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EVALUATION METHOD OF SCALING INHIBITORS ACTION EFFECTIVENESS

A research of different composition and structure inhibitors' effectiveness using a cooling scale loop modeling equipment in dynamic conditions. Simulated conditions of water circulating two industries. The optimal molecular weight for carboxylic polyacids as well as the optimal dose for carboxylic polyacids and organophosphorus compounds for use in these systems were estimated.

Introduction. To ensure optimal temperature rate in industrial production water cycles are widely used. All water circulating systems can be roughly classified into one of three types of structures that represent a set of water facilities and the sequence of their location on the terrain: open recirculating systems (direct-flow with water reuse), direct-flow systems and closed recirculating systems (reverse).

Continual tightening of ecological regulations and the rising cost of water abstracted from natural sources cause the reduction of water consumption by industrial enterprises by the way of upgrading water circulation systems with increasing evaporation rate.

Therefore the issue of scale deposits in the pipes of the cooling water circulation systems, and especially on the heat exchanging surfaces of the equipment is a very topical.

The rate of formation of scale deposits in water circulation systems, and their quantity directly depends on the operating system parameters, as well as on water quality indicators such as hardness, alkalinity, pH value, TDS (total dissolved solids), etc. In general case, a water stability indicator is used. Water is considered to be stable, if it does not form and dissolve hardness depositions and thus enables continuous operation of a cooling circulating system for a long time [1]. The deviation scope of the water system from the stable state shows its disposition to scale formation or corrosion. Thus, it is possible to predict to some extent the speed and the quantity of scale deposits being produced.

To simplify practical calculations empirical criteria are introduced to determine the saturation index, or water stability, for example Langelier saturation index, etc. [2].

Langelier saturation index (LSI) is calculated by the formula

$$LSI = pH - pH_s,$$

where in pH – measured water pH value; pH_s – pH value corresponding to the equilibrium CO_2 content in the solution depending on the temperature and the concentration of Ca^{2+} cations, the total alkalinity level and salinity. The latter figure (pH_s) is determined using nomograms.

The aggressiveness of water is evaluated by the value of Langelier saturation index. If the index value is less than 0, then this water can dissolve calcium carbonate, eliminating the possibility of a protective carbonate film formation on the surface of pipelines and equipment, which causes corrosion process.

At a positive index value water is non-aggressive and promotes the carbonate deposits formation. If the value of Langelier saturation index is close to 0, water is considered to be stable. The value of the saturation index grows with increasing of evaporation coefficient value, and accordingly, the tendency to form scale deposits increases dramatically. To compensate this negative effect the specific chemical compounds are brought in water composition – scale formation-inhibitors the use of which allows the water system to remain stable at elevated saturation index for a long period of time.

There are various methods for effectiveness evaluating of the inhibitory effect of reagents [3]. However, most methods are characterized by complexity, stringent demands for test conditions and purity of the reagents being used. A common shortcoming is the lack of study possibilities of sedimentation processes in dynamic environments and the associated complexity of phase study of carbonate sedimentation on the surface of various materials.

In this work, the installation simulating the sedimentation processes under dynamic conditions PMAC SCL-30P-2A (UK) was used to evaluate the effectiveness of the reagents as scale inhibitors (Fig. 1).

The operation principle of the apparatus is a dynamic measurement increasing as a result of scale formation, a differential pressure in the metal capillary at varying or constant experiment parameters.

Solutions of calcium and magnesium chloride, and sodium bicarbonate of certain concentration from the containers *1* and *2* are fed via peristaltic pumps *3*, *4* the capillary *6* with a constant volume velocity. Before mixing and feeding to a capillary the solutions pass through heat exchangers (not shown in the diagram) placed in a thermostat *7*, for achieving a predetermined temperature. The formation and sediment deposition takes place in the

capillary under dynamic conditions. Thickness growth of deposits on capillary walls increases the hydrodynamic resistance of the system that is fixed by means of a differential manometer *5*.

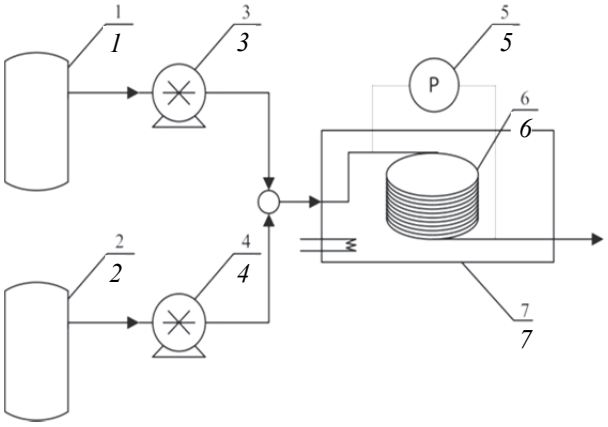

Fig.1. Installation scheme,
simulating sedimentation processes:
1, *2* – containers; *3*, *4* – pumps; *5* – differential pressure gauge; *6* – capillary; *7* – thermostat

The time interval, during which the scale layer, leading to an increase of differential pressure in the capillary from zero to a certain value is formed, is used as an index characterizing the effectiveness of preventing or slowing down (inhibition) sedimentation. The given value is a relative value – it indicates the inhibiting process of sedimentation in the capillary compared to the control non-reagent option. The smaller is the pressure increase in a capillary within a certain period of time, the more effective is the reagent and more optimal the used dose. This installation allows to evaluate the tendency of the water used in a particular water recirculation systems to scale formation.

