

## DEVELOPMENT OF HARDNESS SALT DEPOSIT AND CORROSION INHIBITOR IN AQUEOUS ENVIRONMENT ON THE BASIS OF ORGANIC PHOSPHONATE FOR THE WATER RECYCLING SYSTEMS OF CHEMICAL AND BY-PRODUCT COKING INDUSTRIAL ENTERPRISES

G.V. Ushakov, G.A. Solodov, S.V. Mochalnikov

Kuzbas State Technical University, Kemerovo

E-mail: sna.httt@kuzstu.ru

*The results of laboratory investigation showing that composition of organophosphorous complexon OMED (salt of 1-oxyethylidenediphosphonic acid with 2-dimethyl-amino-methylphenol) and zinc sulphate is an efficient inhibitor of corrosion and salt deposit in aqueous environment are presented. Therefore it can be applied in the recycling cooling systems of industrial enterprises.*

At present time water rotating cycles (WRC) are used at chemical and by-product coking enterprises with low coefficients of circulating water evaporation. The calculations show that growth of evaporation coefficient from 1,5 to 2,0 allows decreasing river water application for feeding water rotating cycle in 3 times, and bleed water evacuation in 5...7 times. Taking into account high capacity of circulating water cooling systems, such change of their operating conditions results in vast water saving and decrease of disposed wastes consumptions [1–3].

Growth of coefficient of circulating water evaporation results in proportional increase of its salt-content, alkalinity, hardness, suspensions concentration, organic and inorganic substances. As a result of this a fouling processes in water recycling system are intensified, circulating water stability is disturbed and its corrosive activity increases. Disturbance of circulating water stability results in extraction of calcium carbonate in solid state from the solution and its deposit on heat-exchanging surfaces.

In the water recycling systems corrosion processes of heat-exchanging equipment and fouling processes also occur. Solid products of these processes and also particulate pollutants, brought into the system with air (in cooling towers) and makeup water, deposit on heat-exchanging surfaces simultaneously with calcium carbonate, forming deposits, which thick often achieve several millimeters. These deposits possess low thermal conductivity and sufficiently impair heat transfer process. Owing to this the productivity of technological devices decreases, product quality deteriorates, raw material losses increase etc.

Thus, simple growth of evaporation of circulating water impairs thermal conditions of heat exchanging equipment, increases the number of its shutdowns for cleaning, reduces service life. Therefore, in the practice of water supply, the problem of stability retaining of circulating water, decrease of its corrosive activity and tendency to fouling became particularly urgent. At present time the most effective way of its solution is circulating water treatment with inhibitors of corrosion and salt deposits [4, 5].

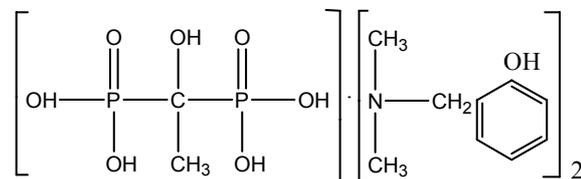
Increase of coefficient of circulating water evaporation and application for this purpose inhibitors of corrosion and salt deposits in the water recycling systems with open cooling elements (cooling towers) is connected with two negative moments. The first one is the appearance of inhibitor components in circulating water, removed from the system for stabilization of mineral com-

position of circulating water. This water is called bleed water and disposed into storm sewage of industrial enterprise. The second negative moment is connected with condensed moisture emission into the atmosphere of industrial stage from the cooling towers of WRC, consequently, with additional atmospheric air pollution. Therefore, inhibitors applying in water recycling systems, along with high efficiency of heat-exchanging equipment protection from corrosion and hardness salt deposits must possess low toxicity [6].

Development of efficient low-toxic inhibitors of corrosions and salt deposits in aqueous environment is a difficult problem, requiring solution of the following questions:

- investigation of inhibitory and stability properties of compounds, used as inhibitors of corrosion and salt deposits;
- development of inhibitory and stability compositions, including the given complexones and admixtures, increasing degree of metal protection from corrosion and fouling.

