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RESULTS OF SERVICE TESTS OF INDUSTRIAL WATER CYCLE IN BLOWOFF FREE CONDITIONS USING ZINK-BICHROMATE-PHOSPHATE CORROSION INHIBITOR AND HARD SALT ACCUMULATION

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Transformation of water cycle at an industrial enterprise into blowoff-free operation mode permitted dumping recycled water into industrial storm sewage to be excluded and total amount of industrial storm sewage waters, dumped into Tom river, to be decreased. Besides, flow of fresh river water for water cycle makeup decreased.

Water recycling system is one of the most important elements of technological complex at enterprises in many branches of industry.

Processing equipment efficiency, quality and prime cost of the product, discharge intensity of raw materials and electric energy depend on quality and efficiency of water recycling system operation [1].

Thus, ensuring qualitative operation of water recycling systems gives the opportunity to mobilize large reserves of manufacturing capacities and obtain significant efficiency increase and economy of industrial enterprises operation.

The main consumers of river water at chemical and by-product-coke enterprises are water cycles (WC), which spend it for losses compensation due to evaporation, droplet entrainment and dumping a part of recycled water into sewage system. The losses of recycled water due to evaporation and droplet entrainment are unrecoverable and determined by operation mode of heat-exchange equipment as well as meteorological conditions on the platform around a cooling tower (temperature and humidity of ambient air, strength and direction of wind etc.).

At WC operating recycled water is subjected manifold and sequentially to physicochemical influence. It is heated, cooled, aerated, contact manifold with heat-exchange surface. As a result, water becomes step-by-step more mineralized. On reaching a certain degree of mineralization water loses stability and acquires the ability to deposit mineral salts. To prevent this phenomenon and support the required composition of recycled water, a portion of water is substituted by raw river water.

Recycled water removed of water recycling system is dumped into enterprise storm sewage through overflow pipes in cooling towers bowls (WC blowoff) or through drainage pipe-lines in technological departments (process losses). Recycled water dumped from WC in aggregate with storm water forms industrial-storm drain at the enterprise. This drain consumption often achieves 80...85 % of total consumption of all sewage water at the enterprise.

Industrial storm sewage contains relatively high concentrations of suspensions dissolved in organic and inorganic compounds. Therefore, it can not be used repeatedly in technological water supply without preliminary treatment. Such drain purification to the quality, at which it can be used repeatedly, is a complex task requiring significant capital investment.

One of the trends for significant reduction of sewage water volumes at chemical and by-product coke enterprises is termination of recycled water dumping of WC. It is connected with WC transformation into blowoff-free operation mode, i. e. the exception of the cause of blowoff water formation itself. It allows minimizing water consumption scales of the enterprise and water supply source contamination, contributes considerably to the environmental control.

However, in maintaining water recycling systems in blowoff-free operation mode the problem of salt depositions in heat-exchange equipment becomes critical, the productivity of biofouling increases intensifying corrosion processes. Therefore, the efficient corrosion and scaling inhibitors should be applied as well as the biofouling problem should be solved for ensuring normal operation of blowoff-free systems. One of the trends in solution of these problems is circulating water treatment by corrosion and salt depositions inhibitors.

Among a large number of inhibitors, synthesized to the present time [2–4], the most widely used in domestic practice is zinc-bichromate-phosphate corrosion and depositions inhibitor (ZBP 2-3-3) [5] for treatment of circulating water of water cycles performing in blowoff-free operation mode. This inhibitor has being applied for years at one of Kemerovo chemical enterprises for heat-exchange equipment protection from corrosion, hardness salt depositions and biofouling in WC, performing in blowoff-free operation mode.

The given paper is devoted to the results of service tests of industrial WC performance in blowoff-free operation mode applying the ZBP 2-3-3 inhibitor. The researched WC had circulating water productivity of 9000 m³/h and was provided with cooling tower.

WC maintenance in blowoff-free operation mode was performed meeting a number of requirements imposed upon such systems when applying the ZBP 2-3-3 inhibitor [6]:

1. Circulating water alkalinity should not be less than 3 mg-equiv/l and should not increase 5,0 mg-equiv/l.
2. pH values of circulating water should be in the range of pH from 7,8 to 8,8. In this pH range the resistance of bacterial suspension is ensured and bacteria capability for adsorption on metal surface decreases.
3. Circulating water should not contain wares, such as hydrocarbons used by microorganisms as a material

for constructive metabolism. Besides, hydrocarbons presence perturbs bacterial suspension resistance, causes agglutination of microorganisms and their coarse-grained flocks settling on metal surface. In these conditions the ZBP 2-3-3 inhibitor loses its efficiency as the inhibitor of biofouling.

