June 29, 2010

MEMORANDUM TO: Gregory F. Suber, Chief
Low-Level Waste Branch
Environmental Protection
and Performance Assessment Directorate
Division of Waste Management
and Environmental Protection
Office of Federal and State Materials
and Environmental Management Programs

FROM: Nishka Devaser, Project Manager **/RA/**
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SUBJECT: JUNE 1, 2010 TELECONFERENCE BETWEEN U.S. NUCLEAR REGULATORY COMMISSION STAFF AND U.S. DEPARTMENT OF ENERGY AND ITS CONTRACTORS CONCERNING SALTSTONE MONITORING ACTIVITIES

U.S. Nuclear Regulatory Commission (NRC) staff held a teleconference with Savannah River Site (SRS) staff to discuss the type of reference electrode used for saltstone Eh measurements and whether the reported values were corrected for the particular reference electrode used (i.e., referenced to a standard hydrogen electrode) or were read directly from the instrument. The oxidation state of saltstone is important to the release of certain key radionuclides and the NRC staff wants to ensure that the redox potential of the saltstone system is accurately reported.

Enclosure:
Meeting Summary

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Meeting Summary: U.S. Nuclear Regulatory Commission Staff Teleconference with U.S. Department of Energy and Contractors Concerning Saltstone Monitoring Activities

On June 1, 2010, the U.S. Nuclear Regulatory Commission (NRC) staff held a teleconference with Savannah River Site (SRS) staff to discuss the type of reference electrode used for measuring the Eh of saltstone, such as the Eh values reported in Kaplan, et al. (2008) (SRNS-STI-2008-00045), and whether the reported values were corrected for the particular reference electrode used (i.e., referenced to a standard hydrogen electrode) or were read directly from the instrument. The Eh value is defined as the redox potential referenced to a standard hydrogen electrode. Reference electrodes other than the standard hydrogen electrode (e.g., Ag/AgCl, saturated KCl) are commonly used in making laboratory measurements of the redox potential. However, if a reference electrode other than the standard hydrogen electrode is used, it is necessary to adjust the values reported by the instrument to account for the half-cell potential of the particular reference electrode used. The NRC staff was interested in this question because the oxidation state of saltstone is important to the release of some of the key radionuclides, such as Tc. If the saltstone is less reducing than was reported, it is more likely that the Tc would be in the highly soluble TcO4- form, and the release of Tc may be higher than predicted.

SRS site staff stated that the electrode used in their experiments was a Ag/AgCl electrode and that the reported values were read directly from the instrument and were not corrected for the particular electrode used. It is the conclusion of the NRC staff that these redox potentials were incorrectly reported as Eh values. Based on the half cell potential of the Ag/AgCl electrode, the true Eh in this system would be 200 mV higher, or less reducing, than was reported.

During this phone call, SRS site staff also stated that during the experiments they observed that the redox condition of the system reached equilibrium slowly and that the redox potentials measured became more reducing with time. Because of this observation, they believe that the experiments may not have been run long enough to capture the steady state reducing conditions, and that the actual system may be more reducing than the experimental results indicate. NRC staff noted that if the Eh of the system reaches equilibrium slowly, the reducing conditions may not be reached in cracks or fast flow paths in the full-scale system.

Staff from Center for Nuclear Waste Regulatory Analyses (CNWRA), NRC's contractor, asked about the basis for the selection of the mineral phases in the geochemical modeling performed in support of the performance assessment, particularly the basis for selecting the highly reduced pyrrhotite phase. SRS site staff stated that the Eh values reported in Kaplan, et al. (2008) were not used as the basis for the phases selected in the geochemical modeling. NRC staff previously asked an additional question about the basis for selection of the initial mineralogy in the geochemical modeling in the Request for Additional Information dated March 31, 2010 (Request for Additional Information number SP-8).

CNWRA staff also asked if there was evidence that Tc is in the reduced state in saltstone. SRS staff stated that research described in Lukens et al. (2005) in Environmental Science and Technology provided this evidence. However, NRC staff noted that in the research described in the Lukens paper the reducing agent Na_2S was added to the waste simulant to reduce it, while this reducing agent is not added to the salt waste processed at the Saltstone Production Facility. The strong reducing agent Na_2S was added because the purpose of the research described in this paper was to evaluate the oxidation of reduced Tc, not to determine if the Tc would become reduced in reducing cementitious wasteforms. Therefore, the NRC staff does not believe that the research described in the Lukens paper addresses the question of whether Tc is in the reduced form in the saltstone wasteform. NRC staff suggested that it would be useful for experiments to be performed to determine the oxidation state and behavior of Tc in the saltstone wasteform.

Enclosure