ResearchGate

See discussions, stats, and author profiles for this publication at: https://www.researchgate.net/publication/261181914

A Calculation Method for Determining the Concentration of Potentially Acid Substances in Feedwater of Once-Through Boilers

Article *in* Thermal Engineering · January 2008

CITATIONS
0

READS
248

1 author:

M. Kamran Bhatti
NFC Institute of Engineering & Technology Multan
50 PUBLICATIONS **156** CITATIONS

SEE PROFILE

Some of the authors of this publication are also working on these related projects:

WSN Node lifetime improvement via cross-layer optimization View project

STATCOM Implementations View project

All content following this page was uploaded by M. Kamran Bhatti on 31 March 2014.

The user has requested enhancement of the downloaded file.

ISSN 0040-6015, Thermal Engineering, 2008, Vol. 55, No. 4, pp. 313–318. © Pleiades Publishing, Inc., 2008.
Original Russian Text © B.M. Larin, E.N. Bushuev, A.B. Larin, M.K.L. Batti, V.N. Vinogradov, S.V. Kiet, 2008, published in Teploenergetika.

A Calculation Method for Determining the Concentration of Potentially Acid Substances in Feedwater of Once-Through Boilers

B. M. Larin, E. N. Bushuev, A. B. Larin, M. K. L. Batti, V. N. Vinogradov, and S. V. Kiet

V. I. Lenin Ivanovo State Power Engineering University (IGEU), Rabfakovskaya ul. 34, Ivanovo, 153003 Russia

Abstract—The problem of chemically monitoring the products resulted from destruction of organic substances in the steam–water path of a supercritical-pressure power unit is considered. The level at which the concentrations of acetic and formic acids have to be measured is determined, and the results from measurements of electric conductivity and pH in feedwater and steam are given. A procedure that allows the conditional concentration of acetic acid in steam to be calculated from measured electric conductivity in feedwater and steam is presented.

DOI: 10.1134/S0040601508040083

The feedwater of once-through boilers for supercritical steam conditions contains almost no mineral admixtures (the electric conductivity $\chi_H < 0.3$ μS/cm) and a small quantity of organic substances. When exposed to the conditions of oxidizing water chemistry with the oxygen concentration ranging from 100 to 400 ppb and with the coolant temperature rising from 300°C at the boiler inlet to 550°C at the boiler outlet, these organic substances undergo deep thermal destruction (thermolysis), during which acidic substances are frequently generated.

Organic substances enter into the feedwater of power-generating boilers together with main condensate [petroleum products, products from destruction of ion-exchange resins used in the condensate polishing unit (CPU), and inleakages of cooling water in turbine condensers and heat network water in delivery-water heaters] and with makeup water from the condensate storage tank. It has been found that acetic acid is the most probable product from thermolysis of such substances [1–3]. When acetic acid and other acidic substances appear in the steam of once-through boilers, the medium circulating in them becomes more corrosive and frequently results in corrosion damage to the tubes of high-pressure heaters and delivery-water heaters that use steam of extractions from the turbine flow path [4, 5].

At present, the Operational Regulations for power-generating boilers installed at Russian thermal power stations (TPSs) do not prescribe the need to monitor organic impurities such as potentially acid substances in feedwater and steam for the lack of reliable measurement tools [6]. The staff of foreign power stations frequently carry out such monitoring using the total organic carbon and total inorganic carbon as indicating parameters. The standard level for the first parameter is equal to 100 ppb [3, 5, 7]. The operating services of Russian power stations make attempts to estimate the quantity of potentially acid substances from measurements of χ and pH of feedwater and steam in once-through boilers [5, 8]. Although easy to implement, such a method provides insufficient information, since the effect on these parameters of impurities contained in water and steam is multifactorial in nature.

