

An Optimal Way to Prevent Corrosion of Equipment at TPP

Karlygash Idrissova, Aitbala Tumanova, Gulzira Koldassova

Abstract: In order to apply polyphosphates as the inhibitors on the running pulp line, it is necessary to clean beforehand the inner surface of pipes from the essential part of corrosion products or apply high concentrations (more than 100 mg/l) of the inhibitor, which is unacceptable for economic and social aspects. In real pipelines having been operating for at least 10 years with a significant amount of corrosion products on the internal surface of the pipeline, introduction of polyphosphate inhibitor has no significant impact on the reduction of absolute corrosiveness of water [1]. The fight against internal corrosion of pipelines of the hydraulic ash removal system gives the maximum effect when carried out in a timely manner, immediately after the putting the pipeline into operation. Slowing corrosion by stabilizing water treatment or installation of inhibitors would be effective if the protective film is formed on the surface of the tubes rapidly and has good adhesion to the metal surface. Great influence on the adhesion has the state of the inner surface of the metal. Presence of significant amounts of corrosion products greatly reduces the efficiency of anti-corrosion treatment of water, and requires high doses of inhibitors, yet, the degree of protection is still much lower than with the new pipes.

Key words: thermal power plants, corrosion inhibitors, the corrosion rate, depth indicator of the corrosion rate.

I. INTRODUCTION

Corrosion of inner surface of steel pipes is a complex, multifactorial process. When choosing optimal methods of protection of metal corrosion and development of water treatment regime for a particular object, the most important is to determine the mechanism and the main factors influencing the rate and nature of the corrosion processes [2].

For lowering the corrosion of equipment rate at thermal power plants (TPP), corrosion inhibitors are widely used nowadays. The protective effect of these reagents is specified by alteration of state due to adsorption or formation of sparingly soluble compounds with metal ions. The latter cover the surface with pellicle (form coating), which reduces the area of active metal surface and results in changing the activation energy of electrode reactions limiting the complex corrosion process [3, 4].

Complexity of the mechanism of action and diversity of factors influencing the effectiveness of inhibitors still make it impossible calculation of the possibility of their application. Therefore, experimental methods are usually applied to assess the effectiveness of complexons in various conditions.

Our research has been focused on determination of the corrosivity of the filtered slurry, selected from the slurry pipeline and the corrosion rate of pipeline material in the system of hydraulic ash and slag removal at thermal power plants. The experiment was carried out in operational conditions similar to those of a pipeline, completely filled with slurry, under constant hydrodynamic regime.

II. MATERIALS AND METHODS

From the analysis of the existing methods of determining corrosion rate it was found that the gravimetric method proves to be the most accurate. Its advantages – the relative ease of implementation and obtaining the most accurate and reliable information, considering the specificity of conducting the experiments on the loss of metal caused by corrosion. The method is based on measuring the difference in weight of the control samples before and after the test in corrosive environment. Determination of the corrosion rate by this method does not require application of special equipment and devices. Their visual inspection allows to reveal the nature of the corrosion damage, and, with the use of special methods, to determine the rate of occurrence of local corrosion processes. Application of the method requires a long contact of the test specimens with a corrosive environment. The technique of application of the method is regulated by the ISO 8044 and the State obligatory standards GOST [5-7].

The method involves placing specially prepared specimens-testifiers of size 50×20×2 mm, made of steel St.3, with polished surface, into the reactor in the environment of model solution or filtered slurry. The working surface of a sample area of about 6 cm² is sufficient for the formation of corrosion products in an amount necessary for photocolometric definition of the amount of iron for the period of a 14-days experiment.

Thorough mechanical preparation of samples before the experiment took place to obtain reliable and reproducible for the corrosiveness of water data, and it consisted in cleaning its side surface with abrasive cloth of various sizes. To avoid crevice corrosion and eliminate edge effects, the samples were pre-oxidized. After the final cleaning of the samples to high finish, there were no visible marks, scratches or other mechanical defects.

