Phase identifications in crud from commercial boiling-water reactors at the Idaho National Laboratory by transmission electron microscopy

Dawn E. Janney, Douglas L. Porter, Joshua L. Peterson[1]

Center for Nuclear Fuels and Materials Research, Idaho National Laboratory, Idaho Falls, ID 83415

[1]Present address: University of Texas, Austin

INTRODUCTION

Activated corrosion products ("crud") from light-water reactors are important to the nuclear power industry because they can lead to fuel-rod failures and cladding breaches. Crud can also become detached and circulate in the cooling-water system, causing additional radiation exposure to plant workers. Knowing which phases are present in crud is vital to understanding how it forms and predicting how it will behave. Previous approaches to understanding crud formation include studying corrosion products formed in boiling water with a composition similar to that in reactor cooling systems, predicting minerals expected to form based on modeling effects of radiolysis of water, and attempting to infer the phases present from analyses of samples involving large numbers of crystals.

Although each of these approaches provides important information, none of them directly identifies the phases present in actual crud. The present study addresses this need.

SAMPLES AND METHODS

As part of a continuing effort to improve the Department of Energy's ability to address problems in currently operating commercial nuclear reactors, the Electric Power Research Institute (EPRI) arranged for the Idaho National Laboratory (INL) to be sent four samples of crud from three commercially operating boiling water reactors. Sample A (from Reactor A) was collected at the 90-inch (~229 cm) elevation of a failed two-cycle rod that had a cumulative burnup of 38.3 GWd/MTU. Sample B (from Reactor B) was collected from the 30-inch (~76 cm) elevation on a three-cycle sound rod that had a cumulative burnup of 40.7 GWd/MTU. Both rods had thick deposits of tenacious crud, and both samples were from plants that used Zn addition and Noble Metal Chemical Addition (NMCA). Sample C (from Reactor C) is from the ~ 45 cm elevation of a sound one-cycle bundle with 21.9 GWd/MTU burnup, and Sample D (also from Reactor C) is from the ~254 cm level of a sound 2-cycle bundle with 22.2 GWd/MTU burnup.

Small particles from each sample were suspended in de-ionized water and dispersed on a commercially prepared carbon-coated formvar substrate supported by a gold grid and analyzed using transmission electron microscopy (TEM). The phases present in a number of particles from each sample were identified using a combination of energy-dispersive x-ray spectroscopy (TEM-EDX), which measures chemical compositions at specific points, and electron-diffraction data (which contains information about crystal structures).

RESULTS

Sample A:

Both nanocrystalline areas and single euhedral crystals of franklinite ($ZnFe_2O_4$, also known as zinc ferrite) were observed in Sample A. Hematite (α-Fe_2O_3) was observed both as single crystals and in a nanocrystalline iron-oxide mixture that also probably includes goethite (α-FeOOH) and magnetite (Fe_3O_4) or maghemite (γ-Fe_2O_3) but does not include significant quantities of akaganéite (β-FeOOH)or lepidocrocite (γ-FeOOH). Other phases in Sample A include crystalline silica (probably quartz, α-SiO2), and a high-Ba, high-S phase that could not be identified from diffraction data. Sample A also contained small quantities of halite (NaCl) and sylvite (KCl), both water-soluble phases that probably precipitated onto the sample as the water used in sample-preparation dried.

Sample B:

Phases identified in Sample B include euhedral crystals of franklinite, a single crystal of willemite (Zn_2SiO_4), several areas of nanocrystalline akaganéite, amorphous silica, and an unidentified phase with a Fe:Cr ratio of ~4:1 and significant concentrations of Ni and Si. Sample B also contained large amounts of halite.

Sample C:

Numerous examples of hematite were observed in this sample, and showed a wide variation in crystal sizes and shapes. Other data suggest the presence of magnetite and lepidocrocite, and at least one kind of clay. A single particle of a high-Pb phase was also observed. Several particles have thick, high-Zr central parts surrounded by thin areas consisting of Fe oxides (primarily hematite); these particles may represent fragments of the cladding and immediately adjacent crud.

Sample D:

Phases identified in Sample D include corundum (α-Al_2O_3), hematite, an unidentified aluminosilicate that is probably a clay, and a high-Zr phase that was not analyzed in detail but may be fragments of cladding.

DISCUSSION

The TEM data suggest that crud consists of a complex mixture of iron oxides, possibly including hematite, magnetite, goethite, lepidocrocite, and akaganéite, many of which occur as nanocrystals. Crud samples from both of the plants using Zn addition also contained Zn minerals (franklinite and willemite). Precise identification of these phases is important because the shapes, sizes, and identities of iron oxides are well known to be sensitive to small changes in formation conditions. Further, different iron oxides may have different thermal and mechanical properties, in turn affecting the likelihood that they can cause fuel pin failure or become detached and spread contamination throughout the cooling system.

One surprising result of the present research is the presence of chlorides in two of the samples. Formation of these phases requires concentrations of chloride far higher than would be tolerated in an operating reactor, indicating that the chlorides are contaminants introduced between the time the crud left the reactor and its arrival at the INL. Despite its nominal formula, akaganéite is a chloride-bearing phase, and thus probably also formed after the crud was removed from the reactor. Alumina, clays, and perhaps silica are also likely to be contaminants. The presence of contaminants can greatly complicate the interpretation of chemical-analysis data, and suggests a need for developing better techniques for collecting “clean” crud samples.

Despite its unique value, TEM data is only rarely statistically representative. Thus, this data should be interpreted in combination with that from techniques with lower spatial resolution such as SEM and bulk chemical analyses.