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TECHNICAL PROBLEMS AND ECOLOGICAL RISKS IN CONNECTION WITH OPERATION OF COOLING WATER SYSTEMS

TECHNICZNE PROBLEMY I ZAGROŻENIA EKOLOGICZNE ZWIĄZANE Z EKSPLOATACJĄ SYSTEMÓW WODY CHŁODZĄCEJ

Abstract: Industrial water consumption in Poland is very high and reach over 10 billion m^3/year, which forces the implementation of appropriate programs and technological solutions to reduce water consumption in industrial activity. Depending on the design system, operating conditions of water-powered cooling systems, they are exposed to varying degrees of corrosion, precipitation and deposition of sediments and the growth of microorganisms in water circulating. So important are measures aimed at raising the technical level of operation of industrial water systems. One of the most promising ways to prevent negative phenomena in the operation of cooling water systems is the use of organic inhibitors of complex multi-functional system to protect against corrosion, deposition of sediments and the development of microorganisms in the water circulation.

Keywords: cooling water systems, corrosion, phosphonic compounds

A major problem in the operation of cooling systems, in which water is acting as the coolant, is the occurrence of adverse processes such as corrosion, precipitation and deposition of mineral sediments as well as microbial contamination of the environment and the formation of biological sediment.

Losses due to corrosion in Poland are estimated on 6–10 % of the gross domestic product. The 20–30 % of general corrosion losses and in the municipal economy even more than 40 % are losses associated with the operation of water systems [1].

In Poland, in many cooling water systems is still applied raw water, or untreated and non-inhibited water demonstrating the high corrosivity (carbon steel corrosion rate of 0.6–0.8 mm/year) and susceptibility to the formation of sediment. This is due to

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generally high-pass system, which leads to excessive water consumption [1–3]. Particularly important are efforts to reduce water consumption, because the fresh water resources in Poland are very small. In Europe, the average amount of water per capita is 4.560 m^3, while in Poland is three times smaller. In 2008 in Poland were used 10.234 billion m^3 of water, of which 7.504 billion m^3 are used for industrial purposes including chemical plants and 353.3 million m^3 [4]. Excessive consumption of water for industrial purposes can be reduced by reconstruction of the circular flow systems as well as by use of multi-inhibitors preparations. These activities would not only reduce water consumption, but also allow to apply effective system protection against corrosion, sludge formation and development of microorganisms even at high concentration of circulating water. The scale of the savings on water consumption in the operation of the cooling water circulation system can be assessed based on the make-up water demand and wastewater discharges to water, depending on the concentration ratio of circulating water (Table 1). The biggest savings in water consumption of 64–66 % is achieved by increasing the concentration of circulating water to 3.5–4.0. In a higher concentrating of water to 5.0–7.0 is achieved both a reduction in water consumption by 70–72 % and less water to reduce the discharges of wastewater but it greatly increases the risk of corrosion and deposition of sediments during the operation of systems [1].

Table 1

Demand up water desalination and size depending on the concentration ratio n (constant evaporation losses amount to100 m^3/hr) [1]

Concentration index [n]	Make-up water demand [m^3/hr[	Size of desludging [m^3/hr]
1.5	300	200
2.0	200	100
2.5	166	66
3.0	150	50
3.5	140	40
4.0	133	33
5.0	125	25
7.0	117	17

Proper exploitation of industrial cooling water circulating system plays an important role in raising the level of technical installations and increasing the competitiveness of many industries and products offered articles through national market on background of European market. However, it is also important that the technological solutions fulfill the conditions for sustainable development and particularly in the field of safe technologies and rational use of raw materials, energy and other materials, due to the protection and preservation of the environment. The methods of preparation and treatment using inhibitors will also let to use low quality water and wastewater from manufacturing processes for cooling purposes. Corrosion inhibitors may be introduced directly into the water to protect the circuit and all the installations, equipment and apparatus in contact with water, thus ensuring high economic effectiveness of the protection and maintenance of cooling systems [1, 3, 5–7].

Technical problems in the operation of cooling systems

Raw unfiltered water contains soluble and insoluble minerals, microbiological organisms, and dissolved gases in water that may cause during operation of the exploitation of cooling circulation reducing the efficiency of heat exchange. Due to its construction, open recirculating cooling systems are primarily exposed to the accumulation of pollutants by concentrating circulating water.

