EXPIRED

IAPWS Certified Research Need - ICRN 3

Solubility of Spinels in the Chemical Conditions of Nuclear Reactors

The IAPWS Working Group - Power Cycle Chemistry has examined the published work in the area of the solubility of spinels in aqueous solutions which is of interest to the electric power industry.

IAPWS recognizes that there is a requirement for work to be pursued in this field and has prepared this document to assist potential investigators obtain sponsorship. The knowledge of the solubility of the spinels which constitute the corrosion products in the primary circuit of a PWR is necessary to predict transport and activation of these corrosion products. Experimental results are available for magnetite solubility in a wide range of pH and at temperatures up to 350°C, but this is not the case for mixed ferrites, especially those containing cobalt.

Although encouraging this work, IAPWS is not able under its statutes to provide financial support. The IAPWS contact can provide any further development information and will act as a liaison between research groups.

Issued by the

International Association for the Properties of Water and Steam

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Solubility of Spinels in the Chemical Conditions of Nuclear Reactors

The knowledge of the solubility* of the spinels which constitute the corrosion products in a primary circuit of a PWR is necessary to predict transport and activation of these corrosion products. Several experimental works on magnetite solubility [1,2,3], in a wide range of pH and at temperatures up to 350°C give a good knowledge of its behavior in chemical conditions of the primary circuit, but this is not the case for mixed ferrites, especially for cobalt containing ferrites, which are the most important species regarding contamination.

It is therefore important to know the solubility of the species $Co_xNi_y(Fe,Cr)_{3-x-y}O_4$. Chromium being less labile, it is not necessary to consider its behavior in a first stage of an investigation and only $Co_xNi_yFe_{3-x-y}O_4$ will be taken into account.

Two complementary types of approach may be considered:

1) Solubility measurements of mixed ferrites representative of corrosion products in primary circuit conditions.

2) Determination, or theoretical evaluation, of some of the equilibria involved in the dissolution of ferrites, possibly determined with a better precision than solubility in the conditions of 1), and evaluation of thermodynamic functions of the species involved would provide support for interpretation and extrapolation of available solubility data. This second part is especially the object of this ICRN.

1. Solubility measurements in primary circuit conditions.

Direct solubility measurements of the ferrites involved in primary circuit conditions, for different values of x and y [4,5,6], and fitting of the available experimental results to a set of solubility equations, determined from thermodynamic considerations [8,9] were performed or are in progress in several laboratories.

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*The word *"solubility"* is used for convenience but is not rigorous in the considered case which deals with chemical equilibrium involving different species in the liquid and solid phases.

The measurements are performed in boric acid-lithium hydroxide solutions which contain hydrogen and are oxygen free. The parameters varied are pH (boric acid and lithium hydroxide concentration), temperature (200-350°C), hydrogen pressure.

The solubility equilibria of a mixed ferrite, generally considered when fitting the experimental results, are:

(1) $Co_xNi_yFe_{3-x-y}O_4 + H_2 + 6H^+ = xCo^{++} + yNi^{++} + (3\text{-}x\text{-}y\text{-})Fe^{++} + 4H_2O$ K_O

(2) $Fe^{++} + nH_2O = FeOH^{(2-n)+} + nH^+$ $K_{Fe(n)}$

(3) $Ni^{++} + nH_2O = NiOH^{(2-n)+} + nH^+$ $K_{Ni(n)}$

(4) $Co^{++} + nH_2O = CoOH^{(2-n)+} + nH^+$ $K_{Co(n)}$

with $n = 1,2,3$.

Some authors consider also the presence of Fe^{+++} and associated hydrolysis equilibria [2,9]:

(5) $Fe^{+++} + nH_2O = FeOH^{(3-n)+} + nH^+$ $K'_{Fe(n)}$

This approach is nevertheless limited by the experimental precision of the data. The solubilities are very low, which involves experimental uncertainties in the determinations, and agreement between different laboratories is not obtained even on the temperature coefficients of the solubility. The dependence of hydrogen pressure is also not clear. Continuation in this direction necessitates exchanges between the laboratories involved to compare the experimental procedures, preparation mode of the spinels, and to try to determine the best experimental conditions. No results seem reliable enough at the present time to serve as a guide for a recommended procedure.

