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RESEARCH ARTICLE

Contemporary approaches to reducing scale formation in heat-exchange equipment

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Abstract
Objectives. Scale formation and corrosion are serious problems for heat and power equipment. These processes, when intense, can completely block the operation of the system, accelerating corrosion and leading to clogging, local overheating, and burnouts and ruptures of boilers and pipes, which in turn can lead to major environmental problems. Therefore, protecting surfaces from scale formation and corrosion is an important task. Promising methods for preventing the development of undesirable consequences include changing the composition of polymer coatings, e.g., by introducing microencapsulated corrosion inhibitors, as well as surface modification approaches, such as hydrophobization of the polymer coating surface. The purpose of the present work is to analyze methods for reducing scale formation and the rate of corrosion processes, as well as to study the efficiency of modification of paints and coatings by introducing microencapsulated corrosion inhibitors.
Methods. The study was based on the use of accelerated corrosion tests.
Results. Existing methods for reducing scale formation and corrosion rate on the surfaces of heat and power equipment were analyzed. The efficiency of modifying protective polymer materials by introducing microcapsules containing an active phosphonate additive was compared with approaches involving the surface modification of such protective materials.
Conclusions. It was determined that the modification of paints and coatings by introducing microencapsulated active additives can significantly reduce the rates of both scale formation and corrosion. By implementing state-of-the-art methods for modifying polymer coatings, a new generation of agents for efficiently preventing scale formation and corrosion processes can be developed for maintaining the high performance of heat-exchange equipment.

Keywords: scale formation, corrosion, inhibition, polymer coatings

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НАУЧНАЯ СТАТЬЯ

Современные подходы к снижению накипеобразования в теплообменном оборудовании

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Резюме

Цели. Процессы накипеобразования и коррозии являются серьезной проблемой для оборудования теплоэнергетического комплекса. Их активное развитие может полностью заблокировать работу системы, ускорить коррозию и привести к закупориванию, местным перегревам, прогарам и разрывам котлов и труб. Это, в свою очередь, может привести к катастрофическим последствиям и масштабным экологическим проблемам. Важной задачей является защита поверхностей от накипеобразования и коррозии. Перспективными методами предотвращения развития нежелательных последствий являются модификация состава полимерных покрытий за счет введения микрокапсулированных ингибиторов коррозии, а также поверхностная модификация, а именно, гидрофобизация поверхности полимерного покрытия. Целью работы являлся анализ методов снижения накипеобразования и скорости коррозионных процессов, а также исследование эффективности модификации лакокрасочных покрытий (ЛКП) посредством введения в их состав микрокапсулированных ингибиторов коррозии.

Методы. В работе использовались методы ускоренных коррозионных испытаний.

Результаты. Проанализированы существующие методы снижения накипеобразования и скорости коррозии на поверхностях теплоэнергетического оборудования. Исследована эффективность модифицирования защитных полимерных материалов за счет введения в их состав микрокапсул, содержащих активную фосфонатную добавку, а также их поверхностное модифицирование.

Выводы. Установлено, что модифицирование ЛКП за счет применения микрокапсулированных активных добавок позволяет существенно снизить скорость как накипеобразования, так и развития коррозионных процессов. Внедрение современных методов модифицирования полимерных покрытий позволяет получать составы нового поколения, эффективным образом препятствующие накипеобразованию, развитию коррозионных процессов, и дает возможность сохранять высокую производительность теплообменного оборудования.

Ключевые слова: накипеобразование, коррозия, ингибирование, полимерные покрытия

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INTRODUCTION

The formation of scale and corrosion on the internal sides of heat-transfer walls presents serious problems for heat and power equipment. A typical situation consists in the formation of a layer of scale, which comprises by corrosion products of metals used in water-cooling systems (circulating water pipelines, water chambers, and heat-exchanger tubes) along with limescale from water (both in the form of suspensions and dissolved salts). At an early stage, such buildups result in an increase in fuel consumption and a decrease in the reliability, efficiency, and operability of heat-exchange equipment and pipelines. At a more advanced stage, scale build-up can completely block the operation of the system, which accelerates corrosion processes leading to clogging, local overheating, and burnouts and ruptures of boilers and pipes. Ultimately, this can result in catastrophic consequences including major environmental problems [1, 2].

