The development of a neutralizing amines based reagent for maintaining the water chemistry for medium and high pressures steam boilers

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Abstract. An overview of the development for neutralizing amine based reagent for water chemistry of steam boilers for medium and high pressures was given. Total values of the neutralization constants and the distribution coefficients of the compositions selected as a main criteria for reagent composition. Experimental results of using this new reagent for water chemistry in HRSG of power plant in oil-production company are discussed.

1. Introduction
The problems of safety and reliability of the operation of thermal power plants inextricably connected with the organization of the optimum water chemistry of steam boilers. Water chemistry is supposed to ensure not only the reliability of the equipment but also a high efficiency of its operation in all operating modes. It was found that the main operational costs associated with the damage of power boilers and HRSG by 50-70% depend on the state of the cycle chemistry [1,2,3].

Today the main forms of chemical conditioning for the fossil plants with drum boilers are water chemistry with the addition of ammonia and hydrazine to the condensate or feedwater and tri-sodium phosphate and sodium hydroxide to the boiler water.

At phosphate treatment, sodium phosphates added to the boiler water for the reaction (1) to form hydroxylapatite, which released into the solid phase as a dispersion slurry. As it can be seen from reaction (1), hydroxyl ions are necessary for precipitation:

$$10Ca^{2+} +6PO_4^{3-} +2OH^- \rightarrow 3 Ca_3(PO_4)_2 \times (Ca(OH)_2)$$

(1)

The phosphate treatment used at the plants in several types. Tri-sodium phosphate and acidic phosphates applied the most often.

The reason for choosing particular water treatment is the quality of the coolant and especially feedwater alkalinity. Thus, because of hydrolysis of carbonates and bicarbonates, the boiler water is enriched with hydrates, and as a result its alkalinity increases. For waters with increased alkalinity, the dosage of acidic phosphates ensures compliance with the standardized values of the pH of the boiler water. Treatment with the presence of free sodium hydroxide is called caustic treatment. In case of low alkalinity, addition of acidic phosphates brings to zero the concentration of free sodium hydroxide and it is called the pure phosphate alkalinity treatment. However, the lack of necessary amount of hydroxyl
ions for the reaction (1) creates conditions for the formation of crystalline scale on the pipe surfaces and the risk of understatement the pH of the boiler water. With such noncompliance, conditions are created for intense corrosion with hydrogen depolarization and the formation of iron phosphate scales. Therefore, at phosphate treatment one of the requirements to the quality of the boiler water is the pH of the boiler water in the drum, which must be at least 9.3[4]. At the same time, creating pH of the boiler water by increasing the concentration of free sodium hydroxide creates the risk of alkaline and intercrystalline corrosion, which damage appears in the form of cracks formed when flow hydrodynamics are disturbed in the places of drying of water with the formation of concentrated solutions of sodium hydroxide [4,5]. There is also a possibility of foaming and transfer the boiler water to steam, which can increase its moisture. Therefore, maintaining the pH of the boiler water at sodium hydroxide dosing mode requires careful monitoring and cannot be recommended as the only solution.

The problem of maintaining the standardized pH of boiler water also relevant for FFAP water treatment [6,7,8]. FFAP (such as Helamin, Purotech, Cetamine, VTIAMINE) contain substances such as film forming and neutralizing amines, alkalizing amines, reducing agents, and dispersants (e.g., polycarboxylates). Of the whole composition, only the neutralizing amines can influence the pH of the water to a greater extent. However, increasing the dose of FFAP to create normal pH values can lead to overdosing of components and a significant increase in the cost of water treatment. Thus, this problem most often solved by additional dosage of strong alkali.

2. Neutralizing amines reagent development
Given the above, there is an actual target to create a product that excludes the dosing of strong alkali. The authors of the article consider the possibility of creating a neutralizing amines based product, which maintains normal target pH of boiler water values and provides reliable protection of the equipment.

