
**WATER TREATMENT
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Qualitative and Quantitative Analysis of Organic Impurities in Feedwater of a Heat-Recovery Steam Generator

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Abstract—In recent years, combined-cycle units with heat-recovery steam generators have been constructed and commissioned extensively in the European part of Russia. By the example of the Kazan Cogeneration Power Station no. 3 (TETs-3), an affiliate of JSC TGK-16, the specific problems for most power stations with combined-cycle power units that stem from an elevated content of organic impurities in the feedwater of the heat-recovery steam generator (HRSG) are examined. The HRSG is fed with highly demineralized water in which the content of organic carbon is also standardized. It is assumed that the demineralized water coming from the chemical water treatment department of TETs-3 will be used. Natural water from the Volga River is treated to produce demineralized water. The results of a preliminary analysis of the feedwater demonstrate that certain quality indices, principally, the total organic carbon, are above the standard values. Hence, a comprehensive investigation of the feedwater for organic impurities was performed, which included determination of their structure using IR and UV spectroscopy techniques, potentiometric measurements, and element analysis; determination of physical and chemical properties of organic impurities; and prediction of their behavior in the HRSG. The estimation of the total organic carbon revealed that it exceeded the standard values in all sources of water comprising the feedwater for the HRSG. The extracted impurities were humic substances, namely, a mixture of humic and fulvic acids in a 20 : 80 ratio, respectively. In addition, an analysis was performed of water samples taken at all intermediate stages of water treatment to study the behavior of organic substances in different water treatment processes. An analysis of removal of the humus substances in sections of the water treatment plant yielded the concentration of organic substances on the HRSG condensate. This was from 100 to 150 $\mu\text{g}/\text{dm}^3$. Organic impurities in boiler water can induce internal corrosion and deposits containing products of their degradation.

Keywords: heat-recovery steam generator, feedwater, IR and UV spectroscopy, potentiometry

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The available international experience with designing new and retrofitting existing thermal power stations suggests that the basic activities for improving their efficiency should be focused on development and commercial implementation of combined-cycle units (CCU). In doing so, CCUs with an HRSG where gas turbine unit (GTU) exhaust gases generate steam in the HRSG are most widely used due to their higher efficiency. Since 2014, CCUs have been constructed and commissioned in the Republic of Tatarstan: a 77 MW GE 6FA—part of 220 MW GTU—was put into operation at the Kazan TETs-2, an affiliate of JSC Tatenergo, in December 2014; a 388.6 MW GE 9HA.01 GTU was put in operation at the Kazan TETs-3, an affiliate of JSC TGK-16, in April 2017; a 77 MW GE GTU is being constructed as part of a 230 MW CCU and is to be put into operation at the Kazan TETs-1, an affiliate of JSC Tatenergo, in March 2018.

Among the problems encountered in implementation of CCUs is the need to meet the requirements for the quality of feedwater for HRSG, which are much stricter than the requirements for the feedwater of power units with a drum or once-through boilers. The feedwater quality must comply with the standards outlined in pars. 4.8.16, 4.8.21, and 4.8.36 of the “RF Power Stations and Networks Operation Code” [1]. Moreover, there is a standard for the content of organic impurities. According to the procedure developed by JSC VTI [2], the total organic carbon in the feedwater for HRSGs should not exceed 100 $\mu\text{g}/\text{dm}^3$. The fact that the feedwater quality requirements become more and more strict leads us to a new view of the water treatment problems [3].

A GTU was commissioned at the Kazan TETs-3 (KTETs-3) in June 2017. A heat-recovery steam generator manufactured by the Podolsk Machine-Build-

Table 1. Actual quality indices of chemically treated water (CTW), evaporator distillate (ED), and main turbine condensate (MTC) for the makeup of HP drum boilers at KTETs-3

Quality indices	2015			2016		
	CTW	ED	MTC	CTW	ED	MTC
Electrical conductivity, $\mu\text{S}/\text{cm}$	0.8	1.19	0.7	0.79	1.1	0.62
Total hardness Ht, $\mu\text{mol}/\text{dm}^3$	1.0	0.5	0.5	1.0	0.5	0.5
Content, $\mu\text{g}/\text{dm}^3$:						
sodium	45.5	36.25	47	54	28.25	43
silicic acid (as SiO_2)	45.8	28.3	35.2	61	29.2	32.4
total organic carbon	610	105	151	603	101	150
iron	12.9	14.56	14.53	11.6	14.9	15.4
copper	1.2	1.8	2.54	2.0	2.6	2.75
oil and grease	120	107	—	151	101	—

ing Factory is provided for recovery of the GTU exhaust gas heat. Its characteristics are as follows:

