IAPWS Certified Research Need – ICRN

Corrosion mechanisms related to the presence of contaminants in steam/water circuits, particularly in boiler water.

The IAPWS Power Cycle Chemistry Working Group is aware of widespread information on the corrosion of steam generating plants that can arise as a result of the presence of contaminants in feedwater and boiler water. Non-volatile solutes are able to concentrate in the liquid phase as steam is generated, producing local chemical conditions that are very different from those existing in the bulk water phase. A number of corrosion mechanisms, including general corrosion, pitting and cracking processes such as corrosion fatigue, stress corrosion cracking and hydrogen damage can then ensue.

IAPWS recognises that certain contaminants are regarded as more likely to cause corrosion than others. Acidic chlorides present a substantial threat that is frequently encountered. Other contaminants (sulfates, bromides, fluorides, nitrates, acetates, etc.) all contribute corrosion risks that may be less severe. Currently, there remains a need for a comprehensive technical explanation of the variability and the potential of aggravated corrosive conditions that may be established through combinations of ionic impurities in the feed water. There can also be a serious corrosion risk if highly alkaline conditions are allowed to develop. This corrosion requires appreciably more concentrated solutions than those that are able to support acidic attack but the development of these conditions is possible because of the high solubility / low melting point of compounds such as sodium hydroxide.

Although encouraging work in this area, 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.

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International Association for the Properties of Water and Steam

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Background

Whenever boiling occurs there is a possibility of stimulating chemical changes in the liquid and vapor phases. In a boiler producing steam for power plant or process applications, any volatile solutes will be preferentially located in the vapor phase while non-volatile solutes are predominantly retained in the liquid phase. Ammonia and some amines that are used for feedwater treatment are volatile and their loss from the boiler water can result in a reduction in pH in the remaining liquid [1, 2]. Contaminant ions such as sodium, potassium, chloride, bromide, sulfate, nitrate, etc. constitute non-volatile solutes, which can concentrate to a very high level, particularly when heat flux is high and where porous deposits have accumulated in the boiler.

In practical terms, the corrosion risk associated with contaminants is managed by limiting the allowable concentrations of the ionic/soluble species and by the additional dosing of small amounts of alkaline solutes to the boiler water in order to prevent the development of acidic concentrates. For example, the IAPWS Technical Guidance Document for Volatile treatments for the steam-water circuits of fossil and combined cycle/HRSG power plants describes the limits at various locations in the feedwater train for sodium and conductivity after cation exchange (CACE) to boilers operating using volatile amines for alkalinity control [3]. There is a secondary risk if excessively alkaline conditions are allowed to develop, either as a result of ingress to the circuit of alkaline contaminants or from over-dosing of the alkaline solutes. The IAPWS Technical Guidance Document for Phosphate and NaOH treatments for the steam-water circuits of drum boilers of fossil and combined cycle/HRSG power plants recommends limits for phosphate concentration and CACE and describes various action levels to mitigate the effects of excessively alkaline chemistry conditions [4].

In addition to the effect of concentration of impurities by boiling, the formation of corrosive acidic conditions can be stimulated by the action of oxidising agents (residual oxygen, ferric ions, cupric ions, etc.). In some cases, this has led to the use of reducing agents added to the feedwater to suppress the concentration of oxidising impurities. This practice has a detrimental effect on the solubility of protective iron oxides, and is no longer universally adopted.

It is generally recognised that chloride contamination provides the greatest risk of boiler corrosion, particularly in combination with the presence of oxidising agents. However, the relative risks associated with other common contaminants are not fully quantified and the factors controlling these risks have not been comprehensively evaluated. Additionally, it is not well understood how the combination of various ionic impurities may interact to create a complex corrosive solution.

Possible risk factors

All corrosion processes rely on mechanisms for removing a proportion of the corrosion product from the metal surface, enabling on-going access of the corrosive medium to the substrate [5].

This implies that the following chemical parameters need to be quantified in order to provide an advanced understanding:
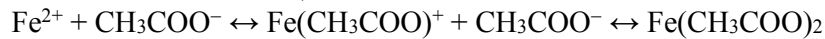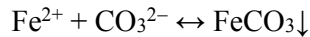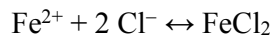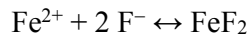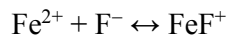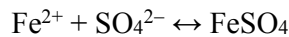
Acid strength / dissociation

The anions of strong acids can generate lower pH at the corrosion site. Anions migrate in the electric field within the solution, accumulating at anodic corrosion sites. Additionally, the hydrolysis of corrosion product cations can generate acidic solutions provided the accumulating anions form strong acids [6]:

e.g., $Fe^{2+} + H_2O \leftrightarrow FeOH^+ + H^+$

$Fe^{2+} + 2 H_2O \leftrightarrow Fe(OH)_{2\,(aq)} + 2 H^+$ etc.
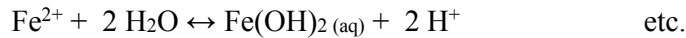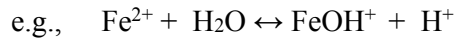
There is a strong interaction between the dissolved ions or aqueous species and the solid-phase species that are invariably present.

