Technologies for monitoring and cleaning the return manufacturing condensate in the energy-technological complex of heat power plant – petrochemical facility

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Abstract. Condensate reuse as feed water for boilers reduces the costs of the used natural resource, improving the environmental and economic efficiency of the facility. The return condensate during condensation of steam supplied from thermal power plants for the implementation of technological processes at many petrochemical facilities is an aqueous mixture of petroleum products and mechanical components with a small amount of inorganic components. The return condensate samples obtained from plants for the production of butyl rubber, synthetic rubber, styrene and polyester resins were used to determine the quantitative and qualitative composition of organic impurities. On the basis of obtained results, physical and chemical purification methods have been developed. According to the analysis results, it is recommended to bring the return condensate to the required standards by flotation with air bubbles of small diameter.

1. Introduction
For large plants and industrial facilities, the most effective is to cooperate with heat power plants (HPP) creating energy-technological complexes, primarily related to the supply of steam, as well as electricity and hot water. In Tatarstan, such complexes currently include Kazan Thermal Power Station-3 – Kazan organic synthesis plant and Nizhnekamsk Thermal Power Station-1 – Nizhnekamsk petrochemical plant. The input steam, which in petrochemical facilities, depending on the technology, participates in the production cycles of organic components, water washing and product cooling, is returned by chemical plants to HPP in the form of return condensate. Thus, return condensate from petrochemical industries is characterized by low content of inorganic substances and high content of organic pollutants in the form of dispersed particles, resin emulsions and dissolved hydrocarbons of volatility various degrees.

Return condensate, depending on the parameters of the boiler units of combined heat and power plants or steam generating plants, must meet the quality standards given in table 1 [1].

| Indicators               | Units of measurement | Values of indicators |
|-------------------------|----------------------|----------------------|
| Hardness total          | µg-eq/dm³            | ≤50                  |
| Fe                      | µg/dm³               | ≤100                 |
| Cu                      | µg/dm³               | ≤20                  |
| Na                      | µg/dm³               | ≤100                 |
| nSiO₂·mH₂O              | µg/dm³               | ≤120                 |
| Oil products            | µg/dm³               | ≤0.5                 |
8.5-9.5
≤5
≤1000

In case of inconsistency between the return condensate quality and the stated requirements, the condensate purification [2,3] or disposal is necessary; this, however, is associated with material costs and environmental problems. In some cases it is more profitable to use the condensate heat than to bring its quality to the required parameters [4].

2. Materials and methods
For quantitative and qualitative analysis of organic impurities, the return condensate samples were taken from the butyl rubber plant (sample 1), synthetic rubber plant (sample 2), styrene and polyester resins plant (sample 3). Based on the obtained results, physical and chemical methods have been developed to clean the return condensate samples.

For the initial analysis and at the intermediate stages of sample cleaning, color, pH, electrical conductivity (SEC), and permanganate oxidation were determined. The electronic absorption spectra of the solutions were recorded on a SHIMADZU UV-1800 spectrophotometer in relation to the solvent (distilled water) in quartz cuvettes (1 cm). Lamps were switched at a wavelength of 340 nm. Physical and chemical methods of exposure for the removal of organic impurities included sedimentation, boiling, flotation, flocculation, coagulation, ion exchange, and sorption procedures.

The sedimentation was carried out in the light, in open containers for 3-4 days.

Samples were boiled in open flasks for 5 minutes.

Flotation of air bubbles of small diameter to increase the area of exposure was realized for 1 hour.

Flocculation was performed with a 1% starch solution in the amount of 3 ml – 500 ml of the sample.

Coagulation was performed with a 5% solution of FeCl₃ in the amount of 6 ml – 500 ml of the sample.

Ion exchange was carried out with an organ-absorber MP 800 (anion exchange resin), previously converted to the OH form by washing with 6% NaOH.

The impurities were absorbed from the samples by charcoal (brand BAU) or activated (medical) coal. Pre-ground charcoal was boiled for 10 minutes in distilled water and then washed with distilled water. Activated (medical) coal was not subjected to preliminary preparation. Due to the fact that identical results were obtained by passing samples through both charcoal and activated (medical) coal, the term “coal” is used in the description of the procedure. Before passing through the coal, the samples were subjected to sedimentation or flotation. Then the samples were placed for 1 hour in coal (5 g of coal with 50 ml of the sample). The solution was filtered through a double filter paper, prewashed with distilled water.

