

Original Paper

## Evaluation of pH Increment due to Hide-out of Phosphates in High Temperature Water

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With a view of elucidating the buffering effect of sodium phosphates in high temperature water, the dissociation constants of phosphoric acid are estimated by using of reported data and isocoulombic equation principle, and then pH of sodium phosphate solutions is calculated at boiler water temperature. The results indicated that in term of pH the sodium phosphate solutions were close to sodium hydroxide solution with temperature raising and the molar ratio of sodium to phosphate was not a significant factor in controlling pH of bulk water at boiler water temperature. This means that there is little need to perform the blow-down of boiler water and reinject di-sodium hydrogen phosphate, even though the hide-out occurred, as long as the concentration of phosphate species in boiler water is kept above the lowest level for prevention of hardness ion precipitation.

Key Words: hide-out, high temperature water, sodium phosphate treatment, dissociation constant

### 1. Introduction

Sodium phosphates are widely used in drum-type boilers to serve as a pH buffer for corrosion control and for prevention of scale deposition by precipitation of hardness ions. The concentration of phosphate species and the molar ratio of sodium to phosphate are regulated to be within the range of 0.1 to 3 ppm, and 2.5 to 2.8, respectively, based on corrosion tests, field experiences<sup>1) 3)</sup> and dependence of pH on the molar ratio at room temperature. It is, however, not easy to maintain the regulation in practical boiler operation<sup>4)</sup>, because boiling induces concentration and/or precipitation of phosphate compounds on the heat-transfer surface of boiler tubes. In particular,

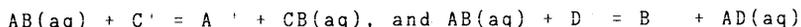
phosphate species in boiler water concentrate preferentially on heated surfaces compared to sodium, resulting in a significant increase in molar ratio in boiler water. This phenomenon, known "Hide-out", is supposed to make boiler water caustic, and cause caustic corrosion of boiler materials.

In order to avoid such problems, many efforts have been taken for maintaining the regulated values with countermeasures such as frequent blow-down of boiler water containing the high ratio of sodium, and/or injection of fresh  $\text{Na}_2\text{HPO}_4$  solution. This procedures however are not only troublesome for operators, but also cause heat loss in the high temperature water circuit and decrease in thermal efficiency of electric power generation.

With a view of elucidating the buffering effect in high temperature water, the dissociation constants of phosphoric acid in high temperature solution are estimated by using reported experimental data<sup>5)</sup> and the isocoulombic equation principle<sup>6) 7)</sup>. pH of sodium phosphate solutions is calculated at the current boiler water temperature. Based on these data, we discuss the influence of the molar ratio on pH, and questions on the current regulation and its application to cycling boiler.

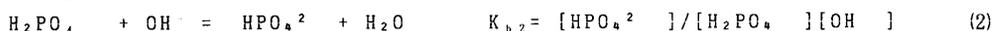
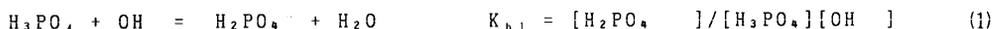
## 2. Estimation of dissociation constant

The dissociation constants were measured experimentally up to 300 °C<sup>5)</sup>. Based on these data, it is necessary to make a prediction for the constants at boiler water temperature 350 °C. A lot of attempts have been made to find a method for the estimation<sup>8)</sup>. Lindsay reported that a straight line relationship was obtained between temperature and the dissociation constants of weak acids and strong bases, or reverse<sup>6)</sup>, in considering the equilibrium constant on following isocoulombic neutralization reactions :



The isocoulombic reactions are formulated by combination of the dissociation reaction of acids or bases with the ionization reaction of water for which detailed thermodynamic data are now available over a wide range of temperatures and pressures<sup>9)</sup>. Although an ionization reaction is accompanied by significant changes in heat capacity and volume due to ion-water interactions in the products, the isocoulombic equation involves no change in the number of ionic charges, and a large portion of the changes due to the ion-water interactions are cancelled out between the products and reactants. Hence the changes in heat capacity and volume are small, and thermodynamic equilibrium constants can be extrapolated from room temperature to high temperature and pressure.

