Determination of Phosphate Concentration in Boiler Water using Conductivity Measurements

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Abstract—The impossibility of unambiguously estimating phosphate concentration by measuring boiler-water conductivity in a high-pressure drum boiler ($p_b = 13.8$ MPa) is shown. Mathematical models of ion equilibria in boiler water, which allow one to determine the concentration of phosphates and other ion admixtures from the measurement data obtained with the use of standard (conductormeters and pH-meters) in cooled samples of feedwater and boiler water, are described.

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Obtaining the decrease in acceptable phosphate excess specified in the 15th edition of Rules for Operation [1] requires reliable monitoring, with an automated monitoring being desirable The system of chemicaltechnological monitoring (SCTM) functioning at many thermal power stations (TPSs) is capable of rendering timely information on water chemistry to the staff and fulfilling monitoring and diagnosing functions. At the present time, there is no automated measuring of phosphate concentrations. In addition, sodium concentrations in the boiler water are not measured as well, although knowledge of this data would expand SCTM diagnostic potentialities.

The measurement of specific conductivity (hereafter referred to as conductivity) aimed at determining phosphate excess has been attracting the attention of specialists for many years [2-4]. The unique linear dependence of conductivity on phosphate concentration measured under laboratory conditions for smallconcentration water solution of sodium phosphate differs from that obtained for the boiler water in a clean compartment (CC) of boiler drums at various cogeneration plants (Fig. 1). We see that, even in a narrow phosphate concentration range of 0.5-2.0 mg/l, which is typical for clean compartments, the dependence $[PO_4^{3-}] = f(\kappa)$ cannot be described unambiguously. This is explained, in particular, by the fact that, at low phosphate excess values, sodium chlorides and carbonates significantly contribute to the boiler water conductivity, while such a contribution to the conductivity of CC boiler water is attributed to ammonia. Due to this, conductivity measurements cannot give reliable information for organizing automated phosphate metering. Traditionally, phosphates are metered proportionally to the steam or feedwater flowrate. Adjustment of the phosphate metering based on the conductivity data complicates the introduction of an automated phosphatizing regime. Figure 2 gives daily monitoring records of the automated conductivity recorders for an industrial boiler in the case in which the medium flows in the drum from right to left. The data given point to the complexity of the problem of monitoring phosphate concentrations based on the data on measured boiler water conductivity. In addition, based on the results of conductivity measurements of cooled boiler water samples alone, it is impossible to unambiguously determine phosphate concentrations.

Our paper is aimed at indirect determination of phosphate and ion admixtures concentrations in the boiler water from the data obtained with the use of standard automated chemical monitoring system measurement devices (conductometers and pH-meters) and application of the mathematical model of the boiler water ion equilibria, the schematic diagram of which is given in Fig. 3. This model is based on data from automatic measurements of conductivity and pH index of feedwater and boiler water from the salt compartments (SCs) and clean compartments of the drum.



Fig. 1. Dependences of phosphate concentrations on boilerwater conductivity in clean compartments of different TPSs (experimental data). (1) Mosenergo TETs-26 (1988, VTI data), (2) Mosenergo TETs-26 of (2005, authors' data), (3) Saransk TETs-2 (2005, authors' data), (4) Petrozavodsk TETs (2005, MEI data), and (5) Ivanovo TETs-3 (2005, authors' data).



Fig. 2. Variations in the specific conductivity $\kappa_{\rm H}^{25}$ (at 25°C) of feedwater, boiler water, and steam of the drum boiler (p_b = 13.8 MPa) during tests (automated recording data). Values of specific conductivity, μ S/cm: (0) feedwater upstream of the boiler, (1) in right clean compartment no. 1, (2) in right clean compartment no. 2, (3) in the left clean compartment, (4) in the left salt compartment, and (5) superheated steam downstream of the boiler (specific conductivities of points 0, 1, 3, and 5 should be read at the left axis and those of points 2 and 4 at the right axis).



Fig. 3. Schematic diagram of the mathematical model of ion equilibria in the boiler water.