3. Results
The results of preliminary analysis of the samples are presented in table 2.

| indicators | sample 1 | sample 2 | sample 3 |
|------------|----------|----------|----------|
| color, transparency | transparent, colorless | transparent, colorless | transparent, primrose |
| smell | weak sweet-bitter smell | strong smell of organic substances | moderate smell of organic aromatic compounds |
| pH | 11.3 | 7.1 | 9.1 |
| SEC, MS/cm | 5.43 | 0.104 | 0.117 |
| theoretical salt content, mg/l | 3530 | 68 | 76 |
| oxidability, mg/l | not determined | 23.44 | 13.84 |
According to the results of the preliminary physical and chemical analysis, it was decided not to continue the study of the sample 1 due to its high salinity.

On the UV spectrum of an unpurified sample 2 (figure 1), three peaks have been determined: a peak with a wavelength of 251 nm is characteristic of a benzene ring, that with a wavelength of 219.5 nm – for butadiene and 195.5 nm - for butyl alcohol. These substances are the main components of the rubber synthesis. The peak with a wavelength of 251 nm is wide and low, the peaks at 219.5 and 195.5 nm are high and narrow.

![Figure 1. Comparison of UV spectra of sample 2 before purification (line 1) and after settling (line 2).](image1)

Judging by the UV spectrum (figure 2), the sample 3 contains predominantly organic substances involved in the production cycle of styrene and synthetic resins. There are high and intense peaks at 190 nm (ethylene glycol), wide and gentle ones at 220.3 nm (aromatic ring), and two small peaks at 310 nm and 317 nm (terephthalic acid and phthalic anhydride, respectively).

![Figure 2. Comparison of UV spectra of sample 3 before purification (line 1) and after settling (line 2).](image2)

Chemical methods of exposure, i.e., the treatment with an organic absorber and the flocculant dosing, did not have any significant positive effect on the samples cleaning from organic impurities. After passing the samples through the organic absorber on the UV spectra, intense bands with a wavelength of 200 nm appeared in addition to the existing ones. When dispensing a flocculant, visible changes of the samples were not observed, including after settling the solutions with the flocculant for a day.

After the coagulant dosing, the sample 2 turned yellow and remained transparent. The coagulant dosing into sample 3 resulted in a cloudy solution. After 1 day of settling and the coagulant adding, a dense brown precipitate fell out. The solution above the precipitate became transparent obtaining primrose tinge and subtle smell. The results of physical and chemical measurements have shown a decrease in pH - 7.3 and an increase in SEC - 148 μS / cm relative to...
baseline values. A UV spectrophotometer was used for the solution spectrometry above the sediment of the sample 3 after the coagulant adding and settling. The spectrum has dramatically changed and almost all the peaks have disappeared from it. The curve have smoothed out (figure 3).

![Figure 3. Comparison of UV spectra of sample 3 after flotation (line 1) and the coagulant addition (line 2).](image)

It may be assumed that organic matter coagulation with iron salts occurred with precipitation. Judging by the UV spectrum, almost all organic compounds precipitated from the solution. However, the primrose color of the sample after deposition and the oxidation index indicate the residual content of iron salts in the treated coagulant solution (table 3).

Samples subjected to physical methods of exposure (settling, flotation, boiling) have been largely cleared of organic impurities.

After settling in the light in open containers for 3–4 days, the smell became subtle, the transparency and color remained almost unchanged, and the precipitate did not fall out. The results of the SEC and the pH of the sedimentation samples remained almost unchanged, but the UV spectrum smoothed out, especially for sample 2 (figure 1). The peaks have almost disappeared, the intensity (height of the peaks) has decreased, and the spectrum has become similar to the aromatic organic compounds spectrum. The spectrum of the ATP sample has changed, but not so significantly (Figure 2). Some peaks have disappeared and the height of the peaks has decreased. Peaks remained at 190 nm and became narrow, 220 nm and 317 nm. The permanganate oxidability of the samples 2, 3 decreased and reached the required values (table 3). Therefore, settling for 3 days eliminates a significant amount of organic impurities from the samples, and judging by the intense odor, they become very volatile. In comparison with a longer settling of the samples for 7 days, additional effects have not been recorded.

