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Using an APK-051 Analyzer in a Chemical Engineering Monitoring System

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Abstract—The capabilities of an APK-051 automatic analyzer for directly measuring the standardized indicators used for automatic chemical monitoring and indirectly determining the concentration of ammonia in water coolant are described.

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Deviations from the standard quality of coolant used in power units equipped with superhigh- and supercritical-pressure boilers occur primarily due to inleakages of cooling water in turbine condensers, inadequate quality of makeup water, or improper metering of correcting chemical agents. Under such conditions, chemical monitoring must give reliable and timely information on the standardized parameters of water chemistry by direct measurement or indirect determination (by calculation) of the appropriate indicators [1, 2].

According to the operational regulations, the following indicators should be monitored at different locations of the condensate–feedwater path of a power unit:

—specific electrical conductivity of a direct sample χ and an H-cationated sample χ_H, pH, concentration of ammonia $[NH_3]$ and sodium ions $[Na^+]$, and total hardness H_t and alkalinity A_t and

—concentrations of iron, copper, oxygen, and others.

The first group of indicators characterizes galloping deviations from normal water chemistry, and it should be pointed out that only χ, χ_H, and pH can be measured using automatic industry-grade instruments (conductivity meters and pH meters) with good reliability and high accuracy. These instruments constitute the principal part of the fleet of measurement devices used in an automatic chemical engineering monitoring system for power units at thermal power stations. The measurement accuracy is determined by the accuracy class of instruments for automatic chemical monitoring. The measurement error is equal to 1.5–2% for a conductivity meter and 0.05 units of pH for a pH meter provided that they are calibrated and checked in accordance with the instrument's certificate. However, calibration of these instruments carried out using standard solutions becomes nonrepresentative during measurements in infinitely diluted solutions, such as turbine condensate and feedwater of power-generating boilers, and doubt may be cast on the correctness of direct and indirect measurements.

The results of measurements carried out with the instruments for automatic chemical monitoring should be processed using the calculation procedures described in GOST (State Standard) 8.207-76.

Table 1 gives the values of χ, χ_H, pH, and sodium ion concentrations measured using automatic chemical monitoring instruments: a conductivity meter, a pH meter produced by Alpha BASSENS Co., and an Aton-101 MP ion meter under conditions of regular chemical monitoring at OAO Mosenergo's TETs-9 cogeneration station; Table 2 gives results obtained from processing of these data.

It can be seen from analysis of the data given in Table 2 that the specific electrical conductivity of an H-cationated sample has a minimal interval of changes, which corresponds to a stably low mineralization of turbine condensate. This interval is somewhat larger in pH and χ, which is attributed to the unstable mode in which ammonia is metered into the coolant circuit. The parameter $[Na]^+$ has the largest interval of changes, which is due to low accuracy of measurements carried out using the ion meter. If measurement results do not fall within the interval of true values, they are regarded

Table 1. Values of indicators characterizing the quality of steam turbine condensate measured using the instruments of the automatic chemical monitoring system

χ_H, μS/cm	χ, μS/cm	pH	$[Na^+]$, μg/dm^3
0.290	6.5	9.31	1.6
0.287	6.5	9.32	9.5
0.275	6.5	9.4	3.0
0.282	6.4	9.3	7.0
0.239	4.7	9.2	2.8
0.245	4.9	9.3	3.2
0.238	5.0	9.3	4.0
0.245	5.0	9.3	9.0

Table 2. Results obtained from processing the measured values of the parameters being monitored (see Table 1)

Indicator	χ_H	χ	pH	$[Na^+]$, μg/dm^3
Arithmetic mean	0.263	5.69	9.3	5.01
Variance of arithmetic mean	0.008	0.30	0.019	1.06
Sum of random and systematic measurement errors $\Delta a_{rand} + \Delta a_{syst}$	0.019 + 0.005 = 0.024	0.71 + 0.005 = 0.715	0.045 + 0.017 = 0.062	2.51 + 0.017 = 2.527
Interval of true values of the quantity measured	[0.239; 0.287]	[4.98; 6.41]	[9.24; 9.36]	[2.48; 7.27]

Table 3. Kinds of galloping deviations from normal water chemistry of feedwater in a superhigh-pressure drum boiler SVD (p_d = 13.8 MPa)

