Using of Pourbaix diagram for evaluation of water chemistry recommended for ultra-supercritical parameter of water coolant

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Abstract. An important indicator the reliable operation of the steam-water cycle at power plants is water chemistry. Special chemicals are used to correct water chemistry. At designing a new unit the selection of the chemicals is determined by the parameters of the water and steam and materials, used in different parts of the cycle. Oxygen and ammonia are used to correct water chemistry at units with supercritical parameters In the presence of these reagents the protective film is formed on the surface of the metal.

The transition to ultra-supercritical parameters requires the using of new materials, used in the water-steam cycle. Austenitic steels are recommended to replace on inconel steels. Oxygenated treatment and all-volatile treatment under oxidizing conditions were recommended to apply at units of ultra-supercritical parameters. However to select the optimum water chemistry is necessary to have date on the conditions of formation the protective film on the inconel surfaces.

On the basis of Pourbaix diagram is proposed to evaluate the influence of water chemistry on the forms of existence the oxides of nickel and chromium on the surface of inconel at high parameters of water coolant. The results of calculations are compared with the experimental data.

At present, in Russian energy sector the tendency exists to implement ultra-supercritical steam parameters (USC) [1]. Temperature increase up to 700 °C and pressure increase up to 35 MPa result in necessity for obtaining of data on construction materials and chemical-water treatments, which can be used for power units with USC. Implementation of new parameters makes problematic the option for austenitic steels use as the main structural material for boilers equipment of thermal electric power plants. The need to replace the austenitic steels is associated with the process of protective film formation on the steam side. For power units, where oxygenated treatment (OT) and all-volatile treatment under oxidizing conditions (AVT(O)) is used, the main protective film on the alloy surface is magnetite (Fe₃O₄) [2]. Formation of an oxide layer on the surface of austenitic steel in the steam medium occurs in accordance with the reactions as follows:

\[3Fe + 4H_2O_{(steam)} \leftrightarrow Fe_3O_4 + 4H_2\]  \hspace{1cm} (1)

\[Fe + H_2O_{(steam)} \leftrightarrow FeO + H_2\]  \hspace{1cm} (2)

\[3FeO + H_2O_{(steam)} \leftrightarrow Fe_3O_4 + H_2\]  \hspace{1cm} (3)
Each of these reactions is characterized by its own equilibrium constant: 

for reaction 1

\[ K_p = \frac{p_{H_2}^4}{p_{H_2O}^2} \]  

(4)

for reaction 2

\[ K_p = \frac{p_{H_2}}{p_{H_2O}} \]  

(5)

for reaction 3

\[ K_p = \frac{p_{H_2}}{p_{H_2O}} \]  

(6)

where \( p_{H_2} \) and \( p_{H_2O} \) are the partial pressures of hydrogen and steam, respectively.

The dependence of the equilibrium constants on the temperature is graphically expressed by the Shodron diagram, see Figure 1.

![Shodron diagram](image)

**Figure 1.** Shodron diagram [2]

The above diagram testifies that at the temperatures lower, than 570 °C, this is the equilibrium constant of the reaction 3 plays the main role, this results in magnetite formation, which is more thermodynamically stable compound up to the temperature of 570 °C, being formed in accordance with the reaction (1), to which the equilibrium constant (4) corresponds. At the temperatures above 570 °C, ferrous oxide is more thermodynamically stable compound, being an iron oxide formed in accordance with the reaction (2), to which the equilibrium constant (5) corresponds; the above oxide does not exhibit protective properties.

As it was noted earlier, steam temperature in the boiler with USC is much higher than 570 °C. Consequently, in the steam area, a protective film of magnetite cannot be formed in the USC power units. For this reason, it was proposed to use Inconel alloys for USC power units. These alloys are practically free from iron and consist mainly of nickel (50-60%) and chromium (20-25%), and other
alloying components. Table 1 presents the composition of alloys, which are recommended for implementation at power units with USC [1].

**Table 1.** Structural materials for manufacturing of boiler equipment at thermal electric power plants with ultra-supercritical parameters [1]

| Alloy | Alloy composition | Field of application               |
|-------|-------------------|-----------------------------------|
| 617   | 55Ni-22Cr-9Mo-12Co-Al-Ti | Superheater, re heater, pipelines, heaters |
| 230   | 57Ni-22Cr-14W-2Mo-La | Superheater, re heater, pipelines, heaters |
| 740H  | 50Ni-25Cr-20Co-2Ti-2Nb-V-Al | Superheater, re heater, pipelines, heaters |
| 282   | 58Ni-10Cr-8.5Mo-2.1Ti-1.5Al | Pipelines, heaters |

The experimental data are practically not available to estimate the above construction materials behavior under the above conditions in the stream media [3]. These structural materials were tested mainly in the hot air [4].