When the principle is applied to the dissociation of phosphoric acid. The isocoulombic neutralization reactions and its equilibrium constants are :



The equilibrium constants were obtained from the dissociation constants of phosphoric acid and water in the temperature range of 0 ° to 300 °C. The constants were plotted against the reciprocal of temperature, and the linear relationships are shown in Fig. 1. In extrapolating this line to 350 °C, the neutralization constants of equations (1) and (2) were found to be  $2.8 \times 10^6$ ,

$1.0 \times 10^2$  respectively. These values may have a little surplus bias, because the experimentally measured constants for hydrolysis of some weak acids and bases have a tendency to curve concavely downward and deviate from the straight lines over  $250^\circ\text{C}$  gradually<sup>10)</sup>

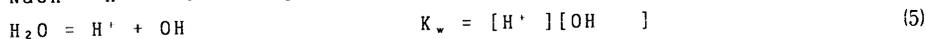
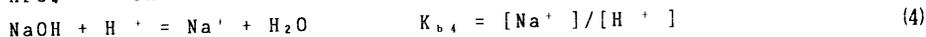
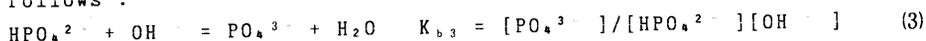
### 3. Calculation of pH of sodium phosphates solution

Simultaneous equations for calculation of pH were set up from the following relationships :

- (a) All the equations of equilibrium constants relating to neutralization of all postulated species.
- (b) The equation of electroneutrality between ionic species.

(c) Mass balance equation pertaining to a material remaining in water. The procedure was applied to neutralization of sodium phosphate, which contains the six ions -  $\text{H}^+$ ,  $\text{OH}^-$ ,  $\text{Na}^+$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{HPO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ .

The neutralization reactions, in addition to the equation (1) and (2), are as follows :



It was known that the equilibrium constant of the equation (3),  $K_{b3}$ , was smaller than 3 over  $150^\circ\text{C}$  and then the concentration of  $\text{H}^+$  formed from dissociation of  $\text{HPO}_4^{2-}$  is smaller than that from water<sup>5)</sup>. Sodium hydroxide completely dissociates in bulk boiler water<sup>11)</sup>. Equation (3) and (4), and the concentration of  $\text{PO}_4^{3-}$ , therefore, may be disregarded when calculating pH at elevated temperatures.

The equation of electroneutrality is :

$$[\text{Na}^+] + [\text{H}^+] = [\text{H}_2\text{PO}_4^-] + 2[\text{HPO}_4^{2-}] + [\text{OH}^-] \quad (6)$$

The mass balance equation in water is :

$$[\text{A}] = [\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}] \quad (7)$$

where [A] is the total concentration of all phosphate species.

From equation (1) and (2) and  $K_w = 5.01 \times 10^{-13}$  :