The research in the direction of developing inhibitor of corrosion and salt deposits were carried out, as a basis of which salt of 1-oxyethylidenediphosphonic acid with 2-dimethyl-amino-methylphenol (complexon OMED) was selected. Pilot runs of this complexon were synthesized at Sterlitamak pilot petroleum chemical plant by the technology, developed by Kazan chemical-engineering institute. The formula of complexon has the form

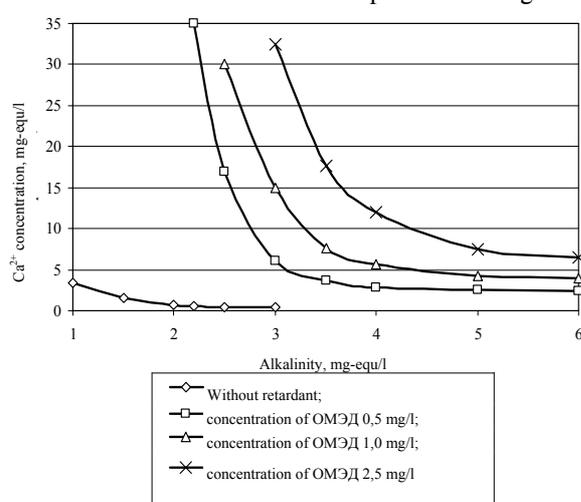


### Water stability in presence of complexon OMED

To determine water stability a specific method is developed. The essence of this method is that dependence of equilibrium concentration of calcium carbonate is determined on researched water alkalinity. According to this method 7 cone flasks are filled up with 200 ml of water each with certain content of calcium ions. Then the flasks are placed at magnetic stirrers and the given amount of sodium carbonate solution is added to each one

while stirring. Concentration and quantity of  $\text{Na}_2\text{CO}_3$  solution are chosen so that in 2...3 last samples calcium carbonate precipitates and in the first samples there is no precipitate. Solutions in the flasks are stirred at magnetic stirrers during 2 hours and are abandoned for 24 hours. After that water is filtered and its alkalinity and calcium ions concentration are determined. The last data of analysis of the last flask, where there is no calcium carbonate deposit, are taken as equilibrium values of these coefficients. Then concentration of calcium ions is increased in researched water and defining is repeated again. As a result the second equilibrium values of water alkalinity and concentration of calcium ions in it etc. are obtained.

Using the described above method water stability in presence of different amounts of complexon OMED is researched. The data obtained are presented in fig. 1.



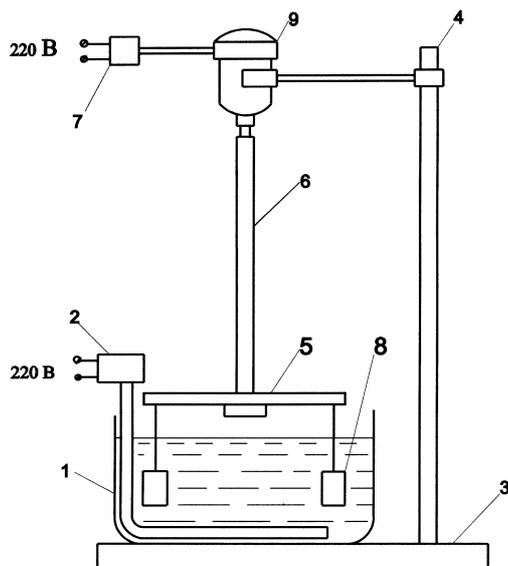
**Fig. 1.** Equilibrium curves of calcium ions in water in presence of inhibitor OMED

Physical meaning of dependences, presented in this figure consists in the fact that at values of calcium ions concentration and alkalinity, being on the left of equilibrium curves, water possesses stability and does not extract calcium carbonate as a precipitate. At values of calcium ions concentration and alkalinity of circulating water, being on the right of equilibrium curves, water is not stable and it extracts calcium carbonate precipitate. It is seen from figure 1 that in the range of OMED concentrations in water 1...3 mg/l water stability retains at its alkalinity equals to 3...5 mg-eq/l in the range of equilibrium curves calcium ions concentration in water 2,5...30 mg-eq/l.