4. Continuous chlorination of circulating water is inadmissible. In blowoff-free systems of water recycling the chlorination of circulating water is not the technique for biofouling prevention. However, periodical chlorination of circulating water is necessary for improving sanitary and hygienic parameters of blowoff-free systems.

Inhibition and reagent treatment of circulating water

WC transformation into blowoff-free operation mode was achieved due to termination of circulating water dumping into industrial storm sewage through a bleed pipe branches in cooling tower bowls, through the hydraulic locks of processing equipment, water tanks in toilets, pumps gaskets in manufacturing departments. Then inhibition and reagent treatment of circulating water was started.

Inhibition was carried out by a complex zinc-bichromate-phosphate corrosion and depositions inhibitor, which consists of the following components:

- sodium bichromate;
- zinc sulfate;
- sodium hexametaphosphate.

Reagent treatment of circulating water was performed with sulfuric acid and water solution of sodium hypochlorite. Sulfuric acid was used for correcting circulating water alkalinity, i. e. its support in the range, which ensures circulating water stability with the inhibitor. Circulating water treatment with sodium hypochlorite (chlorination) was carried out for suppression biofouling on heat-exchange surfaces of heat-exchange equipment.

The inhibitor components (sodium bichromate, zinc sulfate, sodium hexametaphosphate) were periodically dipped into the grout tank, set near the cooling tower bowl. The capacity of the grout tank was 1,5 m³. The components dissolving in circulating water was carried out in ideal mixing mode. For this purpose two nipples were welded into upper and lower parts of tank shell tangentially to its circle. Circulating water was supplied to the lower nipple of the grout tank through the pipeline, laid from hot circulating water collector. The solution of the inhibitor component was self-flowing into the cooling tower bowl through the upper nipple of the grout tank. Sulfuric acid and sodium hypochlorite solution was supplied into cooling tower bowl from movable capacities with volume of 2 m³ each made of stainless steel.

Chemistry operation conditions of blowoff-free water cycle

Chemical conditions have been monitored during the whole period of experimental-industrial tests of WC performance in blowoff-free operation mode. Circulating water samples were selected in cooling tower bowl.

The diagram of changing alkalinity, circulating water hardness, concentration of calcium and magnesium ions in it is presented in Fig. 1. It is seen from this diagram that at the beginning of the tests, when WC was operating with system blowoff (May-July), circulating water hardness was 3,3...4,9 mg-equiv/l. It started increasing since transition to the blowoff-free operation mode and in September it was 12,2 mg-equiv/l and then it started decreasing and in October it was equal to 5,38 mg-equiv/l. The reason for such change is the fact that WC performance in blowoff-free operation mode from October to November was suspended for technical and technological reasons, its blowoff was resumed and its feeding was correspondingly increased.

After resuming WC performance in blowoff-free operation mode the hardness of circulating water started increasing again. Its maximal value was achieved only in a year of testing in August and amounted 32,5 mg-equiv/l. Then, circulating water hardness started decreasing and in two years of testing (September – October) it amounted 5,8...8,5 mg-equiv/l. The similar dynamic is also typical for concentration of calcium and magnesium ions. It is seen from Fig. 1 that circulating water alkalinity has changed in considerably more restricted range, than its hardness and it amounted 0,3...4,3 mg-equiv/l.

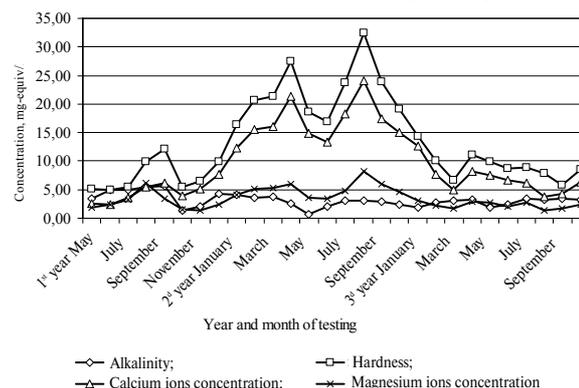
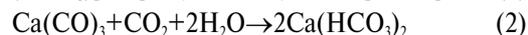


Fig. 1. Diagram of changing circulating water alkalinity and hardness, concentration of calcium and magnesium ions in it in the period of testing WC blowoff-free operation mode

The reasons for increasing circulating water hardness values are:

- increase of circulating water evaporation coefficient, stipulated by WC transformation into blowoff-free operation mode;
- circulating water treatment with sulfuric acid at the presence of which the following chemical reactions occur in water



The reaction (1) occurs very rapidly and decreases circulating water alkalinity supporting it in the required range (not more than 5 mg-equiv/l). Besides, it converts carbonate hardness into non-carbonate (constant) one. Reaction (2) is connected with dissolving carbonate deposits existing in the system. Its rate depends on both

concentration of CO₂ dissolved in water and amount of carbonate deposits existing in the system. Therefore, while testing the blowoff-free operation mode the circulating water hardness first increases and then decreases achieving, finally, the standard. This process is considerably slower and takes about 2 years (Fig. 1).