As a result of evaporation of water, pollution and present salts in water, undergo the accumulation in system, which may lead to intensification of adverse processes such as: corrosion, sediment formation and development of microorganisms. These processes are interdependent and have mutual influence on each other (Fig. 1). Corrosion processes and the accompanying adverse events occur in both closed and open cooling systems. However, due to a very complicated structure and operation of open recirculating systems dedicate them considerably larger attention [2, 5, 8–9].

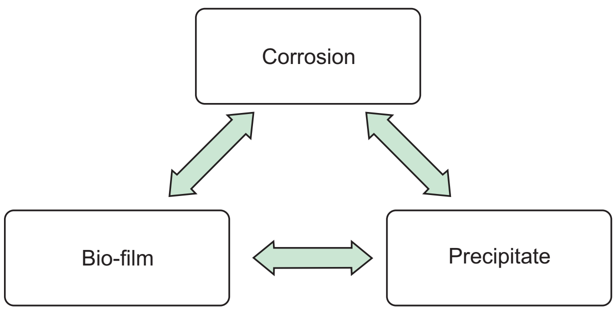

Fig. 1. The relation between the processes determining the state of cooling systems [8]

Proper operation of the water systems with recirculation require that such system has to remained 'clean', that is not formed any corrosion products and should not precipitated solids that favor the growth of microorganisms in the water circulation [1]. On the other hand, there is no clear requirement to be met by an open feed water cooling system. The current recommendations are usually determined based on experimental data developed by designers and engineers. Recommendations for water used regulate only a few key parameters, which include: general parameters, pH, hardness and salinity of the water. The individual limits specified parameters may vary among themselves to some extent, depending on construction materials used for the system [10].

Factors affecting the increase in water consumption during operation of the cooling system can be divided into two categories – physicochemical and biological. Physicochemical factors are responsible for such negative processes as precipitation of deposits on heated surfaces and corrosion of structural materials [11].

Corrosion processes of cooling systems are contingent on the type of construction materials, as well as the composition of the cooling water. Typical cooling systems are generally made of carbon steel, copper and brass. Cooling waters are contained in the Mercer's definition as inert corrosive environments. According to this definition, aquatic environments are neutral-phase systems, containing at least 50 % of the water about pH in range 5.5–10.0. Metal constructional materials in such solutions are covered with layers of durable natural oxide formed on the air. Under such conditions, these layers do not react with H^+ ions and OH^- to form soluble products. However, when in solution are present aggressive anions (Cl^-, SO_4^{2-}, HCO_3^-) layer can undergo electrochemical digestion. Neutral water environments are the most aggressive corrosive environments. Only in neutral aqueous environments may occur separately or simultaneously three types of corrosion cells (macro- and microcells, concentration cells, differential temperature cell) associated with electrochemical corrosion of metals [1, 12].

Electrochemical corrosion of metals is the dominant processes proceed in neutral aqueous environment, accompanied by an anodic oxidation reaction of metal. In the case of carbon steel (most often used constructional material) can be summarized as follows:

$$Fe \rightarrow Fe^{2+} + 2e$$

and the cathodic oxygen reduction reaction (when in solution are not present stronger oxidants). In aqueous environment at pH > 7 the reduction of oxygen proceeds according to the following reaction:

$${}^1/_2O_2 + H_2O + 2e \rightarrow 2OH^-.$$

Reactions of anodic metal oxidation and cathodic reduction of oxygen occur at the same rate, while the cathodic reaction is limited by diffusion of oxygen to the metal surface. Depending on the prevailing conditions, as a result of secondary reactions on the surface of the metal can be formed a layer constituting the barrier to the diffusion of oxygen. This layer consists of iron(II) hydrated oxide or iron(II) hydroxide. Dissolved oxygen is present in the water oxidizes the outer part of the layer of iron(III) hydrated oxide or iron(III) hydroxide

$$Fe(OH)_2 + H_2O + {}^1/_2O_2 \rightarrow 2Fe(OH)_3\downarrow \rightarrow Fe_2O_3 + 3H_2O.$$

There are cases where, because of unfavourable conditions, the oxide layer formation does not occur on metal surface but in volume of solution. The consequence of this is the formation of large quantities of precipitate that accumulate in such places where the flow rate is reduced. In such places also permanent water pollutions as well as biological deposits are accumulating [1].

