Medium pressure boiler water chemistry optimization using neutralizing amine mixture reagent AMINAT™ PK-2 at CEPP "Borovichi Refractories Plant" of JSC "BKO"

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Abstract. An overview of the neutralizing amine based reagent AMINAT PK-2 usage for water chemistry of steam boilers for medium pressure boiler was given. Long term experiment showed that new reagent allows to decrease corrosion rate comparing with old water chemistry based on ammonia only. Two dosage schemes in different cycle places discussed. Scheme with two points on injection showed better results. Results of corrosion rates experiments and photos of tubes inner surfaces are presented. Based on fuel savings due to reducing scale formation the total annual economy for last year was 5.1 million Russian roubles.

1. Introduction
Water chemistry’s task to minimize corrosion and scale formation on the heat transfer surfaces of steam generating facilities is an actual problem. The main source of impurities in heat carriers (feed water, steam etc) and his quality decrease is a corrosion in a condensate part. These corrosion processes take place during steam condensation due to some residual oxygen and carbon dioxide and are followed by an oxygen and hydrogen depolarization respectively.

The hydrazine-ammonia water chemistry with maintaining of feedwater pH to 9.1±0.1 is recently the most widely used to provide an oxygen binding and a carbon dioxide neutralization. A broad implementation of ammonia and its derivatives was justified by their high volatility and neutralization ability. However, the high distribution coefficient of ammonia between the steam and water phases leads to its domination in a steam, but not in a condensate. Thus it results in a non-uniform distribution of ammonia in a condensate. The required value of pH in condensate is therefore not provided along the whole steam paths. At the same time an increase of ammonia content in the last portions of a steam may lead to the corrosion of copper alloys used in equipment. On the other hand a limitation of ammonia content in a feedwater to level 1 mg·dm⁻³ does not give a desirable result, especially when a simplified scheme of feedwater treatment is used.
About 20 years ago application of the complex amine-based reagents with film-forming amines, neutralizing amines and dispersants such as polyacrylates and polycarboxylates becomes popular at the power plants as an alternative to the hydrazine-ammonia chemistry. An advantage of the complex amine-based reagent is associated mostly with a water chemistry simplification. However, until recently there are no any guidelines for the most appropriate reagent selection [1]. Despite the fact that the quality of feedwater for steam boilers is strictly regulated, taking into account the variety of conditions of the equipment and possible variations in the quality of feedwater and boiler water is often impossible in the case of application of complex reagent. The adjustment of dozes of complex reagents is complicated by the fact that the composition of the reagents and the ratio of its components is unknown for specialists responsible for maintaining the water chemistry at the power plant. All this leads to the mixed results of their implementation on Russian thermal power plants and requires additional dosing of reagents (ammonia, strong alkalis).

Separate optimization of the water chemistry is the dozing of neutralizing amines. At the same time in Russian practice, there is experience of application as single neutralizing amine, and a reagent which is a mixture of several neutralizing amines.

In 2005-2006 at Rostov and at Balakovskaya nuclear power plants the morpholine and ethanolamine water chemistry have been implemented respectively for the secondary coolant circuits [2]. Then in 2010-2011 the more advanced chemistry with a combined dozing of ammonia and amines have been applied [3].

Combined dozing of ammonia and amines becomes reasonable in the case of a simplified scheme of water pretreatment. In 2007 at Zakamskaya thermal power plant No. 5 with medium pressure steam boilers an effective combined chemistry with ammonia and a reagent AMINAT™ PK-2 produced by OOO "NPF "Travers" (Moscow) as a blend of three different amines, was reported [4]. This composition meets a requirement of a low total distribution coefficient as well as of high neutralizing ability. This experience was used in a present work for an improvement of medium pressure steam boilers operation at a central electric power plant (CEPP) of "Borovichi Refractories Plant" (CEPP JSC "BKO").

2. Equipment at CEPP JSC "BKO"

CEPP JSC "BKO" uses steam boilers TP-30, E-50-3.9-440GMA, TP-35U and SP-25/2 for the steam and electric power generation. Most of the steam produced used after turbo-generators for boilers heating and then it is returned in a form of a condensate to the boilers as a feedwater. The recycled condensate constitutes 90% of a boiler feedwater.

The water via technical water pipe is taken from the Msta river and transported to the water treatment unit. There it passes mechanical filters filled with dispersed anthracite. Then the clarified water goes to the double-step sodium softening facility and to an atmospheric deaerator DSA-100, where mixed with condensate and used as a feedwater for steam boilers.