Feedwater treatment capacity, t/h	500 (max. 520)
Working pressure, MPa:	
primary circuit	4.5
secondary circuit	13
Maximum blowdown, t/h	15

The HRSG should be fed with demineralized water. According to the contract, the HRSG manufacturer does not deliver a water treatment plant for chemical water treatment. It is assumed that all demineralized water will be supplied from the TETs' chemical department. At present, the demineralized water at TETs comes from different sources:

(1) Chemically demineralized water (CDW) from a two-bed demineralizer with a capacity of 500 t/h (of Phase I and II);

(2) Evaporator distillate (ED) from the evaporating water treatment unit with a capacity of 360 t/h; and

(3) Main turbine condensate (MTC).

These three types of demineralized water mixed in different proportions will make up the HRSG feedwater. Mixed bed filters with internal regeneration are also installed for additional feedwater treatment. Natural water from the Volga River is used as raw water for preparation of demineralized water.

Table 1 presents mean quality indices of the demineralized water fed from different sources in 2015–2016.

It is evident that certain quality indices, particularly, the total organic carbon, of the demineralized water exceed the limits set forth in the applicable standards. A decrease in the content of organic impurities requires identification of their nature and source.

The objectives of this investigation are as follows:

(1) A qualitative and quantitative analysis of organic impurities in HRSG feedwater;

(2) An analysis of chemical impurities for components using physicochemical analysis techniques (such as chromatography, IR and UV spectroscopy, potentiometric measurements, or element analysis);

(3) Prediction of physical and chemical properties of organic impurities and their behavior in the HRSG.

The problems related with organic impurities in the feedwater of evaporators or steam generators were previously dealt with extensively in the RF leading research centers, such as MPEI, IGEU, and VTI [4–8]. Many organic impurities belonging to different classes of compounds were found in the raw water and process water used at TETs. It is generally agreed that organic substances and/or products of their thermal degradation can cause erosion and corrosion damages in steam generators and turbines.

PROCEDURE FOR EXTRACTION OF ORGANIC COMPOUNDS FROM WATER SAMPLES

For the preliminary assessment, the water was analyzed at intermediate stages of the water treatment process. The samples were tested for color, chemical oxygen demand (using permanganate and dichromate as the oxidant), and optical density in a spectrophotometer. To ascertain the chemical structure of organic substances, they were extracted from the process water using Grade AG-3 activated coal. The coal was prewashed with 0.1% NaOH solution, acetone, and HCl solution. After that, the coal was rinsed with plenty of distilled water. Portions of the water under investigation were made to flow through the treated coal. Then the organic compounds were extracted by fractions. First, elution with acetone containing 10% water (by volume) was performed. After that, the coal was rinsed with water. Acidic organic substances adsorbed on the coal was removed by washing with 0.5% NaOH solution. The final stage included purification and concentration of the desorbed organic substances. The acetone extract was carefully evaporated at 40°C. The alkaline eluate was neutralized with

Table 2. Content of organic substances in the feedwater at Kazan TETs-3

Characteristic	December 2015			January 2016		
	CTW	ED	MTC	CTW	ED	MTC
Organic matter, mg/dm ³	1.050–1.320	0.450	0.520	1.430	0.300	0.265
The same as TOC, mg/dm ³	0.500–0.620	0.212	0.244	0.627	0.141	0.125

Table 3. Analysis of basic fractions of organic substances extracted from the raw Volga water and demineralized water from different sources at KTETs-3

Component	Element content, wt %				
	C	H	O	N	S
Humic acids	51.2 ± 3	4.7 ± 0.6	40.4 ± 3.8	2.6 ± 1.6	1.1 ± 0.3
Fulvic acids	46.7 ± 4.3	4.2 ± 0.7	45.9 ± 5.1	2.3 ± 1.07	1.2 ± 0.7

hydrochloric acid and passed via KU-2 cationite in the H-form. All the eluate was then evaporated at a maximum temperature of 40°C to obtain a volume of approximately 100 mL. The solutions with sediments were put into bags from semipermeable (dialysis) cellophane, which were placed into tanks with distilled water. Specimens from the dialysis bags were transferred to Petri dishes and dried in a vacuum oven above CaCl₂. The specimens were then put into weighing cups and lastly dried in a desiccator above CaCl₂.