The problem of creating an effective composition can be solved by combining various organic amines. While developing such a composition, it is necessary to take into consideration the basic properties of neutralizing amines, such as the value of the distribution ratio, the neutralizing ability, the thermal stability at various parameters of the equipment operation.

The most important property of organic volatile amines is their neutralizing ability with respect to acidic impurities. Thus, when a neutralizing amine added to a water containing carbonic acid, there are following reactions goes on:

\[ B + H_2O = BH^+ + OH^- \]  
\[ H_2CO_3 = H^+ + HCO_3^- \]  
\[ H^+ + OH^- = H_2O \]

Neutralizing ability of amines is estimated by the neutralization constant, according to the equation:

\[ K_N = \frac{C_{BH^+} C_{OH^-}}{C_B} \]  

where B are the molecules of neutralizing amines.

The practical value in determining the neutralizing ability of any of the amines is to determine the required dose of the compound to the desired pH. Numerous authors have published a data on the dissociation constants of neutralizing amines. Therefore, it was decided to conduct experiments to determine the dissociation constants of some amines and compare them with the available published data.

Four neutralizing amines selected for the experiment: dimethylethanolamine, morpholine, monoethanolamine, cyclohexylamine. Aqueous solutions of amines with different concentrations were prepared by adding them to a fixed volume of distilled water. Then the pH of the solution was measured with a certain concentration of amine and the concentration of hydroxyl ions from the
equation of the ion product constants was calculated. According to the reaction (2), amounts of the BH+ and OH- ions are equal, so the neutralization constant was calculated by the equation:

$$K_N = \frac{C^2_{\text{OH}^-}}{C_B}$$

(6)

Table 1 shows the averaged values of the dissociation constants of the neutralizing amines obtained in the course of the experiment, as well as the $K_N$ from the literature data.

**Table 1.** The dissociation constants of neutralizing amines and carbonic acid

| Compound                           | Molecular weight | $K_N$ from the literature data [9, 10] | Experimental $K_N$ |
|------------------------------------|------------------|----------------------------------------|--------------------|
| Carbonic acid (first stage dissociation) | 44               | 4.4·10$^{-7}$                          | -                  |
| Dimethylmethanolamine              | 87               | 6·10$^{-6}$                            | 10$^{-5}$          |
| Morpholine                         | 89               | 5.6·10$^{-6}$                          | 1.73·10$^{-6}$     |
| Cyclohexylamine                    | 99               | 4.4·10$^{-4}$                          | 1.95·10$^{-4}$     |
| Monoethanolamine                   | 61               | 5·10$^{-5}$                            | 10$^{-5}$          |
| Composition 1                      | 77               | 7.6·10$^{-5}$                          | 7.4·10$^{-5}$      |
| Composition 2                      | 76,1             | 1.28·10$^{-4}$                         | 4.9·10$^{-5}$      |
| Aminate™ PC-1                      | 87,8             | 3.7·10$^{-5}$                          | 2.33·10$^{-5}$     |
| Aminate™ PC-2                      | 91               | 1.1·10$^{-4}$                          | 6.1·10$^{-5}$      |

As it can be seen from the table 1, experimental values of the dissociation constants of the amines are close to the values from the literature data. Therefore, obtained values of $K_N$ were used for creation the composition.

Initially, when choosing the components and quantitative composition of the formulations, the task was to obtain the maximum neutralizing ability. Its calculation based on the principle of independence and additivity [11], according to which the $K_N$ of composition is determined from the relation:

$$K_N^\text{mix} = (\Sigma C_i \times K_N^i)/\Sigma C_i$$

(7)

where $C_i$, $K_N^i$ are the percentage of the i-th component in the mixture and its dissociation coefficient respectively.

Based on the calculations performed, the two most effective compositions selected. Since the obtained values on the dissociation coefficients of compositions 1 and 2 are comparable to the $K_N$ of Aminate™ PK-1, Aminate™ PK-2, the total distribution coefficient should be considered as the determining factor.