The authors of this paper have measured χ and pH of feedwater and steam in once-through boilers at several TPSs. An analysis of the obtained results and data available from the literature (Table 1) shows that the electric conductivity of samples (or the electric conductivity of H-cationated samples if ammonia is metered into feedwater) increases from 0.05 to 0.20 μS/cm and the pH value of samples decreases by 0.1–0.3 as a transition occurs from feedwater to steam. Such changes are stable in nature and occur in all likelihood as a result of thermolysis of organic impurities contained in feedwater [9]. In Table 2 we find some results from analyses of feedwater and steam sampled in power-generating boilers for the content of products from thermolysis of organic impurities in coolant according to the data of [10–12].

The results from the investigations specialists of the All-Russia Thermal Engineering Institute carried out on CPUs at two district power stations have shown that the average quantity of lactic and acetic acids that enters into condensate downstream of these units is in the range from 20 to 40 μg/dm^3 for each of them. However, the major portion of sorbed organic substances escaped from the CPU in the second half of the filtration cycle if mixed-bed filters were installed in the CPU. These substances were observed escaping from the polishing unit during almost the entire filtering cycle if separate H–OH ion-exchange treatment was used in the CPU. The results from analyses of feedwater and steam in supercritical-pressure drum boilers

Table 1. Electric conductivities and pH values of feedwater and steam and their differences for TPS units equipped with once-through boilers

Power unit	Feedwater		Steam		Steam–water difference	
	χ, μS/cm	pH	χ, μS/cm	pH	Δχ, μS/cm	ΔpH
Reftinsk district power station	0.15	7.9	0.25	7.6	+0.10	–0.3
Mosenergo's TETs-26 cogeneration station, the 250-MW power unit:						
before the replacement of CPU ion-exchange filters (1997)	–	–	–	–	+0.10	–0.40
after replacement of CPU ion-exchange filters (2005)	0.10	7.0	0.15	6.8	+0.05	–0.20
Perm district power station	0.1	8.08	0.16	7.87	+0.06	–0.19

Table 2. Results form analyses of samples for the content of acetic and formic acids

Characteristic of a sample	Concentration, μg/dm^3 of	
	acetic acid	formic acid
Turbine condensate of a 300-MW power unit (after the CPU) [10]	10…60	–
Cogeneration power unit equipped with a drum boiler (p = 14 MPa) with distillate from a multistage evaporating plant (MEP*) used as makeup water [3]:		
feedwater	18.7	2.5
superheated steam	28.1	4.8
Cogeneration power unit with a drum boiler (p = 14 MPa) with chemical demineralization of makeup water [3]:		
feedwater	500…750	10…100
superheated steam	75…90	2…4
Superheated steam at the cogeneration station of Moscow Power Engineering Institute [11]	0…60	0…25
Power unit at the Saransk TETs-2 cogeneration station equipped with a drum boiler (p = 15 MPa) during abnormal operation of the MEP [12]:		
feedwater	60…90	3…4
superheated steam	40…100	2
Kazan TETs-3 cogeneration station (1997) [12]:		
chemically demineralized water	215	2
distilled water from the MEP	54	2
superheated steam (p = 14 MPa)	82	2

* MEP – multistage evaporating plant.

[11, 12] have revealed that the concentrations of acetic acid in water and steam are considerably higher in them (50 to 100 μg/dm^3) than they are in once-through boilers. The generalized results of studies carried out by foreign researchers [9] are in agreement with the data obtained in Russia: the concentration of acetic acid in steam is in the range from 1 to 7 μg/dm^3 if a CPU is in operation and from 9 to 120 μg/dm^3 if a CPU is not used.

We proposed a method for calculating the concentration of products from destruction of organic compounds in a once-through boiler recalculated for acetic acid, which is the most probable product of thermolysis. It is assumed that there are no other sources from which acidic substances could enter into boiler steam. The values of χ, χ_H, and pH of feedwater and steam measured by means of regular instrumentation are used for calculations [13, 14]. The concentrations of mineral impurities in feedwater are thus determined.