SPECTROSCOPIC INVESTIGATION PROCEDURES

IR transmission spectrums of the investigated specimens were determined using a Bruker Vector 22 FT-IR spectrometer. The spectrums were recorded in the frequency range between 400 and 4000 cm⁻¹ with a resolution of 4 cm⁻¹. Bruker's OPUS software was used for data processing. Specimens for IR-spectroscopy were prepared as follows. A specimen (weight of 0.0015 g) was ground in an agate mortar together with KBr powder (0.15 g) until a homogenous mixture was obtained. The prepared mixture was used for making a 13-mm diameter disc specimen in a press mold at a pressure of 10 t/cm². For comparison, an identical tablet was made from pure KBr powder without ant additives.

Electronic absorption spectrum of solutions were recorded in a Shimadzu UVmini-1240 with reference to the solvent (distilled water) in quartz cells (1 cm). The lamps were switched over at a wavelength of 340 nm.

DISCUSSION OF THE RESULTS

Using the above-described procedure, organic substances in a pure form were extracted from the Volga raw water and the demineralized water from different sources. Their content in the feedwater in the period from December 2015 to January 2016 is given in Table 2. Since the analysis of organic substances was

determined, Table 2 also presents the calculated values of TOC.

These results agree well with each other. The presented data for the feedwater at Kazan TETs-3 (in 2015 and 2016) enable us to make the following conclusions:

(1) The content of organic substances in the chemically treated water is above 1 mg/dm³ (or 600 µg/dm³ as TOC) at all times.

(2) The content of organic substances in distillate from the evaporator varies from 0.20 to 0.45 mg/dm³ (or 100 to 200 µg/dm³ as TOC).

(3) The content of organic substances in the main turbine condensate is slightly higher than in the evaporator distillate and varies from 0.25 to 0.55 mg/dm³ (or 125 to 250 µg/dm³ as TOC).

The extracted organic substances were crystalline or resinous substances ranging in color from brown to black and partly insoluble in acidic water. An assumption that these were humic substances, namely, a mixture of humic and fulvic acids, was taken as the basis [4]. Fractional precipitation or acidation of the extract enables the organic substances to be broken down easily into two basic fractions: humic acids (HA) and fulvic acids (FA). The ratio of humic fractions (HA/FA) in the raw Volga water is 20/80. Hematomelanin acids can be extracted from HAs precipitated with ethanol. Table 3 presents the analysis of factions extracted from the raw and demineralized water at KTETs-3.

A set of indications enabling one to unambiguously determine the features of humic substances, such as specific composition, the structure of the "core" of macromolecules from benzenecarboxylic acids, the presence of nonhydrolyzed nitrogen, and the specific of electronic and IR spectrums, was proposed in [9–11] based on processing of abundant data on the structure and properties of humic substances.

Based on physical and chemical characteristics, elemental composition, UV and IR spectrums (Figs. 1, 2), it has been established that the chemical composition of the organic fraction of the raw water

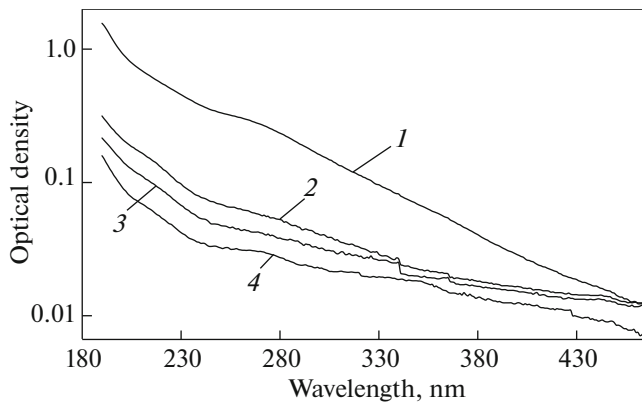


Fig. 1. UV absorption spectra for the (1) raw Volga water, (2) evaporator distillate, (3) main turbine condensate, and (4) chemically demineralized water at KTETs-3.

and the feedwater correspond to that specific for humic substances.

