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DEPOSITS IN WATER - BASED COOLING SYSTEMS

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The paper discusses phenomena that cause scale and sludge formation in water-based cooling systems. Results of experimental research into cooling water treatment in an industrial cooling installation with the application of ammonium salts of strong acids have been presented. It has been found that a stoichiometric dose causes carbonate hardness removal. Adequately higher doses bring about crumbling and insignificant dissolving of the scale. Simultaneous application of an inhibitor of corrosion and incrustation prevents corrosion losses and advantageously influences water treatment.

key words: cooling water, water treatment, scale, cooling system, inhibitors

INTRODUCTION

Cooling water systems operate practically in all sectors of the industry. In the year 2001 total consumption of water in Poland amounted to 7.308 km³, out of which 55% has been used in the power engineering industry and most (about. 95%) of the water consumed by that sector has been applied for cooling purposes (Statistical Yearbook of 2003; Spoz, 2000). Situation illustrated by those data is typical for majority of industrialized countries (Veil, 1999).

In Poland, cooling systems apply raw water that, due to the lack of treatment or inhibitor additives, exhibits aggressively corrosive and deposit-forming properties. It results from a considerable flow-capacity of those systems, which causes excessive consumption of the water and creates an economic barrier for its rational treatment. This unfavorable situation can be improved by replacing once-through systems by recirculating ones. At the same time it is possible to apply multi-functional inhibitor preparations that could protect the systems against such phenomena as corrosion, de-

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posit formation and development of microorganisms, even at a high condensation degree of the recycled water.

It is important to reduce water consumption in Poland because fresh water resources are extremely poor there. In Europe an average fresh water amount per capita is 4560 m³, while in Poland it is by three times less.

At late 90-ties of the 20th century fresh water consumption in Poland has been reduced by 25% owing to shutdowns of cooling systems. The mentioned water consumption reduction has unquestionably contributed to the improvement of water quality in Polish rivers (Spoz,2000).

COOLING SYSTEMS

Although in the pertinent literature many kinds of cooling systems are described all of them can be classified into three principal types: once-through systems, open recirculating and closed recirculating ones (Ahmed, 2000).

CORROSIVE AND DEPOSIT-FORMING PROPERTIES OF WATER

Properties of water that is commonly used in industrial cooling installations cause corrosion and incrustation, which brings about many technical problems and considerably raises operation costs of those installations.

Depending on the water quality and construction materials the following weakly or firmly adherent deposits can form on heat exchange surfaces,

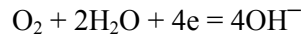
- corrosion products forming as a result of the reaction of water or its components with metal
- incrustation products that form so-called *scale* composed mostly of sparingly soluble calcium compounds
- suspended solids in the form of *sludge* resulting from the sedimentation of mineral and biological particles that are present in cooling water.

The deposits impair operation of cooling water installations by bringing about such disadvantageous phenomena as:

- frequent and difficult repairs
- costly overhauls and related system outages
- induced use of oversized apparatus
- increased water consumption
- energy losses following from additional resistance to the water flow due to the formed deposit layers.

CORROSION OF WATER COOLERS

Corrosion processes occurring in metals that heat exchangers are made of depend on a composition of the construction material as well as on the cooling water composition. Standard cooling water installations usually are made of carbon steel, zinc-coated steel, copper and brass. Oxygen in the cooling water makes the most frequent corrosive agent. Metal elements corrode in oxygenated neutral water when the metal oxidation potential is more negative than the equilibrium potential of cathode depolarization:



Corrosion rate grows along with the increase of:

- temperature (value of the oxygen diffusion coefficient grows)
- oxygen concentration in water
- water flow rate (decrease of the diffusion layer also called boundary layer).

In specific conditions carbon steel exchangers can undergo passivation, although an increase of oxygen concentration in water at higher temperatures and in the presence of chlorides can lead to the occurrence of strong pitting corrosion (Kubicki, 1994).

Carbon dioxide makes another corrosion-accelerating agent in cooling systems.

The effect of various salts dissolved in water on corrosion depends on the kind of salts. Chlorides and sulfates considerably intensify corrosion processes, while phosphates, silicates, and carbonates cause passivation of carbon steel.

Significant share in the total of corrosion damages has the activity of various kinds of microorganisms that destroy the apparatus, armature, constructions, and protective coats on their surfaces.