Decrease in hardness is stipulated by reducing the quantity of calcium and magnesium cations delivered into circulating water due to carbonate deposits dissolving as well as their removal into atmosphere with circulating water aerosol. The final result of WC processes is dissolution of carbonate deposits existing in WC system.

The dynamic of changing the total salt content of circulating water, sulfates, chlorides and suspensions content in it are presented in Fig. 2. Variations of sulfate-ions and chloride-ions concentrations in circulating water are stipulated by three reasons:

- reagent treatment mode of circulating water with sulfuric acid and sodium hypochlorite;
- change of water-thermal operation mode of water cycle, therefore, the evaporation coefficient of circulating water;
- change of the ions concentration in makeup water.

The determining reason for these is the one connected with rather large quantities of sulfuric acid and sodium hypochlorite introduction into circulating water.

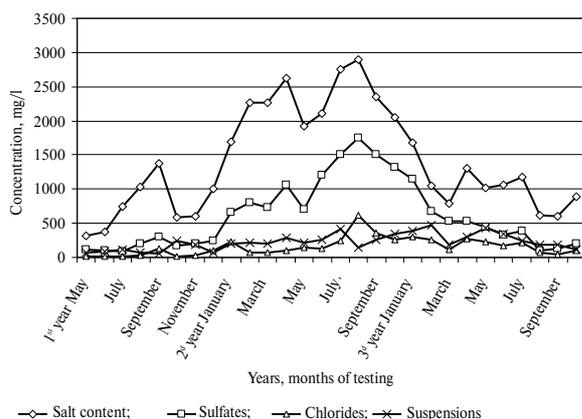


Fig. 2. Diagram of changing salt content, sulfates, chlorides, suspensions concentration in circulating water during WC blowoff-free operation mode testing

Stable operation of WC at such abnormally high indices of its chemistry conditions was achieved by entering the inhibitor component – sodium bichromate, zinc sulfate and sodium hexametaphosphate as well as reagents – sulfuric acid and water solution of sodium hypochlorite. Concentrations of inhibitor components at testing of blowoff-free mode have changed in the following range: for Cr⁶⁺ ion – 1,02...1,84 mg/l; for Zn²⁺ ion – 0,46...1,99 mg/l; for PO₄³⁻ ion – 2,18...3,48 mg/l.

Circulating water corrosiveness with ZBP 2-2-3

Circulating water corrosiveness in WC was estimated by corrosion rate of carbon steel samples in it (St. 3), which represented plates of 20×40 mm size and 2...3 mm thick. Before being installed in WC the plates had been polished

with abrasive paper and brightened with diamond paste for achieving smoothness of their surface not lower than the 8th level, ungreased in acetone and weighted.

The corrosion rate was determined by gravimetric way (in samples weight descending). For this purpose in preset time the samples were taken out of WC, treated mechanically off corrosion and put into 5 % hydrochloric acid, inhibited with urotropin for 1...3 min. Then the samples were washed with water and acetone, dried and weighed.

Corrosion rate was determined by the equation

$$v = \frac{G_1 - G_2}{Ft}, \text{ g}/(\text{m}^2 \cdot \text{h}),$$

where G_1 is the initial sample weight, g; G_2 is the weight of sample after contact with circulating water, g; F is the surface of sample, m²; t is the contact time of sample with water, h.

At the beginning of testing the corrosion rate of carbon steel and iron samples was determined for WC blowoff operation mode, when circulating water was not undergone the inhibition and reagent treatment. For this purpose the samples were put into special container which was set in cooling tower bowl. Then the corrosion rate of these metal samples was determined after the beginning of inhibition and reagent treatment. The results of these corrosion testing are presented in the Table. The data show that as a result of circulating water treatment with the ZBP 2-3-3 inhibitor the corrosion rate of iron and carbon steel decreased more than 10 times.