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The samples were oxidized, butt-ends were covered with chemically resistant lacquer. For degreasing of samples alcohol was used.

The amount of pulp investigated was 0.5 l. The water temperature in the glass beaker was maintained within the required temperature.

By difference of total iron ΔFe concentration in the test solution before and after the experiment, it is also possible to determine the absolute corrosive pulp activity by the formula:

$$H = \frac{\Delta Fe_{total}}{S}, mg/cm^2 \quad (1)$$

where S – the surface of the sample, cm^2 . Absolute corrosive activity of slurry solution was assessed by a special scale.

The corrosion rate was calculated using the formula:

$$K_m = \frac{(m_1 - m_2)}{S\tau} \quad (2)$$

where m_1 – mass of the sample before the test, in grams;
 m_2 – mass of the sample after the test, g;
 S – sample surface area, m^2 ;
 τ – time of exposure, h.

The area of the surface of the sample was calculated using the formula:

$$S = 2 \times \left[\left(ab - \frac{\pi d^2}{4} \right) + h \times \left(a + b + \frac{\pi d}{2} \right) \right] \quad (3)$$

where a – length of the sample, m;
 b – width of the sample, m;
 h – thickness of the sample, m;
 d – diameter of the sample, m.

Corrosion depth parameter indicative of thinning the sample per unit of time was calculated by the formula:

$$P_{Fe} = K_m \frac{8760 \times 10^{-3}}{7.87} = 1.1131 K_m \quad (4)$$

where P_{Fe} – depth indicator of the corrosion rate, mm/year;

8760 – number of hours per year;

.87 – iron density, g/cm^3 .

The extent of metal corrosion protection (Z , %) was calculated by the formula:

$$Z = \frac{K_{m0} - K_m}{K_{m0}} \times 100 \quad (5)$$

where K_{m0} – corrosion rate in the uninhibited environment of $g/m^2 \cdot h$.

Results and discussion

For calculations by the above formulas, we used the data obtained from our analysis of the TPP pulp solutions which are presented in Table 1.

Table 1 Characteristics of TPP pulp samples

| Sample | pH | Total hardness, mg-eq/l | Calcium hardness, mg-eq/l | Magnesium hardness, mg-eq/l | Alkalinity total, mg-eq/l | Content of Fe^{3+} , mg/ml |
|---------------------------------------|------|-------------------------|---------------------------|-----------------------------|---------------------------|------------------------------|
| The pulp after the ash-removal system | 4.49 | 2.4 | 2.0 | 0.4 | 2.0 | 1.13 |

The results show that the pulp after the ash-extraction plant is acidic by nature and aggressive to the environment. Tables 2 - 4 show that the average corrosiveness of the filtered pulp, taken after the ash-extraction plant, determined from 3 replicate experiments, with respect to the steel St3 was $0.1436 g/m^2 \cdot h$, i.e. the degree of activity is "high".

Tables 2 - 4 also show the results of the gravimetric determination of Steel 3 corrosion rate in pulp solutions in the absence and in the presence of corrosion inhibitors: zinc orthoethylidendiphosphonate (OEDPZn), Gilufer and trisodium phosphate. The choice of these inhibitors is predetermined by their resistance to thermal and corrosive environments, as well as the ability to film formation [8].

