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Thermodynamic modeling of the processes in a boiling water reactor to buildup the magnetic corrosion product deposits

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1. Introduction

The practice of reagent additions in reactor water is a key issue for the Nuclear Power Plants (NPP). Additives are spiked into the feed water for various reasons, for example, hydrogen addition aiming to reduce oxidizing conditions due to radiolytic decomposition of water in the core [1]. The issue of additives and subsequent material deposition may be relevant for all NPP internals in contact with the coolant. One of the most important processes occurs at the fuel elements where the water is heated up to around 558.15 K. In Boiling Water Reactors (BWR), since boiling begins already in the lower parts of the fuel element; some dissolved components may concentrate in the water, leading to the precipitation of secondary solid phases in the surroundings of the cladding surface. Early-discovered such deposits at the Canadian "Chalk River Nuclear Laboratories" have lead to the term CRUD after "Chalk River Unidentified Deposits" [2].

Zinc has been added to reduce the cobalt deposition and activity buildup on recirculation lines. However, this addition and the CRUD deposits produced thereof have disturbed the Eddy-current (EC) based measurements of the fuel cladding corrosion layer thickness at BWR Kernkraftwerk Leibstadt (KKL) [3,4]. These investigations have shown that the magnetic layer consists of microcrystalline Zn, Ni and Mn ferrite spinel phases that were deposited during the NPP operation. Interpretation of μ XAFS spectra, made it possible to estimate the extent of inversion in spinels

ABSTRACT

The buildup of corrosion product deposits (CRUD) on the fuel cladding of the boiling water reactor (BWR) before and after zinc injection has been investigated by using Gibbs Energy Minimization (GEM-Selector code) calculations of thermodynamic equilibrium at in situ temperatures and pressures. Under the BWR water chemistry conditions, Zn addition together with the presence of Ni and Mn induce the formation of (Zn,Ni,Mn)[Fe₂O₄] spinel solid solutions. GEM calculations applied to the boiling zone match with the electron probe microanalysis (EPMA) and Extended X-ray Absorption Fine Structure (EXAFS) findings, indicating that zinc-rich ferrite spinels are formed on BWR fuel cladding mainly at lower pin elevations under Zn water chemistry conditions. GEM results have helped to explain the existence of magnetic product deposits on the surface of the fuel element and the processes that take place in the reactor.

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and to obtain spinel structural formulae: $(Ni_{0.013}^{2+}Mn_{0.09}^{2+}Zn_{0.675}^{2+}Fe_{0.29}^{3+})[(Fe_{1.71}^{3+}Zn_{0.075}^{2+}Mn_{0.03}^{2+}Ni_{0.127}^{2+})O_4]$ at lower and $((Ni_{0.025}^{2+}Mn_{0.16}^{2+}Zn_{0.495}^{2+}Fe_{0.29}^{3+})[(Fe_{1.71}^{3+}Zn_{0.055}^{2+}Mn_{0.04}^{2+}Ni_{0.225}^{2+})O_4])$ at higher elevations of the investigated fuel pin [5].

This study deals with the modeling of the possible composition of the CRUD layer depending on the chemistry of the coolant. These processes, considered as partial chemical equilibria, were modeled with the Gibbs Energy Minimization GEM-Selektor code [6].

2. Modeling methodology

2.1. Gibbs Energy Minimization (GEM) approach

The GEM approach is based on a mass balance for the entire system, which is set up by specifying the total amounts of chemical elements and a charge balance only. These elements and electric charge are called "Independent Components" (IC). All chemical species, in all phases, are called "Dependent Components" (DC), since their stoichiometries can be built from ICs. In the GEM system formulation, thermodynamic *phases* (each including one or more DCs and additional properties, such as the parameters of non-ideal mixing) are considered explicitly. Each component (DC) is provided at input with its elemental stoichiometry and value of the standard molar (or partial molal) Gibbs energy G° , taken from the database and corrected to the *P*, *T* of interest, if necessary.