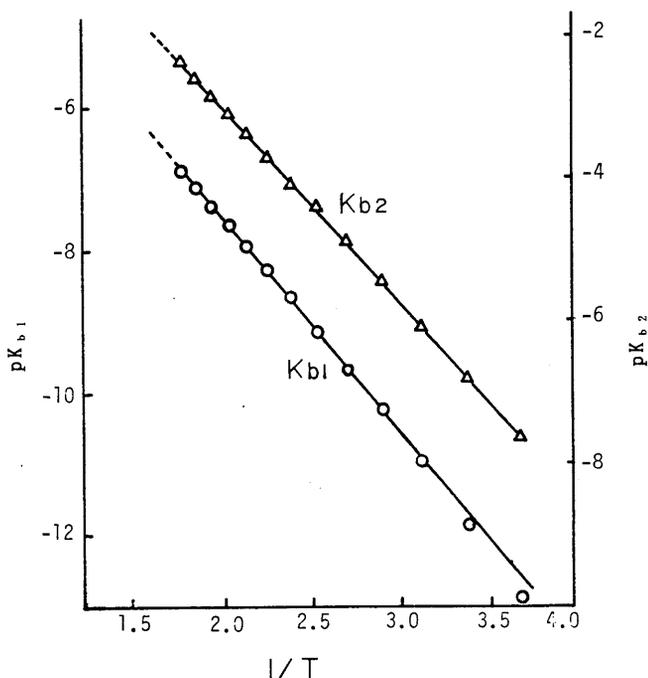


Fig. 1 Temperature dependence of the equilibrium constant for neutralization of phosphate ions

$$K_{b1} = \frac{[\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4][\text{OH}^-]}$$

$$K_{b2} = \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-][\text{OH}^-]}$$

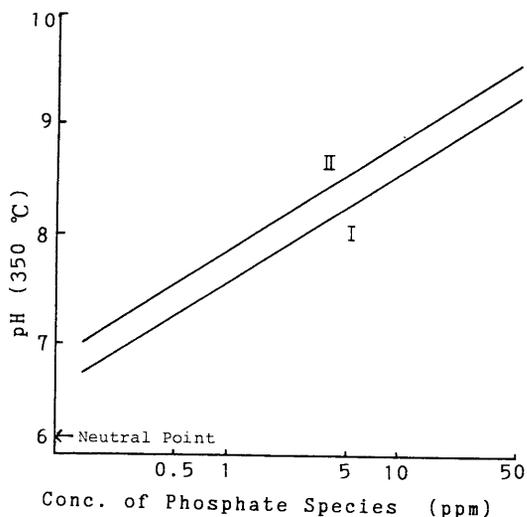


Fig. 2 pH of dilute  $\text{Na}_2\text{HPO}_4$  solution and effect of disappearance phosphate species due to hide-out at 350 °C  
 I :  $\text{Na}_2\text{HPO}_4$ ,  
 II : Complete disappearance of phosphate species from bulk water

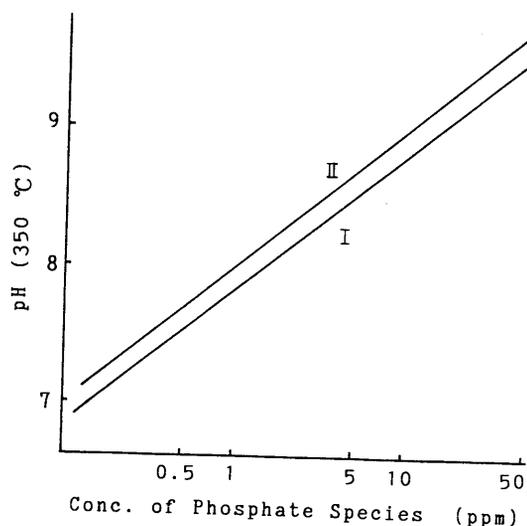


Fig. 3 pH of dilute  $\text{Na}_3\text{PO}_4$  solution and effect of disappearance phosphate species due to hide-out at 350 °C  
 I :  $\text{Na}_3\text{PO}_4$ ,  
 II : Complete disappearance of phosphate species from bulk water

$$[\text{H}_2\text{PO}_4^-] = [\text{H}_3\text{PO}_4][\text{OH}^-] \times 2.8 \times 10^6 = 1.4 \times 10^{-6} [\text{H}_3\text{PO}_4]/[\text{H}^+] \quad (8)$$

$$[\text{HPO}_4^{2-}] = [\text{H}_2\text{PO}_4^-][\text{OH}^-] \times 1.0 \times 10^2 = 7.1 \times 10^{-17} [\text{H}_3\text{PO}_4]/[\text{H}^+]^2 \quad (9)$$