The source mathematical model (for a sample cooled down to 25°C) of ion equilibria with participation of the boiler water admixtures regards the following equations:

(i) electric dissociation in lean electrolytes characterized by corresponding equilibrium constants:

$$H_2O \implies H^+ + OH^-; \quad K_w = a_{H^+}a_{OH^-} = 1 \times 10^{-14}; \quad (1)$$

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$$CO_{2} + H_{2}O = H^{+} + HCO_{3}^{-};$$

$$K_{1}^{H_{2}CO_{3}} = \frac{a_{H^{+}}a_{HCO_{3}^{-}}}{C_{H_{2}CO_{3}}} = 4.5 \times 10^{-7};$$
(2)

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-};$$

$$K_{\rm II}^{\rm H_2CO_3} = \frac{a_{\rm H^+}a_{\rm CO_3^{2-}}}{a_{\rm HCO_3^{-}}} = 4.8 \times 10^{-11};$$
 (3)

$$NH_4OH \Longrightarrow NH_4^+ + OH^-;$$

$$K^{\rm NH_4OH} = \frac{a_{\rm NH_4^+}a_{\rm OH^-}}{C_{\rm NH_4OH}} = 1.76 \times 10^{-5};$$
(4)

$$H_{2}SiO_{3} \longrightarrow H^{2} + HSiO_{3};$$

$$K_{I}^{H_{2}SiO_{3}} = \frac{a_{H^{+}}a_{HSiO_{3}}}{C_{H_{2}SiO_{3}}} = 2.2 \times 10^{-10};$$
(5)

$$HSiO_{3}^{-} \rightleftharpoons H^{+} + SiO_{3}^{2-};$$

$$K_{II}^{H_{2}SiO_{3}} = \frac{a_{H^{+}}a_{SiO_{3}^{2-}}}{a_{HSiO_{3}^{-}}} = 1.6 \times 10^{-12};$$
(6)

(ii) phosphate hydrolysis in the boiler water:

$$PO_{4}^{3-} + H_{2}O \implies OH^{-} + HPO_{4}^{2-};$$

$$\frac{K_{w}}{K_{III}^{H_{3}PO_{4}}} = \frac{a_{OH^{-}}a_{HPO_{4}^{2-}}}{a_{PO_{4}^{3-}}};$$
(7)

$$HPO_{4}^{2^{-}} + H_{2}O \Longrightarrow OH^{-} + H_{2}PO_{4}^{2^{-}};$$

$$\frac{K_{w}}{K_{II}^{H_{3}PO_{4}}} = \frac{a_{OH^{-}}a_{H_{2}PO_{4}^{-}}}{a_{HPO_{4}^{2^{-}}}};$$
(8)

$$H_{2}PO_{4}^{-} + H_{2}O \iff OH^{-} + H_{3}PO_{4};$$

$$\frac{K_{w}}{K_{II}^{H_{3}PO_{4}}} = \frac{a_{OH^{-}}a_{HPO_{4}^{2-}}}{a_{H_{3}PO_{4}}};$$
(9)

(iii) electrical neutrality:

$$[Na^{+}] + [NH_{4}^{+}] + [H^{+}] = [OH^{-}] + [C1^{-}]$$

+
$$[HCO_{3}^{-}] + 2[CO_{3}^{2-}] + [HSiO_{3}^{-}] + 2[SiO_{3}^{2-}] \quad (10)$$

+
$$[H_{2}PO_{4}^{-}] + 2[HPO_{4}^{2-}] + 3[PO_{4}^{3-}];$$

(iv) the electric conductivity equation:

$$1000\kappa = \lambda_{H^{+}}[H^{+}] + \lambda_{Na^{+}}[Na^{+}] + \lambda_{OH^{-}}[OH^{-}] + \lambda_{NH_{4}^{+}}[NH_{4}^{+}] + \lambda_{CI^{-}}[CI^{-}] + 2\lambda_{CO_{3}^{2-}}[CO_{3}^{2-}]$$
(11)
+ $\lambda_{HCO_{3}^{-}}[HCO_{3}^{-}] + \lambda_{H_{2}PO_{4}^{-}}[H_{2}PO_{4}^{-}] + 2\lambda_{HPO_{4}^{2-}}[HPO_{4}^{2-}] + 3\lambda_{PO_{4}^{3-}}[PO_{4}^{3-}] + \lambda_{HSIO_{3}^{-}}[HSIO_{3}^{-}] + 2\lambda_{SIO_{3}^{2-}}[SIO_{3}^{2-}].$

(when using H-cationization of water samples, this system is supplemented with corresponding equations for an H-cationized sample under the following assumptions: in an H-cationized sample, the equilibrium of bicarbonate dissociation in accordance with (3) is markedly shifted to the left; thus, we can neglect both the presence of CO_3^{2-} ions in such a sample and not calculate their concentrations; during ion exchange in an H-cationite, nearly all Na⁺ cations are substituted by H⁺ cations; all forms of sodium phosphate salts are pass into the phosphoric acid dissociated at the first phase);

