First Principles Calculations Predict Stable 50 nm Nickel Ferrite Particles in PWR Coolant

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Abstract: Thermodynamic calculations that combine experimental data with the results of first principles calculations yield negative free energies for {111} surfaces of nickel ferrite for the temperature, pressure and ion concentrations typical of Pressurized Light Water Reactor (PWR) coolant. When combined with a positive bulk free energy of formation, the negative surface energies predict that thermodynamically-stable octahedral nickel ferrite particles with diameters of ~50nm should be present in PWR coolant during operation. These particles would not be removed by mixed bed demineralizers and would be below the filter pore sizes typically used in Chemical and Volume Control Systems. The calculations also predict that these particles are not thermodynamically stable in coolant under ambient conditions. Based on these results it is proposed that solvated nickel ferrite particles, which are predicted to be stable and likely long-lived in PWR primary coolant, contribute to the nucleation of metal oxide scale on PWR fuel rod cladding and that conventional methods for purifying the primary coolant may be ineffective in removing these species.

I. Introduction

Changes in U.S. energy policy have led to renewed efforts toward meeting the challenges associated with expanding nuclear power as a primary energy source.[1] One of these challenges is increasing reactor efficiency, reliability and fuel lifetime by eliminating the porous metal oxides that form on the fuel rods in Pressurized Light Water Reactors (PWRs) during operation.[2] [3] Termed CRUD for Chalk River Unidentified Deposits (an acronym based on where it was first observed), these deposits reduce heat transfer, contribute to fuel rod corrosion, and contain trapped boron[4] [5] that can reduce local neutron flux in a process called a CRUD-induced power shift.

In PWRs CRUD deposits are found near the top of the fuel rods, and are associated with sub-cooled nucleate boiling. CRUD is composed chiefly of condensed nickel ferrite (NiFe_2O_4) and nickel oxide particles, with the addition of various boron, lithium, zinc, and zirconium containing compounds depending on operating conditions and CRUD thickness.[4] [5] The nickel ferrite particles in CRUD are typically found to have an octahedral morphology. Bonaccordite (Ni_2FeBO_5), a rare, water-insoluble hard mineral, has also been found in CRUD;[4] its presence has been taken as evidence for extreme conditions in the interior of CRUD relative to the coolant.[4] The outer region of CRUD is porous and contains a series of vents called boiling chimneys. It is believed that the coolant flows in through the porous regions, boils, and then escapes through the boiling chimneys. Depending on the thickness, CRUD may also contain a denser region near the fuel cladding.

CRUD modeling efforts traditionally address one of two processes, nucleation of CRUD[6] or coolant flow and boiling in the porous CRUD leading to growth from dissolved species.[7] [8] [9] The current understanding of the nucleation process is that some colloidal (or relatively large) species are deposited from the coolant to the fuel cladding during subcooled nucleate boiling by micro-layer evaporation and dry out. In this process suspended particles are transported to a fluid-bubble interface. Evaporation into the bubble removes the solvent from the suspended particles, and they condense to form a porous solid.[6] In experiments designed to study this process suspended particles are introduced into the fluid, and porous solid deposits are found at surfaces that are in the vicinity of bubble nucleation sites. In PWRs such particles are assumed to be present in the coolant as products of the corrosion of the piping that carries the coolant between the fuel rods and steam generator. However, the composition, structure, size and exact origin of these particles have not been well characterized.

Several recent studies have modeled fluid and heat transport as coolant flows through the porous regions of the CRUD, and then escapes as steam through the boiling chimneys.[7] [9] [10] The most sophisticated of these models include chemistry coupled to the thermal hydraulics. Modeling of this type by Henshaw *et al.*[7] and by Short *et al.*[8] have both suggested extreme conditions of temperature, concentration and pH within the CRUD that

depend on the CRUD thickness, and that are very different from conditions in the coolant. The evaporation process in the CRUD adds dissolved species into the solid, although apparently suspended particles are not necessary for CRUD growth, in contrast to the nucleation process.

To reduce concentrations of various species from the coolant and hence mitigate the CRUD nucleation and growth processes, PWRs use a Chemical and Volume Control System (CVCS) that filters suspended particulates larger than about 500 nm, and that removes dissolved ions using mixed bed demineralizers.[11] The coolant temperature and pressure in the CVCS is typically reduced from those in the reactor to avoid damage to the demineralizing resins and the water pumps.