INCRUSTATION PROCESSES

In the case when cooling water does not meet the chemical requirements it can cause precipitation of the following kinds of deposits:

- mineral crystalline
- mineral amorphous.

The main reason for the mentioned precipitation is high carbonate hardness and excessive salinity of cooling water. Salts that are dissolved in the water get condensed as water evaporation proceeds and usually precipitate when the solubility product gets exceeded. The process runs in heat exchangers (and in cooling installations) that make an advantageous environment for the beginning of solid phase crystallization.

Scale deposits that form in cooling water systems are polycrystalline porous substances with amorphous inclusions. Their physical - chemical and mechanical properties are variable depending on many factors such as:

- the kind and concentration of substances contained in the recycled water - both pollutants and substances purposefully added to enhance properties of the water
- local heat load
- the kind of crystallization base
- hydrodynamic conditions
- contact with polluted atmospheric air
- corrosive power of water against construction materials
- development of biological life in water.

Depending on the prevailing content of carbonate, sulfate or silicate compounds-three main types of scale can be distinguished (Stańda, 1999):

- carbonate scale that contains mainly calcium and magnesium carbonates as well as magnesium hydroxide
- sulfate scale (gypsum), that contains more than 50% of calcium sulfate
- silicate scale whose basic components are calcium and magnesium silicates and aluminosilicates.

Considerable content of calcium bicarbonate in raw water that is used for cooling purposes, its low solubility and favorable conditions in recirculating cooling systems are the reason why carbonate scale occurs the most frequently and its basic component is calcium carbonate which can form as a result of:

- temperature increase in the system
- pH changes
- concentration increase following from the solution condensation.

COOLING SYSTEM PROTECTION AGAINST DEPOSIT PRECIPITATION

Methods for preventing scale formation can be developed in the two following directions:

- introduction of supplementary water with most of the scale-generating pollutants removed
- treatment of the recycled water by adding inhibitors.

INHIBITOR PROTECTION

An analysis of the pertinent literature reports of the recent 10 years and opinions based on practical experience leads to the conclusion that inhibitor protection, sometimes also coupled with biocide, makes the most effective and economical method for preventing scale formation and corrosion in industrial cooling water systems of the recirculating type.

The key to elaborate a good program for the cooling water treatment in recirculating systems is its chemical composition when it gets condensed.

The best regulator for the economics and reliability of the applied chemical treatment method is the recycled water reaction.

According to Ascolese Ch.It R., (1998) water treatment programs can be classified into two groups:

- a neutral program in the operation conditions of $6.8 < \text{pH} < 7.8$
- an alkaline program when $7.8 < \text{pH} < 9.0$.

Till recent times many inorganic metallic compounds such as chromates, molybdates and zinc compounds as well as some non-metallic ones like phosphates (polyphosphates and orthophosphates), silicates, nitrites and also azoles that effectively protect copper alloys have been applied as corrosion inhibitors.

Disadvantages of inorganic inhibitors such as: toxicity (chromates), low stability (silicates and polyphosphates) or selective protective action (nitrites) as well as increasingly rigid ecological standards, have turned the interest of researchers to the application of organic compounds as potential inhibitors of multifunctional properties (Amjad, 1997).

Within the 10 recent years, many water treatment technologies based on phosphonate acid compounds have been elaborated. They exhibit relatively high efficiency both in inhibiting corrosion of ferrous metals as well as in water treatment and preventing scale formation.

REMOVAL OF DEPOSITS AND PREVENTING THEIR FORMATION IN INDUSTRIAL COOLING INSTALLATION

The testing has been performed in a recirculating cooling installation *Lacpol* in Gdynia. The installation has been composed of four shell-and-tube ammonia condensers of the SRS type and fan coolers. All condenser and cooler elements that contact water have been made of ST3 steel. Surfaces of heat exchangers have been covered with scale layer of 3mm of average thickness.

REFERENCE CONDITIONS

Chemical analysis of the scale has shown that it has contained 95% of CaCO_3 , about 3% of iron compounds, and 2% of HCl-insoluble components (including organic ones). Table 1 presents properties of the cooling water. It follows from the analyses of the feeding and recycled waters that condensation coefficients have the values given in the last column of Table 1. The condensation coefficient of chlorides (the best soluble salts) that almost 2-fold exceeds the condensation value of general and carbonate hardness proves the occurrence of precipitation of calcium and magne-

sium carbonates. As t/n is 0.75, it can be calculated that 25% of hardness introduced to the system precipitated in the form of scale.