PRIMARY METHODS FOR REDUCING SCALE FORMATION AND CORROSION RATE

In a heat-exchange apparatus, e.g., the main steam condenser of the turbine of a nuclear power plant (NPP), the number of tubes can be very large, reach 100 000 or more. Therefore, the repair and reconstruction of such apparatuses present complex technical problems. In general, 2–5% of heat-exchanger tubes in such steam condensers have become unserviceable due to corrosion and erosion damage. Evaluation of the corrosion state of equipment at several thermal power plants (TPPs) and NPPs showed [3] that 30% of tubes are highly likely to form corrosion holes in the near future. Although these tubes can be plugged off, this will lead to an unacceptable decrease in the efficiency of the heat-exchanger equipment.

A successful solution of the problem of scale formation will ensure the cleanliness of the surfaces of water systems, helping to save fuel and energy resources, as well as preventing possible catastrophic consequences [4].

At present, the heat-exchange equipment of power systems is made mostly of copper–nickel alloys (MNZh 5-1, GOST 492-2006[1]), brass L68 (GOST 15527-2004[2]), stainless steel, and titanium alloys.

A significant variation in the conditions according to which corrosion processes develop in heat-exchange apparatuses of power plants is mainly due to the composition and temperature of the cooling water used. While NPPs typically either use natural freshwater from cooling ponds and rivers or seawater, the recycled water supply generally used for cooling TPPs is stored in cooling towers, allowing the use of special additives, e.g., for controlling the build-up of scale. Meanwhile the salt content of cooling water can differ considerably depending on the season and the cooling pond makeup conditions; in cooling water of enclosed water bodies, it can reach 100–3000 mg/L.

Based on the experience of repairing and inspection of heat-exchanger tubes of condensers of power plants, it can be concluded that the development of local corrosion is the main cause of leakage. However, local corrosion damage does not account for more than 70% of the total number of defects. Although the operating conditions and materials of heat exchangers differ, the following forms of corrosion damage are typical:

- destruction of tubes and tube sheets in the rolling zone by flow-accelerated corrosion and galvanic corrosion;
- development of unit corrosion pits or clusters of pits throughout the length of the internal surface of tubes (on the side of the cooling liquid). Pits can differ very widely in size and depth, all the way down to holes. This type of corrosion damage of tubes made of copper-nickel alloys, brasses, and stainless steels was detected both in both freshwater and seawater contexts [5].

Among the main types of corrosion damage of heat-exchanger tubes are the following:

- corrosion pits growing further into cracks due to the stress corrosion cracking mechanism;
- clusters of small-size pits (pitting) occurring primarily in the lower part of heat-exchanger tubes;
- intercrystalline, transcrystalline, and mixed-type cracking;
- corrosion over large-areas of insignificant depth.

In general, corrosion cracking of the metal of heat-exchanger tubes is caused by corrosive impurities in the form of chlorides and sulfates contained in the boiler water of steam generators [6].

The evaporation of some of the water circulating in the system from cooling towers and the surface of open ponds and water treatment facilities results in an increase in the concentration of salts and scale-forming compounds in the water. Significant quantities of corrosive compounds, mechanical suspensions, and microorganisms can accumulate in repeatedly reused water. All of this causes an intense scale build-up leading to local overheating, leading to corrosion of condensing and cooling equipment, impairing heat transfer, and weakening the mechanical strength of the metal of coil tubes and housings of apparatuses.

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[1] GOST 492-2006. Interstate Standard. Nickel, nickel and copper-nickel alloys treated by pressure. Grades. Moscow: Standartinform; 2011 (in Russ.).

[2] GOST 15527-2004. Interstate Standard. Pressure treated copper zinc alloys (brasses). Grades. Moscow: IPK Izd. Standartov; 2004 (in Russ.).

Scale formation in demineralized water generator is inhibited by a number of methods, in particular:

- acidification of water and using scale control additives;
- addition of granular additives (seeds);
- contact stabilization;
- using special designs of evaporators with moving and self-cleaning heat-transfer surfaces;
- magnetic, ultrasonic, and radiation treatment of feed water.

The choice of one or another method for cleaning internal surfaces, which can be divided into chemical, mechanical, and physical approaches, is also largely determined by the type of scale.

Chemical methods of scale removal by possible simultaneous inhibition in different technological streams are typically performed by mixing a chemical treatment agent with a technological stream to ensure the treatment of hard-to-reach surfaces. However, chemical treatment methods that include the use of complex-forming agents and corrosion inhibitors are increasingly widely used due to a number of significant advantages.

The means by which complex-forming agents partially or fully convert insoluble scale into well-soluble salts or other compounds has been described in detail [7–9]. There are also methods based on the conversion of scale into substances that are insoluble in water but soluble in other chemical reagents [10–12].