#### Carbon steel corrosion in circulating water in presence of complexon OMED

In laboratory environment water corrosive activity in presence of complexon OMED has been studied. As a subject of inquiry purified river water from the technical water supply system of Kemerovo OAO «Azot» was used.

To determine water corrosive activity the laboratory setup and the method of defining rate of metal samples corrosion were developed. The scheme of the setup is presented in fig. 2.



**Fig. 2.** Setup for defining water corrosive activity: 1) reservoir with researched water; 2) heater with automatic temperature regulator; 3) tripod; 4) arm; 5) rotating disk, 6) axis, 7) laboratory autotransformer; 8) check samples; 9) electric motor

The essence of the method consists in dipping check samples made of carbon steel into researched water, being in the reservoir – 1 and their attaching to the disk – 5, which is brought into rotation by the electric motor – 9. Rotation rate is specified so that linear velocity of samples motion conforms to the rate of water flow motion in the tubes of industrial heat exchangers. On the expiry of prescribed time the samples are extracted from the setup and put into 5 % hydrochloric acid, inhibited with urotropin, which dissolves corrosion products. After that the samples are washed with distilled water, dried and weighed on analytical balance.

Water corrosive activity in the presence of complexon OMED was estimated by the corrosion rate of the samples of carbon steel in it (St. 3). Corrosion rate was defined by decrease of samples weight, dipped into water for 24 hours at temperature 20...25 °C.

Samples corrosion rate was defined according to the formula

$$K = \frac{\Delta G}{F t},$$

where  $\Delta G$  is the decrease of sample mass, g;  $F$  is the sample surface area,  $\text{m}^2$ ;  $t$  is the experiment time, h.

**Table 1.** Water corrosive activity in the presence of complexon OMED

Test number	Concentration, mg/l		Alkalinity, mg-eq/l	Corrosion rate, g/( $\text{m}^2 \cdot \text{h}$ )	Corrosion type
	OMED	$\text{Zn}^{2+}$			
1	0	0	1	0,91	Pitting
2	0,1	0	1	0,26	Sharpened
3	0,1	0	3	0,32	Pitting-sharpened
4	0,1	0	5	0,60	
5	0,5	0	1	0,40	
6	1,0	0	1	0,67	

The obtained data are presented in table 1. They show that presence of 0, 1...1,0 mg/l complexon OMED in water decreases corrosion rate 1,3...3 times in comparison with uninhibited water in.

Visual study of samples surface showed that in the absence of complexon OMED corrosion is pitting. Its introduction in water changes corrosion nature and makes it pitting-sharpened. Therefore, the conclusion was made that use of only complexon OMED as a inhibitor of corrosion and salt deposit is undesirable. In the composition of inhibitor of corrosion and salt deposit the second component, removing sharpened corrosion is required.

#### Search of admixture to complexon OMED in composition of two-component inhibitor of corrosion and salt precipitate

Zinc sulfate, nickel nitrate and sodium silencer, containing correspondingly ions  $Zn^{2+}$ ,  $NO_3^-$  and  $SiO_3^{2-}$ , inhibiting processes of metals corrosion in water environments were studied as possible admixtures to complexon OMED.

The experiment was carried out at modeling setups, corresponding reservoirs with circulating water, into which the sample plates of carbon steel were dipped. The conditions of the experiment are as follows: temperature 23...25 °C, stirring, air saturation, time of the experiments 48 h. Time was selected on the basis experimental data on kinetics of samples corrosion in circulating water, which results showed that corrosion rate in 40 hours amounts to 60...80 % of maximal value and further it does not significantly change during the time of experiment.