The value of the total distribution coefficient of composition 1 and composition 2 also determined by the additivity principle. For calculations, both literature data on $K_P$ of individual amines and a data obtained in the course of researches of the amines properties [11,12] used. Table 2 shows the distribution coefficients of Aminate™ PK-1 and Aminate™ PK-2 which were obtained at the experiment [11,12]. Almost for all temperature ranges, the obtained $K_P$ values of compositions 1 and 2 were 1.3-1.5 times lower in comparison with Aminate™ PK-1 and Aminate™ PK-2, which indicated their advantage not only in limiting carbon dioxide corrosion of the equipment, but also in maintaining the pH of the boiler water in the alkaline region.

**Table 2.** Distribution coefficients depending on the operating parameters of the boilers

| Product/Operating parameters | Composition 1 | Composition 2 | Aminate™ PK-1 | Aminate™ PK-2 |
|-----------------------------|--------------|--------------|---------------|---------------|
| 7 bar/165 °C               | 1.5          | 2.07         | 1.6           | 2.8           |
| 40 bar/250 °C              | 1.58         | 1.63         | 2.1           | 2.1           |
| 100 bar/310 °C             | 1.65         | 1.40         | 2.33          | 2.26          |
Compositions 1 and 2 have been certified under the trade mark Aminate and named Aminate™ PK-4 and PK-6, respectively.

The results of pilot tests on the HRSG of hydrogen production plants of JSC Slavneft-YANOS confirmed the correctness of neutralizing amines products development approach. Initially (pilot tests in 2016), Aminate™ PK-2 and Aminate™ PK-4 were proposed for the organization of chemical conditioning at HRSG in order to prevent scale formation on heat transfer surfaces. Pilot tests results are shown at the table 3.

### Table 3. Indicators of the quality of the water in HRSG during the introduction of reagents Aminate™

| Sample point          | pH limits  | Aminate™ PK-2 | Aminate™ PK-4 |
|-----------------------|------------|---------------|---------------|
|                       | pH         | C/C, mg/l     | PO₄³⁻, mg/l   | pH            | C/C, mg/l | PO₄³⁻, mg/l |
| Feedwater             | 8.5-9.5    | 8.9-9.1       | -             | 8.7-9.3       | -         | -          |
| Boiler water          | 9.5-10.5   | 7.6-7.7       | 23-35         | 6-15          | 9.5-10.5   | 35-70       | 4-6       |
| Saturated steam       | 6.0-9.0    | 8.9-9.2       | 2.5-4.0       | -             | 8.8-9.0   | 3-5        | -         |
| Turbine condensate    | 8.5-9.5    | 9.0-9.2       | -             | 9.0-9.5       | -         | -          |

As it can be seen from the table, the product Aminate™ PK-2 reliably protected the equipment from carbon dioxide corrosion and provided normal pH values in saturated steam condensate and turbine condensate.

Application of phosphate-based product did not allow maintaining the pH of the boiler water at the normal limits due to the low buffering of the feedwater (demineralised make-up water).

At the retesting in 2017, Aminate™ PK-2 replaced by Aminate™ PC-4. The test results at the Table 3 showed that the application of Aminate™ PK-4 allowed to increase the pH of boiler water to the normal values. Maintained phosphate excess during the dosage of Aminate™ KO-4 did not exceed the limit.

Results of repeated pilot tests have shown the effectiveness of the Aminate™ KO-4 and Aminate™ PK-4 keeping reliable chemical conditioning at HRSG, which uses demineralized water as a feedwater.

### 3. Conclusion

This article describes a neutralizing amine based products developing process, which use the total values of the neutralization constants and the distribution coefficients of the compositions as a main criteria.

Based on experimental and calculation data, Aminate™ PK-4 and PK-6 have developed. These products application allow correcting both the pH values of steam and condensate and the pH values of the boiler water.

The results of pilot tests at JSC Slavneft-YANOS showed that application of Aminate™ PK-4 and Aminate™ PK-6 for chemical conditioning at the medium pressure HRSG with demineralized water make-up provided the normal pH values.

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