



UNITED STATES
NUCLEAR REGULATORY COMMISSION
ADVISORY COMMITTEE ON NUCLEAR WASTE
WASHINGTON, DC 20555 - 0001

ACNWR-0247

October 12, 2006

The Honorable Dale E. Klein
Chairman
U.S. Nuclear Regulatory Commission
Washington, D.C. 20555-0001

Dear Chairman Klein:

**SUBJECT: WORKING GROUP MEETING ON EVALUATING THE LONG-TERM
PERFORMANCE OF CEMENT BARRIERS FOR NEAR-SURFACE WASTE
DISPOSAL**

Licensees of the U.S. Nuclear Regulatory Commission (NRC) have used cementitious materials such as grouts¹ and concrete² (referred to as "cement" hereafter) for decades to stabilize wastes physically and prevent subsidence of waste disposal facilities. Some of the beneficial attributes of cement are intrusion deterrence, reduced water infiltration, and favorable chemical conditions. Quantitative credit is often taken for these attributes in performance assessments. For example, the NRC staff has identified the long-term performance of cement as having high risk significance for performance assessment evaluations of the saltstone disposal facility at the Savannah River Site.

Taking credit for the beneficial attributes of cement raises a fundamental question that is important to NRC reviewers, as well as operators of radioactive waste disposal facilities: How long can the various beneficial attributes of cement be assumed to be effective? This question is important to the performance of cement as a waste stabilization medium and as a construction material in waste disposal facilities. To address this question, a 1-day working group meeting (WGM) on evaluating the long-term performance of cement for near surface disposal of radioactive waste was held on July 18, 2006, during the 172nd meeting of the Advisory Committee on Nuclear Waste (Committee). The WGM included presentations by experts during three sessions and associated panel discussions as follows:

¹ Grout is a mixture of cement, water, and other materials that is pourable when fresh. Grouts may be mixed with waste, used to encapsulate waste, and used in caps and barrier walls that isolate wastes from water.

² Concrete is a mixture of cement, water, and aggregate, such as stones, typically used as a structural material.

Session 1 – Addressed the uses of cement in near-surface disposal of radioactive wastes and the emergence of cement as an assumed barrier to radionuclide migration in some performance assessments. This session included presentations by Dr. Christine Langton from the Savannah River National Laboratory, and Professor David Kosson from Vanderbilt University.

Session 2 – Addressed failure modes of cement and the causes of failure. This session included presentations by Dr. Rachel Detwiler from Braun Intertec Corporation, and Professor Barry Scheetz from Pennsylvania State University.

Session 3 – Addressed the current state of technology in predicting cement performance over time. This session included presentations by Professor Fred Glasser from Aberdeen University in the United Kingdom, Dr. Leslie Dole from Oak Ridge National Laboratory, and Dr. Edward Garboczi from the National Institute of Standards and Technology (NIST).

NRC staff from the Office of Nuclear Regulatory Research and the Office of Nuclear Material Safety and Safeguards collaborated with Committee staff in preparing the agenda for the WGM and also participated in technical discussions during the meeting.

Summary and Observations from the Working Group Meeting

The following sections summarize the highlights of the presentations and the Committee's observations based on the information received at the WGM.

Where Is Cement Used and How Is It Important to Performance?

- Important beneficial attributes of cement in near-surface waste disposal applications are its:
 - Strength: Cement can stabilize wastes in a disposal site against subsidence or collapse and impede intrusion by humans, animals, and vegetation.
 - Low Permeability: Cement can impede the infiltration of water to the waste, and subsequent contact with and mobilization of radionuclides.
 - Chemistry: Cement can alter the chemistry of infiltrating water to reduce radionuclide solubility and mobility by establishing alkaline and reducing conditions in infiltrating water.
- Cement properties can be tailored to meet a wide range of situation-specific performance criteria under a variety of environmental conditions by adjusting the type and proportion of materials used to prepare cement. However, the performance criteria

and environmental conditions often lead to competing requirements (e.g., low strength may reduce cracking, but also provide less deterrence to intruders). Formulations ultimately selected for a particular application often represent a compromise among the requirements.