Curves 2–4 in Fig. 1 are nearly identical, thereby demonstrating that the organic fraction of all three types has the same composition. The untreated raw water contains much greater organic impurities, which is confirmed by the deviation of curve 1.

A comprehensive analysis of the structure of organic impurities can be done using an IR-spectroscopy technique. Several spectrums are presented in Fig. 2: curves 1 and 2 represent spectrums of fulvic acids and curves 3 and 4 represent spectrums of humic acids extracted from the process water at KTETs-3.

All the spectrums contain bands specific for humic substances: a wide band 3420–3440 cm^{-1} represents valence vibrations of the bound OH-group; a 2920–2950 cm^{-1} band represents CH_2 - and CH_3 -groups; a 1710–1730 cm^{-1} band stands for a CO-group; a 1640 cm^{-1} band represents deformation vibrations of the CN-bond in amides; a 1330–1370 cm^{-1} band corresponds to deformation vibrations of the CH-bond; valence vibrations of the CO-group of alcohols and ethers are found in the range 1122–1170 cm^{-1} .

There are differences between spectrums 1 and 2 or 3 and 4 specific for fulvic or humic acids, respectively. Thus, 1070 and 1270 cm^{-1} bands seen in spectrums 1 and 2 are caused by symmetric and asymmetric valence vibrations of the carboxyl group, while clear bands at 2490 and 2602 cm^{-1} represent carboxylic acids. An intense band at 1010 cm^{-1} is specific for the OH-group in carbohydrates. On the other hand, spectrums 3 and 4 contain bands in the range between 1400 and 1620 cm^{-1} , thereby confirming the presence of a considerable amount of aromatic fragments. One more distinguishing feature is the existence of a band at 3430 cm^{-1} indicating that there are bound OH-groups.

The behavior of IR-spectrums suggests that fulvic acids essentially contain aliphatic carboxyl-acid and amino-acid fragments and polysaccharides, while humic acids contain highly oxidized aromatic fragments (such as benzenecarboxylic acid). Hematome-lanic acids (black resinous substances) resemble sub-

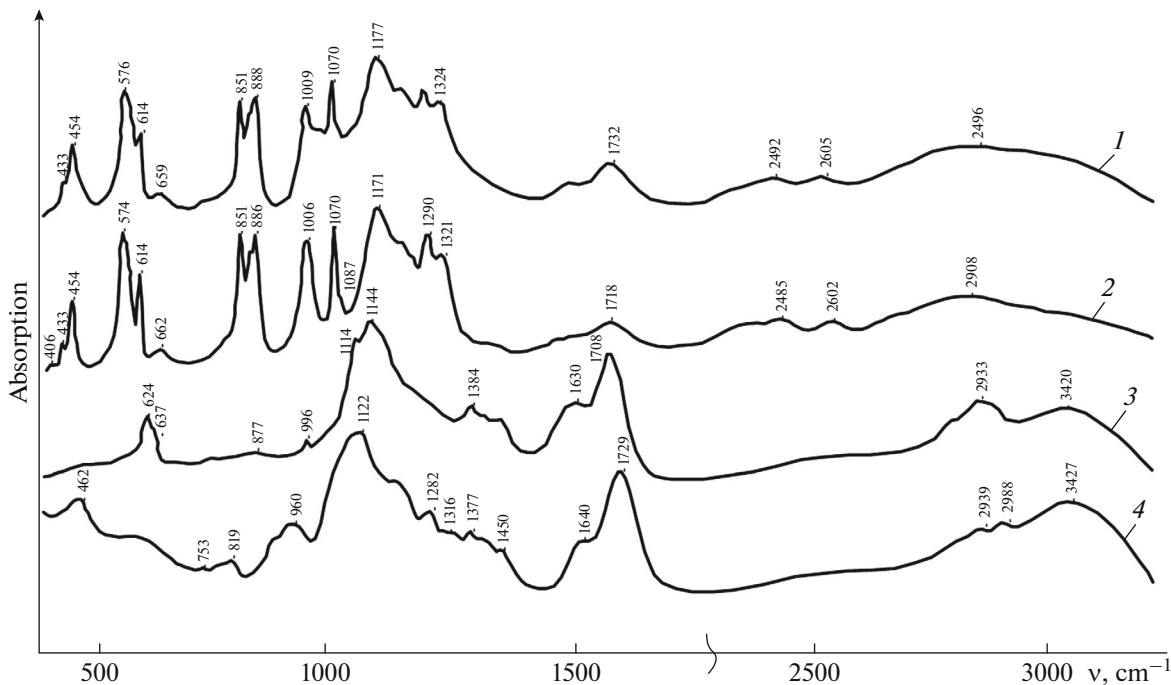


Fig. 2. Spectrums of organic fractions obtained by IR-spectroscopy. 1—ED fractions not removed in activated carbon; 2—fraction separated from the acetone extract of ED filtrate; 3—fraction extracted using acid from the evaporator blowdown water (HA); 4—fraction separated from evaporated CTW extract.