Corrosion of the steam-generating circuit basically can be regarded as an electrochemical process, the course of which depends upon the presence of oxidizing agents or of reducing agents, which create one or another oxidation-reduction potential (ORP) in the working environment. Corrosion products are mainly weak electrolytes, which behavior depends upon the pH of the medium. Thus, for any given temperature, the main physical & chemical parameters, which allow controlling corrosion activity of the medium, are pH and ORP. To perform this control, it is necessary to know the boundaries of thermodynamic stability of corrosion products being formed at a given temperature at various pH and ORP values [5]. The pH - ORP diagrams are also called the Pourbaix diagrams.

The main Inconel alloys components are chromium and nickel that is why the main possible reactions of these elements in the water medium were considered, see table 2 and table 3.

**Table 2.** Reactions equations for Cr - H₂O systems

| Compound | Reaction |
|----------|----------|
| Cr⁺⁺⁺⁺ | Cr = Cr⁺⁺⁺⁺ + 2e⁻ |
| Cr⁺⁺⁺ | Cr = Cr⁺⁺⁺ + 3e⁻ |
| Cr⁺⁺ | Cr⁺⁺⁺ + e⁻ |
| CrO | Cr + H₂O = CrO + 2H⁺ + 2e⁻ |
| CrO | Cr⁺⁺ + H₂O = CrO + 2H⁺ |
| Cr₂O₃ | 2Cr + 3H₂O = Cr₂O₃ + 6H⁺ + 6e⁻ |
| Cr₂O₃ | 2CrO + H₂O = Cr₂O₃ + 2H⁺ + 2e⁻ |
| Cr₂O₃ | 2Cr⁺⁺⁺ + 3H₂O = Cr₂O₃ + 6H⁺ |
| CrO₄⁺² | Cr⁺⁺⁺ + 4H₂O = CrO₄⁺² + 8H⁺ + 3e⁻ |
| CrO₄⁺² | Cr⁺⁺⁺ + 4H₂O = CrO₄⁺² + 8H⁺ + 6e⁻ |
| CrO₄⁺² | Cr₂O₃ + 5H₂O = 2CrO₄⁺² + 10H⁺ + 6e⁻ |
| CrO₂⁺ | CrO₄⁺² + 2H₂O = CrO₄⁺² + 4H⁺ + 3e⁻ |
| CrO₂⁺ | Cr₂O₃ + 2H₂O = CrO₂⁺ + 4H⁺ + 3e⁻ |
| CrO₂⁺ | Cr₂O₃ + H₂O = 2CrO₂⁺ + 2H⁺ |
| CrO₂⁺ | CrO + H₂O = CrO₂⁺ + 2H⁺ + e⁻ |
Table 3. Reactions equations for Ni - H\textsubscript{2}O systems

| Compound | Reaction |
|----------|----------|
| Ni\textsuperscript{2+} | \(Ni = Ni^{2+} + 2e^-\) |
| NiO | \(Ni + H_2O = NiO + 2H^+ + 2e^-\) |
| NiO | \(Ni^2+ + H_2O = NiO + 2H^+\) |
| Ni\textsubscript{3}O\textsubscript{4}2H\textsubscript{2}O | \(3NiO + 3H_2O = Ni_3O_4 \cdot 2H_2O + 2H^+ + 2e^-\) |
| Ni\textsubscript{3}O\textsubscript{4}2H\textsubscript{2}O | \(3Ni^{2+} + 6H_2O = Ni_3O_4 \cdot 2H_2O + 8H^+ + 2e^-\) |
| Ni\textsubscript{3}O\textsubscript{4}2H\textsubscript{2}O | \(3HNiO_2^- + H^+ = Ni_3O_4 \cdot 2H_2O + 2e^-\) |
| HNiO\textsubscript{2}^- | \(Ni + 2H_2O = HNiO_2^- + 3H^+ + 2e^-\) |
| HNiO\textsubscript{2}^- | \(NiO + H_2O = HNiO_2^- + H^+\) |
| HNiO\textsubscript{2}^- | \(Ni^{2+} + 2H_2O = HNiO_2^- + 3H^+\) |

The above equations testifies that two reaction types take place in water medium, i.e. oxidation-reduction reactions and replacement reactions.

This is the Nernst equation, which is the major equation describing oxidation-reduction process on the metal surface under the impact of the contact medium.

Nernst equation

\[
E = E^0 + \frac{2.3 \cdot RT}{n \cdot F} \log \left( \frac{a_{\text{ox}}}{a_{\text{red}}} \right)
\]

where \(E^0\) is standard electrode potential; \(R\) is gas constant; \(F\) is the Faraday constant; \(T\) is temperature; \(n\) is the quantity of electrons; \(a\) is activity of oxidized and reduced forms.