2. Determination of involved equilibria and of thermodynamic functions

If equilibria 1-5 are separately well known, and if an empirical rule determining the relation between the ratios of concentrations of different compounds in solution and the composition of the solid is found, it would be possible to calculate all equilibrium concentrations in any conditions. Although it would be unrealistic to expect to obtain a complete determination of solubilities in this way, some of these equilibria may be easier to determine precisely than the total solubility and may help to validate and interpret solubility data. To reach this purpose, 3 research projects are needed:

Determination of hydrolysis constants for cobalt ions

Hydrolysis constants for iron and nickel ions were determined [8,9] from fitting of solubility results of magnetite [1,2] and of nickel oxide [7]. Several sets of hydrolysis constants are available, not always in complete agreement but of the same order of magnitude.

Cobalt ions hydrolysis is less well known. Experimental determination of the solubility of CoO in a wide range of pH and temperature would allow determination of hydrolysis constants and therefore, as the species CoO is well known, thermodynamical functions for the different ions could be determined.

As the cobalt concentration in equilibrium with CoO is expected to be much higher than the one in equilibrium with cobalt-containing ferrites, and as the oxide is easy to obtain as a pure substance, the solubility determination would probably allow determination of hydrolysis constants which may be employed when fitting the ferrites solubility data.

The experimental device could be the same as that used for ferrite solubility measurements.

Determination of the equilibrium constant K_0

Solubility measurements of nickel ferrites, cobalt ferrites, and mixed nickel cobalt ferrites of different compositions in acidic solutions where no hydrolyzed ions are present, would give a direct access to reaction (1). The concentrations in these mediums will be relatively high, allowing more precise results, and the fitting of equations will be better than in the case of primary circuit chemical conditions, because only one equilibrium is involved. It should be then possible to work in a large range of compositions and temperatures, to measure the Fe/M (M=Co or Ni) ratio as a function of x and to obtain K_0 values to be used in solubility data fitting.

Gibbs function of formation of spinels

In order to interpret the results and especially the variation in concentration of given species in equilibrium with different spinels, it is necessary to know the Gibbs energy of formation of spinels as a function of their composition. In a first approximation it can be considered that a spinel $M_xFe_{3-x}O_4$ is an ideal mixture of MFe_2O_4 and Fe_3O_4.

(6) $$\Delta G_{M_xFe_{3-x}O_4} = x\Delta G_{MFe_2O_4} + (1-x)\Delta G_{Fe_3O_4} + \Delta S_{\text{mixing}}$$

the entropy term is small.

The validity of this hypothesis is to be tested. On the other hand, it is also known that spinels may accept some deviation to stoichiometry (presence of vacancies) which may be compatible with incongruent dissolution. The thermodynamics of this phenomena should be investigated.

This can be approached by 2 ways:

1) *From the experimental determination of K_0*

For a given ferrite composition, the relations:

$\ln K_0 = -\Delta G/RT$

will allow, at each temperature, the calculation of the Gibbs function change of the reaction, and as thermodynamic functions for the simple ions Fe^{++}, Fe^{+++}, Co^{++}, Ni^{++} are rather well known, an evaluation of the Gibbs function of the ferrite may be performed.

The evolution of this Gibbs function with the composition of the spinel, and essentially the eventual deviation from the value determined from relation (6) may yield important information.

2) *From theoretical approach*

A model of mixed oxides allowing evaluation of the trends of the variation of Gibbs function when different cations are substituted or when vacancies are produced would help to choose the way of fitting thermodynamic data on experimental results. This necessitates the intervention of a solid physics laboratory.

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