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Simonenko Vladimir, Doctor of Technical Sciences, Professor, Department of Open Cast Mining, National Technical University «Dnipro Polytechnic», Ukraine, e-mail: simonenko.v.i@nmu.ua, ORCID: http://orcid.org/0000-0002-9409-7813

Pavlychenko Artem, Doctor of Technical Sciences, Associate Professor, Head of Department, Department of Ecology and Technologies of Environmental Protection, National Technical University «Dnipro Polytechnic», Ukraine, e-mail: pavlychenkoa@nmu.org.ua, ORCID: http://orcid.org/0000-0003-4652-9180

Chuprova K. et. al., Researcher, Institute for the Design of Mining Enterprises, National Technical University «Dnipro Polytechnic», Ukraine, e-mail: chernyaev.aleksey82@yandex.net, ORCID: http://orcid.org/0000-0003-4652-9180

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Shuryberko M., Gomelya M., Shablyt T., Chuprova K.

DEVELOPMENT OF REAGENTS FOR PROTECTION OF EQUIPMENT OF WATER SUPPLY SYSTEMS FROM SCALE AND CORROSION

Об’єктом дослідження є екологічно безпечні водоциркуляційні теплообмінні системи в промисловості та комунальних господарствах. На діючих підприємствах в процесі модернізації систем водокорундування часто переходять на використання інгібіторів корозії металів та накипоутворення. Після тривалого періоду експлуатації цих систем загроза обладнання не проводиться. Одним з найнебезпечніших проєктів реконструкції є навіяння продуктів накипоутворення та корозії на внутрішній поверхні теплообмінного обладнання. Ці утворення знижують ефективність теплопереносу і нівелюють ефективність інгібіторів корозії та стабілізаторів накипоутворення.

В роботі проведено оцінку ефективності композицій, запропонованих в якості травильних розчинів для очищення поверхонь металу від осадовідкладень, а також в якості стабілізаторів накипоутворення. В кінці дослідження визначено, що на універсальній агресивність серед розглянутих варіантів характеризується композиція Р-29. Глибший показник корозії 0,118907 mm/рік. Показник руйнування уротропіну, уротропіну з тіокарбамідом.

Результати досліджень вказують, що найменшою корозійною агресивністю серед розглянутих варіантів характеризується композиція Р-29. Глибший показник корозії 0,118907 mm/рік. Показник руйнування уротропіну, уротропіну з тіокарбамідом.

1. Introduction

At existing enterprises, in the processes of modernization of water use systems, in particular, cooling systems, they often switch to the use of corrosion inhibitors for metals and scale formation. However, after a long period of operation of these systems, full replacement of pipelines and equipment is not performed. The internal surfaces...
of heat exchange equipment and pipelines are covered with scale and corrosion products [1], which significantly reduce the efficiency of heat transfer and almost completely eliminate the effectiveness of corrosion inhibitors and scale builders.

To ensure the proper effectiveness of the reagents, it is necessary either to increase their concentrations by tens to hundreds of times, or to pre-clean the internal surfaces of pipelines and heat exchangers from deposits. The first option is inexpedient both from ecological and economic points of view. In the case of a successful selection of a composition for cleaning the surfaces of deposits from scales, the result of the further use of inhibitors is economically viable and time consuming.

Therefore, research in the field of protection of metal structures against corrosion and scale is relevant. In particular, the creation of complex and inexpensive inhibitors of corrosion and scale of deposits, which are effective in a wide temperature range and universal for various types of metals and solutions of different chemical composition.

2. The object of research and its technological audit

The object of research is environmentally friendly water-exchange systems in the energy, industry and utilities. In industry and energy, approximately 80 % of water is used in water cooling systems. In the absence of pretreatment of water for cooling systems in order to maintain the salt balance in the system, 8 to 30 % of water is discharged daily into the hydrosphere. At the same time, physical (thermal) and chemical (copper and brass capacitors) pollution of reservoirs is observed.

On the other hand, an important issue is the protection of metal structures against corrosion in water and aqueous solutions. High corrosivity of environments leads to significant costs of materials, water and energy.

Therefore, the priority is creation of effective ways of water conditioning. This will allow moving to closed cooling systems, which, in turn, will ensure a reduction in fresh water intake for industrial facilities and a reduction in industrial wastewater [2].

One of the ways to solve this problem is to use metal corrosion inhibitors and scale formation stabilizers in water treatment processes. The main requirements for modern compositions are their high efficiency, complexity of action and non-toxicity [3]. That is, inhibitors that are used in circulating systems must protect metals from corrosion and simultaneously reduce scale deposits on the surface of heat exchange equipment.