- While the use of cement by NRC licensees to stabilize radioactive wastes for near-surface disposal has decreased over the last 15 years, cement is commonly used to stabilize radioactive wastes in other countries, DOE sites, and hazardous waste disposal facilities. Cement is also used in the U.S. and other countries for subsurface barriers and disposal vaults.
- The NRC staff is currently evaluating draft performance assessments being used by DOE to support its proposed determinations that certain wastes resulting from nuclear fuel reprocessing are not high-level waste. Credit is being taken for the beneficial attributes of cement in these performance assessments. The DOE is also expected to take credit for the beneficial attributes of cement in decommissioning.

How Does Cement Degrade?

- Cement is thermodynamically unstable in essentially all environments relevant to waste disposal. Environmental constituents that react with cement are water and air containing oxygen, carbon dioxide, and other trace chemicals. These constituents, which are an inevitable part of the environment at near-surface waste disposal sites, degrade the beneficial attributes of the cement by:
 - Reacting with the matrix that binds the cement constituents together which results in cracking. The density of the degradation products is greater than that of the original cement. The resulting shrinkage leads to stress-induced cracking and somewhat reduced bulk strength. Reduced strength is not as critical in waste applications as it is in structures, because soil typically surrounds and supports cement containing disposed waste. There is concern that shrinking and cracking over time could degrade beneficial properties of concrete and have a negative impact on performance.
 - Reacting with cement constituents that establish reducing conditions (e.g., blast furnace slag) until the capacity to maintain these conditions is depleted. As infiltrating water and air containing oxygen move through the cement by matrix diffusion and flow through cracks, reducing conditions would be neutralized and oxidizing conditions would prevail. Many radionuclides are more soluble under oxidizing conditions.
 - Reacting with alkaline cement constituents like calcium hydroxide until the capacity to maintain alkaline conditions is depleted. Carbon dioxide acidifies the cement as infiltrating water and air move through the cement by matrix diffusion and flow through cracks. Many radionuclides, the actinides in particular, are more soluble under acidic conditions.

- The rate at which cement degrades can be reduced by: (a) minimizing its contact with infiltrating water and air; and (b) creating cement that minimizes cracking. The greater the surface area exposed to infiltrating water and moist air by matrix diffusion and cracks, the greater the rate at which environmental constituents react with the cement and degrade its beneficial attributes. Even uncracked cement has significant matrix permeability to water and air, as compared to materials such as glass.
- Cracking during curing can be reduced, but not eliminated, by using additives and ensuring that the cement temperature increase during curing is not excessive. Reaction of environmental constituents with cement can result in additional cracking. Reactions that lead to matrix shrinkage and additional stress-induced cracking result in increased surface area that is available for degradation reactions. However, in some circumstances, it is possible for the products of cement degradation to fill cracks and form a protective layer on a cement surface which reduces the area available for degradation reactions.
- Participants reported there is no comprehensive list of chemicals that lead to induced degradation of cement and the relevant properties of the chemicals. They recommended that a thorough literature search organized into a readily accessible database would allow easy access to the required information for most chemicals of interest.
- Exposure to ionizing radiation can degrade cement. The levels of gamma and neutron radiation in foreseeable waste disposal applications appear to be well below those that would have a significant impact on cement degradation. However, the effects of prolonged exposure of cement to alpha radiation are not well known.
- The experts noted that even the best of cement formulations are often compromised by inadequate quality control during preparation and emplacement which may lead to premature degradation.

How Well Can Cement Degradation be Predicted?

- Predicting the performance of cement mixed, or in contact, with waste containing a complex mixture of radionuclides and chemicals (dirty cement) relies on predicting the performance of standard construction cement (clean cement).
- The important beneficial attributes of clean cement are maintaining adequate strength and, in some cases (e.g., dams) maintaining sufficiently low permeability when exposed to typical environmental constituents (e.g., moist air and water containing carbon dioxide and common chemical species such as chloride and sulfate).
 - Experience and computer models can be used together to yield defensible predictions of cement cracking, strength, and permeability for clean cements exposed to typical environmental constituents for at least 50 to 100 years, and perhaps a few hundred years.

