NDT
	Radiation Stability	Maintain leach resistance and dimensional stability after irradiation	• Dimensional changes <3%, no significant cracking or spalling • Leach rate must meet above guidelines	No Standard Method*, Follow by Compressive Strength Test
	Freeze/Thaw Stability	Maintain leach resistance and dimensional stability after temperature cycling	• Dimensional changes <3%, no significant cracking or spalling • Leach rate must meet above guidelines	No Standard Method*, Follow by Compressive Strength Test
	Wet/Dry Stability	Maintain dimensional stability after wet/dry cycling	• Dimensional changes <3%, no significant cracking or spalling • <25% reduction in integrity or strength	ASTM B-4843[14]**, Follow by Compressive Strength Test or NDT

* Where a standard test is not available an interim procedure has been suggested.

** Use the apparatus and procedure only, do not use the failure criteria in Section 6.15 of the ASTM Test Method.

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