EXPIRED

IAPWS Certified Research Need - ICRN 9

Thermodynamic Models for Transition - Metal/ Water Systems under Steam Generator Conditions

The IAPWS Working Group - Physical Chemistry of Aqueous Solutions has examined the published work in the area of the solubility of transition metal oxides 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. Thermodynamic constants for the formation of aqueous transition metal species are required to model equilibrium aspects of the solubility, mass transport, and corrosion mechanisms of corrosion products in the primary circuits of nuclear reactors and in the boilers of fossil power stations. Relevant parameters include heat capacity and volume function for soluble species, hydrolysis constants, and equilibrium solubility data over a wide range of pH and oxidation potentials at temperatures up to 350 °C.

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 liaise between research groups.

Issued by the

International Association for the Properties of Water and Steam

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IAPWS

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Thermodynamic Models for Transition - Metal/ Water Systems under Steam Generator Conditions

Models to describe the solubility and stability of transition metal oxides and ferrites are required for chemical control in thermal and nuclear steam generators, and in the primary coolant circuits of nuclear reactors.

The temperature range of interest is 250 °C to 350 °C for thermal units and 225 °C to 300 °C for PWR systems. Under normal operation, the alkalinity of the bulk water is 10^{-5} to 10^{-3} mol kg $^{-1}$ KOH, NaOH or LiOH. However the local concentration in crevices or under deposits may exceed 1 mol kg^{-1} in caustic <u>or</u> acid released by corrosion reactions or incongruent precipitation. Models for corrosion product transport and crevice corrosion require a description of solubility gradients, dissolution and precipitation kinetics, colloid transport and corrosion kinetics. This ICRN addresses the aspects of the problem related to equilibrium solubilities of oxides and equilibrium speciation of aqueous transition metals in high temperature water.

Lambert (1) and many workers have identified the critical need for:

1) Accurate equilibrium solubility data for transition metal oxides over a wide range of pH and temperature.

and

2) Accurate solubility and solid phase thermodynamic data to describe the dissolution and sorption behaviour of mixed ferrites.

Unfortunately, technical problems associated with the very low solubilities (10^{-7} to 10^{-9} mol kg $^{-1}$) and the need to characterize the equilibrium redox condition and surface phase make these measurements EXTREMELY difficult (1-6). Hence a further priority is:

3) The development of accurate models for <u>predicting</u> the solubility of transition metal oxides from known room temperature data or molecular properties.

Direct Solubility Measurements of Transition Metal Oxides

The need for direct solubility measurements and some of the experimental problems have been summarized by Lambert (1). Palmer and coworkers (7) have evaluated two of the most detailed studies on the solubility of Fe_3O_4 by Sweeton and Baes (2) and Tremaine and Leblanc (3). Further work on Fe_3O_4 is needed. However, if attempted, new measurements should be at a level of sophistication that addresses the unanswered questions in these two studies related to the oxidation state of the dissolved species, equilibrium pH, and the nature of the equilibrium surface phase.

Mixed Ferrites and Chromites

Data for mixed oxides and ferrites such as Ni_x, Co_y $Fe_{3-x-y}O_4$ are needed to model equilibrium aspects of activity transport in PWR systems. The technical problems are described by Lambert (1) and others (6, 8, 9). Meaningful solubility measurements are even more difficult than those described above because the composition of the solid phase may not be uniform due to incongruent dissolution or precipitation.

Predictive Thermodynamic Models for Aqueous Species

The temperature and pH dependence of oxide solubility are principally controlled by the stability of the aqueous metal ion, and its complexes with hydroxide. For example the solubility of Fe_3O_4 under boiler conditions is controlled by the ferrous and ferric species $Fe^{II}(OH)_2^\circ$, $Fe^{II}(OH)_3$ $Fe^{III}(OH)_3^\circ$ and $Fe^{III}(OH)_4^\circ$. There is considerable uncertainty in the speciation of iron(II) and iron(III) under these conditions. The solubility data are so uncertain that calculations based on estimated stabilities of these species are needed to determine which experiments are clearly wrong. The best results would then be used to refine the calculations. Attempts to do this were made in the 1970's using the Criss-Cobble method (10). The application of the Criss-Cobble method to hydroxy-complexes at temperatures above 200 °C. has since been discredited. More recently, there have been two advances:

(i) Mesmer and Baes (11) have reported very approximate correlations for estimating the properties of hydroxy-complexes at elevated temperatures.

(ii) Helgeson et.al. (12) and others (13-16) have used simple thermodynamic models based on the Born equation for the heat capacity of solvation to predict high-temperature properties for simple M^+ and M^{+2} ions with good accuracy.

There is a critical need to develop physico-chemical models for estimating the thermodynamic properties of aqueous transition metals and their complexes so that reasonably accurate predictions of oxide stability and mass transport can be made under steam-generator conditions.

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ICRN Issue Date: September 1994

ICRN Expiration Date: September 1997

Bibliography

1. I. Lambert, "Solubility of Spinels in the Chemical Conditions of Nuclear Reactors", IAPWS Certified Research Need (December 1992).
2. F.H. Sweeton, C.F. Baes, J. Chem. Thermodynamics, 1970, 2, 479.
3. P.R. Tremaine, J.C. Leblanc, J. Sol. Chem. 1980, 9, 415.
4. P.R. Tremaine, J.C. Leblanc, J. Chem. Thermodynamics, 1980, 12, 521.
5. C.F. Baes Jr. and R.E. Mesmer, The Hydrolysis of Cations (Wiley, 1976).
6. E.W. Thornton, S.M. Walker, TPRD/B/10011/R87 CEGB 1987, (See also TD/RP8/REP/0016 CEGB 1990).
7. D.A. Palmer and S.E. Drummond, J. Phys. Chem. 1988, 92, 6795; (See also D.A. Palmer, K.E. Hyde Geochim Cosmochim Acta 1993, 57, 1393).
8. Y.L. Sandler, R.H. Kunig, Nucl. Sci. and Eng., 64, 866, 1977; (See also 77, 211, 1981).
9. D. Barbour and D. Lister, Int. Atomic Energy Agency Paper IAEA - SM-264/15, 1982.
10. D.D. Macdonald and P. Butler Corrosion Sci. 1973, 13, 259; (See also Atomic Energy of Canada Limited Reports AECC 4136, 4137, 4138, and 4139 (1972).)
11. C.F. Baes Jr. and R.E. Mesmer, Amer. J. Sci. 1981, 281, 935.
12. H.C. Helgeson, D.H. Kirkham and G.C. Flowers, Amer. J. Sci. 1981, 281, 1249.
13. E.L. Shock and H.C. Helgeson, Geochim. Cosmochim. Acta, 1988, 52, 2009.
14. J.K. Hovey, P. Tremaine, Geochim. Cosmochim. Acta, 1986, 50, 453.
15. J.K. Hovey, L. Hepler and P. Tremaine, J. Phys. Chem., 1982, 92, 1323. See also Properties of Water and Steam, M. Pichal and O. Sifner eds. (Hemsphere, 1989, p 351.
16. P. Tremaine, Proc. Symp. on Chemistry in High-Temperature Water EPRI NP-6005, 1990.