- There is presently no evidence to verify these predictions beyond a few hundred years. Obtaining this evidence may be possible through analysis of cement analogs which are discussed below.
- Ancient anthropogenic and natural analogs of modern cement exist in the form of 2000- and 6000-year old cement used in places such as the Roman empire and Nabatea, respectively, and certain metamorphic rocks. None is a direct analog for modern clean cement because these cements were composed of different ingredients and made under different or unknown conditions. To use these analogs as a basis for predicting the long-term performance of modern cement requires understanding molecular-level phenomena that occurred as they aged. Achieving this level of understanding has been beyond available technology. However, a combination of advanced thermodynamic and kinetic modeling such as that being pursued at NIST, and analytical tools that allow cement degradation processes to be observed at the molecular level bring the capability to obtain information from analogs that would be directly related to the degradation of modern clean cements within reach.
- Potentially important beneficial attributes of dirty cement are its strength, low permeability, and ability to maintain reducing and alkaline conditions.
 - Historically, the primary emphasis in making dirty cement has been on meeting more modest strength requirements than those imposed on clean cement, and even here there have been notable failures (e.g., grouts that fail to solidify or contain free standing water). More recently there has been some interest in taking credit for the other long-term beneficial attributes of cement. However, quantitative data on the degradation rate of dirty cement is available for times that are a small fraction of the period of performance being analyzed in performance assessments.
 - The performance of dirty cement is much more difficult to predict than that of clean cement. Computational models typically do not account for the interaction of radionuclides and chemicals in the waste with each other and the cement constituents. These models are well beyond state of the art, and would require enhancement of existing models to include thermodynamic and kinetic data for the radionuclides and chemicals in dirty cement, as well as the many unique additives (e.g., fly ash, blast furnace slag) used to tailor the attributes of dirty cement.
- The WGM experts believe that accelerated testing of cement using extreme conditions such as increased temperature or highly concentrated degradation reagents is not a valid predictor of long-term cement performance. Tests conducted under extreme conditions alter the chemical reactions that occur and do not represent what would actually happen.

- The WGM experts were universally negative on the validity of some standardized laboratory tests (e.g., ANSI 16.1) for predicting actual long-term performance of cement. Standardized tests typically last for days and use conditions that are very different from what a dirty cement might experience. Short-term test results are not necessarily representative of behavior in tests lasting a few years. It is difficult to obtain a representative test sample from a large cement monolith created over many days. Finally, a given set of test conditions will be conservative for some species and attributes, and nonconservative for others.
- There is an industry trend to formulate Portland cement to set more quickly. Cement that sets quickly allows for speedier construction resulting in lower cost. Experts believe this trend is likely to have an adverse effect on the durability of cement.
- The composition and amount of infiltrating water to which cement may be exposed are also difficult to predict. This difficulty leads to substantial additional uncertainty in predicting the performance of cement.
- Technology to monitor the performance of large cement monoliths non-invasively is generally not available at this time. Irretrievable monitoring devices could be emplaced when the monolith is being poured, but these devices are likely to fail in a relatively short time and the ability to interpret signals from what will eventually become obsolete technology is questionable. Large cement monoliths can be monitored using existing invasive technologies involving insertion of retrievable devices into penetrations in the monolith. This approach allows monitoring devices to be removed for repair or replacement. Care must be taken to ensure that penetrations used in invasive monitoring do not become a pathway for infiltrating water and air.

Recommendations

The Committee recommends that the NRC consider supporting studies in a number of areas:

- Extending computational capabilities to cement containing mixtures of radionuclides and non-radioactive constituents
- Using a combination of advanced analytical techniques and computational capabilities to analyze aging of analogs, so that the results can be used to evaluate assumptions about the long-term performance of modern cement
- Developing protocols and techniques to test cement samples, and to monitor cement during emplacement and curing, to measure indicators of future cement performance
- Preparing a comprehensive readily accessible database of chemicals that cause degradation of cement, including conditions and processes under which degradation may occur

The Committee believes that these studies will improve the NRC staff's ability to evaluate the performance of cement in waste isolation for waste stabilization and as a structural material. Further, the Committee believes that these insights will lead to better risk-informed performance assessments of radioactive waste disposal using cement.

The Committee looks forward to reviewing the results of the NRC staff's activities related to predicting the long-term performance of cement as they become available.

Sincerely,

/RA/

Michael T. Ryan
Chairman

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