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# Redox Chemistry in Nuclear Materials Storage Matrices Under Ambient and Accelerated Aging Conditions

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**ABSTRACT:**

We seek to (i) develop a non-destructive and extremely high-throughput method for characterizing the redox chemistry of DGR-relevant cements, and (ii) apply this method to link redox chemistry to the causes and consequences of mineralogical transformations that occur from initial curing through cement aging and degradation either by natural or accelerated aging protocols likely to stimulate failure modes. The development of these methods will critically inform hypotheses for long-term mineral chemistry, structural integrity, and radionuclide fate and transport for DGR cementitious barriers in this first-of-its-kind study. To this end, we have identified five specific research objectives:

1. ***Develop a high-throughput instrument for determining metal oxidation state speciation in cements via x-ray emission spectroscopy (XES) in a laboratory setting.*** This enables the study of several thousands of cement samples across the proposed matrix of chemical and aging combinations that will be prepared in this work. Such high-throughput lab-based x-ray spectroscopy is steadily growing as an extension and alternative to synchrotron beamlines for *analytical* applications where more limited technical capability suffices.
2. ***Develop a new analytical procedure for redox characterization of DGR-relevant cements and its relationship to concrete mineralogy and changes thereof.*** The new high-throughput instrument (objective 1) will determine the oxidation state/speciation of redox-active elements, some purposefully doped at low concentration into the DRG-relevant cements. This will be correlated with mineralogy changes seen in x-ray diffraction (XRD). We propose doping cements with a mixture of 3*d* transition metals known to show oxidation state in their x-ray emission spectra, e.g., Cr, Co, Mn, V, Zn, while also measuring S XES to see its theoretical reduction capacity.
3. ***Evaluate accelerated aging modalities and their effect on redox chemistry in DGR-relevant cements.*** Evaluation of thermal, radiation dose, $O_2/CO_2$ cycling, and/or supercritical $CO_2$ cycling on cement redox chemistry will directly address several potential degradation channels for DGR concretes.
4. ***Evaluate the interplay between steel inclusions and the naturally redox chemistry in DGR-relevant cements***. This addresses the induced redox changes due to the interfacial chemistry of the steel storage drums and structural components with the cementitious barriers in DGRs. Realistic consideration of such interactions is required for comprehensive evaluation of DGR plans.
5. ***Compile a test bank of DGR-relevant cements to support longitudinal study of their degradation in this and future research.*** This will include both low- and high-pH cements, prepared with and without 3*d* transition metal (3*d* TM) additives and/or steel inclusions, following the recipes developed in objectives 2, 3, and 4 (detailed below). Curating cements for the purpose of long-term aging studies will provide a set of standard specimens aged naturally for which specimens subjected to accelerated aging protocols may be compared to for assessment of their "true age". This sample library will serve as a unique resource for future DGR research in the United States.