The experience of implementing the water chemistry treatment on the gas-turbine power plant using the AMINAT reagents

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Abstract. Implementation of the program of import substitution considered on the example of pilot tests (PT) of reagents produced by NPF Travers LLC. The existing water chemistry of steam boilers and heat recovery steam boilers of RN-Tuapsinsky Oil Refinery LLC gas-turbine power plant is organized with the use of complex reagent Helamin BWR-150H. Considering the advantages and disadvantages of complex reagents for the organization of water chemistry, it was proposed to conduct PT of reagents AMINAT KO-4 based on a mixture of polyphosphates to prevent scale formation on heat transfer surfaces and AMINAT PK-2 based on mixtures of neutralizing amines to prevent carbon dioxide corrosion. The article presents the results of the PT, which showed that the corrective water chemistry of boilers using reagents AMINAT ensured the maintenance of the regulatory requirements of the regime maps of the equipment, as well as minimizing the processes of corrosion, scale formation and sludge formation during the entire period of work. Based on the results obtained, conclusions were drawn on the technical and economic feasibility of using these reagents.

1. Introduction
In accordance with the Energy Strategy of Russia until 2030, one of the main characteristics of ensuring state energy security is the stability of the energy sector to external and internal economic, technological and natural threats, as well as its ability to minimize the damage caused by manifestation of various destabilizing factors. The energy strategy of Russia until 2030 [1] and the Strategy for the development of power engineering for 2010-2020 [2] set targets for the level of development of import substituting production in power sector. The maximum possible use of a competitive domestic product in all technological processes and projects is included among the most important principles and mechanisms of the state energy policy for ensuring energy security.

For example, an import substitution program is being successfully implemented at RN-Tuapse Refinery LLC. As part of this program, in the first half of 2018, employees of the GTU TPP together with specialists of NPF Travers LLC carried out pilot tests of domestic AMINAT reagents for the treatment of feed and boiler water of steam boilers and waste heat boilers of GTU-TPP RN-Tuapsinsky Oil Refinery LLC.

The thermal scheme of the starting complex consists of three blocks of gas turbine units (GTU) with six waste heat boilers (HB) E-65-4.0-440 and two steam boilers (SB) E-50-3.9-440GM. Water desalination is provided in two-stage reverse osmosis plant (ROP). The permeate after the first stage of
the ROP enters the calciner, then for a deeper removal of carbon dioxide at the second stage of the ROP, strong alkali (NaOH) is dosed into the permeate, also increasing the pH value of the permeate after the second stage. Permeate after the second stage of reverse osmosis is fed to the deaerator.

For the organization of the water chemistry (WC) of the SB and HB GTU TPP, at the project stage, a Helamin reagent was chosen with a pH correction of the boiler water with alkali. In connection with alkalization of the permeate to pH = 8.5-9.5, the dosing of NaOH into the boiler water was excluded. The input of the complex amine-containing reagent brand Helamin BWR-150H was organized in the feedwater pipeline after the deaerator to the inlet of the feed pumps. The dosing of Helamin BWR-150H reagent was monitored by the content of the reagent in the feed and boiler water, as well as in the saturated steam [3].

The advantages of using complex amine-containing reagents include, first of all, the simplification of the organization of chemistry of steam boilers. Due to the fact that the amine-containing reagents do not contain either phosphates or solid alkalis (caustic soda) and do not require their use for corrective treatment of boiler water, the problem of hide-out, i.e. increasing the phosphate content in the boiler water due to their transition from deposits on the surface of the boiler. The presence of film-forming amines in the complex reagent allows preserving the equipment in the shutdown mode, which is most relevant nowadays for many Russian stations and industrial enterprises [4].

In addition to significant advantages, it is worth noting the disadvantages of complex amine-containing reagents. First of all, it is a high cost and a significant consumption of reagent. A number of enterprises have noted the negative effect of film-forming amines on the sensitive elements of sensors of automatic instruments for chemical control of the coolant quality, which requires additional measures by personnel to eliminate these effects [5].

The most discussed problems also include the lack of information on the component composition of complex amino-containing reagents. At the same time, the input quality control of the reagent by the pH value and density offered by the manufacturers does not allow to determine the percentage of the reagent unambiguously. According to the developed document [3], the content of the reagent in the coolant along the path should be 1-5 ppm. To monitor and maintain existing standards used the measurement of polyamines (PA) photocolorimetric method with indicators Bengal Rose or Eosin [6, 7]. According to the developers of this method, the content of only film-forming amines is determined during the analysis. But, as practice has shown, this method allows determination of neutralizing amines. Given the above, the use of complex reagents can lead to ambiguity of the results and requires individual testing of water chemistry for steam boilers and recovery boilers.

2. Using AMINAT reagents

Taking into account the shortcomings described in Helamin water chemistry, in the framework of import substitution program to conduct pilot tests on steam equipment, a gas turbine-based power plant was proposed by domestic agents brand AMINAT. For the organization of the correctional water chemistry of steam boilers and waste boilers, AMINAT KO-4 reagent on the basis of a mixture of polyphosphates was delivered to prevent scale formation on heat transfer surfaces and AMINAT PK-2 on the basis of a mixture of neutralizing amines was delivered to prevent carbon dioxide corrosion and maintain normalized pH values of the water and steam.

