

EXPIRED

IAPWS Certified Research Need - ICRN 4

Interaction Between Sodium Salts (Phosphates, Sulfates, Silicates, Borates) and Transition Metal Oxides

The IAPWS Working Groups - Power Cycle Chemistry and Physical Chemistry of Aqueous Solutions have examined the published work in the area of interactions between anions and transition metal oxides, which are 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 research need is to determine the solubility of sodium sulphates, borates and silicates in contact with  $\text{Fe}_3\text{O}_4$ ,  $\text{NiO}$ ,  $\text{ZnO}$ ,  $\text{Cr}_2\text{O}_3$  and other transition metal oxides at temperatures up to  $360^\circ\text{C}$ .

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 act as a liaison between research groups.

**Issued by the**

**International Association for the Properties of  
Water and Steam**

**President: J.R. Cooper**  
**Queen Mary and Westfield College**  
**London E1 4NS England**

**Executive Secretary: Dr. R.B. Dooley**  
**Electric Power Research Institute**  
**Palo Alto, California 94304 USA**



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## Interaction Between Sodium Salts (Phosphates, Sulfates, Silicates, Borates) and Transition Metal Oxides

Reliability of power station steam generating equipment depends largely on the thermal/mechanical and electrochemical stability of protective oxide layers which coat internal surfaces. In this respect, most stressed areas are where steam raising causes local concentration of dissolved solids, present in bulk boiler water, from a few parts-per-million level to up to 1 mol/kg and perhaps higher. Some chemical compounds may locally in-service reach their solubility limit and precipitate, causing a reduction in their bulk boiler water concentration (chemical hide-out). During low loads and power generating unit shutdown periods the precipitated solids may partially or totally redissolve elevating relevant species' concentrations and a combination of mechanical stress, high temperatures and presence of concentrated solutions often results in corrosion attack. Corrosion risks are particularly high when hide-out process is accompanied by local boiler water pH changes due to incongruent solids precipitation. In this respect, behavior of salts of polyprotic acids is most relevant. The concentration phenomenon and power station equipment corrosion risks are in principle common to both nuclear and fossil fuel fired units.

Although much corrosion research work has been done and published on the impact of concentrated contaminant solutions on integrity of various alloys, relatively little is known about relevant reaction mechanisms at the metal oxide/boiler water interface. Knowledge of reactivity of transition metal oxides and dissolved ionic species with salts of polyprotic acids (such as phosphoric, sulfuric, silicic and boric) is particularly important for establishing correct cycle corrosion protection control strategies.

Recent studies [1,2] have shown that sodium phosphates of certain Na/PO<sub>4</sub> ratios react with magnetite, NiO, and ZnO, forming relatively stable solid reaction products. Reactions such as



consume phosphate and thus can cause Na/PO<sub>4</sub> ratios to rise above 3.0 [3].

It is interesting to note that sodium phosphate is added to boiler water to maintain stable pH and minimize magnetite solubility. The precipitation reaction, which has been studied at temperatures up to 360°C, was found incongruent, generating alkali in liquid phase and conjugate solid acids. In the industry, the



uptake and the release of phosphates can thus be accompanied by large pH excursions, potentially leading to local metal wastage and/or cracking. The reaction mechanism, identified under laboratory conditions, is consistent with the "phosphate hide-out" phenomenon in operating units. Its full understanding permitted adjustment of boiler chemical control strategies and reduced unreliability in related equipment using phosphate treatment.

At present, it is not clear whether salts of other polyprotic acids, such as sulfates, silicates and borates, which are commonly present contaminants in power generation cycles, behave similarly to phosphates potentially also creating corrosive environments. Although scientific reference data is in this respect rather limited, circumstantial coincidence points to some similarities.

The stability of the transition metal sulfates in high temperature water has been examined by Swaddle and co-workers [4]. They found that solutions of iron (II) and chromium (III) all yield the hydrate  $Me_x(SO_4)_y \cdot zH_2O$  / in preference to the oxides or ferrites that are stable in the absence of sulfate. Sawochka reported adsorption of sulphates in an Inconel capillary tubing heated to 300°C [5]. In their field test program on PWR units, Sawochka found that only a fraction of sulfates return to solution during unit power reduction, implying that sulfates formed stable solid reaction products. High temperature solubility of pure sodium sulfate has been studied by Lietzke and Marshall [6] among others.

The rich chemistry of metal-silica systems has been examined in depth, particularly by the geochemical community, and it is not intended to be summarized here. What appears very relevant is the fact that silica plays a major role in altering the kinetics of magnetite dissolution through the formation of acmite  $NaFeSiO_6$  [7].

#### Needed Research Activities

The main research need is to determine the solubility of sodium sulfates, borates and silicates in contact with magnetite, NiO, ZnO, Cr<sub>2</sub>O<sub>3</sub> and other transition metal oxides potentially present in power generation cycles at temperatures up to 360°C. Any study should also determine whether the precipitation reaction is incongruent and, if possible, to fully characterize the solid phases formed.

The reaction product solubility data, generated by these studies can, in principle, be modeled by chemical equilibrium codes and possibly by reaction path codes as well. Near critical non-ideality effects can be described by suitable modern approaches.

The effect of hide-out and hide-out return reactions on protective magnetite and other oxide films should be determined.



**IAPWS Contact:** Mr. J. Stodola  
Ontario Hydro Operations Support  
700 University Avenue  
Toronto, Ontario M5G 1X6 Canada  
Telephone: (416) 506-4615  
Fax: (416) 978-0087

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