(v) lean electrolytes dissociation in the H-filtrate:

$$H_2O \rightleftharpoons H^+ + OH^-; \quad K_w = a_{H^+}^H a_{OH^-}^H = 1 \times 10^{-14}; (12)$$
$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-;$$

$$K_{\rm I}^{\rm H_2CO_3} = \frac{a_{\rm H^+}^{\rm H} a_{\rm HCO_3^-}^{\rm H}}{C_{\rm H_2CO_3}^{\rm H}} = 4.5 \times 10^{-7};$$
(13)

$$H_{3}PO_{4} \rightleftharpoons H^{+} + H_{2}PO_{4}^{2^{-}};$$

$$K_{1}^{H_{3}PO_{4}} = \frac{a_{H^{+}}^{H}a_{H_{2}PO_{4}}^{H}}{C_{H_{3}PO_{4}}^{H}} = 7.5 \times 10^{-3};$$
(14)

(vi) electric neutrality for the H-filtrate:

$$[H^+]_{\rm H} = [Cl^-]_{\rm H} + [H_2 P O_4^-]_{\rm H} + [HCO_3^-]_{\rm H}; \qquad (15)$$

(vii) electric conductivity for the H-filtrate:

$$1000 \kappa_{\rm H} = \lambda_{\rm H^{+}}[{\rm H^{+}}] + \lambda_{\rm CI^{-}}[{\rm C1^{-}}] + \lambda_{\rm H_{2}PO_{4}^{-}}[{\rm H_{2}PO_{4}^{-}}] + \lambda_{\rm HCO_{3}^{-}}[{\rm HCO_{3}^{-}}].$$
(16)

Hydrogen ion concentration in analyzed water depends on pH:

$$pH = -\log a_{H^+}.$$
 (17)

Equations (1)–(17) contain the following values: pH is the value of the hydrogen ion index in the analyzed water; κ , $\kappa_{\rm H}$ are the electric conductivities of the analyzed water and its H-filtrate, μ S/cm; [H⁺], [NH₄⁺], [HCO₃⁻], [CO₃²⁻], [OH⁻], [PO₄³⁻], [HPO₄²⁻], [H₂PO₄⁻], [HSiO₃⁻] and [SiO₃²⁻] are the corresponding ion concentrations in the analyzed water, mol/dm³; [Na⁺] is the

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total concentration of sodium, calcium and magnesium in the analyzed water recalculated to sodium ions, mol/dm³; a_{H^+} , a_{OH^-} , $a_{HCO_3^-}$, are the activities of the corresponding ions, mol/dm³; [Cl] is the total concentration of strong acid anions recalculated to chlorideions, mol/dm³; [H⁺]_H, [HCO_3^-]_H, [Cl⁻]_H, [H₂PO_4^-]_H are the concentrations of corresponding ions in the H-filtrate, mol/dm³; K_w , $K_I^{H_2CO_3}$, $K_{II}^{H_2CO_3}$, K^{NH_4OH} , $K_I^{H_3PO_4}$, $K_{II}^{H_3PO_4}$, $K_{III}^{H_3PO_4}$, $K_I^{H_2SiO_3}$, are the ion-equilibria thermodynamic constants of water and carbon dioxide, at the first and the second phases; ammonia, phosphoric acid, at the first, the second and the third phases, respectively; silicic acid, at the first and the second phases; and λ_{H^+} , λ_{Na^+} , λ_{OH^-} are the equivalent electric conductivities of corresponding ions, S cm²/g-equiv.

To solve the above system of equations, the following assumptions based on laboratory tests with model solutions and on experiments with boiler water are introduced.

1. The boiler-water hardness in the case of phosphates excess is taken to be zero.

2. The concentration of strong acid anions is given, recalculated for chloride ions. The concentration of these ions in an H-cationized sample is equal to their concentration in the sample before H-cationization.

3. The degree of carbon dioxide dissociation and the degree of phosphate hydrolysis at the first phase in a cooled boiler-water sample is taken to be 100%.

4. Taking into account the dissociation constants of phosphoric and carbonic acids at the first phase of the process $(7.5 \times 10^{-3} \text{ and } 4.5 \times 10^{-7}, \text{ respectively})$, the degree of these acids dissociation under the conditions of H-cationized sample is assumed to be 100% for the phosphoric acid and 0% for the carbonic acid.

5. The boiler water in high-pressure boilers ($p_b = 13.8 \text{ MPa}$) is a highly diluted solution ($\kappa_{CC} < 20 \ \mu\text{S/cm}$) and ($\kappa_{SC} < 100 \ \mu\text{S/cm}$). Moreover, the existence of ion pairs such as [Na₂HPO₄⁰], [Na₃PO₄⁰], [NaOH⁰], [Na₂CO₃⁰] can be neglected, i.e., concentrations of such ion pairs should be taken to be to zero. Ion activity in the equations can be substituted by their concentrations.