In the GEM method, the activities and concentrations of the DCs are treated separately for each phase, taking into account the appropriate standard/reference states and activity coefficients. The equilibrium assemblage conforming to the Gibbs phase rule



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is selected automatically from a large list of stoichiometrically possible phases. The equilibrium partitioning in a multiphase system, including for example an aqueous solution, a gas mixture, one or several solid solutions, and, optionally, sorption phases, is computed simultaneously for all phases in a straightforward way. The calculations were carried out using a GEM "Interior Points Method" (IPM) algorithm [7,8]. In addition to the speciation vector $n^{(x)}$ (mole amounts of DCs – the primal solution), IPM computes a complementary dual solution vector u (equilibrium chemical potentials of ICs in the system state of interest). Actually, the power of GEM IPM lies in comparing the DC chemical potentials obtained from primal $n^{(x)}$ and dual u vectors, wherever possible.

The Zn–Mn–Ni ferrite spinel is represented as a solid solution of four end members with bulk stoichiometry: $ZnFe_2O_4$ (franklinite, *fra*); NiFe₂O₄ (trevorite, *tre*); MnFe₂O₄ (jacobsite, *jac*); and FeFe₂O₄ (magnetite, *mag*). The latter end member (*mag*) must be considered in the thermodynamic model for the sake of completeness, even though Fe²⁺ was not detected instrumentally in this particular set of CRUD samples formed at oxidizing conditions. Previous thermodynamic modeling [16] showed that even at such conditions at 573 K, 3–6% of aqueous dissolved iron may still exist as Fe²⁺ ion and its complexes, especially at lower pH. Hence, neglecting of Fe²⁺ in the solid solution model of ferritic spinel would make it less internally consistent regarding redox of the system, and make the potential use of the thermodynamic model impossible in scenarios at more reducing conditions. Thermodynamic properties of the *mag* end member are taken over from the previous work [9,10].

Cation substitutions in spinel solid solution occur simultaneously in two sublattices – one comprised of tetrahedral structural sites (cation multiplicity of 1 per end member formula) and another – of octahedral sites (multiplicity 2). In normal spinels (e.g. chromite $FeCr_2O_4$), divalent cations occupy tetrahedral sites, and trivalent cations – octahedral sites. However, in ferrites, part of divalent cations may occupy octahedral sites, and part of trivalent cations – tetrahedral sites. This phenomenon is called 'inversion'; the extent of inversion decreases with temperature.

In a narrow temperature region of interest, the extent $\alpha^{(inv)}$ of inversion for each spinel end member was assumed constant and expressed through the \bar{G}^{inv} term – an increment to the g_T^o term of the respective end member, evaluated following the approach of Kurepin [9,10].In this approach, the Gibbs energy of mixing in a multi-component spinel solid solution phase is represented as

$$\Delta_{mix} = \Delta G^{inv} + \Delta G^{id} + \Delta G^{ex} \tag{1}$$

where ΔG^{inv} is the inversion contribution; ΔG^{id} is the ideal configurational part, and ΔG^{ex} is the excess part of the Gibbs energy of mixing per mole of the phase. Each of those parts can be represented as the sum of products $\Delta G = \sum_j \bar{G}_j x_j$ of the respective partial mole quantity of *j*-th end member and its mole fraction x_j ; the summation is taken over all end members of the phase. The partial properties of mixing for the *j*-th end member are:

$$\bar{G}_i^{inv} = -TS_c \tag{2}$$

where

$$S_{c} = -R(\alpha_{j}^{(in\nu)} \ln \alpha_{j}^{(in\nu)} + (1 - \alpha_{j}^{(in\nu)}) \ln(1 - \alpha_{j}^{(in\nu)}) + \alpha_{j}^{(in\nu)} \\ \times \ln(\alpha_{j}^{(in\nu)}/2) + (2 - \alpha_{j}^{(in\nu)}) \ln(1 - \alpha_{j}^{(in\nu)}/2))$$
(3)