Normally, the ammonia chemistry used at CEPP JSC "BKO" with phosphate dozing to the boiler water. However, the data analysis revealed that this water chemistry does not provide the required quality of heat carrier. Thus, the measured pH values of a saturated and superheated steam was in the range of 6.2-6.8, while the required values have to be higher than 7.5. At the same time the pH of a boiler condensate was within 7.7-8.3, which was below the recommended values 8.5-9.5.

The iron concentration in a condensate was around 80-300 μg·dm⁻³. The corresponding corrosion products have been transmitted by the condensate to the steam boilers and formed there the secondary iron oxide deposits on the heat-transfer surfaces. The planned outages of boilers since 2010-2011 indicated that an amount of corrosion rate exceeds notably the permissible level (>200 g·m⁻²) [5]. A considerable amount of iron oxide deposit formed within a period 2012-2013 was found in the heating pipes of the back screen of a boiler No.4 (TP-35U).
3. Water chemistry optimization

All these facts led to a conclusion, that an ammonium sulfate dosage was inadequate to suppress the acidic corrosion of the steam and condensate system. For the better carbon dioxide binding and for pH increase, the specialists of "Travers" company proposed and implemented a combined water chemistry based on a simultaneous use of ammonium sulfate and a reagent AMINAT™ PK-2. The last one represents mixture of neutralizing amines.

The general scheme dosing of ammonium sulfate and trisodium phosphate remained unchanged. Both reagents dosage was performed operating from the same vessel. Initially the corresponding vessel was filled with trisodium phosphate. Then an ammonium sulfate was added to this solution. The dosing-pump capacity was manually regulated in accordance with the chemical control data.

A special equipment for AMINAT™ PK-2 proportional dozation has been developed. It was assumed, that a feedwater flow for the steam boilers is not a constant and may change from 3 to 25 tones per hour. Therefore an AMINAT™ PK-2 injection was organized in the additional (softened) water pipeline which supplies atmospheric deaerators of steam boilers. The corresponding dosing pump EMEC KMS MF 0808, was intended to work either in a constant mode or in relevance with water consumption value. The latter have been provided by a pressure sensor Metran 100 DD, responsible for the monitoring of softened water flow to the deaerator. AMINAT™ PK-2 was dozed as a diluted solution with amines concentration around 10%.

To determine the effectiveness of the combined water chemistry of steam boilers in the pipeline of back condensate installed 4 corrosion indicators from the St3 steel [6]. While commissioning also carried out chemical control of the water chemistry of steam boilers to determine the optimal doze of AMINAT™ PK-2, providing a normal pH value for feedwater.

The pre-commissioning operations of ammonia sulfate and AMINAT™ PK-2 implementation have been organized in a stage-by-stage mode starting with a season of 2013-2014. During a preliminary stage at “summer” period (August-September 2013) only ammonia sulfate was used and monitored by the corrosion indicators. The corresponding dosage was within 0.9-1.0 mg·dm⁻³. The next six stages have been performed during the heating season operating with both ammonia sulfate and AMINAT™ PK-2 combined dozation. During this period the ammonia sulfate doze was reduced to a 0.7-0.8 mg·dm⁻³ level, while doze of AMINAT™ PK-2 was corrected in order to adjust the required pH value in steam-and-condensate pipelines.

After each stage the corrosion indicators have been removed, chemically treated, and the corrosion rate was estimated gravimetrically. Then the AMINAT™ PK-2 doze was corrected, and a new set of corrosion indicators was installed before the next stage has started. Table 1 represents the corrosion rates and the mean values of a condensate flow at different stages along with steam and return condensate pH values.

Table 1 data indicates that the mean corrosion rate under a single reagent ammonia sulfate dosation mode is around 0.2 mm/year. Thus the corrosion resistance of St3 under these conditions is low. It corresponds to the level 6 of Russian national standard 13819-68 [7]. Therefore the condensate should be treated as an aggressive matter, while the whole situation with equipment as an emergency one [6].

The pH data demonstrate that a combined application of ammonium sulfate and AMINAT™ PK-2 provides a stable increase of both steam and condensate pH if the amine concentration increases. However, the indicators corrosion rate reveals no clear correlation with AMINAT™ PK-2 concentration. At the same time, it was considerably higher relative to the summer season mode, based on the single reagent (ammonium sulfate) application.