A mixture of sodium tripolyphosphate and a nitrogen-containing compound (ethanolamine borate) has been recommended [13] as a water-soluble inhibitor; this can increase the efficiency of corrosion protection, decrease the salt deposition rate, and protect heat-exchange equipment made of ferrous metals from stress corrosion damage. It was determined that a combination of ethanolamine borate (EAB) and sodium tripolyphosphate (STPP) in a certain ratio (10.0–20.0 wt % EAB : 80.0–90.0 wt % STPP) gives rise to a synergistic increase in the washing, protective and water-displacement properties of the inhibitor.

The appropriate treatment methods, conditions, and reagents can be selected based on the results of chemical analysis of scale [14, 15]. One of the main methods for controlling the surface properties of materials is hydrophobization [16–19].

Water repellent coatings are highly important in many applications, including corrosion protection, self-cleaning, fouling protection, separation of oil from water, anti-icing, energy conversion, drug release, drag reduction in flowing liquids, and antibacterial adhesion, as well asproduction of antifouling paints for boats, windshields, architectural coatings, etc. [20, 21].

Along with hydrophobic coatings proper, a special group of superhydrophobic coatings can be identified. Bionic superhydrophobic coatings of surface attract attention owing to their characteristics and possibilities of application. In nature, superhydrophobic properties are present in the surfaces of some plants and animals, namely, lotus and rice leaves, shark skin, gecko foot, butterfly wing, penguin feather, and others [22, 23].

An efficient approach to reducing metal corrosion or improving metal waterproofing uses superhydrophobic materials to lower surface tension. However, the retention of an air layer as a barrier between the superhydrophobic metal support and the liquid limits the area of contact between the liquids and the surface, significantly decreasing the transfer of heat [24, 25]. Hydrophobic surfaces can be obtained by either creating a specific hierarchical surface roughness, or applying materials with low surface energy to a support. These approaches can be used both separately, and together [26, 27]. Superhydrophobic coatings produced using physical adsorption have short service life because of weak physical interaction [28]. High energies of interaction with a material are characteristic of coatings obtained using chemical adsorption of hydrophobic agents.

The curvature of a surface is one of the control factors. It has been determined that the contact angle on cylindrical and spherical surfaces is larger than that on a flat surface, whereas the contact angle on concave surfaces (nanopores, spherical cavities) is smaller than that on a flat surface of the same chemical composition [29].

At the Massachusetts Institute of Technology, Cambridge, MA, USA, a method was developed to coat the surfaces of a condensing apparatus with a monatomic graphene layer. By testing in a water vapor medium at 100°C, this coating was shown to ensure the transition from film to drop condensation and increase the heat transfer by a factor of 4 in comparison with metallic surfaces, where the condensate formed a water layer.

The short service life of most artificial superhydrophobic surfaces prohibits their widespread use in industry. Moreover, such surfaces tend to lose superhydrophobicity on exposure to an aggressive medium or under a mechanical action. In order to expand the range of application of superhydrophobic surfaces, solving these problems is highly important.

In order to maximize the service life of anti-scale coatings, the following complex properties should be ensured: thermodynamically stable heterogeneous conditions of surface wetting, chemical stability, high adhesion to support, and abrasion resistance.

Despite the above disadvantages and difficulties of obtaining superhydrophobic surfaces, the developed methods and superhydrophobic additives can be very useful for protecting heat-exchange equipment from scale formation and corrosion.

An efficient and widely used method for protecting and restoring tubes used in heat-exchange equipment is to apply a polymer protective coating (lining) to the internal surface. This is due both to the successful development of polymer materials with a high thermal conductivity and to the development of the painting technology, which allows the application of an ultrathin lining to the undamaged surface of a tube in one pass while simultaneously placing reliable polymer plugs for fill both corrosion pits, and corrosion holes [30].

Metallic heat-transfer surfaces are converted to metal–polymer ones by applying a polymer composite lining to the internal surface of a metal tube. The efficiency of this conversion is determined by:

- a significant increase in the service life of the system of lined tubes owing to high chemical and abrasion resistance of polymer linings;
- blocks of corrosion sites, which can be scale formation nuclei;
- a substantially lower adhesion of scale to the polymer surface than to the metal of the tube. This is due to the smoother lining surface (especially in comparison with the surface of a tube with corrosion pits) and lower polarity of the inert polymer surface (in comparison with surface of the oxidized metal) and therefore the absence of conditions for chemical binding of scale;
- the possibility of controlled modification of the surface layer to impart additional anti-scale properties to the surface.