3. The aim and objectives of research

The aim of research is determination of the effectiveness of compositions based on inorganic acids as corrosion-resistant pickling solutions for the restoration of metal pipe surfaces, as well as compositions for permanent use in water conditioning processes.

To achieve this aim it is necessary to perform the following tasks:

1. To evaluate the corrosivity of the compositions of etching solutions for cleaning metal surfaces using the mass metric method and the method of polarization resistance.

2. To establish the dependence of the solubility of calcium sulfate in acidic environments, which differ in chemical composition and concentration.

3. To evaluate the effectiveness of the use of the proposed compositions as stabilizers of scale formation by determining the stabilization and anti-scale effects of aqueous solutions of different composition.

4. Research of existing solutions of the problem

As a result of long-term use of heat exchange equipment at industrial facilities, metal surfaces of pipelines, boilers, etc. are covered with a layer of corrosion products and carbonate-sulphate scale deposits [4, 5]. The simplest and most affordable way to restore the surfaces of pipelines, heat exchangers, boilers is washing them with acidic solutions [6, 7].

However, the use of pure acids for flushing pipes has several disadvantages. The authors of [8, 9] emphasize the danger of using inorganic acids as etching solutions. In particular, the use of sulfuric acid [8] leads to the formation of insoluble calcium sulfate, and hydrochloric acid [9] due to the presence of chlorides – to an increase in the aggressiveness of the environment.

An alternative is the use of organic acids. It is known that sulfamic acid (10 % solution) is an effective reagent for cleaning pipes from corrosion and scale products. However, this solution is corrosive to steel 20. The average polarization resistance \( R_{pav} \) is 70 Ohms [10].

At the present stage, phosphoric acids are the most effective stabilizers of scale formation [2, 11]. And their zinc salts are the most effective inhibitors of metal corrosion [3, 11]. However, the issue remains the use of these acids as etching solutions.

Thus, the results of literary analysis allow to conclude that, despite the long period of use of water circulation systems in industry [1], the issue of recovering metal equipment remains not fully resolved. In particular, there is a lack of effective and at the same time corrosive pickling solutions for cleaning metal surfaces from scales.

5. Methods of research

In preliminary studies [10], it was shown that the composition of thiocarbamide and urotropin exhibits a synergistic effect in protecting the metal surface from corrosion. Therefore, the compositions of etching solutions based on hydrochloric, sulfuric, phosphoric acids in the presence of urotropin or urotropin with thiocarbamide were used in the work.

Evaluation of corrosion of the proposed compositions was carried out in two ways: by the method of polarization resistance and by the mass metric method.

The polarization resistance was determined using the polarization resistance indicator P5126 (Ukraine) and a two-electrode sensor from a UK-2 corrosion-indicating device (Ukraine) with electrodes made of steel 20, previously processed and weighted. The sensor was installed in a 150 cm³ container, and at certain intervals for two hours, the polarization resistance \( R_p \) (Ohm) was measured using the indicator P5126. The magnitude of the polarization resistance is inversely proportional to the corrosion rate of the metal.
Mass metric determination of the corrosion rate was determined by the difference in mass of the sample, corroded, in grams before and after corrosion. The duration of the experiments was 18-23 hours.

The experiments were carried out in stationary environments at a temperature of 15–20 °C in free contact of water with air.

Mass metric indicator of corrosion, g/(m² h):

\[ K_n = \frac{m_1 - m_2}{S \cdot \tau}, \]

where \( m_1 \) – the initial mass of the sample, g; \( m_2 \) – the mass of the sample after the test, g; \( S \) – the sample area, m²; \( \tau \) – the test duration, h.

Deep corrosion rate, mm/year:

\[ R = \frac{K_n \cdot 8.76}{d_{me}}, \]

where \( K_n \) – the mass metric index of corrosion, g/(m² h); \( d_{me} \) – metal density, g/cm³; 8.76 – the coefficient calculated by the number of hours per year (8760) divided by 1000.

Evaluation of the effectiveness of the developed compositions as stabilizers of scale formation was determined by changing the hardness of water when it is heated. Determination of the stabilization effect (SE) was carried out in closed containers at a temperature of 90–100 °C for 5 hours. The anti-scale effect was determined at a temperature of 40–60 °C in open glasses with water evaporation 37.5 % (evaporation coefficient 1.6).

Stabilization effect, %:

\[ SE = \frac{H_{in} - H_{in0}}{H_{in} - H_{or}} \times 100. \]

where \( H_{in0} \), \( H_{in} \) – initial and residual hardness of water, mg-eq/dm³, respectively; \( H_{or} \) – residual hardness of water without the use of a stabilizer, mg-eq/dm³.