Table 2 Gravimetric determination of the rate of corrosion of Steel 3 in the pulp in the absence and presence of the inhibitor OEDPZn ($\tau = 14$ days before)

| No | Concentration of inhibitor OEDPZn, % | m_1 , g | m_2 , g | Δm , g | K_m , $g/m^2 \cdot h$ | K_m middle $g/m^2 \cdot h$ | P_{Fe} , mm/year | Z, % | m-alkalinity, mg eq/l | $C_{Fe^{3+}}$, mg/l |
|----|--------------------------------------|-----------|-----------|----------------|-------------------------|------------------------------|--------------------|------|-----------------------|----------------------|
| 1 | 0 | 23.7105 | 23.6489 | 0.0616 | 0.1432 | 0.1436 | 0.1598 | - | 5.0 | 1130 |
| 2 | | 25.9340 | 25.8640 | 0.0700 | 0.1439 | | | | | |



| | | | | | | | | | | |
|----|------|---------|---------|--------|--------|--------|--------|-------|------|------|
| 3 | | 24.8223 | 24.7565 | 0.0658 | 0.1437 | | | | | |
| 4 | 0.05 | 23.7314 | 23.7105 | 0.0209 | 0.0415 | 0.0445 | 0.0495 | 35.09 | 6.5 | 980 |
| 5 | | 25.9605 | 25.9340 | 0.0265 | 0.0470 | | | | | |
| 6 | | 23.7302 | 23.7060 | 0.0242 | 0.0447 | | | | | |
| 7 | 0.1 | 23.9434 | 23.9080 | 0.0354 | 0.0689 | 0.0629 | 0.0699 | 8,26 | 16.0 | 1430 |
| 8 | | 24.1512 | 24.1200 | 0.0312 | 0.0596 | | | | | |
| 9 | | 26.0266 | 25.9949 | 0.0317 | 0.0601 | | | | | |
| 10 | 0.5 | 23.5511 | 23.4062 | 0.1449 | 0.2589 | 0.2275 | 0.2533 | < 0 | 26.5 | 1860 |
| 11 | | 23.2315 | 23.1160 | 0.1155 | 0.2170 | | | | | |
| 12 | | 26.3230 | 26.2053 | 0.1177 | 0.2067 | | | | | |
| 13 | 1.0 | 26.6600 | 26.4838 | 0.1856 | 0.3204 | 0.3784 | 0.4212 | < 0 | 37.5 | 2360 |
| 14 | | 21.8755 | 21.6899 | 0.1762 | 0.3311 | | | | | |
| 15 | | 24.3500 | 24.0804 | 0.2660 | 0.4836 | | | | | |

Varying different OEDPZn inhibitor concentrations in the pulp allowed to establish that the most effective is its concentration of 0.05%, the steel corrosion rate being 0.04448 g/m²·h (table 2). The penetration depth is equal to 0.04951 mm/year, the degree of protection – 35.09%. Increasing the concentration of the inhibitor to 0.1% cases increase of the corrosion rate up to 0.6287 g/m²·h. The depth of penetration – 0.06998 mm/year, the degree of protection – 8.26%. Further increase of the OEDPZn concentration is impractical because increase of the

concentration of the inhibitor leads to reduction of its protective action.

It is known that the inhibiting capacity of the reagent Gilufer appears due to the change in the surface state of the metal as a result of its absorption or formation, with metal ions, of sparingly soluble compounds – protective films [9].

Using Gilufer for inhibiting corrosion of steel in the pulp showed that the optimal concentration is 0.1% (table 3).

Table 3 Gravimetric determination of the rate of corrosion of Steel 3 in the pulp in the absence and presence of the inhibitor Gilufer (τ = 14 days before)

