RESEARCH INFORMATION LETTER, "ASSESSING THE PERFORMANCE OF CEMENT BASED MATERIALS AS ENGINEERED BARRIERS FOR ISOLATING RADIOACTIVE WASTE"

Background

The service life and degradation behavior of cementitious material structures employed as the principal engineered barrier to isolate radioactive waste materials are important factors in assuring credible performance assessments (PA's) of a facility. Cementitious barriers may be used as, (i) concrete structures and vaults in decommissioning actions such as entombment of nuclear and other structures, (ii) low-level waste (LLW) and assured isolation facilities (AIF), (iii) cement grout infills in entombment applications, (iv) cement-grout-encapsulated waste for waste incidental to reprocessing (WIR), and (v) cement-based grout curtains and/or impermeable underground walls to prevent ground water from contacting waste or transporting it away from the site.

Prediction of the service life and degradation of cementitious barriers may be possible by computationally modeling the degradation mechanisms of the barrier. Many of these barriers need to function for hundreds and maybe thousands of years. Physical modeling of the barriers, using the computer degradation code 4SIGHT developed for concrete structures and vaults in an NRC sponsored program at the National Institute of Standards and Technology (NIST), predicts and assesses the barriers ability to isolate waste over a few hundred years. Chemical modeling, which primarily involves the binding and absorption of radioactive species by the highly alkaline cement hydration products, may prolong service life for many hundreds of years, but has not been incorporated in the computational models at this time.

Degradation (physical) modeling, as discussed in this research information letter (RIL), addresses the potential for the releases of radioactive materials to the environment from a cementitious barrier primarily by ground water flow and transport through the degraded barrier. It does not address degradation of the barrier due to the loss of structural integrity by anticipated dead and live loads imposed on the structure. The design and construction quality assurance and quality control (QA/QC) for the barrier and the barriers response to structural loading should be adequately assessed by structural engineers, to ensure the barrier will remain stable under the anticipated loads and safety margins are adequate. This RIL discusses the degradation of the cementitious materials of barriers (by processes such as chloride and sulfate ion attack, alkali-silica reactions, acid attack, and leaching).

Degradation modeling incorporates all the relevant physical processes that impact the barrier and cause it to release radioactive contaminants it was intended to isolate. The most important physical parameters for the modeling are porosity, the formation factor, the water- cement ratio, and the permeability of the barrier. The chemical assessment requires knowledge of the spatial distribution of the ionic species inside and outside the barrier. The most important factor affecting the transport properties of the cementitious barrier is the existence of cracks that extend through the barrier. The following pages discuss the results from the research program to date, the significant regulatory findings and the remaining limitations and sources of uncertainty. All references identified in the RIL can be accessed at http://ciks.cbt.nist.gov/jackal/homepage.html and http://ciks.cbt.nist.gov/monograph. Technical reports noted as drafts have been reviewed by the research project manager but do not have a NIST or NUREG/CR number and are not yet available on the Web site.

Research Summary

(A) Concrete Structures/Vaults

(i) Degradation Mechanisms

"Service Life of Concrete" (NUREG/CR-5466, NISTIR 89-4086, 1989) discusses the major environmental degradation processes that affect concrete: sulfate attack, corrosion of reinforcing steel/carbonation, alkali-aggregate reactions and leaching by acidic subsurface water. Other degradation mechanisms are freeze-thaw deterioration, and microbiological attack. Sulfate attack on concrete can be severe, resulting in cracking of the concrete and in some cases, its disintegration. The highly alkaline environment of cement concrete normally passivates the steel. However corrosion of steel embedded in concrete is a serious problem in the presence of chloride ions. Alkali-aggregate reactions are usually internally contained in concrete and are not dependent on the diffusion of an aggressive solution into the cement-based material. Serious cracking of the concrete occurs when the reaction results in the formation of expansive products. When siliceous (i.e., alkali-silica reactions) and dolomitic (i.e., alkali-carbonate reactions) limestone aggregates are used, expansive alkali-aggregate reactions are known to occur. Buried concrete, in contact with percolating subsurface water, can undergo deterioration by the dissolution of the common constituents of cement paste, the alkali salts, and sodium hydroxide. Leaching can reduce the pH of the concrete, as well as make it more porous for subsurface water. Freeze-thaw deterioration of concrete can be reduced substantially by preventing ponding of water adjacent to the structure and incorporating air voids in the concrete mix. Some bacteria can attack cement-based materials by transforming ammonia into nitrites or nitrates or by producing lactic acid or butyric acid. In the normal design life of conventional structures, bacterial action does not seem to be a major cause of deterioration. However, for service life periods of hundreds of years, the impacts of bacterial activity have not been assessed and may be difficult to predict.