Table. Circulating water corrosiveness, determined in cooling tower bowl

Sample material	Contact time with water, h	Concentration in circulating water, mg/l			Corrosion rate, g/(m ² ·h)
		Zn ²⁺	Cr ⁶⁺	PO ₄ ³⁻	
Steel St.3	470	0	0	0	0,387
Iron	470	0	0	0	0,435
Steel St.3	400	1,2	1,8	1,7	0,021
Iron	400	1,2	1,8	1,7	0,052

Control of WC circulating water corrosiveness was performed during its whole operating period in blowoff-free mode. To increase the obtained data reliability the carbon steel check samples were put into heat-exchanger, being in processing department. The samples were set into tubing string of heat-exchanger in which circulating water entered for cooling technological product. The technological product with temperature 140...150 °C entered into tube space of this heat-exchanger.

On the basis of the results of carried out investigations the dependences of carbon steel corrosion rate on contact time with circulating water with ZBP inhibitor were plotted. They are presented in Fig. 3. It is seen from the Fig. that carbon steel corrosion rate with zinc-bichromate-phosphate inhibitor is 0,075...0,02 g/(m²·h). And the highest corrosion rate is observed from the start time of the contact of samples with water.

Thus, after WC transformation to blowoff-free operation mode, inhibition and reagent treatment of circulating water, the samples corrosion rate at the input into heat-exchanger was 0,01...0,089 g/(m²·h), at the heat-exchanger output it was from 0,005...0,085 g/(m²·h). It

proves that the ZBP 2-3-3 inhibitor protects efficiently the equipment from corrosion in circulating water after WC transformation into blowoff-free operation mode.

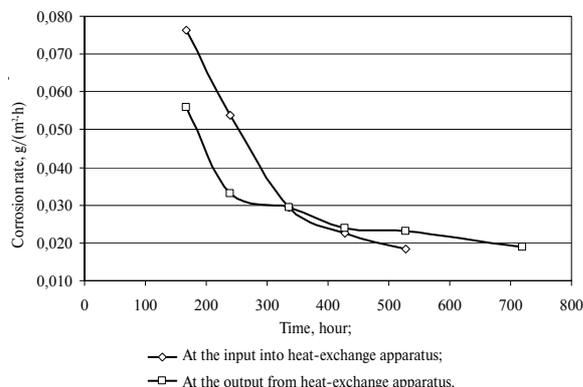


Fig. 3. Dependence of carbon steel corrosion rate on contact time with circulating water of blowoff-free WC with ZBP 2-3-3 inhibitor

Circulating water tendency to hardness salt deposition with ZBP

Circulating water tendency to hardness salt and suspensions deposition was estimated by increasing of stainless steel samples weight after their contact with circulating water. The samples were of 20×50 mm size, 4...6 mm thick and were set in cooling tower bowl and heat-exchanger tubes simultaneously with the carbon steel samples. After the samples being taken out of circulating water, they were undergone to airing not less than 48 h, and then they were weighted on analytical balance. The obtained results are given in Fig. 4.

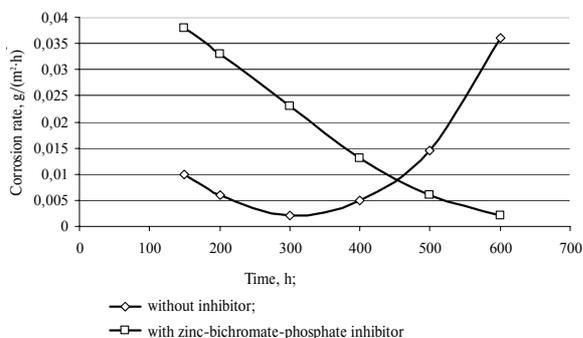


Fig. 4. Dynamic of suspensions deposition on stainless steel samples in WC circulating water

It is seen from Fig. 4 that at contact time of samples with water from 150 to 300 h the deposition rate in circulating water, without inhibitor, decreases, and then increases. Deposition rate in circulating water containing inhibitor decreases steadily at increasing contact time of the samples with water.

At contact time of samples with water to 450 h the rate deposition in circulating water containing inhibitor is higher than in water without inhibitor. At increasing contact time of samples with water over 450 h the deposition rate in circulating water containing corrosion inhibitor becomes significantly higher than in water without inhibitor.

Defining calcium and magnesium salts in depositions on the samples showed their complete absence. Therefore, suspensions depositing on the surfaces of heat exchanging equipment at WC performance in blowoff-free mode with zinc-bichromate-phosphate inhibitor are the products of microorganisms and animalcular activity developing in circulating water volume.