The spontaneous process of transition of the system to an equilibrium state is characterized by a change in the Gibbs energy (\(\Delta G_p\)), which value can be calculated by the equation 8:

\[
\Delta G_p = \sum G_{pr} - \sum G_{bas}.
\]

where \(\sum G_{pr}\) is Gibbs energy products of reaction, \(\sum G_{bas}\) is Gibbs energy basic compound.

The change in Gibbs energy of the oxidation-reduction reaction, related to the standard electrode potential, is described by equation 9:

\[
E^0 = \frac{\Delta G_p}{n \cdot F}
\]

The equilibrium constant of any chemical reaction is characterized by the equilibrium constant. The relationship between the change in Gibbs energy and the equilibrium constant is expressed by the equation 10:

\[
\Delta G_p = -RT \cdot \ln(K_p)
\]

From the above equations, it follows that the main variable is the change in Gibbs energy. Experimental data on the change in Gibbs energy are mainly available only for the temperature of 25 °C [6,7]. For high temperatures, the \(\Delta G_p\) values were determined by calculation. The calculations were made for the reactions presented in Table 2, according to which the following compounds are formed at the temperature of 373 °C: Ni\textsuperscript{2+}, NiO, Ni\textsubscript{3}O\textsubscript{4}2H\textsubscript{2}O, HNiO\textsubscript{2}-, Cr\textsuperscript{2+}, Cr\textsuperscript{3+}, CrO, Cr\textsubscript{2}O\textsubscript{3}, CrO\textsubscript{4}\textsuperscript{2-}, CrO\textsubscript{2}-. As a result of the calculations, the regions of existence of individual nickel and chromium compounds at the water-metal interface were determined for various ORP and pH values Figure 2 and Figure 3.
Figure 2. Diagram pH – ORP for Ni-H₂O system at the temperature of 373 C.
The dashed lines are the boundaries of forms of existence at concentration in water of 10⁻⁷ mol/dm³; the solid lines are boundaries of forms of existence at concentration of 10⁻⁶ mol/dm³.

It follows from the above diagram, that at ORP > 0, the region of formation of Ni₃O₄.2H₂O, which is supposed to be protective film, is in the pH range from 5 to 7.

Figure 3. Diagram pH – ORP for Cr-H₂O system at the temperature of 373 C.
The dashed lines are the boundaries of forms of existence at concentration in water of 10⁻⁷ mol/dm³; the solid lines are the boundaries of forms of existence at concentration of 10⁻⁶ mol/dm³.
It follows from the diagram that for ORP values $> 0$, the formation region of $\text{Cr}_2\text{O}_3$, which is a protective film, is in the pH range from 2 to 6. When pH increase, the $\text{CrO}_4^{2-}$ ion becomes thermodynamically more stable compound.

In accordance with PTE standards [8] at thermal power plants with supercritical parameters in the neutral-oxygen chemical water treatment, the pH of the feed water is normalized in the range of 6.5 - 7.5, and in the case of ammonia oxygen the feed water is normalized in the range 7.5 - 8.5. Due to the fact that in the diagrams the pH values are presented for the temperature of 373 °C, and in PTE standards the pH values are presented for the temperature of 25 °C, the pH values were recalculated for pH25 in accordance with the dependence given in [9].

For $\text{Ni-H}_2\text{O}$ system, pH25 range is 6.2 – 8.2; for $\text{Cr-H}_2\text{O}$ system, pH25 range is 3.2 – 7.2. It follows from the results presented above, that implementation of OT is preferable for nickel and chromium oxides protective films formation.

Surveys of a number of supercritical steam parameter and USC power units in China, where high chromium steels were used as structural materials, revealed the presence of $\text{CrO}_4^{2-}$ ion in the feedwater and in water steam in the course of oxygen-ammonia chemical water treatment [10].

It was found out, that when operating the thermal electric power plant, under the conditions of transfer from supercritical steam parameter to USC, increase of water temperature in the economizer results in increase of $\text{CrO}_4^{2-}$ ions concentration. In authors' assumption, significant differences in content of this ion are resulted from the values of concentration of oxygen, pH value, chromium content in the alloy, and temperature of the coolant. The results obtained in the course of operation of the supercritical steam parameter and USC power units do not reveal the reason for the increase in the $\text{CrO}_4^{2-}$ ion content in the feedwater. From the obtained diagram for the $\text{Cr-H}_2\text{O}$ system ‘see Figure 3’, it can be concluded that the region of existence of the $\text{CrO}_4^{2-}$ ion in the feedwater increases with increase pH. The upper limit of pH25 values according to IAPWS [11] standard, i.e. 9.8, corresponds to pH value of 8.6 at 373 °C. At the given pH value, the formation of the $\text{CrO}_4^{2-}$ ion occurs in the range of ORP from -0.3 to 0.1 V.

The results of calculations of existence of nickel and chromium forms in water coolant with USC are correlated with the data on operation of existing power units. The results of the calculations can be recommended for use in the design of power units with USC.

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