$$\bar{G}_i^{id} = RT lna_i^{(cnf)} \tag{4}$$

$$\bar{G}_{j}^{ex} = RTln\gamma_{j} \tag{5}$$

Here, $\bar{G}_i^{(nv)}$ is the partial Gibbs energy related to the extent of inversion $\alpha_j^{(hv)}$ (see below), S_c is a configurational entropy of ordering that corresponds to the difference between inversed and non-in-

versed spinels. \bar{G}_j^{id} is the ideal contribution to the partial Gibbs energy of *j*-th end member; $a_j^{(cnf)}$ is the configurational part of end member activity. \bar{G}_j^{ex} is the excess partial Gibbs energy, and γ_j is the respective activity coefficient related to energy of non-ideal interactions between substituting cations. This gives the following expression for the chemical potential of *j*-th end member used in the GEM-Selector calculations:

$$\mu_j = g_{T,j}^o + RT ln \chi_j + RT ln \lambda_j \tag{6}$$

where g_{ij}^o is the standard Gibbs energy function of the 'normal' (noinversion) end member and λ_j is the apparent activity coefficient expressed as

$$\ln \lambda_j = \frac{G_j^{(inv)}}{RT} + \ln a_j^{(cnf)} - \ln x_j + \ln \gamma_j \tag{7}$$

To simplify the solid solution model, the end members were defined according to the structural formula $[M^2,M^3]_{tet}[(M^3,M^2)_2]_{oct}O_4$. For example, the trevorite end member with the extent of inversion $\alpha^{(inv)} = 0.8$ has the structural formula $[Ni_{0.2}Fe_{0.8}]_{tet}[Fe_{1.2}-Ni_{0.8}]_{oct}O_4$. In such cases, the ideal and non-ideal parts of Gibbs energy of mixing are easier to express through cation site fractions $y_{s,m}$ where *m* is the index of cation on the respective *s*-th site.

The $a_j^{(cnf)}$ term was calculated with the following equation [11,12]:

$$a_{j}^{(cnf)} = \prod_{s} \prod_{m} \left[\frac{n_{s}}{r_{m}} y_{s,m} \right]^{r_{m}}$$
(8)

where *s* is the index of site (sublattice), n_s is the multiplicity of site *s*, and r_m is the number of cations on site *s* in *j*-th end member. At each iteration of GEMS, site fractions of cations y_m were computed from mole fraction of end members as

$$y_{s,m}=\frac{1}{n_s}\sum_j r_m x_j.$$

The excess Gibbs energy of mixing term was calculated (following [19], Kulik & Wagner, in preparation) as

$$RT\ln\gamma_j = \sum_{s} RT\ln\gamma_{mj} \tag{9}$$

$$RT\ln \gamma_{m,j} = \frac{r_m}{n_s} \sum_{w} W_{ab} \left(y_a \ y_b \right) \left[\frac{Q_m}{y_{s,m}} \frac{r_m}{n_s} - 1 \right]$$
(10)

where W_{ab} is the regular Margules interaction parameter, and Q_m is the number of a and b subscripts equal to m (0 or 1); the summation is taken over the list of all non-zero interaction parameters. The above calculations are built-in in the in-house GEMS v.3 code (http://gems.web.psi.ch) used in the present work.

2.2. Thermodynamic data for the investigated system

For a deeper insight into the processes taking place during operation in the reactor, it is necessary to improve the understanding of the system by combining the experiment and the thermodynamic modeling. For this reason, the thermodynamic properties of the pure normal spinel end members $ZnFe_2O_4$, $NiFe_2O_4$, $MnFe_2O_4$ and $FeFe_2O_4$ were collected. To assess the extent of inversion and the involved non-ideality in cation substitutions, some binary solid solutions between these end members have been evaluated, as described below.

The thermodynamic data for pure normal $ZnFe_2O_4$ and $NiFe_2O_4$ was taken from [9,13]; that for $MnFe_2O_4$ from [14], and for $FeFe_2O_4$ from [9], as summarized in Table 1.

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