Anti-scale effect, %:

\[ AE = \frac{H_{or}}{H_{in}} \times 100. \]

The residual calcium concentration in the samples was determined using trilonometry with eriochrome black T indicator.

6. Research results

A fairly common alloy that has been used in the machine-building industry for a long period is steel 20. In particular, its mechanical properties determine the widespread use of this brand in boiler-making, the manufacture of pipes and heating elements for various purposes. Therefore, all studies in the work carried out with steel 20.

As can be seen from the above results (Fig. 1), in static conditions the polarization resistance of tap water in the Kyiv (Ukraine) is insignificant and amounts to 305–316 ohms. Solutions of hydrochloric, sulfuric, phosphoric acids, in concentrations of 10 %, cause significant corrosion of steel 20. The polarization resistance of these solutions is respectively 5.3; 8.4 and 15.1 ohms. Adsorbing on the surface of the metal, these anions form compounds that have good solubility. This leads to an increase in the corrosion rate of steel. The most aggressive are chloride anions, which are able to easily penetrate protective surfice films of the metal.

The presence of urotropin in a concentration of 5 g/dm³ in the solution leads to an increase in the polarization resistance, that is, to an increase in the protective effect. The maximum protective effect after 2 hours is observed:

- for a mixture of hydrochloric acid and urotropin in a ratio of 100:5, and the polarization resistance increases to 164.5 ohms;
- for sulfuric acid with urotropin (100:5), this indicator rises to 75.3 ohms;
- for a mixture of phosphoric acid and urotropin (50:5), it reaches 94.5 ohms.

However, the corrosion rate in these environments is large compared to tap water.

The result of adding thiocarbamide is not straightforward. So, its use in a mixture with hydrochloric acid and urotropin (100:5:1) has a negative effect — the polarization resistance is reduced to 49.6 ohms. In the presence of phosphoric acid under the same conditions, this indicator reaches the values of tap water and is 365 ohms. An impressive effect is observed when used in a mixture of sulfuric acid: the polarization resistance increases to 1136 ohms.

The reliability of the obtained results is confirmed by experiments carried out by the mass metric method (Table 1).

As can be seen from results in the Table 1, all compositions have a greater corrosive aggressiveness than tap water, the deep corrosion rate of which is 0.015618 mm/year. The least corrosive aggressiveness among the options considered is characterized by the P-29 composition. The metric corrosion rate of this composition is 0.106881 g/(m² h), the deep corrosion rate, respectively, is 0.118907 mm/year. A P-29 composition, created on the basis of orthophosphoric acid: the polarization resistance increases to 1136 ohms.
acid, is used as a reagent for removing scale formation products – calcium carbonates and sulphates. Its rate of destruction of chemically scaled gypsum is at least 90%. Therefore, let’s assume that the P-29 composition is an effective corrosion-insensitive reagent for cleaning the equipment of water supply systems from salt decomposition and corrosion.

| No. | Solution                  | Concentration, g/dm³ | Corrosion rate Mass metric, g/(m²·h) | Deep corrosion rate, mm/year, (mass metric method/method of polarization resistance) |
|-----|--------------------------|----------------------|--------------------------------------|----------------------------------------------------------------------------------|
| 1   | Tap water                | –                    | 0.014012                             | 0.015618                                                                          |
| 2   | HCl 50                   |                      | 2.903103                             | 3.229766                                                                          |
| 3   | HCl 100                  |                      | 5.192697                             | 5.779891/10.63969                                                                 |
| 4   | HCl urotropin 50         | 5                    | 0.203566                             | 0.226472                                                                          |
| 5   | HCl urotropin 50         | 10                   | 0.247372                             | 0.275206                                                                          |
| 6   | HCl urotropin 100        | 5                    | 0.324675                             | 0.361209/0.392655                                                                |
| 7   | HCl urotropin 100        | 10                   | 0.373634                             | 0.415676                                                                          |
| 8   | H₃PO₄ 50                 |                      | 2.591353                             | 2.882938/2.734004                                                               |
| 9   | H₃PO₄ 100                |                      | 3.865855                             | 4.300849/2.897846                                                               |
| 10  | H₃PO₄ ammonia 50         |                      | 0.302843                             | 0.336919                                                                          |
| 11  | H₃PO₄ ammonia thioucarbamide 100 5 |                  | 0.131168                             | 0.145927                                                                          |
| 12  | H₃PO₄ ammonia thioucarbamide 50 5 |                  | 0.183512                             | 0.204161                                                                          |
| 13  | P-29 (pH=1.66)           |                      | 0.106881                             | 0.118907                                                                          |