Researched water had the following values range of determined coefficients:

pH	7,4...8,3
Alkalinity, mg-equ/l	1,4...2,7
Hardness, mg-equ/l	2,9...3,7
Salt content, mg/l	510...695
Chlorides, mg/l	210...280
Sulfates, mg/l	19,8...33,1
CPC	10,1...11,0

**Table 2.** Corrosion rate of carbon steel in water in the presence of OMED and various admixtures

OMED concentration, mg/l	Admixture		Corrosion rate, g/(m <sup>2</sup> ·h)	Rate of deposition, g/(m <sup>2</sup> ·h)
	Formula	Concentration, mg/l		
0	–	–	0,235	0,002
3	–	–	0,545	0,000
3	ZnSO <sub>4</sub>	1,0	0,041	0,000
3	Ni(NO <sub>2</sub> ) <sub>2</sub>	2,0	0,200	0,000
3	Na <sub>2</sub> SiO <sub>3</sub>	10,0	0,266	0,000

Circulating water stability in the presence of complexon OMED and investigated admixtures was defined simultaneously with corrosion testing. Circulating water stability was estimated by the rate of hardness salt precipitation on the samples of stainless steel, which were put into circulating water together with the samples of carbon

steel. The rate of precipitation was determined by increase of samples mass before and after the contact with water.

The results of the experiments are presented in table 2. From this table it is seen that the most efficient admixture to complexon OMED is zinc sulfate.

#### Corrosion of carbon steel and hardness salt precipitates in the presence of two-component inhibitor OMED – zinc sulfate

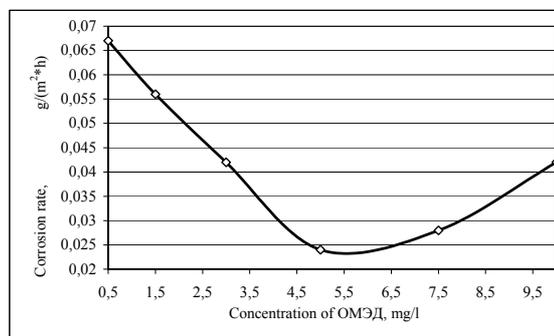
The aim of the given investigations was to define operating concentrations of zinc ions and complexon OMED in water at treatment of circulating water of WRC by two-component inhibitor OMED – zinc sulfate.

The investigations were carried out in two stages. At the first stage operating concentration of ions in water was defined. For this purpose corrosion rate of carbon steel in water was determined according to above-stated method. Concentration of zinc ions in the experiments was equal to 1 and 2 mg/l. Concentration of complexon OMED amounted to 0,5...1,0 mg/l. The results of the experiments are presented in table 3.

**Table 3.** Water corrosive activity in the presence of complexon OMED and zinc sulfate. Alkalinity is 1 mg-equ/l. Pitting corrosion

Test number	Concentration, mg/l		Corrosion rate, g/(m <sup>2</sup> ·h)
	OMED	Zn <sup>2+</sup>	
1	0	0	0,91
2	0,1	1	0,083
3	0,5	1	0,076
4	1,0	1	0,059
5	0,1	2	0,035
6	0,5	2	0,051
7	1,0	2	0,042

It follows from the data of table 3 that addition of zinc ion in amount of 1...2 mg/l to complexon OMED as the second component decreases corrosion rate of carbon steel in 10...11 times. In this case pitting corrosion does not occur. Therefore Zn<sup>2+</sup> concentration, equal to 1...2 mg/l, may be taken as operating one for two component inhibitor OMED – zinc sulfate.



**Fig. 3.** Dependence of corrosion rate of carbon steel on complexon OMED concentration at water treatment with two component inhibitor OMED – zinc sulfate

At the second stage of investigations the experiments in defining corrosion rate in water, in which zinc ions concentration was constant, equal to 1 mg/l, and com-

plexon concentration was changed were carried out. The obtained data are presented in figure 3. It is seen from this figure that at OMED concentration equal to 4...8 mg/l corrosion rate has the smallest values. Therefore these concentrations may be taken as operating ones.