In industry, the water enters the water recirculation systems from natural surface or underground sources. Depending on the origin the impurity content in the water can vary considerably. So, the company PJSC "Mineral Wax Plant" uses water from artesian wells, and the PJSC "Grodno Azot)" – river water (Table)

The aim of this work is to simulate the operation of the cooling water circulating cycles, as well as the effectiveness study of scaling inhibitors of different composition under dynamic conditions.

Main part. As model systems solutions of sodium hydrogen carbonate, calcium and magnesium chlorides were used, taken in amounts corresponding to the water parameters from the real water circulation systems of enterprises "Mineral Wax Plant" and PJSC "Grodno Nitrogen". The pH value was adjusted by means of sodium hydroxide.

As scaling inhibitors the following set of compounds was used: succinic acid, adipic acid, sebacic acid, polyacrylic acid having a molecular weight (MW) 2,000–16,000 polymethacrylic acid (MW 5,100) hydroxyethylenediphosphon (HEDP) amintrimetilphosphon (ATMP), 2-phosphonbutan 1,2,4-tricarboxylic acid (PBTK). The scaling inhibitor was fed to the unit separately. The inhibitor concentration quantity in the solutions being studied is selected in such a way as to ensure a pressure change in the capillary within an hour. The reagent doses being used are equal within the same system.

As a comparative characteristics of the reagent effectiveness there served a relative indicator – time interval (τ), during which in the capillary there is formed the scale layer, which leads to a differential pressure increase from zero to a certain value, similar for all experiments (in our case – to 4 psi). The results of studies are presented in Fig. 2.

Experiments have shown that when bringing the dicarboxylic acids (succinic acid, adipic acid, sebacic acid) in the system, the inhibition duration does not increase substantially as compared with the control.

Carrying the polymeric carboxylic acids (polyacrylic acid, polymethacrylic acid, and their copolymers) leads to an increase of inhibiting duration by 1.2-1.3 times. When using as inhibitors organophosphorus compounds (hydroxy-ethylenediphosphon, amintrimetilphosphon 2-phosphonbutan-1,2,4-tri-carboxylic acid) the system work duration increases by 2,6-3 times compared with the control, reagentless option.

Quality values of the circulating water samples at enterprises

Water		Alkalinity, mmol / l	Ca^{2+}, mg/l	Mg^{2+}, mg/l	pH	LSI
PJSC ”Mineral Wax Plant” (artesian water)						
Feeding (K_y = 1)		5	49.9	12.7	7.46	0.9
Cycle (K_y = 2)		7.84	100.1	25.3	8.8	2.5
Cycle (K_y = 3)		10.6	149	37.9	9	3.1
PJSC “Grodno Asot (Nitrogen) (river water)						
Feeding (K_y = 1)		2.83	154	55.5	8	1.5
Cycle (K_y = 2)		5.07	308	111	8.4	2.5
Cycle (K_y = 3)	7.61	462.1	166.6	8.7	3	

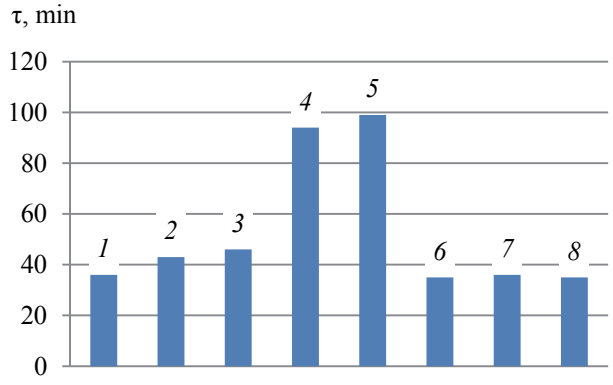

Fig.2. Time interval for scaling (τ)
in the modal system without additions (*1*)
with reagents (*2–8*):
1 – without additions; 2 - PMAA (0.1 mg / l, $MW_{2,100}$);
3 - PAA (0.1 mg / l, $MW_{2,100}$) 4 - HEDP (0.1 mg / l);
5 - ATMP (0.1 mg / l) 6 - succinic acid (0.1 mg / l);
7 - adipic acid (0.1 mg / l) 8 - sebacic acid (0.1 mg / l)

The study of PAA samples with different molecular weights (500, 2,100, 5,100, 8,100 and 15,100) results into the fact that the inhibitory action effectiveness with increasing molecular weight initially increases and then decreases (Fig. 3).