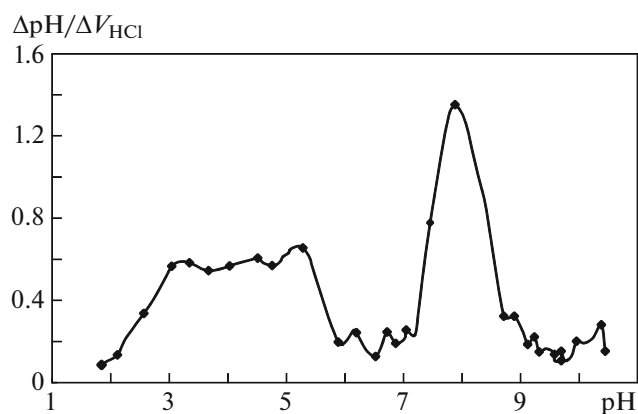


Fig. 3. Differential curve of potentiometric titration of the organic fraction from the natural Volga water (December 2015; the permanganate demand is $6.4 \text{ mg O}_2/\text{dm}^3$).

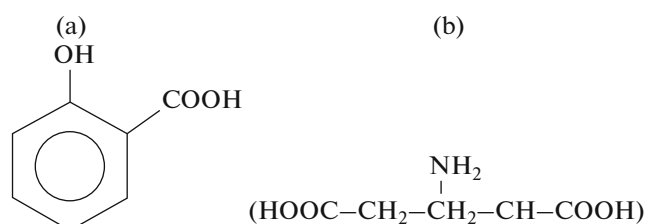


Fig. 4. Structural formulae of (a) salicylic and (b) L-glutamic acids.

stituted phenols according to the specifics of their spectrum.

Using various organic solvents and solutions (such as acetone, ethanol, and sodium acetate water solution), the fulvic acids were fractionated into crenic and apocrenic acids. Sharp differences were revealed in the composition between the fulvic acid parts eluted with acetone or anodized with alkali according to the content of nitrogen and oxygen as well as the acidity.

Humic substances, which are a mixture of biochemically stable high-molecular compounds, are the major organic substances present in natural river water in the European part of Russia that are responsible for colority and chemical oxygen demand with permanganate as the oxidant. The mixtures consist of humic and fulvic acids. Their chemical structures are similar and represent a polymeric compound consisting of substituted benzoic rings linked with linear fragments. For a substitute, carboxylic and hydroxylic groups, amines, amides, and imines offering acidity ranging from pH of 3–5 to 8–10 prevail. Humic substances contain a considerable amount of absorbed compounds of silicon and iron.

Potentiometric measurements were used for investigating the raw Volga water for the content of organic substances and the organic substances for their acidity. A curve of pH-metric titration (pH-spectrum) of the Volga water organic fraction is presented in Fig. 3.

Humic and fulvic acid can be considered as dibasic acid. As a first approximation, salicylic ($pK_a^{(1)} = 2.98$ and $pK_a^{(11)} = 13.6$) and *o*-phthalic ($pK_a^{(1)} = 2.943$ and $pK_a^{(11)} = 5.432$) acids having a similar chemical structure and close values of pK_a (here, pK_a is the constant of dissociation of carboxyl and hydroxyl groups) can be considered for a monomer of humic acids (Fig. 4). A better approach to a monomer of fulvic acids is offered by L-glutamic acid ($pK_a^{(1)} = 4.31$ and $pK_a^{(11)} = 9.67$). An additional advantage of selecting monomeric acids as an analogue of humic and fulvic acids lies in the fact that complexes of these acids with ions of metal usually contained in natural water have been thoroughly studied.