The use of raw water as a coolant in open cooling systems in the industry is characterized by: high total hardness, alkalinity (balance carbonate), the presence of silicates and sulphates, which contribute to the formation of deposits in pipes, heat exchangers and other parts of installation. The formed sediments are the cause of development of underdeposit corrosion and increased action of microorganisms [13, 14]. In order to limit processes of the grow of deposits resulting from dominating interferences of the carbonate balance in the cooling system a stabilization of water is being conducted, which gives it such a property to ensure the storage and transmission of water without causing changes in the physical, chemical and biological agents. Various methods of the stabilization of water are being used for it without removing soluble salts, gasses and pollutants in stabilized water. Stabilization of water can be carried out by physical and chemical methods, or using a combination of both. Physical stabilization does not pollute the water and its scope includes: treating water in a magnetic, electromagnetic field, or by using ultrasonic waves. Methods of chemical stability of water rely on the introduction to the relevant chemicals. This creates a greater possibility of water treatment regardless of its composition (pH, salinity, dissolved gases) and the technical conditions of operation of the cooling system. The compounds for the chemical stabilization should among others create long-lasting but soluble complexes with ions Ca(II) and Mg(II), well dispersed organic sediments and should be safe for the environment [1, 3, 15]. Formation of complexes between the compounds and the stabilizing cations present in the water helps to reduce the concentration of these ions. The result is a lower rate of sediment deposition in the water.

The use of chemical stabilization can also reduce corrosion aggressiveness of water used in industrial cooling systems. A suitable method for the stabilization of water enables utilization for industrial purposes, poor quality of surface waters and waste-waters from manufacturing processes as a coolant in the working systems.

The presence of microorganisms (bacteria, fungi, algae) in circulating water is also undesirable from the corrosion point of view. Their presence is conditioned with the lack of microbiological stability of water and hydraulic conditions in the system. Microorganisms in the metabolic process breath (take oxygen) and produce metabolites--substances that can strongly stimulate the electrode processes, such as aggressive organic acids, sulphides [16]. Besides of this, microorganisms absorb the ingredients in the metabolism of the passive layer and corrosion-inhibiting substance particles. Cathode activity of microorganism manifests mainly by fabricating hydrogen ions by them. Local oxygen consumed in the process of respiration leads to the formation of the biofilm aeration alternating microcells, and the place of the oxygen-depleted surface are becoming privileged sites for the development of anaerobic bacteria. These bacteria in course of life processes produce metabolites such as H_2S, sulphides, polysulphides or thiosulphate, which are stimulators of corrosion of iron, especially in an environment containing hydrogen ions [17, 18]. Operation of the system in which microorganisms are present can lead to negative effects – from creating an insulating layer and inhibiting the flow of biofilm on heat transfer surfaces by microbial corrosion of structural materials. A common cause of accelerated corrosion of metals covered with a biofilm detachment of the biofilm clusters strongly associated with the original products of corrosion and surface display of open fragments exposed to aggressive environmental effects. Biological corrosion occurs more frequently at the impured than the pure metal, but the same kind of microorganisms for some metals may promote corrosion, and the other may lead to the inhibition [19].