Despite modeling efforts aimed at understanding the physical and chemical processes leading to CRUD formation, and the use of CVCSs and coolant chemistry tuning[12] to control CRUD formation, CRUD continues to be a major hurdle to fully optimizing reactor efficiency and lifetime. One of the unsolved issues in PWRs is the composition, size and origin of the particles suspended in the coolant that are thought to be responsible for CRUD nucleation.[6][8]

We recently used a first-principles informed thermodynamics scheme[13][14] to calculate temperature-dependent surface energies of nickel oxide and nickel ferrite, two compounds that are known to be present in PWR CRUD.[5][4] One unanticipated result of these calculations is that nickel ferrite was found to have a negative free energy for the formation of several different surfaces under typical PWR coolant conditions, but a positive bulk free energy of formation with respect to dissolved species under the same conditions. In this paper we show that this result leads to a prediction of thermodynamically-stable (and hence long-lived) nickel ferrite particles with an octahedral morphology and sizes of about 50 nm in PWR coolant. Based on these results, we propose that these particles are responsible for the nucleation of CRUD and that removal of these particles by physical (e.g. filtration) or chemical means should be explored as a new route for mitigating CRUD nucleation.

II. Details of the Calculations

Temperature-dependent effective chemical potentials (ECPs) $\mu^0(T)$ for metal and oxygen ions in various solid oxides are determined by solving a system of linear equations of the form

$$\Delta_f G_{A_x B_y O_z}^0(T, P) = E_{A_x B_y O_z}(0K) - \frac{z}{2} \mu_{O_2}(T) - x \mu_A^0(T) - y \mu_B^0(T). \quad (1)$$

As described in the Appendix A of reference 13, the change in free energies $\Delta_f G_{A_x B_y O_z}^0$ are derived from four parameter fits to experimental heat capacities for the various solid oxides at temperatures ranging from 298.15K to 898.15K, and $E_{A_x B_y O_z}$ are energies from Density Functional Theory (DFT) calculations at 0K.[13] The results presented here use ECPs that were determined from a least squares fit to data for NiO, ZnO, Fe₂O₃, Fe₃O₄, FeO(OH), Cr₃O₄,

CoFe₂O₄, ZnFe₂O₄ and NiFe₂O₄. [13,15-17] ECPs for water and solvated metal cations are determined from the expressions

$$\left(\Delta_f G_{H_2O}^0(T, P)\right)_l = \left(\mu_{H_2O}(T, P)\right)_l - \frac{1}{2}\mu_{O_2}^0(T) - \mu_{H_2}^0(T) \quad (2)$$

and

$$\left(\Delta_f G_{M^{n+}}^0(T, P)\right)_{aq} = (\mu_{M^{n+}}(T, P))_{aq} - \mu_M^0(T) + \frac{n}{2}\mu_{H_2}^0(T) - n(\mu_{H^+}^0(T, P))_{aq} \quad (3)$$

respectively, using data from [18] and [19], and the conventional chemical potential form

$$\mu_{H^+}(T) = \mu_{H^+}^0(T_r) + RT \ln(10^{-pH}) \quad (4)$$

is used for the solvated proton. This scheme avoids having to perform DFT calculations on H₂ and O₂ molecules, it extrapolates data from DFT calculations on oxides to higher temperatures, and it provides a straight-forward method for incorporating the properties of solvated phases with the results of DFT calculations.

Surface energies were determined from DFT slab calculations that were carried out using the Vienna *Ab-initio* Simulation Package [20-22] and the generalized gradient approximation with the exchange-correlation functional of Perdew, Burke, and Ernzerhof [23,24] plus on-site Coulomb interactions (GGA+*U*). The on-site Coulomb interactions were implemented using the formulation of Dudarev, *et al.* [25] in which the single parameter, $U_{\text{eff}} = U - J$, describes the Coulomb repulsion. Values of 4.5 eV and 6.0 eV were used for U_{eff} for all Fe and Ni atoms, respectively, in the oxides [26,27].

