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Energy for the Future

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Chemical Gradients in Crud on Boiling Water Reactor Fuel Elements
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Abstract

Crud (radioactive corrosion products formed inside nuclear reactors) is a major problem in commercial power-producing nuclear reactors. Although there are numerous studies of simulated (non-radioactive) crud, characteristics of crud from actual reactors are rarely studied. This study reports scanning electron microscope (SEM) studies of fragments of crud from a commercially operating boiling water reactor. Chemical analyses in the SEM indicated that the crud closest to the outer surfaces of the fuel pins in some areas had Fe:Zn ratios close to 2:1, which decreased away from the fuel pin in some of the fragments. In combination with transmission electron diffraction analyses (published elsewhere) that were used to identify the crystal structure of particles of this crud with specific Fe:Zn ratios as franklinite and several iron oxides, these results suggest that the innermost layer of crud in some areas may consist of franklinite ($ZnFe_2O_4$, also called zinc spinel), while outer layers in these areas may be predominantly iron oxides.

Introduction

Corrosion products from boiling water reactor components (such as those constructed of stainless steel or brass) can be transported into the reactor core by the cooling water, where they can be deposited on the outside of the fuel pins to form crud. If these radioactive deposits break loose and circulate through the plant, they can cause safety hazards for plant workers. They can also interfere with cooling water circulation around the pins causing fuel failures. Numerous attempts to prevent and control crud formation and circulation by changing the water chemistry have been made (e.g., ref. 1); none has been fully successful. The samples in this study were from a plant in which zinc had been added to the water.

Despite numerous attempts to understand the formation of crud (primarily using non-radioactive surrogates) and to control its formation and characteristics by altering water chemistry, there is little fundamental understanding of what crud is, how it forms, and how its characteristics might be modified to make crud less damaging to plant operation and worker health.

The present study reports data from scanning electron microscopy (SEM) of crud fragments from a commercially operating power-generating nuclear reactor. The fragments were chosen because they allowed the interface between the cladding that forms the outer surfaces of the fuel pins and the inner surfaces of the crud to be viewed approximately edge-on (Fig. 1). This orientation was chosen because it allows observation of any compositional or microstructural layers that might have formed.

Samples and Methods

The crud sample in this study is one of three provided by the Electric Power Research Institute (EPRI) to the Idaho National Laboratory (INL) as part of an on-going effort to build the capabilities of the INL to address problems of current concern to the nuclear power industry. The sample consisted of fragments of crud that had been scraped from the outer surfaces of fuel pins in a hot cell.

SEM samples were prepared by transferring a few particles of crud to a carbon "sticky dot" on a standard SEM stub using tweezers and a small, freshly purchased paintbrush in a glovebox. Individual particles were too small to readily see and manipulate, and no effort was made to control their orientations.

Several crud particles in which the interface between the crud and cladding was approximately vertical were identified in the SEM. Back-scattered electron images of these particles were recorded, and energy-dispersive X-ray (EDX) spectra from points uniformly spaced along lines crossing the interface were recorded to examine variations in chemical compositions. Concentrations of Fe, Zr, Zn, Cr, Mn, and Ni (all previously reported as important elements in crud and detected in at least some spectra in this study) were normalized to a total of 100%. Because of the rough surfaces of the samples, the compositions should not be considered quantitative; however, major variations in ratios of elements present in significant concentrations are considered significant. The volume of sample represented by each measurement is estimated as an approximately spherical or hemispherical region a few micrometers across and deep. Thus, the volumes of material represented by compositions measured within a few micrometers of each other overlap, making sharp distinctions in composition appear gradual but also ensuring that small areas with unique compositions are not inadvertently skipped.

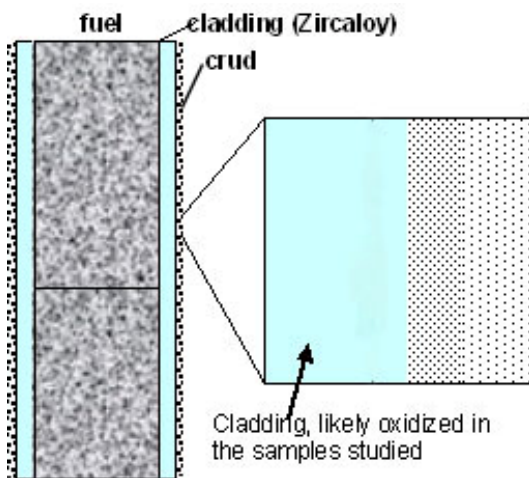


Figure 1 – Sketch of fuel pin cross-section showing fuel, cladding, and possible layered structures in crud

Results

Although no attempt was made to control the orientation of individual particles of crud during sample preparation, several relatively large particles were found in which the interface between the cladding and the adjacent crud was oriented approximately edge-on.