Reduction of corrosivity of water in cooling systems

The protection of industrial water systems has the aim to reduce corrosion rate of construction materials, reducing the amount of mineral precipitate and accumulation it on the surface as well as to prevent microbial growth. Among many methods of protection against corrosion deserves a special attention the inhibitors protection, due to its simplicity, efficiency and versatility [3]. Research undertaken in the last 30 years concerning the application of corrosion inhibitors to protect the cooling systems have shown that the most effective are organic compounds containing phosphorus, which have multidirectional action. Organophosphorus compounds introduced into the system simultaneously provide corrosion inhibition, reducing the amount of deposits set aside, and their dispersion [20, 21]. Obtained desirable results are well show in the literature [3]. In one of the Polish Institutions of Nitrogenous Industry was used multifunctional blend inhibitor VFZ (the main component was trimethylophosphonic acid N-[$N(CH_2PO_3H_2)_3$]) for protection the cooling system with a capacity of 18000 m^3. This system was supplied with decarbonized water**.** During operation of the system followed by absorption of ammonia and reduction water pH 5.6–6.0. Circulation water was periodically contaminated by ions Cu(II), which increased the risk of corrosion and sediment formation. The corrosion rate of carbon steel and copper operation in such conditions was, respectively: 0.71–0.89 mm/year and 0.05–0.27 mm/year. The rate of sediment deposition was 11.47–12.38 g/(m^2day). Introduction of corrosion protection by VFZ inhibitor reduced the corrosion rate of both carbon steel 0.12 mm/year and the corrosion rate of copper to 0.013 mm/year. It was also limiting the rate of precipitation to 0.95 g/($m^2 \cdot$ day). Application of this inhibitor caused a reduction in consumption of decarbonized water to supply the 1.100 thousand m^3 (before safe annual water consumption was 2.424 thousand m^3 and after the introduction of inhibitor – 1315 thousand m^3). Therefore it has limited scope and frequency of repairing works about 50 %.

The use of multifunctional inhibitor reduces water consumption for industrial purpose, reduces the corrosiveness of water and the introduction of unnecessary chemicals to enhance the effectiveness of the protection of the cooling system.

Despite the many advantages of corrosion inhibition these compounds have also disadvantages. These compounds are characterized by too much phosphorus in its molecule. Phosphorus found in the water contributes to growth of phytoplankton, resulting the formation of so-called algal bloom on its surface. From 1 January 2000 applicable regulation introduced in 1991 by the Minister of Environment and Natural Resources and Forestry, which establishes the reduction of total phosphorus in the wastewater entering the flowing waters and see waters from the amount of 5 mg/dm^3 to 1.5 mg/dm^3 [21]. Therefore, the research began looking for new organophosphorus compounds, with smaller quantities of the phosphonic groups, but with the same good inhibition properties.

Conclusion

Long-term, failure-free work of cooling system, while maintaining its full capacity, is associated with the provision of adequate water treatment. This requires taking into consideration process of processing of water treatment and circulation [10, 11]. A build-up of adverse phenomena will be a consequence of wrong preparing water and the bad exploitation of the cooling system. They may be the result of frequent breakdowns, renovation breaks, the use of oversized equipment, increased water consumption, energy losses due to additional resistance to water flow because of the layers of sediment formed.

Effective and yet economical solution is to use multifunctional organophosphorus inhibitors. However, due to increasingly restrictive regulations regarding protection of natural environment led to research on finding new compounds. They should be characterized by: high corrosion performance and anti-scaling performance at low concentrations, non-toxicity, stability and duration of action as well as availability of raw materials for their manufacture. One of the promising possibilities for the production of these compounds is the use of waste materials from industry. This will also help to reduce the amount of generated wastes, which will positively affect the environment.

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TECHNICZNE PROBLEMY I ZAGROŻENIA EKOLOGICZNE ZWIĄZANE Z EKSPLOATACJĄ UKŁADÓW WODY CHŁODZĄCEJ

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Abstrakt: Zużycie wody przemysłowej w Polsce jest bardzo duże i wynosi ponad 10 mld m^3/rok, co zmusza do wdrażania odpowiednich programów i rozwiązań technologicznych w celu zmniejszenia zapotrzebowania na wodę. W zależności od rozwiązań konstrukcyjnych, warunków eksploatacji układów chłodzących zasilanych wodą, narażone są one w różnym stopniu na korozję, wytrącanie i odkładanie się osadów oraz rozwój mikroorganizmów w wodzie obiegowej. Dlatego ważne są działania mające na celu podnoszenie poziomu technicznego eksploatacji przemysłowych układów wodnych. Jednym z najbardziej perspektywicznym sposobem zapobiegania negatywnych zjawisk występujących przy eksploatacji układów wody chłodzącej jest stosowanie ekologicznych wielofunkcyjnych inhibitorów kompleksowo chroniących układ przed korozją, odkładaniu się osadów i rozwojem mikroorganizmów w wodzie cyrkulacyjnej.

Słowa kluczowe: układy wody chłodzącej, korozja, związki fosfonowe