The temperature-dependent free energy of formation $\gamma(T, P)$ for nickel ferrite surfaces formed from ions in solution was determined from the ECPs through the expression

$$\gamma(T, P) = \frac{1}{2A} \{ [G_{\text{slab}} - \Gamma_{\text{Fe}} \mu_{\text{Fe}^{+2}}^E - \Gamma_{\text{Ni}} \mu_{\text{Ni}^{+2}}^E - \Gamma_{\text{NiFe}_2\text{O}_4} g_{\text{NiFe}_2\text{O}_4} - n_{\text{H}_2} \mu_{\text{H}_2}^E] - [\Gamma_{\text{Fe}} + \Gamma_{\text{Ni}}] \cdot (2\mu_{\text{H}^+} - \mu_{\text{H}_2}^E) \}. \quad (5)$$

In this equation A is the surface area from the slab calculation, G_{slab} and $g_{\text{NiFe}_2\text{O}_4}$ are the DFT energies for the surface slab and bulk reference cell, respectively, the μ_i^E 's are environment-dependent chemical potentials, and the surface excess quantities Γ_i are given by

$$\Gamma_{\text{Fe}} = n_{\text{Fe}} - n_{\text{O}_2} + \frac{n_{\text{H}_2}}{2} \quad (6a)$$

$$\Gamma_{\text{Ni}} = n_{\text{Ni}} - \frac{n_{\text{O}_2}}{2} + \frac{n_{\text{H}_2}}{4} \quad (6b)$$

$$\Gamma_{\text{NiFe}_2\text{O}_4} = \frac{n_{\text{O}_2}}{2} - \frac{n_{\text{H}_2}}{4} \quad (6c)$$

When the stoichiometry of the slab and reference cell are the same, $\Gamma_{\text{Fe}} = \Gamma_{\text{Ni}} = 0$ and $\Gamma_{\text{NiFe}_2\text{O}_4} = 1$, and Eq.(5) reduces to the traditional definition of surface energy. When the surface is non-stoichiometric with respect to bulk nickel ferrite, the surface formation energy becomes

dependent on the environment through the chemical potentials. These are related to the ECPs through the molal concentration x_i by

$$\mu_i^E = \mu_i(T, P) + RT \ln[x_i] \quad (7)$$

In the prior work temperature-dependent free energies were reported for 23 surfaces with five orientations and several different cuts along particular high-symmetry directions.[14] Of these surfaces 11 did not contain any additional surface termination beyond that determined by the orientation and cutting plane of the bulk nickel ferrite crystal. The remaining 12 surfaces had additional water, OH or H groups terminating the surface. Further details are given in references [13] and [14].

III. Results and Discussion

Plotted in Figure 1 is the calculated free energy of formation for the nickel ferrite (111) surface with and without a surface termination referenced to dissolved ions as a function of temperature under PWR conditions of pressure = 15.5 MPa, pH = 7.2, and concentrations $[Ni^{2+}] = 1.66 \times 10^{-14}$ and $[Fe^{2+}] = 4.17 \times 10^{-13}$ mol/kg.[7, 28] These concentrations are taken from prior calculations that used a detailed reaction scheme that included water radiolysis chemistry.[28] Hence while radiolysis is not explicitly considered in our scheme, it is implicitly included through the concentrations. These (111) surfaces are calculated to have the lowest free energies. For reference, the next lowest energy surface is a (101) surface with a free energy of formation ranging from about -7 J/m² to about -6.5 J/m² over the same temperature range. A Wulff construction using these surface energies predicts that only the (111)

Figure 1. Calculated free energies of formation for nickel ferrite (111) surfaces with (dashed line) and without (dotted line) dissociated and chemisorbed water on the surface (both curves correspond to the axis on the left). The solid line is the free energy of formation for bulk nickel ferrite (the curve corresponds to axis on the right). In each case the free energies are relative to dissolved species under PWR coolant conditions.

crystallographic

surface orientations would appear at equilibrium. The same calculations yield a positive surface free energy for nickel oxide,[13] and similar calculations by other groups have yielded negative surface energies for alumina[29] and zinc oxide.[30]

Illustrated in Figure 2 are structures of the two surfaces that correspond to the energies plotted in Figure 1. Red spheres represent oxygen, white spheres represent hydrogen, and blue and pink spheres represent nickel and iron, respectively. The top panel is for a 'c-cut' (see reference [14] for details) that leaves a primarily metal terminated surface, while the bottom panel is for the same interface but containing chemisorbed water and hydroxyl groups. The initial structure for the latter consisted of hydrogen atoms terminating the exposed oxygen atoms and hydroxyl groups terminating the exposed metal atoms. During relaxation some of the hydrogen atoms reacted with the hydroxyl groups to create water molecules that are bound roughly parallel to the surface along surface channels as can be seen in the figure. The remaining hydroxyl groups are oriented roughly normal to the surface and sit at sites that span pairs of surface nickel atoms. Alternatively, rather than hydroxyl groups, the OH surface structures can be considered surface oxygen atoms originating from the bulk that are terminated with hydrogen atoms.