The equations of electric neutrality can be written as follows:

for an H-cationated sample of live steam,

$$[H^+]_H^{l.s} + [Na^+]_H^{l.s} = [Cl^-]_H^{l.s} + [HCO_3^-]_H^{l.s} + [CH_3COO^+]; \quad (1)$$

and for an H-cationated sample of feedwater,

$$[H^+]_H^{fw} + [Na^+]_H^{fw} = [Cl^-]_H + [HCO_3^-]_H^{fw}. \quad (2)$$

In these equations, the concentrations of sodium ions and chloride ions in feedwater and steam are equal to each other, i.e., $[Na^+]_H^{l.s} = [Na^+]_H^{fw}$ and $[Cl^-]_H^{l.s} = [Cl^-]_H^{fw}$ provided that these impurities transfer completely from water to steam. Then, the difference of Eqs. (1) and (2) gives the expression

$$[H^+]_H^{l.s} + [H^+]_H^{fw} = [CH_3COO^-] - ([HCO_3^-]_H^{fw} - [HCO_3^-]_H^{l.s}). \quad (3)$$

The concentration of acetate ion in Eq. (3) can be taken approximately equal to the total concentration of acetic acid, i.e., $[CH_3COO^-] = C_{ac}$. The value the ratio of the forms $[CH_3COO^-]/C_{ac}$ has for an H-cationated cooled sample for the usual values of pH of around 6.0 or higher is equal to 20 : 1 or higher; hence, the adopted assumption is valid within the limits of a 5% error.

The equations of electric conductivity in an H-cationated sample can be written in the following form:

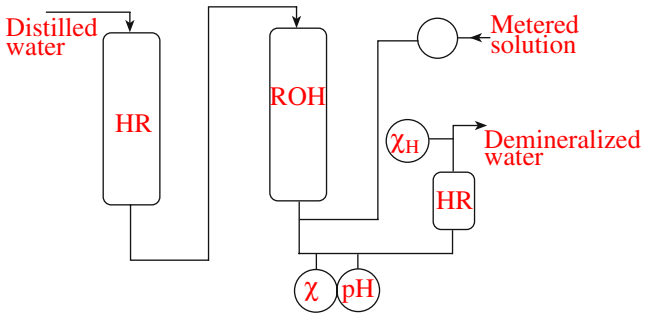

Fig. 1. Circuit arrangement for metering ammonia and acetic acid at the laboratory setup.

for live steam,

$$1000\chi_H^{l.s} = \lambda_{H^+}[H^+]_H^{l.s} + \lambda_{Na^+}[Na^+]_H^{l.s} + \lambda_{Cl^-}[Cl^-]_H^{l.s} + \lambda_{HCO_3^-}[HCO_3^-]_H^{l.s} + \lambda_{CH_3COO^-}[CH_3COO^-]_H^{l.s}; \quad (4)$$

and for feedwater,

$$1000\chi_H^{fw} = \lambda_{H^+}[H^+]_H^{fw} + \lambda_{Na^+}[Na^+]_H^{fw} + \lambda_{Cl^-}[Cl^-]_H^{fw} + \lambda_{HCO_3^-}[HCO_3^-]_H^{fw}. \quad (5)$$

Subtracting expression (5) from Eq. (4), substituting (3) into the result, and taking the adopted assumptions into account, we obtain:

$$1000(\chi_H^{l.s} - \chi_H^{fw}) = (\lambda_{H^+} + \lambda_{CH_3COO^-})C_{ac} - (\lambda_{H^+} + \lambda_{HCO_3^-})([HCO_3^-]_H^{fw} - [HCO_3^-]_H^{l.s}), \quad (6)$$

where $\chi_H^{l.s}$ and χ_H^{fw} are the measured values of the electric conductivity of H-cationated samples of live steam and feedwater, μS/cm; and λ_{H^+}, $\lambda_{HCO_3^-}$, and $\lambda_{CH_3COO^-}$ are the reference values of the limiting electric mobilities of H^+, HCO_3^-, and CH_3COO^- ions.