(ii) Condition Assessment of Concrete Structures and Vaults

The length of time that any concrete structure must remain effective in isolating its contents depends on the quantity of specific radionuclides present in the structure and the time necessary for potential radiation exposures to be reduced through radioactive decay. The concrete engineered barrier needs to perform adequately for the duration of the isolation period to mitigate the leaching and migration of radionuclides to the environment and ensure that the relevant regulatory criteria are met. "Condition Assessment of Concrete Nuclear Structures Considered for Entombment" (NISTIR 7026, 2003) discusses the assessment of the concrete entombment structures and the probabilistic calculation of the service life of the structures. The concrete material modeling assessment relied primarily on the effects of degradation mechanisms (e.g., sulfate and chloride ion attack, leaching) on the concrete, the permeability of the intact concrete, and the characterization of cracks in the concrete and their contribution to fluid flow.

Although NISTIR 7026 refers to nuclear structures undergoing decommissioning by the entombment option, any concrete structure for isolating radioactive waste should be evaluated and characterized in a similar manner prior to loading the structure with waste. In the modeling, both the material properties of the intact concrete and a careful characterization of the concrete crack properties (i.e., crack width, crack spacing and crack penetration depth) are essential for evaluating the flow properties of fluids through the concrete and estimating service life. Uncertainty in material parameters is addressed with guidelines for sampling and parameter distribution characterization. Crack width and penetration depth have the greatest impact on concrete bulk permeability.

(iii) Modeling of Degradation Mechanisms: Development of 4SIGHT

The program 4SIGHT (NISTIR 5612, 1995) was developed as a tool for estimating the service life of underground concrete structures for isolating waste. To have the most versatility, degradation modeling incorporates all the physical and chemical processes that may occur. The physical parameters for modeling include the porosity, the formation factor, the water-cement ratio and the permeability of the concrete. The chemical assessment requires knowing the quantity, the spatial distribution, and concentration of the ionic species (e.g., sulfate, chloride ions) inside the concrete and immediately exterior to it. The factor that most affects the transport properties of the concrete is the existence of cracks within the structure. Enhancements to the code were made based on validation tests of the code's transport model (NISTIR 6747, 2001). In addition, a cracking model and a Monte Carlo simulation based on parameter uncertainty were incorporated (NISTIR 6519, 2000) to address the inherent uncertainty in concrete property parameter estimation. The 4SIGHT code incorporates multiple degradation mechanisms by using a single transport equation for ions. Previously, models for predicting concrete performance were developed for a specific degradation process, and none could realistically incorporate the effects of simultaneous degradation processes. These effects include the coupled effect that one degradation mechanism (e.g., leaching) could have on another (e.g., chloride diffusion and subsequent corrosion of the steel reinforcement). The 4SIGHT program models these coupled effects by modeling the transport and reaction of ionic species within the pore space. Based on the stoichiometry of possible reactions between the ionic species and available soluble minerals, the pore space would change through either dissolution or precipitation of the solid phases. Using computer models of cement paste hydration, empirical relations are established between changes in porosity and corresponding changes in the transport coefficients that characterize the solid microstructure. By coupling between reaction and transport, 4SIGHT is able to simulate the simultaneous effects of multiple degradation mechanisms.

(iv) Cracking

Cracking in concrete is due to a number of mechanisms. During placement, if the evaporation rate is great enough, the concrete surface can develop tensile stresses sufficient to crack the concrete. These plastic-shrinkage cracks typically extend through the entire concrete member because they can occur when the concrete is still plastic. Cracking can also be caused by settlement of the concrete member, by flexural stresses, and by thermal effects. The continued removal of water by the hydration process generates a chemical-shrinkage stress that can initiate autogenous shrinkage cracks. Subsequent drying due to ambient conditions also generates shrinkage stress, which generates drying-shrinkage cracks. The incorporation of crack modeling by 4SIGHT is limited to the effects of flexural and shrinkage cracking and their effect on transport (NISTIR 6519, 2000).