After the flotation procedure, there were no visible changes of the samples, pH or SEC, but the smell almost disappeared. The UV spectrum of sample 2 after flotation coincides in intensity with the spectrum after settling for 3 days. There are 2 peaks that have the same wavelength as in the untreated sample (252 and 219 nm), but with a significant decrease in the height and area under the peak curve (figure 4). Therefore, one hour of flotation of the sample 2 is equivalent to 3 days of settling.

The UV spectrum curve of sample 3 compared to the settled sample 3 smoothed even more (Figure 2, 3). The peak height of 190 nm in the untreated sample decreased by half, and the peak at 220 nm was reduced by 20%. Thus, one hour of flotation of sample 3 exceeds the effect of 3 days of settling.

The permanganate oxidability of the samples after flotation is identical to that after settling (table 3) and additionally testifies to the methods equivalence.

The UV spectra of samples boiled for 5 minutes look like they are settled, but the peaks are higher after boiling. Apparently, these methods could be equally effective, but a longer boiling is necessary, which is unprofitable in terms of energy.

Sorption by coal after settling or flotation eliminates residual odor from the samples and smoothens the spectra, removing all peaks from them. However, a band from coal appears on the UV spectra, overlapping with part of the spectrum (figure 4, 5). There is a wide intense peak in the region of 200–
250 nm. This intense peak appears to be caused by the presence of unwashed resin in the coal. In addition, the passage of samples through coal increases the permanganate oxidation significantly (table 3).

![Figure 4. UV spectra of sample 2 after flotation (line 1) and after flotation-passage through coal (line 2).](image)

![Figure 5. UV spectra of sample 3 after flotation (line 1) and after flotation-passage through coal (line 2).](image)

**Table 3.** Summary table of permanganate oxidation results of samples 2 and 3 (mg/l).

|        | raw  | settling | flotation | settling coal | + flotation coal | + coagulant |
|--------|------|----------|-----------|---------------|-----------------|-------------|
| sample 2 | 23.44 | <2       | 1.84      | 25.6          | 25.04           | -           |
| sample 3 | 13.84 | 5        | 4.44      | 45.2          | 49.04           | 12.4        |

When superimposing the UV spectra of samples 2, 3 after settling – passing through coal and flotation – passing through coal, the graphs merge into one curve. That is, the cleaning with these methods makes the samples very similar in composition, which indicates an almost complete removal of organic impurities.

**4. Conclusion**
1. The sample from the butyl rubber plant was removed from the analysis of organic components due to high salt content, requiring additional purification methods.
2. Passing the samples through the organic absorber and the flocculant dosing do not provide significant positive results.
3. The addition of coagulant FeCl₃ gives the best effect among the used methods, judging by the UV spectrum. That is, the maximum amount of organic impurities is cleared in comparison with other methods, but the results of permanganate oxidation are unsatisfactory, which is apparently due to the iron ions increase in the sample.

4. Determination of the condensate samples from the synthetic rubber plant, styrene and polyester resins plant, within 3 days gives a significant positive result, but takes a lot of time and requires space for organizing the condensate tanks.

5. Flotation with small-diameter air bubbles for 60 minutes provides an effect equivalent to settling the sample from the synthetic rubber plant and superior to settling the sample styrene and polyester resins plant. Permanganate oxidation indicators meet the requirements.

6. Boiling gives the same effect as flotation, but boiling method is more energy consuming.

7. Passing samples through coal after settling and flotation clears samples from odor residues and smooths the spectra, removing all peaks from the bottom. However, a band from coal appears on all UV spectra, overlapping with part of the spectrum. In addition, passing samples through coal increases the permanganate oxidation significantly.

The obtained results served to identify the priority method for removing condensate from the samples from organic impurities from synthetic rubber plant, styrene and polyester resins plant; a flotation procedure with small air bubbles of small diameter can be recommended for 60 minutes.

References
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