#### The influence of two component inhibitor OMED – zinc sulfate on fouling in aqueous environments

Besides corrosion decrease and prevention of hardness salt deposits, the important property of any inhibitor is an ability to suppress vital activity of animalcular organisms, developing in aqueous environments and forming the great bulk of fouling on heat exchanging surfaces. Therefore, after weighing the samples of stain-

less steel, from their surface smears were taken, put on a slide and visually examined under a microscope. The results of investigations showed that two component inhibitor OMED – zinc sulfate does not stimulate fouling processes in aqueous environment.

Thus, the results of investigations, carried out in laboratory environment, indicate the composition of organophosphorous complexon OMED (salt of 1-oxethylidene-diphosphonic acid with 2-dimethylamino-methylphenol) and zinc-sulfate being the effective inhibitor of corrosion and salt precipitate in aqueous environment. Therefore it may be applied for two-bath process of circulating water in systems of recycling cooling of industrial enterprises.

#### REFERENCES

1. Pavluhina L.D., Rakcheeva L.V. et al. Circulating water treatment in the system of water rotation at OAO «Voskresensk mineral fertilizers» // Modern technologies of water preparation and equipment protection from corrosion and scale formation: Reports, theses of the conference. – Moscow, 2003. – P. 57–61.
2. Alferova L.A., Nechaev A.P. Development of closed systems of industrial enterprises and systems water consumption // Chemistry and technology of water. – 1990. – V. 12. – № 6. – P. 534–542.
3. Belichenko Yu.P., Gordeev L.S. et al. Closed systems of chemical industries water supplying. – Moscow: Chemistry, 1996. – 270 p.
4. Talalai A.V., Shukailo B.N., Kolomiets P.V. Stabilization treatment of circulating and extraction water and deposits removal from the surfaces of heating and cooling // Modern technologies of water preparation and equipment protection from corrosion and scale formation: Reports, theses of the conference. – Moscow, 2003. – P. 55–56.
5. Gavrilov N.B. High-performance complex programs of reagent treatment of reverse cooling cycles on the basis of domestic reagents // Modern technologies of water preparation and equipment protection from corrosion and scale formation: Reports, theses of the conference. – Moscow, 2003. – P. 49–54.
6. Sorochenko V.F. Maintenance of water rotating cycles without scale formation with minimal environmental risk // Chemistry and technology of fuels and oils. – 1998. – № 4. – P. 50–52.

Arrived on 22.05.2006

UDC 662.749.33

### HIGH-BOILING COMPONENTS IN STRAW OIL

V.I. Lozbin, S.V. Mochalnikov, G.A. Solodov, A.V. Papin, A.V. Nevedrov

Kuzbas State Technical University, Kemerovo

E-mail: sna.httt.kuzstu@ru

*Investigation of straw oil and polymer quality produced in the process of its regeneration has been carried out. The conclusions about using polymers as a material for base end products are made. Flow scheme of technological treatment of straw oil wastes is suggested.*

In the process of coal coking considerable quantity of resin is generated which contains in its composition enormous quantity of organic compounds the large amount of which is difficult to be obtained in other technological processes. Such condensed compounds as acenaphthene, dibenzofuran, fluorene and others are in resin in quantities more than 1 % (per resin). At the same time there is a real requirement for these compounds as raw materials in different branches of applied chemistry and pharmaceutical chemistry.

The technology of coal-tar resin reprocessing at domestic enterprises of by-product-coking industry is mainly carried out at single-column rectification devices with target fraction selection according to column height. Stripping fraction is usually selected from the

17<sup>th</sup> tray. More than 140 individual compounds are in its composition [1]. The greater bulk is presented by 23 components of aromatic series with boiling temperatures 218...293 °C. Moreover, about 40 nitrogenated compounds and 16 components of phenolic series are in the fraction. Quality of straw oil is determined by absorbing capacity (quantity of methyl-naphthalenes), tendency to crystallization when cooling and tendency to polymerization at high temperatures, for which high-boiling components: acenaphthene, diphenylene dioxide, fluorene are responsible [2–4].

High-boiling compounds emission by means of additional rectification of straw oil solves the problem of both straw oil quality improvement and raw materials for emission of individual high-boiling components. In