Absent environmental conditions which may cause cementitious material degradation, cracking can be the most severe concrete degradation mechanism. Transport through cracks in concrete is only of consequence if the cracks extend throughout the concrete member. Relatively large amounts of water can be transported through a crack, depending on the total potential water head across the fully penetrating crack and on the crack aperture and density. For example, the estimated leakage from a spent fuel pool was calculated using the crack model in the 4SIGHT code. A 1-meter-thick concrete wall with a hypothetical 1-meter-long through crack of 100 micrometers aperture situated 4 meters below the pool surface can conduct approximately 250 gallons of water per day. An evaluation of whether continued hydration of unhydrated cement particles in the concrete structure could seal micrometer sized cracks had mixed results. In the NIST report to NRC on "Effect of Continued Hydration on the Transport Properties of Cracks Through Portland Cement Pastes in a Saturated Environment: A Micro-structural Model Study" (Snyder and Bullard, NISTIR 7265, 2005), NIST's CEMHY3D model was used to investigate whether continued hydration of unhydrated cement causes hydration products to seal small cracks. Continued hydration does not seal cracks in concrete except maybe very small cracks in the 1 or 2-micrometer. Flowing water could deposit fine particles like silt and clay in small cracks and cause some reduction in permeability, but this aspect was not investigated in this study.

(*v) Monitoring Strategy To Confirm Concrete Barrier Performance*

To verify and confirm the service life of a concrete barrier, results from the modeling assessment discussed above must be combined with the monitoring strategy for the barrier. In the draft NIST report, "Long-term monitoring of Concrete-based Structures using non-linear Kalman Filters" (NISTIR xxxx, 2005), the Kalman filter is used in conjunction with the 4SIGHT concrete barrier service life model. The Kalman filter is a set of mathematical equations that provides an efficient computational means to estimate the state of a process. The filter is very powerful because it supports estimations of past, present and future states of the system, and it can do so even when the precise nature of the modeled system is unknown. Specifically, the extended non-linear Kalman filter is applied to both laboratory and hypothetical scenarios to demonstrate its use and applicability. Because 4SIGHT uses only two transport coefficients, porosity and formation factor, the number of state variables in the analysis can be reduced significantly. The Kalman filter is used to refine the estimated transport coefficient obtained from a laboratory fluid flow experiment. The filter is then applied to a hypothetical monitoring scenario to demonstrate a rationale for determining monitoring intervals.

(vi) Potential Limitations and Sources of Regulatory Uncertainty

(a) Radioactive species, redox potential, and the effects of concrete admixtures in the 4SIGHT code

Radioactive species are not included in the current version of the 4SIGHT code. The code should be updated to include radioactive ions and absorptive interactions with cement hydration products. The redox potential of the pore fluid is important in assessing the long-term chemical barrier performance of concrete since it determines the distribution of oxides for a particular element. It is important to know this distribution because some oxides are more mobile than others.

The current version of the code also does not consider the beneficial effects of mineral admixtures in concrete such as silica fume, blast furnace slag, and fly ash. The design and construction of future concrete waste structures (and new nuclear plant structures) will likely incorporate admixtures in their design and construction since the use of admixtures has been demonstrated to significantly increase the service life of concrete.

(b) Nondestructive evaluation (NDE)

As discussed above, one of the first steps in evaluating a concrete structure being considered for isolating waste is to assess the existing condition of the structure. The factor that most affects the permeability of concrete is the existence of cracks within the structure. A 100-micrometer crack can be difficult to detect with the naked eye, and its extent through the structure is almost impossible to estimate from observations of the exterior surface. NDE techniques to identify the presence of such cracks and other flaws in the structure are not currently available. NDE should be developed to detect the cracks and characterize their spacing, width, and depth in order to provide the necessary input to concrete degradation and flow codes. Further, the NDE technique should be robust enough to be applicable to inaccessible parts of the structure (e.g., parts below ground or accessible from only one side of the structure).

(c) Innovative sensor technologies

Since the waste-isolating concrete structure may be expected to be in service for periods exceeding 100 years to satisfy regulatory criteria, it is important to develop monitoring techniques that will remain reliable for such periods. There are no currently available instrumentation or sensors to monitor the response of the structure for such periods of time, particularly for parameters such as formation and growth of surface opening cracks, distribution of deleterious ionic species such as chlorides, and depth of carbonation and corrosion activity of embedded steel in the structure. Timely monitoring data from sensors could be vital in mitigating failures and performing necessary repairs.

(*d) Maintenance and repair strategies*

Currently there are no known techniques to repair concrete structures with micrometer sized through cracks. As noted above, these very small cracks can conduct appreciable flow under the right conditions. This excessive flow concentrated at cracks means that in acidic environments leaching will be concentrated at the crack and may increase crack aperture and the rate of flow through the crack. The facility may be sound structurally and yet allow flow and transport and release of contaminants through it.

(B) Cementitious Grout for Containment of Radioactive Waste (Grout infills/backfills for entombment actions, grouts for waste tanks (WIR), cement based grout curtains).