If the concentration of acetic acid in a cooled H-cationated sample is considerably higher than the change that takes place in the concentration of hydrocarbonates as a transition occurs from feedwater to steam, i.e.,

$$C_{ac} \gg [HCO_3^-]_H^{fw} - [HCO_3^-]_H^{l.s}, \quad (7)$$

the second term on the right-hand side of Eq. (6) can be ignored. The solution of this equation with respect to the concentration of acetic acid (μmol/dm^3) is given by

$$C_{ac} = 1000\frac{\chi_H^{l.s} - \chi_H^{fw}}{\lambda_{H^+} + \lambda_{CH_3COO^-}}. \quad (8)$$

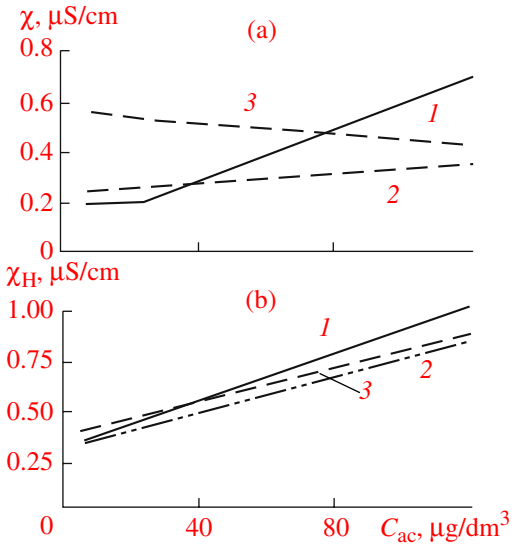

Fig. 2. Electric conductivities of the direct sample (a) and H-cationated sample (b) vs. the concentration of acetic acid. Value of C_{NH_3}, μg/dm^3: (*1*) 3, (*2*) 20, and (*3*) 45.

For a temperature of 25°C, Eq. (8) becomes

$$C_{ac} = 2.56(\chi_H^{l.s} - \chi_H^{fw}). \quad (9)$$

Equation (9) allows us to determine the concentration of potentially acid substances in feedwater of a once-through boiler expressed in terms of C_{ac} in the steam of this boiler from measured values of the electric conductivity of cooled H-cationated samples of steam and feedwater. If no ammonia NH_3 is metered into feedwater, the calculation using Eq. (9) can be carried out for the electric conductivities of direct samples (unlike H-cationated ones) of live steam $\chi^{l.s}$ and feedwater χ^{fw}.

If inequality (7) is not satisfied, the expression for C_{ac} obtained from (6) has a more complicated form, which we do not consider here. Then, Eq. (9) for the concentration of conditional acetic acid (μg/dm^3) becomes

$$C_{ac} = 153.6a(\chi_H^{l.s} - \chi_H^{fw}), \quad (10)$$

Table 3. Results from measurements of electric conductivity and pH and calculation of the concentrations of acetic acid and ammonia from laboratory analyses of water samples

Instrument readings						Measured concentrations of		Calculated concentrations of		ΔC_{ac},%
source water			after metering of NH_3 or CH_3COOH							
χ	χ_H	pH	χ	χ_H	pH	C_{NH_3}, μg/dm^3	C_{ac}, μg/dm^3	C_{NH_3}, μg/dm^3	C_{ac}, μg/dm^3	
0.23	0.30	7.95	0.18	0.46	6.96	–	15	–	24.6	+63.8
0.27	0.25	7.94	0.22	0.48	6.94	–	25	–	34.7	+38.8
0.28	0.27	7.76	0.21	0.45	6.85	–	24	–	27.9	+16.4
0.19	0.15	7.30	0.28	0.57	6.53	–	60	–	63.9	+6.48
0.15	0.24	6.87	0.46	0.85	6.05	–	90	–	93.2	+3.58
0.14	0.25	6.73	0.29	0.31	7.00	20	–	19.2	–	–4.10
0.14	0.23	6.48	0.50	0.30	6.94	40	–	42.6	–	+6.58
0.14	0.22	6.72	0.79	0.35	7.75	80	–	89.6	–	+12.1
0.12	0.22	6.75	0.25	0.36	6.95	19.2	7.7	19.2	8.3	+7.66
0.13	0.23	6.68	0.27	0.41	6.76	19.2	23	9.93	27.3	+18.8
0.15	0.24	6.40	0.32	0.65	6.32	19.2	78	19.0	62.5	–19.9
0.20	0.32	6.84	0.33	0.84	6.56	25	120	22.1	80.1	–33.2
0.15	0.32	6.95	0.53	0.52	7.89	45	27.2	12.6	29.9	+10.1
0.14	0.31	7.24	0.42	0.93	7.55	45	108	35.0	96.1	–11.3