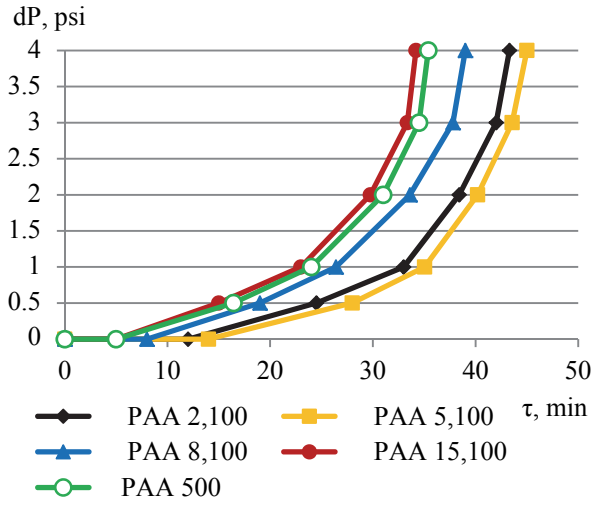

Fig. 3. Differential pressure value
in the system for carboxyl polyacids
with different molecular weights
at a given point of time

Thus, the carrying of samples PAA of MW 8,100 and 15,100 in the system reduces the inhibition time due to the fact that polymers with such a molecular weight value begin to show flocculant properties. In this case there is not only the interaction of the polyelectrolyte polar groups with the calcium and magnesium carbonate crystal surface , but also the bond formation between the remaining in free state "tails" of macromolecules that entails coarsening, the particle aggregation and subsequent sedimentation.

In the case of PAA with MW of 500 and less the inhibition time is also reduced compared with MW 2,100–5,100 because of the fact that the size of the macromolecules does not allow to form an adsorption layer on the surface of the formed crystals, hindering their further correct formation and growth.

To determine the optimal inhibitor dose the number of experiments are carried out and the dependences of the inhibition time on the dose of the input polyelectrolyte are obtained. The graph of dependence is shown in Fig. 4.

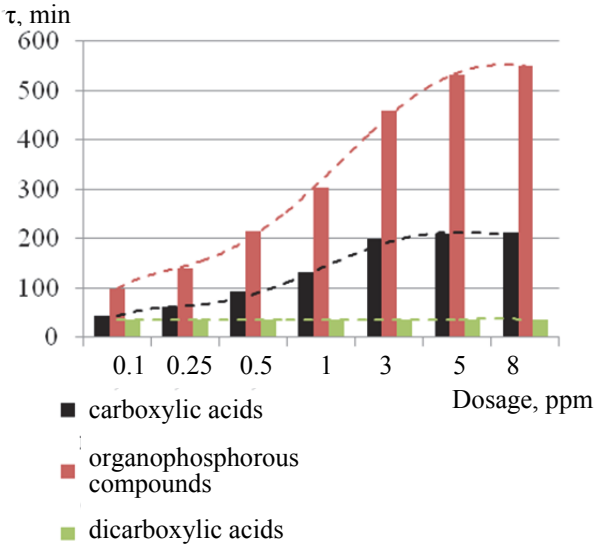

Fig. 4. Scaling duration (τ)
in a model system at various reagents dosages

Fig. 4 shows that the polyelectrolyte dose increase from 0.25 to 3 mg/l greatly improves the inhibiting effect. When increasing PAA concentrations from 3 to 8 mg/l and more – is rising slightly. Therefore, we can conclude that the optimal value of the carboxyl substances concentration in the system is 3.5 mg/l, of phosphorus compounds – 5.8 mg / l.

In the investigated compound series organophosphorus inhibitors showed maximum inhibitory potency that is probably due to their ability to form stable complexes with calcium and magnesium ions. Polymeric carboxylic acids also affect the system stability, but to a lesser extent.

From the study results of the sedimentation inhibiting effectiveness in model systems follows that the use of these substances as inhibitors under practical conditions at PJSC "Mineral Wax Plant" and PJSC "Grodno Azot" will significantly slow down the processes of sedimentation and ensure non-stop operation of the cooling water circulating cycles.

Conclusion. A comparative analysis of the reagents-inhibitors of different composition and structure is carried out under dynamic conditions using the described method of efficiency evaluation, which provides a higher accuracy and reliability of the results in comparison with other methods.

According to the research of the inhibitory action effectiveness of some compounds it has been found that organophosphates are the most effective – sedimentation rate is decreased by 2.6–3 times. In a series of carboxyl compounds the polyacrylic acid with molecular weights from 2,100 to 5,100 has the greatest effect. The optimal dose of the reagents in the system is 5–8 mg/l for phosphorus-containing compounds, 3–5 for carboxylic polyacids.

Comparative characteristics of these substances inhibitory potency, obtained using this method, can serve as a basis for the development of water treatment reagent modes for cooling circulating cycles of industrial enterprises.

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