substituting equation (8) and (9) in (6) and (7), and solving the obtained simultaneous equations,  $\text{H}^+$  concentration can be derived as a function of  $[\text{A}]$  for  $\text{Na}_2\text{HPO}_4$  ( $[\text{Na}^+] = 2[\text{A}]$ ) and for  $\text{Na}_3\text{PO}_4$  ( $[\text{Na}^+] = 3[\text{A}]$ ) respectively :

$$\text{Na}_2\text{HPO}_4 ; [\text{A}][\text{H}^+]^3 + (7.05 \times 10^{-7}[\text{A}] - 2.51 \times 10^{-13})[\text{H}^+]^2 - 3.52 \times 10^{-19}[\text{H}^+] - 1.77 \times 10^{-29} = 0 \quad (10)$$

$$\text{Na}_3\text{PO}_4 ; [\text{A}][\text{H}^+]^3 + (9.40 \times 10^{-7}[\text{A}] - 1.67 \times 10^{-13})[\text{H}^+]^2 - (2.52 \times 10^{-17}[\text{A}] - 2.52 \times 10^{-17})[\text{H}^+] - 1.18 \times 10^{-29} = 0 \quad (11)$$

Values of pH at 350 °C were calculated from these equations with a personal computer. The results were plotted against the total concentration of all phosphate species, as shown in Fig. 2 and Fig. 3.

In order to clarify the increment of pH attributed to a decrease in the concentration of the phosphate species in bulk water, pH was calculated by assuming that the phosphate species have completely disappeared by the hide-out and all sodium ion left in the bulk water. Results were plotted against the original concentration of phosphates in Fig. 2 and Fig. 3. By comparing the curves with those of sodium phosphate, it will be noted that the increment of pH due to the hide-out is only 0.3 pH units even under the extreme condition. Further, it would seem that the increment of pH would be slightly smaller than 0.3 units, because  $K_{b1}$  and  $K_{b2}$  of phosphoric acid have a surplus bias as mentioned above.

## 4. Discussion

As the characteristics of water and aqueous solutions change considerably with increase in temperature, the quality of boiler water should be regulated and controlled on the base of the data obtained under the high temperature and pressure conditions. But we have not yet had any specific method to perform the analysis and measurement under that condition. It is, therefore, necessary to cool boiler water to room temperature, in order to analyze, measure it.

In the case of phosphate treatment, the molar ratio has been regulated for pH adjustment by using data of sodium phosphate solution at room temperature, which is shown in Fig. 4 and Fig. 5. This data indicates that pH increases significantly as the molar ratio increases due to the hide-out of the phosphates. It, therefore, is evident that the molar ratio should be controlled in the narrow range, in order to adjust pH to optimal value for corrosion controll.

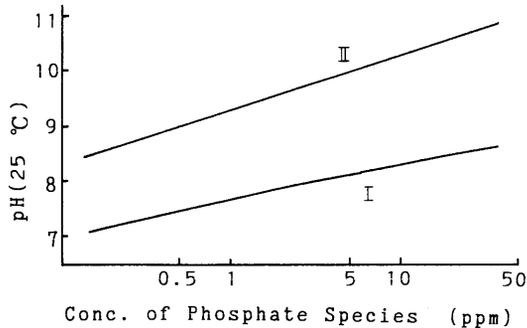


Fig. 4 pH of dilute  $\text{Na}_2\text{HPO}_4$  solution and effect of disappearance phosphate species due to hide-out at room temperature  
I :  $\text{Na}_2\text{HPO}_4$ ,  
II : Complete disappearance of phosphate species from bulk water