Table 4. Results from calculation of the concentrations of acetic acid and ammonia in power units equipped with once-through boilers obtained using the authors procedure

Measured values					Calculated values	
pH^{fw}	χ_H^{fw}, μS/cm	χ_H^{fw}, μS/cm	$pH^{l.s}$	$\chi_H^{l.s}$, μS/cm	C_{NH_3}, μg/dm	C_{ac}, μg/dm^3
8.179	0.090	0.40	7.79	0.13	21.1	6.14
8.083	0.083	0.28	7.74	0.14	10.3	8.76
8.08	0.100	0.31	7.87	0.16	13.8	9.22
8.30	0.103	0.593	8.01	0.125	38.0	3.38
7.99	0.080	0.28	7.9	0.11	14.9	4.62
6.60	0.188	0.153	6.5	0.230	0	6.40
6.60	0.214	0.176	6.5	0.272	0	8.90

where a is an empirical coefficient, the value of which in a first approximation is equal to unity.

Experiments were carried out on a test facility (Fig. 1) to verify the procedure for calculating the indicators characterizing the quality of feedwater and steam in a once-through boiler. Distilled water is fed into an H-cation-exchange filter and then into an OH-anion-exchange filter. The demineralized water downstream of the H and OH ion-exchange filters has high quality (χ = 0.2–0.15 μS/cm) and very low concentration of mineral salts. A solution of ammonia or acetic acid is then metered (to simulate a steam sample), after which χ and pH of mixed solution are measured (a direct sample). Further on, water flows to an H-column, downstream of which χ_H (an H-cationated sample) is measured, and to the demineralized water tank.

The test results are shown in Fig. 2 (for different values of C_{NH_3}). We see that the electric conductivity of a direct sample (Fig. 2a) varies very considerably depending on the combination of acetic acid and ammonia concentrations. Different values of electric conductivity may correspond to the same value of C_{ac}, a circumstance that makes it difficult to determine it by calculation. In contrast, the electric conductivity of an H-cationated sample (Fig. 2b) gives a stable linear dependence on C_{ac} and depends only slightly on C_{NH_3} in the sample.

At a = 1, the calculated values of C_{ac} are in satisfactory agreement (with an average error of 18%) with the measured values (Table 3).

The obtained equation (10) was used for calculating the concentration of the products from thermolysis of potentially acid substances in feedwater of several power units at district power stations equipped with once-through boilers (Table 4).

Thus, a simple calculation formula has been proposed for determining the concentration of potentially acid substances in feedwater of a once-through boiler from the measured electric conductivity of H-cationated samples of feedwater and steam. The obtained calculation results differ from measured data by 18% on the average. The proposed method was presented at the International Conference on Instrumentation for Power Plant Chemistry in Zurich (Switzerland) in September 2006 [15] and received positive appraisal from experts.