Kind of deviation from normal water chemistry	Factor causing the deviation from normal water chemistry	Change in the monitored indicators characterizing the quality of working medium
pH > 9.3	Addition of excessive quantity of ammonia into feedwater	$\chi > 1000$ μS/cm $\chi_H < 1$ μS/cm $[NH_3] > 1000$ μg/dm^3
pH < 8.9	Addition of insufficient or no quantity of ammonia	$\chi < 3$ μS/cm $\chi_H < 1$ μS/cm $[NH_3] < 200$ μg/dm^3
Increase in the content of salts, including an increase of $H_t > 1$ μg-equiv/dm^3	Large inleakages of cooling water in the turbine condenser	$\Delta\chi > 0.1$ μS/cm $\chi_H > 1$ μS/cm $[Na^+] > 100$ μg/dm^3
	Deterioration of makeup water quality with kick-in of alkali or carbonic acid	$\Delta\chi > 0.1$ μS/cm $\chi_H < 1$ μS/cm $\Delta A_t > 0.1\ A_t$ ΔpH > 0.1
	Deterioration of makeup water quality with kick-in of salts	$\Delta\chi > 0.1$ μS/cm $\chi_H > 1$ μS/cm $[Na^+] > 100$ μg/dm^3
Increase in the content of oxygen in turbine condensate above 20 μg/dm^3	Malfunction in deaerator operation	$[O_2] < 50$ μg/dm^3
	Large inleakages of air in the turbine condenser	$[O_2] > 100$ μg/dm^3

as overshoots and are not considered in further processing of measurement results.

The APK-051 instrument developed with participation of the autors for analyzing admixtures in condensate makes it possible to replace measurement of $[Na^+]$ by its calculation using the measured values of χ, χ_H, and pH.

Deviations from normal water chemistry that occur in a drum boiler are often due to degraded quality of feedwater or steam turbine condensate; these events may proceed rather quickly (for 30–60 min). As can be seen from Table 3, galloping deviations from normal water chemistry (except an increase in oxygen concentration) are accompanied by changes in χ, χ_H, and pH. If we take into account changes in these parameters that occur due to malfunctions in the measurement systems of conductivity meters and pH meters, it becomes clear how difficult the diagnosing of a factor that caused a deviation from normal water chemistry is, especially at an early stage.

The readings available from regular measurements within the framework of automatic chemical monitoring by means of conductivity meters and pH meters can be used as a basis for constructing an algorithm (Fig. 1) to search for a factor that caused a deviation from normal water chemistry in the condensate–feedwater path [1]. Violation of the upper standardized electrical conductivity of an H-cationated sample is the main criterion here. A similar logic chart of searching for devia-

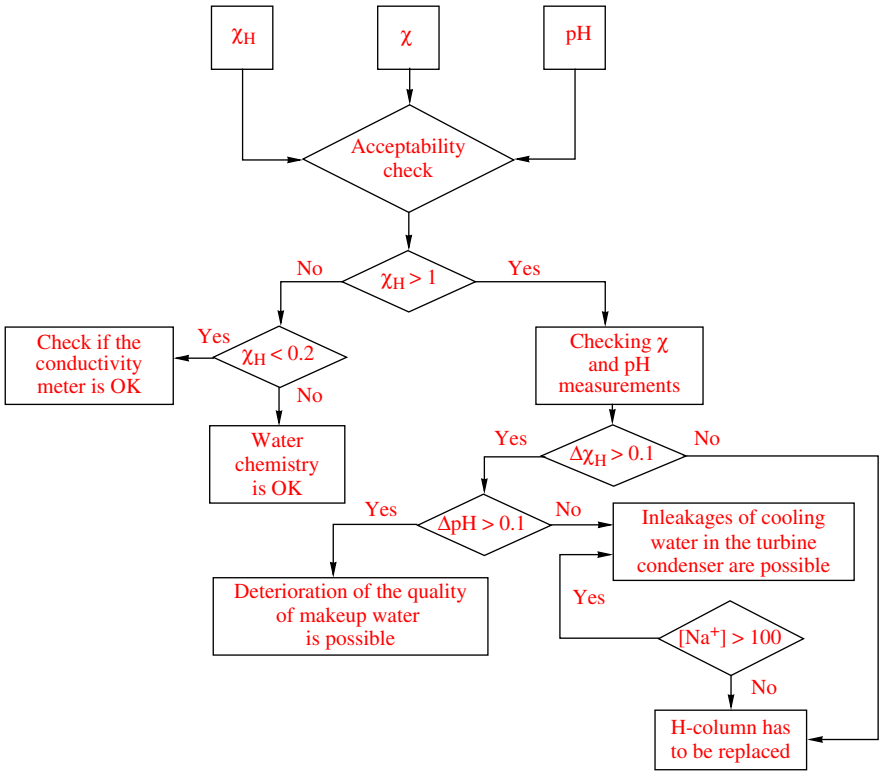

Fig. 1. Algorithm of searching for a factor causing deviations from normal water chemistry in condensate of a cogeneration turbine.

tions from normal water chemistry can be constructed for the pH and electrical conductivity of a direct cooled sample of feedwater.