The following requirements are imposed on polymer materials for coating the heat-transfer surfaces of turbine condensers:

- the working temperature during normal operation should be 0 to +40°C with an option of a short-term increase to +240°C;
- the coating thickness should be no more than 50–60 μm according to the requirement of the minimum effect on heat transfer at a thermal conductivity of the material of the coating in a range of 1–2 W/(m · K);
- the linear thermal expansion coefficient should be close to that of the metal;
- the pull-off adhesion strength of the material to steel should be 50–60 MPa and remain unchanged during operation;
- the material should be resistant to abrasive wear at an abrasive concentration of 3–5% in a water flow;
- the coating should be smooth and gloss without drips and runs;
- the material should be readily manufacturable and inexpensive.

Many commercially-available polymer materials have some of the necessary characteristics. However, some have a limited operating temperature, while others have a high viscosity, resulting in the impossibility of applying a thin layer of polymer material to a metal substrate. If a coating is too thick, this inevitably leads to an increase in the thermal resistance. Polymer materials also differ significantly in terms of thermal and chemical stability, as well as their adhesion to various metals.

Despite all the difficulties, a wide range of polymer materials is currently used to protect the surfaces of heat-exchange equipment. Most materials require some form of modification, which can include hydrophobization of the surface to increase thermal conductivity and adhesion strength, improvement of thermal and chemical stability, abrasion resistance, etc.

At the Laboratory of Corrosion Protection of Metals and Alloys in Highly Aggressive Media at the Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Moscow, Russia, scale formation was successfully inhibited by introducing modifying (anti-scale) additives both as microcapsules to the bulk of a polymer corrosion protection coating, as well as to its surface.

Each of the microcapsules has the shape of a ball with a core made of a phosphonate modifying additive and a shell made of an epoxy polymer material. As a medium enters the microcapsules, the modifying additive is washed out. These microcapsules have been shown to significantly increase both the corrosion resistance and the duration of the anti-scale action of the modifying additives [31–34].

Testing showed that the adhesion of a scale layer to the modified polymer coatings remains very low. This leads to spontaneous peeling and cracking of scale following insignificant external actions or changes in technological parameters (Fig. 1).

Fig. 1. Photograph of a sample after scale formation testing. The upper part of the sample is protected by a polymer coating

Industrial tests have demonstrated that the coatings of this type minimize scale formation on tube sheets and the inlet portions of heat-exchanger tubes of steam condensers of TPPs and NPPs in long-term operation.

Importantly, the modified coatings have a high abrasion resistance (the sand concentration in the pulp is 5%; the flow velocity is 3 m/s), which allows the coatings

Fig. 2. Appearance of a protective coating on a part of the tube sheet and on a bundle of painted tubes of the horizontal network water heater at the Khabarovsk TPP after 7 months of operation

to be used in condenser tube cleaning systems. The wear rate was less than 0.5 μm in 1000 h. This ensures a service life of a 50-μm-thick coating of more than 10 years.

At the Balakovo NPP in Saratov oblast, Russia, coatings prevented scale and deposition formation in heat-exchanger tubes for 4 years. The coatings have no external damage, peels, or cracks. The color and luster of the surface of the coating were preserved; the anti-scale properties of the coating permitted transition to the batch operation of the condenser tube cleaning system [35].

Successful results were obtained in applying modified coatings to a network water heater at the Khabarovsk TPP. Before applying coatings, on tube sheets and the internal surface of tubes of the horizontal network water heater, a layer of deposited products of corrosion of the feeding water line intensely formed. After applying a polymer coating to the tube sheets and the internal surface of bundles of heat-exchanger tubes, the protected heat-transfer surfaces remained in the initial state without visible scale following 7 months of operation at temperatures up to 140°C (Fig. 2).

CONCLUSIONS

Modern methods of modification of polymer coatings by using active microencapsulated phosphonate additives produce agents of new generation that efficiently prevent scale formation and corrosion processes with retaining high performance of heat-exchange equipment. Along with a high functionality of protective coatings, one should note the availability of raw material and the economic efficiency of implementation of the presented approach for reducing scale formation in heat-exchange equipment. The minimum no-failure service life of the developed polymer protective coatings is estimated at 10 years.

Authors' contributions

V.A. Golovin—concept and methodology development, conducting research, collecting data, and scientific editing.

S.A. Tyurina—collecting data, conducting research, writing and editing the text of the article.

V.A. Shchelkov—methodology development, collecting data, and conducting research.

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