Conclusion

Transformation of water cycle at industrial enterprise into blowoff-free operation mode permitted for solution of two problems on protection of river Tom water ponds:

- to remove circulating water dumping from WC into industrial storm sewage and decrease, thereby, the total of industrial storm sewage water dumping into river Tom on the average 1100 thous. m³ per year;
- to decrease raw river water consumption for feeding water cycle on average 1100 thous. m³ per year.

The results of service tests of WC performance in blowoff-free operation mode confirmed the high efficiency of zinc-bichromate-phosphate inhibitor of corrosion and hardness salt deposition. Circulating water treatment with this inhibitor decreased the corrosion rate of carbon steel in more than 10 times and completely excluded hardness salt deposition on metal surfaces. As a result, shutdowns of heat exchanging equipment for cleaning its heat exchanging surfaces were reduced and downtimes of processing equipment by the same reasons were decreased.

WC circulating water treatment with sulfuric acid allowed dissolving calcium carbonate depositions and corrosion from the walls of heat exchanging equipment and improving heat exchanging processes in it. Circulating water treatment with sodium hypochlorite prevented biofouling processes from developing on the surfaces of heat exchanging equipment. As a result, equipment flooding which was observed to the transformation of water cycle into blowoff-free operation mode was stopped.

Costs for service of WC in blowoff-free mode are determined by the prices of the inhibitor and reagents components, the annual expenditure of which was: sodium biochromate was 680 kg; zinc sulfate was 2000 kg; sodium hexametaphosphate was 730 kg; sulfuric acid was 25 t; water solution of sodium hypochlorite was 50 m³.

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MANUFACTURE OF DESIRED END PRODUCTS BY MEANS OF FINE TREATMENT OF COAL TAR RESIN

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The possibility of desired end product manufacture from by-product coke industry wastes is shown. A large number of valuable products can be obtained from different fractions of coal tar resin by their fine treatment. The products obtained in this way find application in medical and chemical industries and etc. Moreover, recycling of by-product coke wastes into end products solves the problem of their utilization.

The flowsheet of chemical coke by-products recycling in the 60–70s of the previous century began undergoing significant changes. From the classical sheet with obtaining of a number of chemicals (pyridine, benzene hydrocarbons, naphthalene, phenols etc.), chemical recycling of coke by-products was substantially transformed to decontamination of coke oven gas for its further using in power engineering. The recycling of crude benzene, fractions of pitch, pyridine bases with extraction of individual substances or their mixtures was planned at special enterprises, at the devices of high unit capacity.

In the course of this tendency, in connection of startup of the powerful by-product coke industry at the West-Siberian metallurgical enterprise, there appeared the real possibility of removing workshops of crude benzene and resin recycling of the nearby by-product coke plants (Kemerovo BPCP and by-product coke industry CMP) from the flowsheet owing to the equipment excessive wear. The recycling of resin at by-product coke industry of 3CMK is of narrow directed character: naphthalene extraction, obtaining of straw oil (for needs of domestic manufacture and nearby by-product coke enterprises) and pitch [1, 2].

The same sheet of resin recycling was carried out at OAO «Altay-coke», built 20 years later. The difference is only in the fact that the end products of resin recycling are pitch and sleeper impregnation oil. Naphthalene, phenolic and significant part of anthracene fractions are sent to cognate enterprises, where there are devices for recycling to end products, or utilized by means of burning with heat release.

These «wastes» hardly bring profit to the enterprise at the existing rail transportation rates. Their marketing carries more environmental directivity than economical appropriateness.

The concept of centralized resin recycling, realized in Germany, USA and other countries in the middle of the 20th century was also seriously examined in domestic coke chemistry. Resin deep recycling into end products was partially realized in Ukraine and at phenolic plants. About 25 individual substances and about 10 chemical agents (while in Rursk region in Germany more than 100 designations of end products and chemical agents) were produced [3].

In Russia such approach to resin recycling is hardly appropriate for economic reasons. Nevertheless, many chemical compounds, which are obtained as products in by-product coking industry, are deficient raw materials for many branches of chemical industry (pharmaceuticals, polymers, semi-products, colorants etc.). There is a requirement in acenaphthene, fluorene, carbazole, pyrene and many other compounds, the manufacturing of which is practically absent in Russia for a variety of reasons.

The following main components with content from 1 % and more are contained in high-boiling resin fractions [4]: acenaphthene, diphenylene oxide, fluorene, phenanthrene, anthracene, carbazole, fluoranthene, pyrene, chrysene. The first three components are concentrated in stripping fraction and influence significantly the temperature of its crystallization at conventional technology of stripping fraction extraction in one co-