| № | Concentration of inhibitor Gilufer, % | m ₁ , g | m ₂ , g | Δm, g | K _m , g/m ² ·h | K _m middle, g/m ² ·h | P _{Fe} , mm/year | Z, % | m-alkalinity, mg-cq/l | C _{Fe3+} , mg/l |
|----|---------------------------------------|--------------------|--------------------|--------|--------------------------------------|--|---------------------------|-------|-----------------------|--------------------------|
| 1 | 0 | 23.7105 | 23.6489 | 0.0616 | 0.1432 | 0.1436 | 0.1598 | - | 5.0 | 1130 |
| 2 | | 25.9340 | 25.8640 | 0.0700 | 0.1439 | | | | | |
| 3 | | 24.8223 | 24.7565 | 0.0658 | 0.1437 | | | | | |
| 4 | 0.05 | 22.5457 | 22.5128 | 0.0329 | 0.0639 | 0.0572 | 0.0636 | 60.17 | 2.0 | 200 |
| 5 | | 23.3146 | 23.2850 | 0.0296 | 0.0571 | | | | | |
| 6 | | 24.0834 | 24.0571 | 0.0263 | 0.0505 | | | | | |
| 7 | 0.1 | 22.9660 | 22.9413 | 0.0248 | 0.0450 | 0.0450 | 0.0501 | 68.66 | 2.5 | 450 |
| 8 | | 20.5093 | 20.4875 | 0.0218 | 0.0446 | | | | | |
| 9 | | 25.4227 | 25.3950 | 0.0277 | 0.0453 | | | | | |
| 10 | 0.5 | 22.9999 | 22.9402 | 0.0597 | 0.0494 | 0.0493 | 0.0887 | 65.67 | 5.0 | 1930 |
| 11 | | 22.3963 | 22.3400 | 0.0563 | 0.0476 | | | | | |
| 12 | | 23.6036 | 23.5403 | 0.0633 | 0.0511 | | | | | |
| 13 | 1.0 | 24.2134 | 24.2106 | 0.0028 | 0.1864 | 0.1842 | 0.1650 | 28.27 | 6.0 | 2420 |
| 14 | | 24.8046 | 24.6700 | 0.0025 | 0.1986 | | | | | |
| 15 | | 23.1366 | 23.1334 | 0.0032 | 0.1678 | | | | | |

At this concentration, the corrosion rate was 0.0450 g/m²·h; the penetration depth of 0.05005 mm/year; the degree of protection was 68.66%. Increasing the concentration of the inhibitor to 0.5% causes a negligible increase in corrosion rate to 0.0493 g/m²·h, while the

penetration depth rises to 0.0887 mm/year; the degree of protection is 65.67%.

In the presence of trisodium phosphate in the slurry, corrosion rate decreases by almost two times: from 0.1436 g/m²·h to 0.0655 g/m²·h at concentration of 0.5% (table 4).

Table 4 Gravimetric determination of the rate of corrosion of Steel 3 in the pulp in the absence and in the presence of an inhibitor of trisodium phosphate ($\tau = 14$ days before)

| № | Concentration of inhibitor Na ₃ PO ₄ , % | m ₁ , g | m ₂ , g | Δm , g | K _m , g/m ² ·h | K _m middle g/m ² ·h | P _{Fe} , mm/year | Z, % | m-alkalinity, mg-eq/l | C _{Fe3+} , mg/l |
|----|--|--------------------|--------------------|----------------|--------------------------------------|---|---------------------------|-------|-----------------------|--------------------------|
| 1 | 0 | 23.7105 | 23.6489 | 0.0616 | 0.1432 | 0.1436 | 0.1598 | - | 5.0 | 1130 |
| 2 | | 25.9340 | 25.8640 | 0.0700 | 0.1439 | | | | | |
| 3 | | 24.8223 | 24.7565 | 0.0658 | 0.1437 | | | | | |
| 4 | 0.05 | 22.5379 | 22.5339 | 0.0048 | 0.0758 | 0.0736 | 0.0818 | 48.77 | 1.0 | - |
| 5 | | 22.7986 | 22.7930 | 0.0056 | 0.0713 | | | | | |
| 6 | | 22.6683 | 22.6635 | 0.0048 | 0.0735 | | | | | |
| 7 | 0.1 | 22.9293 | 22.9210 | 0.0083 | 0.0752 | 0.0740 | 0.0824 | 48.44 | 3.0 | - |
| 8 | | 22.4700 | 22.4637 | 0.0067 | 0.0728 | | | | | |
| 9 | | 22.6997 | 22.6924 | 0.0075 | 0.0739 | | | | | |
| 10 | 0.5 | 25.6946 | 25.6891 | 0.0055 | 0.0659 | 0.0655 | 0.0733 | 49.02 | 15.0 | - |
| 11 | | 24.9360 | 24.9331 | 0.0029 | 0.0655 | | | | | |
| 12 | | 24.1773 | 24.1770 | 0.0003 | 0.0651 | | | | | |
| 13 | 1.0 | 24.2131 | 24.2106 | 0.0025 | 0.0689 | 0.0706 | 0.0786 | 50.79 | 35.0 | - |
| 14 | | 24.1742 | 24.1705 | 0.0037 | 0.0705 | | | | | |
| 15 | | 24.1344 | 24.1302 | 0.0042 | 0.0723 | | | | | |