Table 1. Corrosion rates of indicators during the pre-commissioning operations of combined dosage of ammonia sulfate and AMINAT™ PK-2 in steam boilers at "Borovichi Refractories Plant" CEPP JSC "BKO"
| R&D period, (AMINAT™ PK-2 dose)* | Season and stage duration, days | Condensate consumption rate, m³/hour / m/sec | pH of superheated steam | pH of condensate | Corrosion rate, mm/year |
|----------------------------------|--------------------------------|-----------------------------------------------|-------------------------|-----------------|------------------------|
| Stage 0 – ammonia sulfate dosage only | summer season; 103 | 10 / 0.3 | 6.7-6.8 | 7.5-8.0 | 0.23 |
| Stage 1 (2.5 mg·dm⁻³) | heating season; 41 | 32 / 0.97 | 7.6-7.8 | 8.2-8.4 | 0.38 |
| Stage 2 (4.0-4.5 mg·dm⁻³) | heating season; 42 | 40 / 1.2 | 7.8-8.2 | 8.7-8.8 | 0.41 |
| Stage 3 (8.0-8.5 mg·dm⁻³) | heating season; 41 | 40 / 1.2 | 8.3-8.6 | 9.1-9.2 | 0.36 |
| Stage 4 (4.0-4.5 mg·dm⁻³) | heating season; 27 | 30 / 0.91 | 8.0-8.1 | 8.7-8.8 | 0.35 |
| Stage 5 ammonia sulfate dosage only | heating season; 15 | 40 / 1.2 | 6.8-6.9 | 7.7-8.1 | 0.6 |
| Stage 6 ammonia sulfate dosage only | heating season; 20 | 30 / 0.91 | 6.7-6.8 | 7.5-8.0 | 0.5 |
| Stage 7 (4.0-4.5 mg·dm⁻³) | summer season; 43 | 10 / 0.3 | 8.3 – 8.6 | 8.7-8.8 | 0.007 |

| A combined mode with two AMINAT™ PK-2 dosage complexes |
|-------------------------------------------------------|
| Stage 8 (2.7-3.0 mg·dm⁻³)** | heating season; 48 | 32 / 0.97 | 8.3 – 8.6 | 8.6-8.7 | 0.23 |
| Stage 9 (2.7-3.0 mg·dm⁻³)** | heating season; 50 | 23 /0.7 | 8.2-8.5 | 8.6-8.7 | 0.05 |

* AMINAT™ PK-2 dosage measured by active substance  
** Cumulative AMINAT™ PK-2 dosage measured by active substance

Taking into account the higher boilers condensate consumption and the higher condensate velocities during the heating season relative to the summer season, one can come to a conclusion, that the flow accelerated corrosion processes limit the whole corrosion rate. Notably the pipelines and steam-and-condensate system of the boilers are the most sensitive units to the flow accelerated corrosion. In order of prove this conclusion the fifth and sixth experiment stages have been launched without AMINAT™ PK-2 and under higher condensate consumption. Indicators have been therefore installed one week after the AMINAT™ PK-2 injection was cancelled.

The corrosion tests in presence of solely ammonium sulfate have demonstrated a non-linear dependence of the corrosion rate \( V_{corr} \) on the condensate consumption and its velocity in the pipes \( V \). Some research groups report on the parabolic relationship between \( V_{corr} \) and \( V \): \( V_{corr} = K \cdot V^n \), where \( K \) and \( n < 1 \) are denoted as empirical coefficients [8, 9, 10]. Using this relationship an empirical equation

\[
V_{corr} = 0.519 \cdot V^{0.52}
\]  

was derived for the experiments run at stages 5 and 6 and presented on figure 1.
Figure 1. Results of corrosion tests for a combined reagent and for solely ammonium sulfate treatment

Figure 1 also provides a comparison of combined reagent water chemistry carried out at stages 1-4. Evidently, the combined ammonia sulfate and AMINAT™ PK-2 blend is capable to diminish corrosion rate for 30% at pH 8.7-8.8 (stages 2 and 4). At the same time an increase of pH up to 9.1-9.2 due to a double AMINAT™ PK-2 concentration increase (stage 3), provides the corrosion rate decrease only for 40%. Thus a 4.5 mg·dm\(^{-3}\) dose of AMINAT™ PK-2 was chosen as an optimal value, and kept constant for all 2014 year.

The corrosion rate under these conditions (stage 7) during the summer period corresponds to the 3\(^{rd}\) level of the scale listed in Russian national standard 13819-68 [7] and fits the corrosion resistance as a good one. Meanwhile according to the same document the condensate could be treated as a low aggressive one. Therefore an implementation of rather low concentrations of a combined reagent completely suppressed corrosion for the summer period.