Figure 2 shows one of these large particles. The particle is flat, and standing on one edge. The left side of the figure is a back-scattered electron image, in which the cladding appears white and the crud appears gray. EDX analyses were collected at twelve points evenly spaced along the chartreuse line, which crosses the boundary between the crud and the cladding. The right side of the figure shows relative concentrations of major elements (Fe, Zr, Zn); some spectra also showed low concentrations of Cr and Mn. The iron-to-zinc atomic concentration ratio appears to be about 2:1 throughout the crud layer.

Figure 3 shows a second piece, in which the Fe:Zn ratio is approximately 2:1 in a very thin layer close to the outer surface of the cladding, then increases towards the edge of the particle farthest away from the cladding. Because of the spatial resolution of the EDX data, even abrupt changes in composition would appear somewhat gradual, and it's not clear whether this layer really exists or is an artifact of the EDX spectrum collection. Figure 3 also shows the location of a second line of points. Data from these points followed the general pattern shown in the figure.

Figure 4 shows a point scan from another location on the fragment shown in figure 3. The iron-to-zinc ratio is approximately 2:1 near the cladding surface and remains approximately constant for 5-10 μm . Farther from the cladding, the ratio increases, and the Zn concentration approaches zero at the edge of the fragment farthest from the cladding.

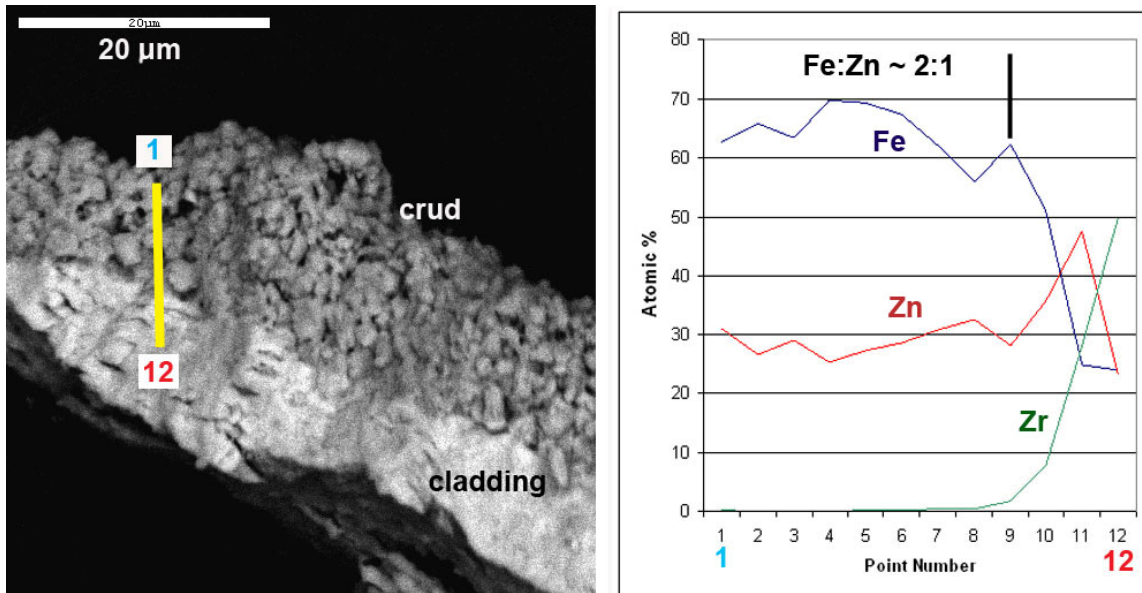


Figure 2 – SEM Backscattered electron image of crud attached to cladding. EDX analysis taken at points 16 to 26 are plotted at right. Points are $\sim 1.3 \mu\text{m}$ apart.