6. Ion forms of dissociation of silicic acid and its compounds is assumed to be absent.

The system of equations, which form the mathematical model, is solved by sequential calculation of ion equilibria, first for the feedwater, then for the boiler water in the salt compartment, and, finally, for the clean-compartment boiler water. To provide for uniqueness of the solution, the following internal tuning parameters determined in the course of laboratory and industrial tests have been introduced:

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(i) K_s , which is the concentrating coefficient of feedwater strong acid anions in the salt compartment, the initial value of which is assumed to be 10:

$$K_{\rm s} = \frac{[{\rm Cl}^{-}]_{\rm b.w}}{[{\rm Cl}^{-}]_{\rm f.w}},\tag{18}$$

where subscripts b.w. and f.w. refer to the boiler water and the feedwater, respectively;

(ii) K_{CC} , which is the coefficient of soluble admixtures concentrating in the salt compartment relative to the clean one:

$$K_{\rm c.c} = \frac{\kappa_{\rm H}^{\rm SC}}{\kappa_{\rm H}^{\rm CC}},\tag{19}$$

(iii) n, which is the ratio of the bicarbonate concentration and the total concentration of strong acid anions recalculated for chloride ions in an H-cationized feedwater sample. The initial value at n is assumed to be unity.

With this, the system of equations of an ion-equilibria mathematical model becomes solvable; for example, for the boiler water in the salt compartment it takes the following form:

$$[Na^{+}] = [OH^{-}] + 2[HPO_{4}^{2-}] + [CI^{-}] + \left(2 + \frac{10^{-pH}}{K_{II}^{H_{2}CO_{3}}}\right)[CO_{3}^{2-}];$$
(20)
$$[OH^{-}] = b_{2}[HPO_{4}^{2-}] + \frac{10^{-pH}}{K_{II}^{H_{2}CO_{3}}}[CO_{3}^{2-}],$$

where b_2 is the coefficient characterizing the presence of acid phosphates of Na₂HPO₄ or excess of NaOH in the working solution fed into the boiler drum. The initial value of it is unity;

$$1000 \kappa = \lambda_{Na^{+}} [Na^{+}] + \lambda_{OH^{-}} [OH^{-}]$$

+ $\lambda_{HPO_{4}^{2-}} 2 [HPO_{4}^{2-}] + \lambda_{CI^{-}} [CI^{-}]$
+ $\left(2\lambda_{CO_{3}^{2-}} + \lambda_{HCO_{3}^{-}} \frac{10^{-pH}}{K_{II}} \right) [CO_{3}^{2-}];$
$$1000 \kappa_{H} = (\lambda_{H^{+}} + \lambda_{CI^{-}}) [CI^{-}]$$

+ $(\lambda_{H^{+}} + \lambda_{H_{2}PO_{4}^{-}}) [H_{2}PO_{4}^{2-}];$
+ $\frac{10^{-pH}}{K_{W^{2}CO_{3}}} [CO_{3}^{2-}] = [CI^{-}] \frac{[HCO_{3}^{-}]_{f.W.}}{2[CI^{-}]_{f.W.}}$

where $[HCO_3^-]_{f.w.}$ and $[Cl^-]_{f.w.}$ are the concentrations of bicarbonates and chlorides in the feedwater determined from measuring $\kappa_{f.w.}$, $\kappa_{Hf.w.}$, and $pH_{f.w.}$ [5, 6].



Fig. 4. Flowchart of the algorithm of boiler-water quality indices calculations in the salt compartment of a drum boiler.

Such a system of equations is solved using the method of iteration approximations with an account of changing the coefficients of admixtures concentrating from the value of the criteria of electrical neutrality of ions expressed by Eq. (20). Figure 4 gives the algorithm of these calculations.

The developed algorithm of ion equilibria calculations for the boiler water was verified as applied to the conditions of operation of TGME-296KhL drum boiler (station no. 5) of the Pechora District Power Station TGME-96B boiler of the Mosenergo TETs-26 (a power unit with a type PT-80-130 steam turbine and the TP-87 drum boiler of the Ivanovo TETs-3 with steam cross ties. The study was aimed at getting experimental and calculation values of phosphate concentrations in the boiler water for a standard operation regime of the power unit (Pechora GRES) and for a regime of variable metering of phosphates into the boiler water and

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Table 1. Results of measurements of pH, electric conductivity, and phosphate concentration in the boiler water of a salt compartment of a TGME-96B boiler during the period of November 14–25, 2005

Results of m of autom	neasurements natic chemica	Results of $[PO_4^{3-}]$		
κ, μS/cm	κ _H , μS/cm	рН	chemical analysis, mg/dm ³	
62.28	38.63	10.41	7.32	
35.80	23.63	9.98	4.74	
16.73	12.70	9.47	3.09	
10.87	7.27	8.34	1.0	
6.30	5.0	8.24	0.55	
32.9	21.01	9.71	3.26	
50.76	30.84	9.26	6.58	

ammonia into the feedwater (the Ivanovo TETs-3 and TETs-26). The results of investigations for the Mosenergo TETs-26 are given in Tables 1 and 2 and in Fig. 5.