Figure 2: Illustration of the surface structures corresponding to the plots in Figure 1. Red spheres represent oxygen, white spheres represent hydrogen, and blue and pink spheres represent nickel and iron, respectively. The top panel is for a 'c-cut' that leaves a primarily metal terminated surface, while the bottom panel is for the same interface but containing chemisorbed water and hydroxyl groups.

Also plotted in Figure 1 is the change in free energy for the formation of bulk nickel ferrite from dissolved ions via

for the same PWR conditions used to calculate the surface free energies. In this case the free energy of formation is positive, i.e. nickel ferrite tends to dissolve.

A Wulff construction with the surface energies in Figure 1 leads to an octahedral particle morphology. This morphology is consistent with hydrothermal synthesis experiments carried out without surfactants that create octahedral nickel ferrite particles with sizes ranging from 60-100 nm. [31] This morphology is also consistent with observations of nickel ferrite particles in CRUD recovered from used fuels.[5]

To calculate the free energy for forming a nickel ferrite particle in solution as a function of size, a net particle surface free energy obtained by multiplying the surface area of an octahedral particle by a (111) surface free energy per unit area is added to the positive free energy for forming bulk nickel ferrite per unit volume times the volume of the particle. Plotted in Figure 3 is the change in free energy for the formation of an octahedral particle in solution from dissolved ions calculated with the data in Figure 1 (using the more negative surface energy), as a function of the characteristic length at different water temperatures. Because the surface area and volume scale differently with particle size, the sum of the surface and bulk energy terms yields a minimum in the free energy of formation as a function of size. At the highest temperature plotted, which corresponds to PWR coolant at operation, there is a minimum in free energy at a size of about 50 nm. At lower temperatures the radius of the free energy minimum and the magnitude of the negative free energy at this minimum both get smaller, until at room temperature the radius is so small that the separation of energy into a bulk and surface terms is inappropriate, and thermodynamically stable particles are not predicted.

These results have several important implications for the nucleation of CRUD in PWRs. First, these particles are predicted to be thermodynamically stable, and therefore will be long-lived rather than transient species. This property and their size under PWR conditions make them leading candidates for nucleating CRUD as discussed above. It should be noted that these are not particles formed on pipe surfaces as a result of their corrosion and transported to the core, but rather they can be formed from dissolved ions. This is a major distinction from the current assumptions for CRUD nucleation.[6][8] Second, these particles would likely not be removed by mixed bed demineralizers and would be below the filter pore sizes typically used in CVCs. Hence once formed they should remain available in the coolant for CRUD nucleation.[6] Third, the calculations predict that these nickel ferrite particles are not thermodynamically stable in coolant under ambient conditions, and might therefore not be observed in post-shutdown conditions depending on the shutdown timescale and associated chemical kinetics. Hence experimental validation of these results would require studies done under PWR coolant operating (or equivalent) conditions.

Figure 3: Change in free energy for the formation of an octahedral nickel ferrite particle in solution from dissolved ions calculated with the data in Figure 1, as a function of the characteristic length at different water temperatures. The inset illustrates the shape and measure of length for the particle.

Although more speculative, these results also have implications for CRUD growth and stability after CRUD nucleation. First, a negative surface energy suggests a thermodynamic tendency to maximize surface area. This may contribute to the stability of porous structure of CRUD. Second, as evident from Figure 1, as temperature increases the free energy of formation for bulk nickel ferrite becomes less positive and the denuded surface comes closer in free energy to the surface with termination. The former leads to larger equilibrium particle sizes, while the latter suggests loss of surface termination. The region of CRUD nearer the fuel rod is known to be more dense and tenacious compared to the porous CRUD that is exposed to the coolant. Our results suggest a possible explanation for this observation; the higher temperature in the CRUD near the fuel rod leads to a thermodynamic and kinetic tendency toward larger particles. This also suggests the incorporation of surface chemical effects as a next step toward modeling the chemistry of CRUD growth.

IV. Conclusion

Recent first-principles informed thermodynamics calculations have predicted a negative free energy for nickel ferrite particles under typical PWR conditions, which combined with a positive free energy of formation for bulk nickel ferrite predicts long-lived 50 nm octahedral nickel ferrite particles in PWR coolant. We propose that these are the source of particles from which CRUD is nucleated via micro-layer evaporation and dry out, and that removal of these particles by physical (e.g. filtration) or chemical means should be explored as a new route for mitigating CRUD nucleation.

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