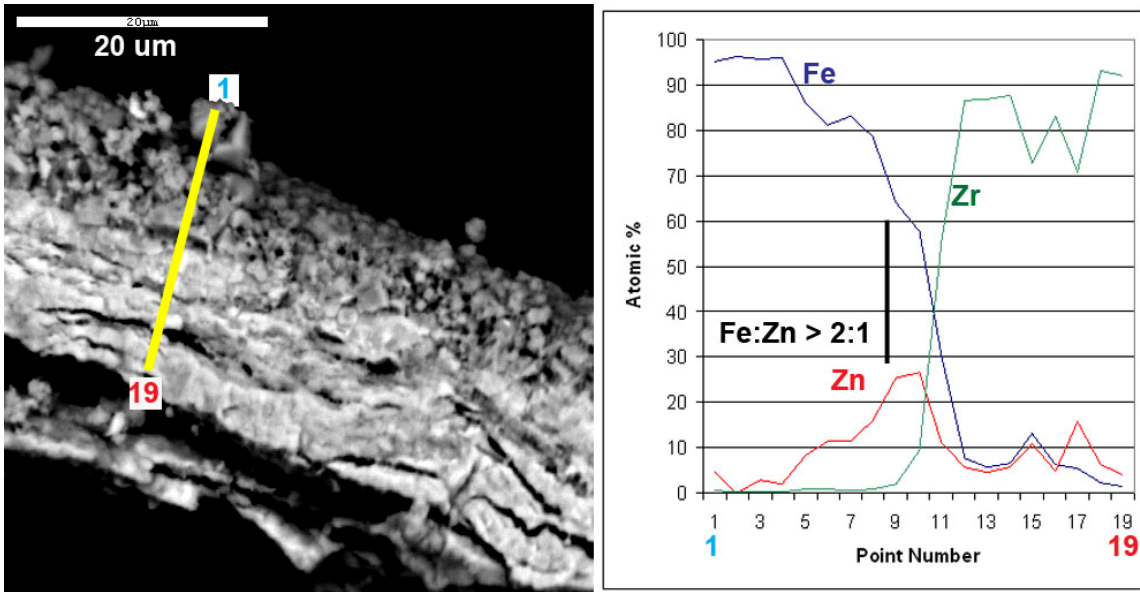


Figure 3 - SEM backscattered electron image of crud attached to cladding material. EDX analysis taken at points 1 to 19 (#1 in crud, #19 in cladding) are plotted at right. Note that the Fe to Zn ratio is less than 2:1 except for a possible very thin layer immediately adjacent to the cladding. Points are approximately one micron apart.