In many enterprises, the problem of scale formation on the heating surfaces of heat exchange equipment is acute. Together with the previous stabilization treatment of water for water systems, a painful issue remains the removal of scale from the surfaces of pipelines and equipment. Scale of calcium sulfate have particular concern, the solubility of which in acids is much less compared with calcium carbonate, as shown in the example of orthophosphoric acid (Table 2). The highest solubility for calcium sulfate has hydrochloric acid. So, for hydrochloric acid with a concentration of 30 g/dm³, this indicator is 24.5–24.9 g/dm³. In a more concentrated solution (10 %), the solubility increases to 36.2–36.7 g/dm³.

Calcium sulfate in phosphonic acids is 2.0–2.5 times less than in hydrochloric acid. For their solutions in concentrations of 10 %, this indicator is about 18 g/dm³. However, their use for laundering equipment is advisable, since these compounds are effective stabilizers of scale formation and metal corrosion inhibitors [11].

Creating compositions based on the considered acids, for example, H₃PO₄+NH₄OH+NTMP, does not always lead to an increase in the effect of dissolution, as is observed in the case of P-29 composition. Although, as can be seen from Fig. 2, there is a definite correlation between the intensity (time) of dissolution and the composition: calcium sulfate ratio. So, with an increase in the volume of the pickling solution under conditions of the same mass of calcium sulfate, a reduction in the time of dissolution of the latter is observed.

The key to effective and long-term use of new and reconditioned heat exchange equipment is the constant use of corrosion and scale inhibitors. The aim of modern developments in the field of water temperature is the creation of reagents with high efficiency and complexity of action both as corrosion inhibitors of metals and scale stabilizers.
Among the known inhibitors, phosphon and nitrile phosphonic acids are also effective. HEDP and NTMP are effective scale stabilizers [11]. Their stabilization effects for tap water at 90 °C are 69.9% and 86.7%, respectively. But they are expensive and their use for large cooling systems is uneconomical.

Based on these acids, a new composition P-33, a reagent to prevent scale, was developed. This mixture showed excellent results under the same harsh conditions (T=90 °C, t=5 h), but in more severe environments (Table 4).

**Table 4. Dependence of stabilization and anti-scale effects on the concentration of reagent R-33 and the composition of the initial solution.**

| P-33 concentration, mg/dm³ | Hardness of water, mg-equiv/dm³ | Stabilization effect, % | Anti-scale effect, % |
|---------------------------|-------------------------------|------------------------|----------------------|
|                           | H₀                           | Hₗ                     |                      |
| Distilled water, 73 g/dm³ NaCl, 10 g/dm³ MgSO₄, 10 g/dm³ CaCl₂ |                           |                       |                      |
| 0                         | 212                          | –                      | –                    |
| 20                        | 228                          | 88.9                   | 99.1                 |
| 50                        | 230                          | 100                    | 100                  |
| 100                       | 230                          | 100                    | 100                  |
| Tap water, 73 g/dm³ NaCl, 10 g/dm³ MgSO₄, 10 g/dm³ CaCl₂ |                           |                       |                      |
| 0                         | 254                          | –                      | –                    |
| 20                        | 282                          | 93.3                   | 99.3                 |
| 50                        | 284                          | 100                    | 100                  |
| 100                       | 284                          | 100                    | 100                  |
| Tap water, 73 g/dm³ NaCl, 20 g/dm³ MgSO₄, 10 g/dm³ CaCl₂ |                           |                       |                      |
| 0                         | 440                          | –                      | –                    |
| 20                        | 468                          | 56                     | 95.5                 |
| 50                        | 490                          | 100                    | 100                  |
| 100                       | 490                          | 100                    | 100                  |
| Tap water, 100 g/dm³ NaCl |                           |                       |                      |
| 0                         | 5.1                          | –                      | –                    |
| 10                        | 5.5                          | 100                    | 100                  |
| 20                        | 5.5                          | 100                    | 100                  |
| 50                        | 5.5                          | 100                    | 100                  |

Even at such high output water hardness (230–490 mEq/dm³), P-33 reagent at a concentration of 20 mg/dm³ provides a stabilization effect at the level of 56.0–93.3%, and an anti-scale effect – 95.5–99.3%. With an increase in the concentration of the reagent up to 50%, the stabilization and anti-scale effects reach 100%.