Using the APK-051 automatic analyzer makes it possible to simplify the task of searching for a factor causing deviation from normal water chemistry of the condensate–feedwater path of a power unit. The software and design of the APK-051 instrument allow χ, χ_H, and pH to be measured and the serviceability of an H-cation-exchange column to be estimated. In addition, the operator can use the software to determine the pH values recalculated for 25°C and calculate the concentrations of ammonium, sodium, and chlorides, as well as alkalinity, parameters from which deviations from normal water chemistry of a condensate–feedwater path can be diagnosed at an early stage (Fig. 2).

The authors of this paper also suggest that the APK-051 automatic analyzer can be used to determine the concentration of mineral impurities in boiler water. The equation for material balance of impurities in a boiler given in [3] can be written in the following form:

$$C_{fw}G_{fw} - C_bG_{bld} - C_bG_b(K_{P\Sigma} + \omega) - C_bG_bP_b = 0, \quad (1)$$

where C_{fw} and C_b are the concentrations of impurities in feedwater and boiler water, μg/l; G_{fw}, G_{bld}, and G_b are the flowrates of feedwater, blowdown water, and boiler water, kg/s; $K_{P\Sigma}$ is the coefficient for distribution of impurity between water and saturated steam; ω is the wetness of steam; and P_b is an empirical coefficient for generation of deposits.

For chlorides we can take $P_b = 0$, $K_{P\Sigma} \approx 0$, and $\omega \longrightarrow 0$.

In this case, Eq. (1) takes the following simple form:

$$[Cl^-]_{fw}G_{fw} = [Cl^-]_{s.c}G_{bld}, \quad (2)$$

where $[Cl^-]_{fw}$ and $[Cl^-]_{s.c}$ are the concentrations of chlorides in feedwater and in the boiler's salt compartment.

For bicarbonates Eq. (1) can be written with $P_b = 0$ and $K_{P\Sigma} \approx 1$, because the maximum quantity of carbonic acid (in CO_2 form) obtained during thermolysis of

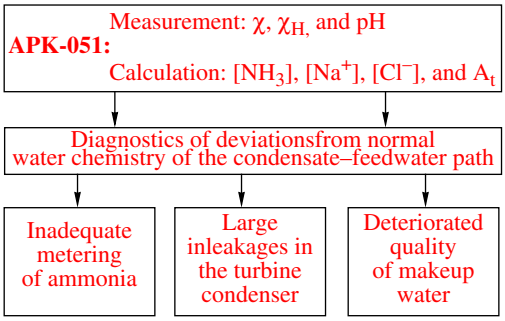

Fig. 2. Flow chart for assessing a deviation from normal water chemistry in the condensate–feedwater path using the APK-051 analyzer.

bicarbonates (in accordance with the following reaction) transfers into steam:

$$2HCO_3^- \longleftrightarrow H_2O + CO_2\uparrow + CO_3^{2-}. \quad (3)$$

It can be seen from (3) that two ions of HCO_3^- give birth to one ion of CO_3^{2-}, which undergoes hydrolysis in a cooled sample in accordance with the following equation:

$$CO_3^{2-} + H_2O \longleftrightarrow HCO_3^- + OH^-. \quad (4)$$

In this case, Eq. (1) of material balance for bicarbonates entering into the boiler with feedwater $[HCO_3^-]_{fw}$ can be written in the form

$$[HCO_3^-]_{fw}G_{fw} = 0.5([CO_3^{2-}]_{s.c} + [HCO_3^-]_{s.c})G_{bld}, \quad (5)$$

where $[CO_3^{2-}]_{s.c} + [HCO_3^-]_{s.c}$ is the total concentration of carbonates and bicarbonates in the boiler drum's salt compartment.

Dividing each term of Eqs. (5) and (2), taking into account the second-stage dissociation constant for carbonic acid K_{II}, we obtain

$$\left(1 + \frac{10^{-pH}}{K_{II}}\right)[CO_3^{2-}]_{s.c} = \frac{2[HCO_3^-]_{fw}}{[Cl^-]_{fw}}[Cl^-]_{s.c}. \quad (6)$$

The APK-051 analyzer can be used for determining the concentrations of chlorides and bicarbonates in feedwater. Then, using Eq. (6) we can easily calculate the concentrations of bicarbonates and carbonates and then also those of chlorides in the salt compartment by measuring χ, χ_H, and pH with the same analyzer. The concentration of phosphates in boiler water can be calculated from the electrical conductivity of an H-cationated sample as shown in [4].

Thus, the APK-051 automatic analyzer can successfully be used for online chemical monitoring of the quality of feedwater and boiler water used in superhigh-pressure drum boilers (p_d = 13.8 MPa). By quantitatively determining the standardized (χ, χ_H, and pH) and diagnostic (NH_3], [Na^+], [Cl^-], and A_t) indicators characterizing the quality of water coolant, it becomes possible to determine the type of deviation from normal water chemistry at an early stage of its development.

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