In May 2014 the steam boiler TP-35U (No. 4) was stopped. The revision of boiler drum revealed the lack of corrosion and any sludge at the bottom of drum. There was also lack of any surface scaling, while the boiler surfaces had the same grey color as indicators. Pipes samples demonstrated the surface scale to be different from that one found during the season of a year 2012-2013. The photos of heating pipes of a boiler No.4 (TP-35U) back screen on figure 2, demonstrate that the scale has higher density and is hardly removable by washing.
The total amount of scale on the tube surface No.36 (season 2013-2014) was twice less (336 g·m⁻²) relative to the season 2012-2013 samples (692-788 g·m⁻²). Meanwhile the scales of a boiler No.4 for all the pipe samples from a 2013-2014 season still exceeded the permissible levels. This was explained by a rather short period of a combined ammonium sulfate and AMINAT™ PK-2 water treatment in a 2013-2014 season: 5 months. Indeed, the longer treatment duration in a season 2014-2015 provided quite acceptable scaling at a level of 240-260 g·m⁻².

The reason of an incomplete scale and corrosion inhibition in by a complex reagent at a CEPP of "Borovichi Refractories Plant" was some steam and condensate consumption from another unit - a firebrick department of the same plant. Thus it was decided to install the second AMINAT™ PK-2 dosage complex in steam pipeline at a cycle part in firebrick department with a same dosing pump EMEC KMS MF 0808 before the beginning of a season 2015-2016. The corresponding data are presented in a table 1 and figure 1 as stage 8 and stage 9 experiments.

Indeed, an installation of two AMINAT™ PK-2 dosage complexes led to a 50% corrosion rate decrease relative to a solely ammonium sulfate treatment (stage 8). Moreover, when the condensate velocity was lowered up to 0.7 m/sec (corresponds to 23 m³/hour condensate flow), then the corrosion rate was decreased for 90% (stage 9). At the same time the reagents provided acceptable levels of the equipment corrosion resistance according to the Russian Standards [5, 6].

In May 2016 the steam boiler TP-35U (No.4) was stopped again. An amount of scale on the surfaces pipes did not exceed 200 g·m⁻². The photo of a pipe No.24 of a boiler No.4 (TP-35U) back screen inner surface on figure 2 demonstrates a thin high density scale layer of about 160 g·m⁻².

It should be noted that an installation of two AMINAT™ PK-2 dosage complexes offered a possibility to reduce the total amount of AMINAT™ concentration up to 2.7-3.0 mg·dm⁻³, and therefore an annual reagent consumption was also decreased. Indeed in 2014-2015 a monthly consumption of AMINAT™ was around 700 kg, while in 2015-2016 it was reduced to 400 kg.

The three years of AMINAT™ application at a CEPP of "Borovichi Refractories Plant" revealed a significant reduction of expenses. The main source of economy was attributed to the fuel savings due to the inhibition of a scale formation. The coal equivalent fuel savings for 2012 year relative to 2016 is equal to 1524 tones. The calculation takes into account purchase costs of reagents and costs of replacement of screen pipes of boilers for repair work. Cost of preservation and carrying out chemical cleaning of the equipment during the repair were not considered since these activities at the station were not carried out.

As a result of calculations it was found that the economic effect due to optimization of water chemistry the CEPP of JSC "BKO" when using reagent AMINAT™ PK-2 was 5.1 million rubles per year.
4. Conclusion
An AMINAT™ PK-2 reagent water chemistry was tested at a CEPP of "Borovichi Refractories Plant". It is found that a combined dozage of ammonium sulfate and AMINAT™ PK-2 becomes the most efficient if last one is injected in two places: into a boiler feedwater and into a steam pipe of a firebrick department of the same plant. An optimal AMINAT™ PK-2 concentration is estimated at the level of 2.7-3.0 mg·dm⁻³ of active substance.

The corrosion test indicated that the corrosion rate of equipment and pipes depends on the condensate flow rate. A corresponding correlation between the corrosion rate and a condensate velocity has been observed. An injection of amines simultaneously in two places reduces the corrosion rate for 50 to 90% in relationship with a condensate flow rate. Almost complete inhibition of corrosion in a steam-and-condensate system can be achieved a condensate consumption below 20 m³·hour⁻¹, which corresponds to the flow rate in the pipes of 0.6 m·sec⁻¹.

An application of AMINAT™ PK-2 provided a scale formation decrease in the steam boilers up to 180-200 gm·m⁻², while the corresponding total cost savings are estimated within 5.1 million rubles per year.

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