**7. SWOT analysis of research results**

**Strengths.** The developed compositions for cleaning pipelines, surfaces of heat exchange equipment based on affordable low-cost reagents, which are dominated by analogues in efficiency, are characterized by low corrosivity and ensure the removal from the metal surface of even poorly soluble chemically resistant substances, including gypsum deposits. In neutral environments, the main components of P-29 reagent are scale inhibitors and corrosion inhibitors. The created P-33 composition surpasses the analogs in that it provides scale stabilization in highly concentrated gypsum solutions in the presence of calcium and magnesium carbonates at high temperatures. The integrated use of reagents for cleaning pipelines and the use of scale formation stabilizers will increase the efficiency and reliability of equipment operation in heat supply systems and in water cooling systems for pipeline protection in the gas and oil producing industry.

**Weaknesses.** The use of acid solutions for cleaning pipelines involves the observance of a number of measures for the safe conduct of technological operations, the use of special acid-resistant containers, acid-resistant dosing pumps and other equipment. Spent solutions must be neutralized and disposed of according to existing regulations. When using scale inhibitors, it is necessary to use high-precision dosing devices.

**Opportunities.** In the case of effective cleaning of metal surfaces of heat exchange equipment with the subsequent use of corrosion inhibitors and scale deposits in water systems, it is possible to increase the service life of heat exchange units by 5–10 times. In addition, in cooling systems it is possible to switch to drainless mode and refuse to discharge circulating water to purge of the system.

**Threats.** In the case of acid cleaning from deposits of surfaces, there is a threat of their insufficiently effective washing of residues of acidic reagents, which can affect equipment corrosion processes when the reaction of the medium in operating systems is acidic. Under normal operating conditions of systems, this threat is unrealistic. With the use of scale stabilizers, the level of water hardness in water systems may increase several times. This helps to reduce the corrosivity of water, but in the case of inadequate control of the dosing of the scale inhibitor, the scale deposition on the heat exchange surfaces is possible. It is also possible the threat of exceeding the permissible concentrations of reagents in the discharge of water during the purge of the system.

**8. Conclusions**

1. As a result of the experimental and computational studies, the corrosivity of the compositions of etching solutions for the cleaning of metal surfaces by the mass metric method and the method of polarization resistance is evaluated. It is shown that all compositions created on the basis of hydrochloric, sulfuric, phosphoric acids in the
presence of urotropin or urotropin with thiocarbamide, have a greater corrosiveness than tap water. The least corrosive aggressiveness among the options considered is characterized by the P-29 composition. The mass metric corrosion rate of this composition is 0.106881 g/(m² h), the deep corrosion rate, respectively, is 0.118907 mm/year. A mixture of P-29, created on the basis of orthophosphoric acid, is used as a reagent for removing scale formation products – calcium carbonates and sulphates. Its rate of destruction of chemically shipped gypsum is at least 90 %. Therefore, it is possible to assume that the P-29 composition is an effective corrosion-insensitive reagent for cleaning the equipment of water supply systems from salt decomposition and corrosion.

2. The dependences of the solubility of gypsum in acidic environments, which are characterized by different chemical compositions and concentrations, are established. It is proved that the solubility of calcium carbonate and calcium sulfate differ significantly. At initial concentrations of orthophosphoric acid 10–100 g/dm³, the solubility of calcium carbonate is 4.5 times greater than the solubility of calcium sulfate. If to compare the efficiency of dissolution of gypsum with various acids, then the highest solubility for calcium sulfate among the considered acids is hydrochloric acid. For hydrochloric acid with a concentration of 30 g/dm³, this indicator is 24.5–24.9 g/dm³. In a more concentrated solution (10 %), the solubility increases to 36.2–36.7 g/dm³. Despite the lower solubility of calcium sulfate in phosphoric acids (2.0–2.5 times) compared with hydrochloric acid, their use for laundering equipment is advisable, since these compounds are effective scale stabilizers and inhibitors of metal corrosion. There is a definite correlation between the intensity (time) of dissolution and the composition: calcium sulfate ratio: with scale stabilizers and inhibitors of metal corrosion. There is a definite correlation between the intensity (time) of dissolution and the composition: calcium sulfate ratio: with equipment is advisable, since these compounds are effective and anti-scale effects reach 100 %.

3. An evaluation is made of the effectiveness of using the developed P-33 composition as scale-forming stabilizers. This mixture shows excellent results in harsh conditions (water hardness 230–490 mg-eq/dm³, T=90 °C, τ=5 h). P-33 reagent at a concentration of 20 mg/dm³ provides a stabilization effect at the level of 56.0–93.3 %, and an anti-scale effect – 95.5–99.3 %. With an increase in the concentration of the reagent up to 50 %, the stabilization and anti-scale effects reach 100 %.

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