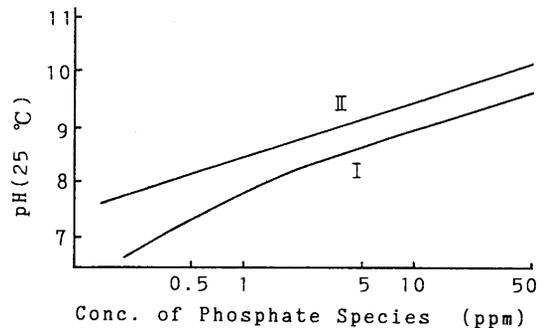


Fig. 5 pH of dilute  $\text{Na}_3\text{PO}_4$  solution and effect of disappearance phosphate species due to hide-out at room temperature  
I :  $\text{Na}_3\text{PO}_4$ ,  
II : Complete disappearance of phosphate species from bulk water

But the characteristics of phosphate solution at high temperature are considerably different from that at room temperature. The results of calculations indicated that pH increment was only slight under boiler water conditions, even if the concentration of phosphate species comes close to zero due to a complete hide-out and the molar ratio increases remarkably. Table 1 shows that the predominant species is di-hydrogen phosphate ion,  $\text{H}_2\text{PO}_4^-$ , at  $350^\circ\text{C}$ , in contrast to hydrogen phosphate ion,  $\text{HPO}_4^{2-}$ , at room temperature. This means that in terms of pH the sodium phosphate solution resembles sodium hydroxide solution with an increase in temperature, and the molar ratio is not a significant factor in controlling of pH of bulk water at the boiler water temperature. Even if the excess of sodium concentrates on the boiling-heat-transfer surface, this is not considered to cause the surface to be highly caustic, because sodium will be neutralized by the phosphate species previously concentrated due to the hide-out on the surface in any form.

Table 1 Share of phosphate species in water  
at room temperature and 350°C

| Phosphates                       | Temperature<br>°C | Share of phosphate species (%) |                                |                                |                               |
|----------------------------------|-------------------|--------------------------------|--------------------------------|--------------------------------|-------------------------------|
|                                  |                   | H <sub>3</sub> PO <sub>4</sub> | H <sub>2</sub> PO <sub>4</sub> | HPO <sub>4</sub> <sup>2-</sup> | PO <sub>4</sub> <sup>3-</sup> |
| Na <sub>2</sub> HPO <sub>4</sub> | 25                | 0                              | 11.1                           | 88.8                           | 0.005                         |
|                                  | 350               | 0.9                            | 98.6                           | 0.5                            | 0                             |
| Na <sub>3</sub> PO <sub>4</sub>  | 25                | 0                              | 0.3                            | 99.5                           | 0.2                           |
|                                  | 350               | 0.005                          | 99.8                           | 0.015                          | 0                             |

Practically, a blowdown of boiler water and reinjection of Na<sub>2</sub>HPO<sub>4</sub> is carried out frequently to keep the molar ratio within the regulation range. Continuous loss of the boiler water which is rich in sodium will deplete sodium inventory in the boiler and reduce total molar ration in the boiler. Further, when the plant load reduced, the phosphate species disappeared by hide-out in normal operation return to bulk water and its concentration increases. Therefore, during load reducing and low load operation, the cumulative loss of sodium and the phosphate return may eventually result in a significant pH depression and require inverse procedure such as injection of Na<sub>3</sub>PO<sub>4</sub>. This is very complicate and burdensome to operators of cycling plants.

From above consideration, it was concluded that there was little need to perform the blow-down and reinjection of sodium hydrogen phosphate in normal operation if it is only for adjustment of pH and the molar ratio, even though the hide-out occurred, as long as the concentration of phosphate species in boiler water is kept above the lowest limit for prevention of scale deposition of hardness ions and leakage of condenser water is not detected. Theoretical estimation of the limit and its dependence on the degree of leakage of condenser-cooling water is an important concern to boiler operators. But it is difficult to estimate the limit theoretically at the present time, because of lack of suitable data on equilibrium constants of reactions between phosphate species and hardness ions under high temperature and pressure. This is considered to be a subject for further discussion.

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