In accordance with the reaction of hydroxylapatite formation in the process of phosphating boiler water in the steam boiler and the recovery boiler, the required amount of AMINAT KO-4 is calculated [8]. Dozing of the reagent AMINAT KO-4 is organized according to the existing scheme of entering alkali directly into the drums of boilers.

The doze of AMINAT PK-2 required for complete neutralization of carbon dioxide and correction of pH of vapors and condensate was calculated depending on the content of carbon dioxide in steam and adjusted depending on the pH of steam and condensate. Pilot tests were decided to be carried out in three stages: stage 1 – maintaining the pH of steam and condensate at pH = 8.5; stage 2 – at pH = 9.0; stage 3 – at pH = 9.5. Dozing of the working solution of the reagent AMINAT PK-2 was carried
out in the line of feed water HB and SB to the suction of feed pumps according to the existing scheme of input of the reagent Helamin BWR-150H.

In the time of pilot tests (PT), the effectiveness of reagents was constantly monitored and evaluated on the basis of chemical analysis of feed water, boiler water, saturated and superheated steam. In this case, the main condition in the course of testing and adjusting the doses of reagents was to ensure the quality standards of the coolant of the steam boiler and the recovery boiler according to the requirements of the approved regime maps. The control of reagent AMINAT PK-2 was carried out using the developed and validated methodology (Certificate No. 205-01/RA.EN.311787-2016/2018).

The pH of steam in the first stage (from 01.03.2018 to 19.03.2018) ranged from 8.5 to 9.1 for SB-1 and from 8.2 to 8.8 for HB-2. Fluctuations of pH values in a wide range associated with the additional setting of dosing equipment in the transition from Helamin water chemistry. At the next stage of PT (from 19.03.2018 to 30.03.2018) the increase in the dose of amines provided a stable increase in the pH of steam to 9.0, and for both boilers the range of oscillations of pH values was quite narrow: from 9.2 to 9.3 for HB-1 and from 9.0 to 9.2 for SB-2. The pH value of the condensate was also maintained mainly at the level of 8.9-9.0. It should be noted that the boiler water indicators were also normal, but the pH of the feed water increased in the second stage to the values of 9.3-9.4 and became close to the upper limit of the normalized pH = 9.5. Based on the analysis of the data obtained in the management of water chemistry, a further increase in the dose of AMINAT PK-2 to maintain the pH of the condensate equal to 9.5 is considered impractical and would only lead to an increase in the consumption of the reagent. This decision is also based on the fact that in the first and second stages the content of iron compounds in feed water and condensates was significantly lower than the normalized values and was in the range of 5-10 ppm, which indicates the achieved minimization of corrosion rates of structural materials.

Therefore, taking into account the results obtained, it was decided to return to the initial dose of the reagent in feed water at the third stage of PT (from 01.04.2018 to 30.04.2018). Limits of change of the normalized indicators of the heat carrier are given in figures 1, 2 and in tables 1-4.

Figure 1. pH of steam for HB and SB at PT.

Figure 2. pH of feed water at PT.
Table 1. Feed water quality indicators during the PT.

| Indicator | Normal range | Doze of AMINAT PK-2, ppm |
|-----------|--------------|--------------------------|
|           |              | 2.6 (01.03–18.03) | 3.75 (19.03–30.03) | 2.6 (01.04–30.04) |
| **SB-1**  |              |                         |                         |                         |
| AMINAT PK-2 concentration, ppm | 2-5           | 2.1-4.5                | 5-6                     | 3.5-5.3                |
| pH        | 8.5-9.5      | 8.9-9.4                | 9.3-9.4                | 9.1-9.3                |
| Fe, ppb   |              | 4.0                     | 4.0-9.0                | 4.0-5.0                |
| **HB-2**  |              |                         |                         |                         |
| AMINAT PK-2 concentration, ppm | 2-5           | 2.3-5.7                | 5-7                     | 3.4-6.5                |
| pH        | 8.5-9.5      | 9.05-9.46              | 9.3-9.4                | 9.15-9.35              |
| Fe, ppb   |              | 2.0-4.0                | 6.0-9.0                | 4.0-5.0                |

Table 2. Boiler water quality indicators during the PT.