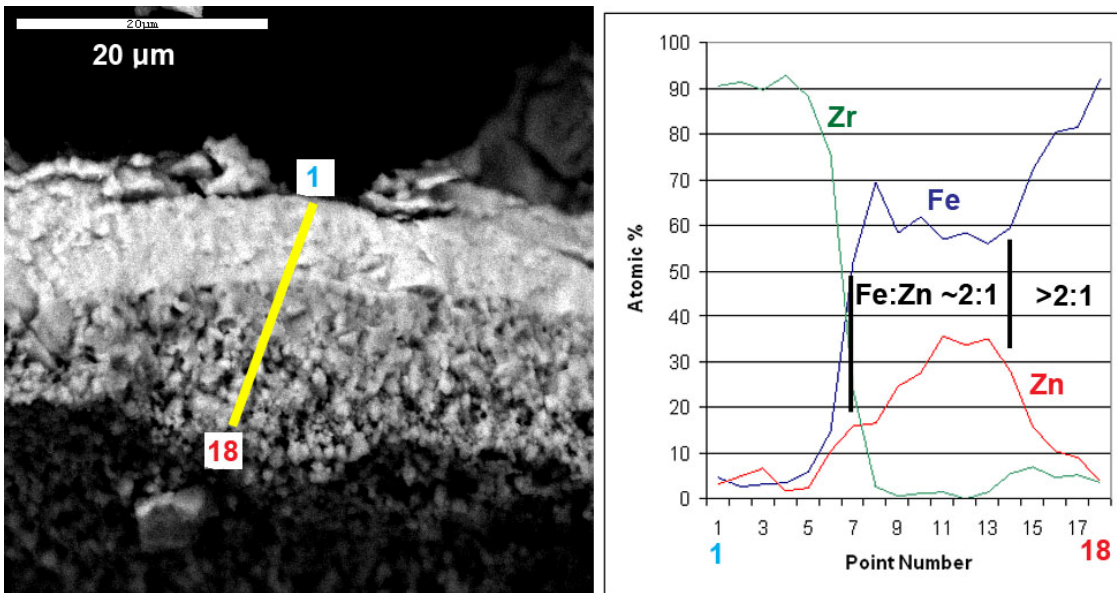


Figure 4 - SEM backscattered electron image of crud attached to cladding material. EDX analysis taken at points 1 to 18 (#1 in cladding, #18 in crud) are plotted at right. Note that the Fe to Zn ratio is less than 2:1. Points are approximately one micron apart.

Discussion

Data presented in Figures 2-4 suggest the presence of a variable-thickness, possibly discontinuous layer of crud with an iron-zinc ratio of ~2:1 adjacent to the outer surface of the cladding. Figure 3 shows this layer as at most a few micrometers thick, while Figure 4 shows a thickness of 5-10 micrometers. Both of these figures show crud farther from the cladding as having a much higher Fe-Zn ratio.

Taken in isolation, the data in Figure 2 show a different pattern, in which the Fe-Zn ratio remains essentially constant throughout the thickness of the crud layer. However, there is no reason to believe that any of the fragments studied here represents the complete thickness of the crud, and Figure 2 may represent the inner portions of a thick layer of crud with an Fe-Zn ratio of 2:1 from which an outer, high-Fe layer has broken away. If this interpretation is true, the maximum thickness of the layer with the Fe:Zn ratio of approximately 2:1 is at least 10 micrometers (measured perpendicular to the cladding surface, not along the line of the EDX data).

By themselves, the SEM data do not allow identification of the specific phases present in the crud. However, TEM studies combining EDX and electron diffraction data conclusively identified franklinite (ZnFe_2O_4 , Fe:Zn ratio 2:1) and iron oxides (primarily hematite, $\alpha\text{-Fe}_2\text{O}_3$) in other particles from this sample (reference 3, Sample A). These data suggest that the material with the Fe:Zn ratio of 2:1 in the SEM data is franklinite, and that layers with higher proportions of Fe contain iron oxides such as hematite.

Although they are not present in the stoichiometric formula for franklinite, low concentrations of Mn have been reported in naturally occurring franklinite (reference 4), and materials with a franklinite-like structure and compositions intermediate between franklinite and ZnCr_2O_4 have been synthesized (reference 5). Thus, the presence of these elements in low concentrations does not necessarily imply that the sample contains discrete high-Cr or high-Mn phases not identified in the TEM data.

Despite the small number of observations presented here, the data suggest the presence of a localized, possibly discontinuous, layer with a Fe:Zn ratio of 2:1 adjacent to the cladding and a higher-Fe material farther away. However, the significance of this result is unclear because of the small number of crud fragments observed. If the pattern is real, it is also not clear why it might occur. Possible reasons include changes in local water circulation patterns or thermal gradients because of the formation of a franklinite layer on the cladding surface. Unfortunately, the data to test these (and other) possible explanations are not available. However, the present study shows both the value of combining TEM and SEM data and the need to combine both kinds of data with information about water chemistry and the local environment in which crud forms.

Conclusions

This study used scanning electron microscopy (SEM) to examine variations in the composition of crud (radioactive corrosion products from nuclear reactors). A material with a Fe:Zn ratio of approximately 2:1 was found adjacent to the cladding in some areas, and some areas showed zinc concentrations decreasing to almost zero farther away from the cladding. Previously published transmission electron microscopy (TEM) analyses of other particles from the same sample suggest that the material with the Fe:Zn ratio of 2:1 is franklinite (ZnFe_2O_4) and that materials with abundant iron and essentially no zinc are iron oxides such as hematite ($\alpha\text{-Fe}_2\text{O}_3$). Although the pattern has not been rigorously established, all of the data are consistent with a crud structure consisting of variable thickness, possibly discontinuous inner layer of franklinite immediately outside the cladding, and an outer layer of iron oxides. Because only crud particles showing the interface between the crud and cladding were studied, compositions of materials more than 10-15 micrometers away from the interface remain unknown.

Although the small number of observations and reactors in the present study do not support inferences about universal patterns of crud formation, the results presented here illustrate the value of SEM data in crud analyses.

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