Complex formation

There is a need to consider reactions such as:

$Fe^{2+} + SO_4^{2-} \leftrightarrow FeSO_4$
$Fe^{2+} + F^- \leftrightarrow FeF^+$
$Fe^{2+} + 2 F^- \leftrightarrow FeF_2$
$Fe^{2+} + 2 Cl^- \leftrightarrow FeCl_2$
$Fe^{2+} + 2 Br^- \leftrightarrow FeBr_2$
$Fe^{2+} + CO_3^{2-} \leftrightarrow FeCO_3\downarrow$
$Fe^{2+} + CH_3COO^- \leftrightarrow Fe(CH_3COO)^+ + CH_3COO^- \leftrightarrow Fe(CH_3COO)_2$

There is some information on all of these equilibria [7]. All equilibrium constants are small at low temperatures (the complexes are barely measureable except for fluoride and carbonate), but are appreciable at boiler temperatures. The acetate equilibria have been studied at high temperatures [8], while measurements of the equilibria for ferrous chloride are available at low temperature [9]. It is necessary to consider the interdependence of the above equilibria with the effect of pH on the anion ligands. This is particularly important for sulfate, fluoride, carbonate and acetate.

Solubility of corrosion product salts

The solubility of corrosion products in high temperature water has been extensively studied [10]; however, the solubility of some of the complexes described above is less well known. Whereas FeF_2 is only slightly soluble, many other anions can generate corrosion products with high solubility ($FeCl_2$, $FeBr_2$, $FeSO_4$, etc.). Knowledge of the solubility of iron-anion complexes is important in that it can influence the transport of corrosion products away from the corrosion site and increase the overall severity of the material degradation.

<u>Combinations of impurity ions</u>

The effect of individual impurity ions is important to identify. However, in practice combinations of several cations/anions are typically present and may interact to produce more aggressive conditions that promote pitting and/or cracking (reduced sulfur species for example). The total ionic charge balance must be considered, including any redox reactions that may complicate deposit/crevice chemistry, to quantify the net equilibrium effect for the reactions described above.

This list of risk factors may not be comprehensive. It does, however, illustrate the fact that knowledge of the underlying equilibria for the reactions described above and their interdependence, which may be formulated by considering the overall ionic charge balance in the solution, are required fully to understand the impacts of impurity ingress into a boiler system.

Sources of contaminants

In practical operation of steam generating plants the following contaminants are frequently encountered:

Chlorides arising from in-leakage of cooling water (particularly at coastal sites).

Chloride and bromide ions arising from thermal decomposition of covalent organo-halide impurities in make-up water.

Sodium, sulfate, chloride and resin decomposition products (potentially including acetate) arising from ion exchanger sources.

Sulfates arising from in-leakage of cooling water (at some river cooled plants).

Fluoride residues from welding fluxes.

Carboxylic acids from the breakdown and oxidation of organic impurities.

Phosphate. Although alkaline phosphates may be deliberately dosed as an additive, acidic phosphates can become corrosive at higher concentrations.

Carbon dioxide / bicarbonate / carbonate from the breakdown and oxidation of organic impurities or from air ingress.

Etc.

The sources of the contaminants vary from plant to plant and must be addressed on a plant-specific basis. The corrosion risk can develop irrespective of source. The above list is given to indicate the range of sources; other possible contaminants may be encountered.

Research Needed

There is a need to quantify the risk factors and to develop a robust ranking procedure for common contaminant species and their combinations that may be encountered during plant operation. While it is desirable to understand all the contributions from all the species listed above, the primary interactions of simple amines used in volatile treatments (ammonia) with chloride and/or sulfate should provide a baseline for comparison.

Specific research needs identified include:

1. Assessment of the equilibrium chemistry at high temperature for various concentrations of ammonia in combination with specific anionic impurities; priority is given to chloride and sulfate.

2. Assessment of the extent to which the complex formation reactions can hold corrosion products in solution and allow their transport away from the corrosion site.

3. Examining the effects of various concentrations of ammonia and chloride on localized corrosion and degradation mechanisms.

4. Examining the effects of various concentrations of ammonia and sulfate on localized corrosion and degradation mechanisms.

5. Examining the effect of combinations of chloride and sulfate on localized corrosion and degradation mechanisms.

The practical outcome would provide a basis for more selective application of monitoring efforts and corrosion countermeasures in steam generating plants.

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