(i) Characterization of Cement Grouts

The draft NIST report to RES "Characterization of Infills/Backfills for use at Entombed Facilities" (NISTIR xxxx, NUREG/CR xxxx, 2005) discusses the use of cementitious grout to isolate radioactive materials under the entombment decommissioning option for nuclear structures. Information in several sections of the report (e.g., the rheology or workability of cement grouts, cement degradation processes, cement performance enhancement, leaching of radionuclides from cementitious grout) is directly applicable to other disposal options where cement grouts are planned to be used as a medium to isolate radioactive waste from the environment, for example, for disposal of wastes incidental to reprocessing (WIR) or in grout curtains (underground walls) built to impede ground water from contacting waste.

The report discusses the state of knowledge in the use and performance of cement grouts to isolate radioactive waste. Past nuclear facility decommissioning actions and closures using cement mixtures are described. Comparisons are made between engineered barrier objectives (10 CFR

Part 61) and entombment decommissioning. Suggested conditions for the effective use of cement-based infills are listed. The conditions include the need to (i) fill voids to physically stabilize the structure, (ii) stabilize contaminants in the waste and debris included in the entombment, and (iii) plug seal penetrations. Special needs are included for shrinkage-compensating cement grouts for plugging penetrations and piping in the structure. However, there are no existing accepted or standardized tests to measure the fundamental rheological and other properties of cement grouts and the grouts ability to be pumped and its setting time. This presents a distinct disadvantage in (i) grout design, (ii) construction quality control, and (iii) confirmation of consistency with proposed performance. Degradation mechanisms that can affect cement-grout performance are discussed in the context of their ability to preclude leaching of radionuclides. Improvements in grout properties to resist degradation mechanisms are noted. For instance, inclusion of pozzolanic materials like fly ash, blast furnace slag, and fumed silica may have significant beneficial impacts on the physical and chemical properties of the final grouted system. Results of leaching tests conducted on cementitious grout mixtures for a variety of radionuclides in an entombment (e.g., cobalt-60, cesium-137) are presented and a tabulation of diffusion coefficients for selected radionuclides in cement waste forms is included. Finally, the report notes that most of the quantitative research done on cementitious waste containment has been limited to degradation reactions that occur on human time scales. Very long-timescale research has been limited to approximations of cement hydration products and material stability based on short-term test results of solubilities and leach rates. A thermodynamic toolkit could be useful to quantify the very long-term stability of cementitious systems. Surface complexation models could be an appropriate way to improve modeling of long-term performance.

(ii) Potential Limitations and Sources of Regulatory Uncertainty

Currently there are no validated computational modeling techniques to assess the short- and long-term performance of grouted wastes. Potential failure modes in grouted wastes such as cracking, disaggregation of materials, shrinkage, and the effects of heat evolution and their impacts have yet to be identified and assessed. There are no standardized tests to measure the fundamental rheology, flow, pumpability, and setting time of cement grouts. There are no QA/ QC procedures and actions to ensure that grouted materials in place are compatible with grout design parameters from small scale laboratory testing.

Estimating the rate of grouted waste oxidation and the effects of oxidation on radionuclide leaching and release is key to assessing the long- term performance of the grout. Current analytical techniques do not address this problem. A thermodynamic toolkit could be useful to quantify the very long-term stability of cementitious systems. The use of surface complexation models could be useful to improve modeling of long-term performance. This could be supplemented with a suitable monitoring strategy, including the use of NDE and sensors to verify modeling predictions.

Regulatory Implications

The NRC research is complete, the 4SIGHT concrete degradation code has been developed, the code’s transport model (NISTIR 6747, 2001) has been validated, a cracking model has been incorporated and a Monte Carlo simulation based on parameter uncertainty (NISTIR 6519, 2000) has been accomplished. It is the only available code capable of predicting the performance of concrete structures employed to physically isolate waste for hundreds of years. Although the

4SIGHT code rigorously solves mathematical representations of fundamental concrete material behavior, there is no assurance that the model is accurate for every possible scenario because test data, either direct or accelerated, is not available for the relevant time periods. At this time, the only way to confirm the predictions of concrete performance using 4SIGHT is through continuous monitoring and periodic testing of the concrete. The computer program in these circumstances can also serve as a useful tool in establishing a testing protocol. The spatial and temporal distribution of the monitoring and testing protocol can be established using the computer program as a guide.

The potential limitations and sources of regulatory uncertainty discussed in the RIL, need to be noted because they apply to current and future needs and for a range of applications from WIR and LLW applications to new reactor licensing. Reliably predicting the performance of complex cementitious grouts in various chemical environments is currently well beyond the state of the art. For both concrete barriers and grouts, performance predictions should be confirmed through systematic long-term monitoring.

References

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