The electrical conductivity of the boiler water in the salt compartment was measured approximately every 2 h; at first, this index decreased during the experiment (one day) from 62 to 6.3 μ S/cm, and then increased up to 50 μ S/cm (see Table 1).

Along with the phosphate concentration (the concentration of $[HPO_4^{2-}]$ ions recalculated to $[PO_4^{3-}]$), the total concentration of strong acid anions recalculated for chloride ions, carbonates, hydrates, and sodium was calculated (see Table 2). The calculation results show that the phosphate concentration values obtained from measuring conductivity and pH correspond to those obtained using a laboratory chemical analysis both for a stationary operation regime and for regimes of varied reagent metering as well. Maximum divergence of the results from the design values was obtained for small phosphate concentrations under conditions when the phosphate metering pump was switched on to increase the excess of phosphates in the boiler water.

The results of measurements and calculations were statistically processed and, as a final result, the relative error in phosphate concentration calculations was determined. A confidence interval of the relative error in phosphate-concentration calculations for a 0.95 confidence probability is 8.91–13.34% for the salt compartment and 11.58–16.34% for the clean one.

The results obtained during industrial tests allowed to assess boiler water chemistry using a state diagram (Fig. 6). The diagram shows the area (the hatched one) of standardized parameters of the boiler water quality (pH and the phosphate excess), within which the measurement data obtained at the Pechora GRES and Ivanovo TETs-3 are mainly kept. Some results obtained in the course of tests conducted at the TETS-26 are beyond these bounds. It attests to the violation of a

Table 2.	Results	of impurity	concentrati	ion cal	lculatio	ons
(mg/dm^3)	for the	salt-compartr	nent boiler	water	based	on
measurem	ient data	L				

[OH ⁻]	[CO ₃ ²⁻]	[Na ⁺]	[Cl ⁻]	[PO ₄ ³⁻]
2.04	2.52	9.32	0.45	8.18
1.25	0.79	5.42	0.52	4.28
0.63	0.07	2.42	0.12	2.78
0.43	0.01	1.53	0.17	1.29
0.24	0.005	0.92	0.05	1.09
1.22	0.58	4.77	0.70	3.11
1.80	1.05	7.83	0.45	6.27



Fig. 5. Dynamics of phosphate concentration variations (calculated values) in boiler-water of salt and clean compartments of drum boiler no. 5 of the Mosenergo TETs-26 during testing.



Fig. 6. Diagram of water-chemistry regimes. The hatched zone is the range specified for pH and phosphate concentration by the Rules of Technical Operation in force [1]. (1) Dependence of boiler-water pH on phosphate concentration at mole ratio $[Na^+]/[PO_4^{3^-}] = 2.8$; (2) the same at $[Na^+]/[PO_4^{3^-}] = 2.2$; (3) the same at $[Na^+]/PO_4^{3^-}] = 3.0$; (4) the same at NaOH excess of 1 mg/dm³; ● Mosenergo TETs-26; + Pechora GRES; ○ Ivanovo TETs-3.

phosphate/alkali ratio in the boiler water. However, such a diagram does not make it possible to get an idea whether the requirements to the boiler water quality, as to its salt content, have been broken. To control the development of such violations in the boiler water chemistry, it is expedient to use the method of indirect determination of phosphate and ion impurity concentrations in the boiler water.

CONCLUSIONS

1. It is expedient to perform permanent chemical control of phosphate and ion admixtures concentrations in the boiler water by measuring both electric conductivity and pH to increase the efficiency of monitoring the water chemistry of drum boilers ($p_b > 10$ MPa).

2. The mathematical model of ion equilibria in cooled boiler-water sample has been developed. The algorithm for calculating phosphate and ion admixtures concentrations in the boiler water based on measurements of conductivity κ , $\kappa_{\rm H}$ and pH of both the feedwater and the boiler water has been suggested. The algorithm has been verified during analysis of the quality of the boiler water at several electric power stations.

3. The method developed is recommended for the systems of automated chemical control for permanent

monitoring of the phosphate water chemistry of power boilers.

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