According to the experimental data, the content of humic substances in a sample of Volga water is $24.1 \text{ mg}/\text{dm}^3$, and the corresponding concentration of acid groups is $0.24 \text{ mmol-equiv}/\text{dm}^3$. The latter value coincides with the experimental humate alkalinity. The content of acid groups of all types is $9.95 \text{ mmol-equiv}/\text{g}$ on a dry basis. If we assume that $\text{pH} (f = 1/2) = pK_a$, where f is the extent of titration, the set of constant pK_a for the tested sample will be 3.05, 4.5, 5.5, 7.9, 9.3, 10.1. According to the published data, the set of $pK_a = 3, 4.77, \text{ and } 10.0$ is specific for humic acids, and the set of $pK_a = 4.3, 8.0, \text{ and } 9.3$ is specific for fulvic acids. With these values of the constants and considering the amount of the consumed titration substance, we obtain that a fraction of humic acids in the tested sample does not exceed 10%, while fulvic acids are responsible for 90%. This fact agrees with the published data indicating that fulvic acids prevail in the water of rivers in the central part of the Russian Federation [8, 11].

Comparison of physical and chemical properties and spectrums of the extracted organic substances demonstrates that the source of organic substances in the feedwater at KTETs-3 is the raw water from the Volga River (allochthonous origin). Water samples taken at all stages of the water treatment process were analyzed for investigating the behavior of organic substances as they enter different water treatment systems.

At the pretreatment stage, approximately 50% of organic substances is removed from the natural water in a clarifier. According to the available data, the coagulant absorbs most apocrenic acids. After that, in preparing chemically treated water in the cation-anion demineralizer, humic substances pass all treatment stages and are basically trapped in the anion exchanger of the second stage. However, the chemically treated water still contains many organic substances. This is explained by the fact that they are not monitored as they pass via the anion exchanger and the standards for their content are not yet established. Since humic substances have a great molecular weight and large sizes, they are likely to break through the mixed bed filter

used as the third stage. These data agree with the conclusions made in [5, 6].

ED and MTC contain much less organic substances since the impurities are nonvolatile high-molecular compounds. This fact was found previously in [5]. The presence of humic substance in ED and MTC is caused by their carry-over by steam in equipment items of the multistage evaporator and in the steam boiler. In this case, the steam carries over the least water-soluble substances, namely, humic acids.

The presented data make it possible to predict the amount of organic impurities that can enter the HRSG. When feeding the HRSG with the water of KTETs-3, the anticipated content of organic substances in the steam condensate will be 100–150 $\mu\text{g}/\text{dm}^3$. Considering the acidity of organic impurities, the problems with corrosion of the equipment may be expected. In addition, since humic substances contain silicon and iron compounds, they can precipitate on the inner surface of HRSG on thermal destruction. Hence, the feedwater for HRSGs required additional treatment for removing organic substances.

CONCLUSIONS

(1) The following content of organic substances in the feedwater from different sources at the Kazan TETs-3 (in 2015 and 2016) was determined:

(i) Above 1 mg/dm^3 (or 600 $\mu\text{g}/\text{dm}^3$ as TOC) in the chemically treated water at all times;

(ii) From 0.20 to 0.45 mg/dm^3 (or 100 to 200 $\mu\text{g}/\text{dm}^3$ as TOC) in distillate from the evaporator;

(iii) From 0.25 to 0.55 mg/dm^3 (or 125 to 250 $\mu\text{g}/\text{dm}^3$ as TOC) in the main turbine condensate that was slightly higher than in the evaporator distillate.

(2) Organic substances in the demineralized water at KTETs-3 include basically natural humic substances. Their source is the natural Volga water. Humic substances are trapped poorly in cation-anion exchangers and, hence, enter the chemically demineralized water. On the other hand, certain fractions of humic substances are carried over by steam since they are thermally stable, and, because of this, they are found in the main turbine condensate and the evaporator distillate.

(3) When feeding the HRSG with water from KTETs-3, the anticipated concentration of organic substances in the HRSG steam condensate will be between 100 and 150 $\mu\text{g}/\text{dm}^3$. Corrosion and deposits on the inside of HRSG that resulted from thermal destruction of organic substances can pose a problem.

(4) The automatic control of HRSG feedwater chemistry at KTETs-3 must include water control for organic substances.

(5) For the HRSG, additional treatment is required of chemically demineralized water for removing

organic substances and of the feedwater for removing all types of mineral impurities.

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