REFERENCES

1. O. I. Martynova, T. I. Petrova, O. S. Ermakov, and A. A. Zonov, "The Behavior of the Products of Thermolysis of Organics in the Two-Phase Region–Boiling Water and Equilibrium Saturated Steam," Teploenergetika, No. 6, 8–11 (1997) [Therm. Eng., No. 6 (1997)].
2. N. V. Golovko and F. M. Tulyupa, "Detection of Fat Acids in Waters of the Steam–Water Cycle of Thermal Power Stations," Energetik, No. 9, 24–25 (1995).
3. V. N. Voronov and T. I. Petrova, "Problems in Organizing Water Chemistry of Thermal Power Stations," Teploenergetika, No. 7, 2–6 (2002) [Therm. Eng., No. 7 (2002)].
4. A. B. Vainman, O. I. Martynova, I. A. Malakhov, et al., "A Study of the Corrosive–Mechanical Damage to the Tubes of the Horizontal District Heat Exchangers of T-250/300-240 Turbines," Teploenergetika, No. 6, 17–22 (1997) [Therm. Eng., No. 6 (1997)].
5. B. S. Fedoseev, "Current State of Water Treatment Plants and Water Chemistry Regimes at Thermal Power Stations," Teploenergetika, No. 7, 2–9 (2005) [Therm. Eng., No. 7 (2005)].
6. *RD (Guidelines) 34.20.501-45: Operating Regulations for Power Stations and Heat Networks, 15th Edition* (SPO ORGRES, Moscow, 1995) [in Russian].
7. O. I. Martynova, "The Behavior of Organics and Dissolved Carbonic Acid in the Steam–Water Path of Power Stations," Teploenergetika, No. 7, 67–70 (2002) [Therm. Eng., No. 7 (2002)].
8. L. V. Koryukova, A. F. Belokonova, N. A. Belokonova, et al., "Ways of Advancing the Water Chemistry for the Supercritical-Pressure Power Units in the Sverdlovenergo Power System," Teploenergetika, No. 7, 30–34 (1999) [Therm. Eng., No. 7 (1999)].

9. A. S. Michal and J. S. Kevin, "Minimizing Levels of Volatile Organic Acids and Carbon Dioxide in Steam–Water Circuits," in *Proceedings of International Conference on Interaction of Organics and Organic Cycle Treatment Chemicals with Water Steam, Stuttgart, Germany, October 4–6, 2005.*
10. B. N. Khodyrev, B. S. Fedoseev, V. A. Korovin, et al., "Mechanism of a Breakthrough of Organic-Acid Anions in the Ion Exchangers of Makeup Demineralizing and Condensate Polishing Units," Teploenergetika, No. 7, 2–6 (1999) [Therm. Eng., No. 7 (1999)].
11. O. I. Martynova, V. I. Kashinskii, A. Yu. Petrova, et al. "Ion Chromatography for Steam and Water Quality Control at Thermal Power Stations," Teploenergetika, No. 8, 39–42 (1996) [Therm. Eng., No. 8 (1996)].
12. A. S. Sedlov, B. M. Larin, and I. P. Il'ina, "Investigating the Entrainment of Organic Substances to the Evaporator Plant Distillate," Teploenergetika, No. 7, 16–19 (1999) [Therm. Eng., No. 7 (1999)].
13. B. M. Larin and N. A. Eremina, "Calculation of the Mineralization and the Concentration of Ammonia and Carbonic Acid in Condensate Type Waters," Teploenergetika, No. 7, 10–14 (2000) [Therm. Eng., No. 7 (2000)].
14. B. M. Larin, E. N. Bushuev, and E. V. Kozyulina, "Increasing the Information Content in Monitoring the Water Chemistry of the Condensate–Feedwater Path of Power Units," Teploenergetika, No. 7, 2–8 (2003) [Therm. Eng., No. 7 (2003)].
15. B. M. Larin, E. N. Bushuev, M. K. L. Bhatti, and A. B. Larin, "Use of Mathematical Model of Ionic Equilibrium for Chemical Monitoring of the Operating Medium Quality of Once-Through Boilers," in *Proceedings of the International Conference on Instrumentation for Power Plant Chemistry, Zurich, Switzerland, 2006,* pp. 18–23.

View publication stats