| Indicator | Normal range | Doze of AMINAT PK-2, ppm |
|-----------|--------------|--------------------------|
|           |              | 2.6 (01.03–18.03) | 3.75 (19.03–30.03) | 2.6 (01.04–30.04) |
| **SB-1**  |              |                         |                         |                         |
| AMINAT PK-2 concentration, clean part, ppm | 5-15           | 3-5                     | 5-7                     | 3.0-5.5                |
| AMINAT PK-2 concentration, salt part left, ppm | 5-20           | 3-5                     | 5-7                     | 3.0-7.0                |
| pH clean part |              | 9.3                     | 10.1-10.9              | 10.1-10.4              | 10.3-10.5              |
| pH salt part left |           | 11.8                    | 11.1-11.3             | 11.0-11.2             | 11.1-11.3             |
| Conductivity clean part, mkSm/cm | ≤ 150          | 40-120                  | 25-80                  | 65-90                  |
| Conductivity salt part left, mkSm/cm | ≤ 800          | 270-450                | 200-520               | 400-570               |
| Phosphates clean part, ppm | 2-6           | 2.5-10                  | 2-7                    | 2.0-6.0                |
| Phosphates salt part left, ppm | ≤ 30           | 23-26                  | 23-25                 | 23-26                 |
| **HB-2**  |              |                         |                         |                         |
| Concentration of AMINAT PK-2, ppm | 5-30          | 2-3                    | 4-6                    | 3.5-7.0                |
| pH        |              | 9.3                     | 10.7-11.1             | 10.4-10.7             | 10.5-10.7             |
| Conductivity, mkSm/cm |              | 500                    | 100-270               | 110-140               | 100-180               |
| Phosphates clean part, ppm | 2-6           | 2-10                   | 2-9                    | 2-6                    |

Table 3. Saturated and superheated steam quality indicators during the PT.

| Indicator | Normal range | Doze of AMINAT PK-2, ppm |
|-----------|--------------|--------------------------|
|           |              | 2.6 (01.03–18.03) | 3.75 (19.03–30.03) | 2.6 (01.04–30.04) |
| **a**     |              |                         |                         |                         |
| AMINAT PK-2 concentration, (saturated steam), ppm | 5-30      | 2-8                     | 5-7                     | 3.3-5.7                |
| pH (saturated steam) |              | 7.5-9.5                | 8.5-9.1               | 9.2-9.3               | 8.3-8.9               |

**b**
As it can be seen from the figures and tables, when comparing the quality of water and steam at the same dose of amines in the first and third stage of the tests, it can be noted that the quality of feed water and boiler water, saturated and superheated vapor in the third stage were maintained in narrower ranges, indicating the adjustment of water chemistry.

Analysis of coolant quality indicators at all stages of pilot tests showed that the use of the reagent AMINAT PK-2 allowed maintaining and adjusting the pH of steam and condensate, as well as reliable protection of the steam condensate path from corrosion processes. During the PT, the minimum dose of AMINAT PK-2 was determined, which provides normalized quality indicators of the SB-1 and HB-2 coolant, equal to 2.6 ppm for the active substance. It was also established that the calculated dozes of the reagent AMINAT KO-4 provided completeness of phosphating processes in boiler water and prevention of scaling processes on heat-transfer surfaces.

At the end of the PT, an internal inspection of the drums of the steam boiler SB-1 and the heat recovery boiler HB-2 was performed to assess the corrosion state of the metal and the presence of salt and sludge contamination during the PT period and compare with the initial state. By the results of survey the acts were drawn, according to which internal surfaces of a drum of the copper and the intra-drum devices were in a satisfactory condition, visible corrosion damages were not available, sludge and salt deposits were absent. During the period of PT a uniform protective oxide film of dark gray formed in the water and steam parts of the drum surface. Existing experience of organizing water chemistry of steam boilers with the use of reagent AMINAT on the basis of neutralizing amines [9] suggests that the presence of such protective films on the inner surfaces of thermal equipment allows the maintenance of minimum corrosion rates of structural materials of the reagent AMINAT based on neutralizing amines for up to 2 months. The studies conducted in the laboratory confirmed this conclusion and allowed us to develop recommendations on the methods for preservation of thermal power equipment under the conditions of use of AMINAT reagents.

### Table 4. Condensate from oil refinery unit quality indicators during the PT.

| Indicator                          | Normal range | Doze of AMINAT PK-2, ppm |
|------------------------------------|--------------|--------------------------|
| |                             | 2.6 (01.03–18.03) | 3.75 (19.03–30.03) | 2.6 (01.04–30.04) |
| AMINAT PK-2 concentration, ppm     | 5-30         | 4.0-6.0                  | 6.5-8.0            | 6.5-7.0            |
| pH                                 | 8.5-9.5      | 8.5                      | 8.9                | 10.5               |
| Fe, ppb                            | ≤100         | 9-12                     | 16-22              | 16-40              |

### Conclusion

The following insights were made on the basis of the results of the pilot tests with the use of domestic reagent AMINAT for processing of feed and boiler water of steam boilers and waste heat boilers, gas turbines, thermal power plants of RN-Tuapsinsky Oil Refinery LLC:
1. Correctional water chemistry of steam boiler and heat recovery boiler of GTU TPP, organized with the use of AMINAT reagents, ensured the maintenance of regulatory requirements of regime maps of the equipment, as well as minimizing the processes of corrosion, scale formation and sludge formation during the entire period of PT.

2. On the basis of operational data the annual requirements for reagents AMINAT PK-2 and AMINAT KO-4 on the maximum and nominal steam production of boilers were calculated. With comparable costs of Helamin and AMINAT reagents, the cost of purchasing AMINAT reagents is significantly lower due to the production at the territory of the Russian Federation, so the use of domestic reagents will significantly reduce the annual cost of purchasing reagents and, as a result, increase the economic efficiency of the customer production activities.

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