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In-Situ Spectro-Electrochemical Studies of Radionuclide Contaminated Surface Films on Metals and the Mechanism of their Formation and Dissolution

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Research Objective

The objective of this research program is to gain a fundamental understanding of the structure, composition, and mechanism of formation of radionuclide-containing surface films on metals that are relevant to the problem of decontamination of piping systems and waste storage tanks at DOE nuclear processing facilities.

Research Progress and Implications

As of May 1998, after about a year and a half of work towards implementing this project, considerable progress has been made in understanding the mechanism and structure of heavy metal ions incorporated into simulated corrosion films of nickel. The nature of iron and chromium oxide films, which are used to model the other components of steels used in piping systems and waste storage tanks in nuclear facilities, has also been elucidated. The principal techniques used in these investigations consist of coupled electrochemical and “in-situ” synchrotron X-ray absorption spectroscopy, as well as vibrational spectroscopy (infrared and laser Raman).

Electrochemically deposited thin films of nickel hydroxide and nickel oxyhydroxide have been used as models for the host hydrous oxide surface layers initially. Contamination by radionuclides is mimicked by the incorporation of stable isotopes of Sr, Ce, Cs, etc. Co-deposition of Sr with hydrous nickel oxide films resulted in the formation of separate domains of Sr(II) oxide/hydroxide phase without lattice substitution into Ni sites or intercalation into the layered structure.The incorporation of Ce occurs in a similar manner with the exception that only Ce(IV) is found codeposited with NiOOH while Ce(III) and Ce(IV) are formed as co-precipitates of alpha Ni(OH)2. In contrast, Cr is incorporated as Cr(III) into lattice vacancies in Ni(OH)2 and as Cr(VI), in the form of a chromate, in the interlamellar layer of the brucite-type structure. We found that hydrous oxide films of Ce and Cr can be prepared by anodic and cathodic deposition processes. The films can differ in structure and chemical reactivity towards oxygen depending on the composition of the electrolyte solution used. Iron oxide/hydroxide films prepared by anodic deposition were found to have a very similar structure to that of the passivation layer on iron. Thus their study would lead to a better understanding of corrosion and passivation phenomena in metals. The knowledge being gained in this work will be useful in developing rational approaches to the cleanup of contaminated corrosion scales via chemical or electrochemical methods. One would anticipate that more drastic procedures will be needed to remove a contaminant that has been incorporated into a lattice site (e.g. Cr) compared to one which is merely adsorbed on the surface. Our results also have implications in the environmental speciation and remediation of Cr. Moreover, there is great interest in the use of Ce and Cr compounds for corrosion inhibition, as well as in other energy technologies, like water electrolysis.

Results of this research are described in 6 publications to date. They have also been presented at 2 recent scientific meetings, i.e., the Materials Research society Meeting, in San Francisco, in April, and the Electrochemical Society Meeting, in San Diego, CA, in May.

Planned Activities

Future work will involve the use of radioactive isotopes in our studies so as to determine the effect of radiation on the structure, composition, and mechanism of ion incorporation into the corrosion films. The investigation of Cs, U, and Pu will be of particular interest. The structure of sorbed species will be studied. A correlation will be made between the local structure of the incorporated metal ion and its facility for removal via chemical or electrochemical dissolution methods. Finally, we will examine the utility of an “electrochemical brush”, which has been invented in the course of this work, as a practical device for the decontamination of real pipes and storage tanks at DOE facilities.