The depth of penetration is 0.0733. But at the same time the degree of protection isn't as high ($Z = 49.02\%$), as that with a 1% solution of the inhibitor.

The research results have been processed in the form of graphic relationships and are shown in Figures 1-3.

III. RESULTS & DISCUSSIONS

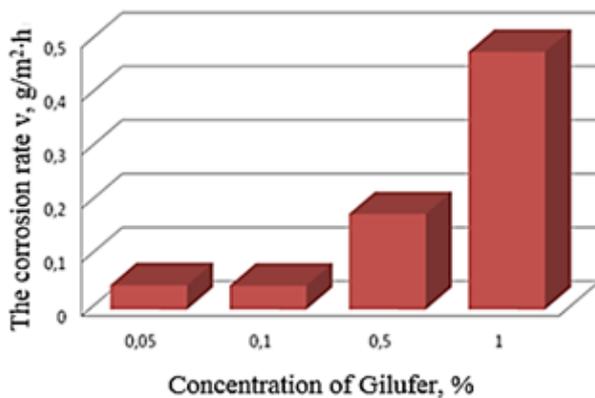


Fig. 2. Diagram of the corrosion rate of steel 3 a pulp concentration of inhibitor Gilufer

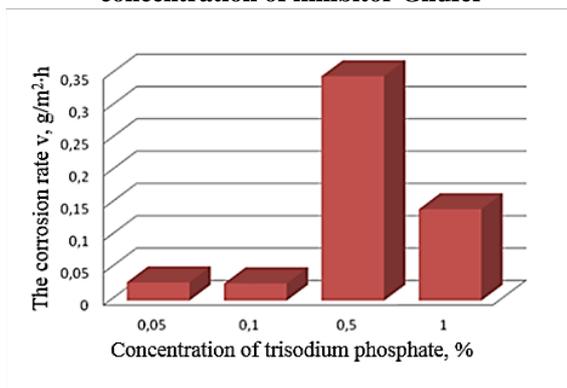


Fig. 3. Diagram of the corrosion rate of steel 3 of trisodium phosphate inhibitor concentrations

IV. CONCLUSION

Treatment of water with the inhibitors makes it possible to ensure effective operation of heat power engineering equipment. Most thoroughly examined in this respect are reagents based on organic phosphonate acids.

For the purpose of protection of the slurry pipeline of TPP ash removal system from corrosion we have carried out researches on pulp inhibiting by the reagents OEDPZn, Gilufer and trisodium phosphate, and selection of optimal concentration of the inhibitors. Gravimetric studies resulted in determining the most effective reagent: addition of Gilufer with the concentration of 0,1% allows to reach the minimal rate of the material corrosion in slurry pipeline (Steel-3). Based on these data we can draw the following conclusion: the most effective inhibitor for lowering the rate of corrosion stage in the pulp is Gilufer with the concentration of 0,1%. The article presents the results of the research work "Research into causes of high corrosive activity of ash pulp in a system of circulating hydro-ash-slag removal at thermal power plants (TPP) and development of technology preventing corrosion of equipment", fulfilled under grant funding of the Ministry of Education and Science (MES) of RK for 2013-2015.

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