Table 1. Properties of the cooling water

No	Indicators	Makeup water	Recycled water	Condensation coefficient
1	pH	7	8.5	
2	general hardness, mval/dm ³	6.6	7.92	1.2 (t)
3	carbonate hardness, mval/dm ³	4.8	5.4	1.2
4	Cl- content, mg/dm ³	36.2	58.2	1.5 (n)
5	SO ₄ ²⁻ content, mg/dm ³	80.0	124.8	1.56

The average water consumption prior to the treatment application:

- in the summer season - 202 m³/day
- in the winter season - 110 m³/day.

In a one-year time, a scale deposit of 3 mm thickness has accumulated and has been mechanically removed every year.

DESCRIPTION OF THE COOLING WATER TREATMENT PROCESS AND DESCALING

A water treatment method elaborated according to the Polish patent No. 102516 (Zagórski et al., 1978) has been applied. Ammonium salt of a strong acid (ammonium chloride and sulfate) has been used as the pH regulator. Sodium polyphosphate (the trade name - *Polifos*) with the addition of zinc sulfate has been applied as the corrosion and incrustation inhibitor while sodium lignosulfonate (known in the market under name of *Klutan*) has acted as a dispersion agent (Szymura et al., 2005).

Because of a great amount of scale in the installation a preliminary dose of ammonium salts of 1.7 of the stoichiometric dose with respect to carbonate hardness has been applied. The proportions of ammonium sulfate and chloride have been calculated in such a way for not to exceed the gypsum solubility product. Analyses of the feeding and recycled waters have been performed twice a week.

An additional system has been elaborated and applied to supply chemicals to the feeding water pipe and direct them together directly to the condenser. The system has been automated. When the salinity meter indication for the recycled water has exceeded by three times the value for the feeding water with chemicals a valve for supplementary water has been opened. It has made it possible to maintain an assumed level of the recycled water condensation. Figure 1 presents a schematic diagram of the cooling installation together with the metering system.

Graph in Fig. 2 presents a course of the cooling water treatment process realized in the discussed installation. Values of the t/n ratio illustrate the decarbonization reac-

tion process ($t/n = 1$). The t/n values of that are higher than unity indicate scale dissolution.

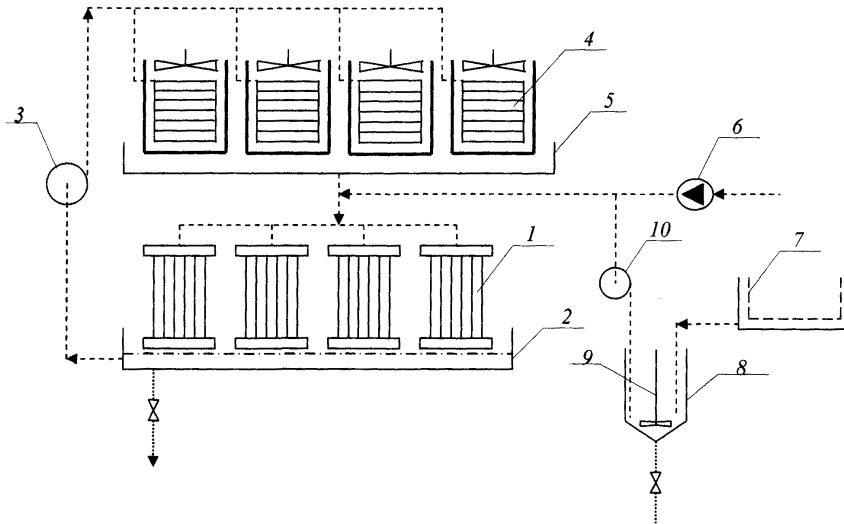


Fig. 1. Diagram of the cooling installation *Lacpol* in Gdynia. 1 -shell-and-tube condenser, 2 - tank under condensers, 3 - recycled water pump, 4 - fan coolers, 5 - trays under coolers, 6 - water meter, 7 - tank with a screen for dissolving chemicals, 8 -mixer, 9 - stirrer, 10 - volumetric pump

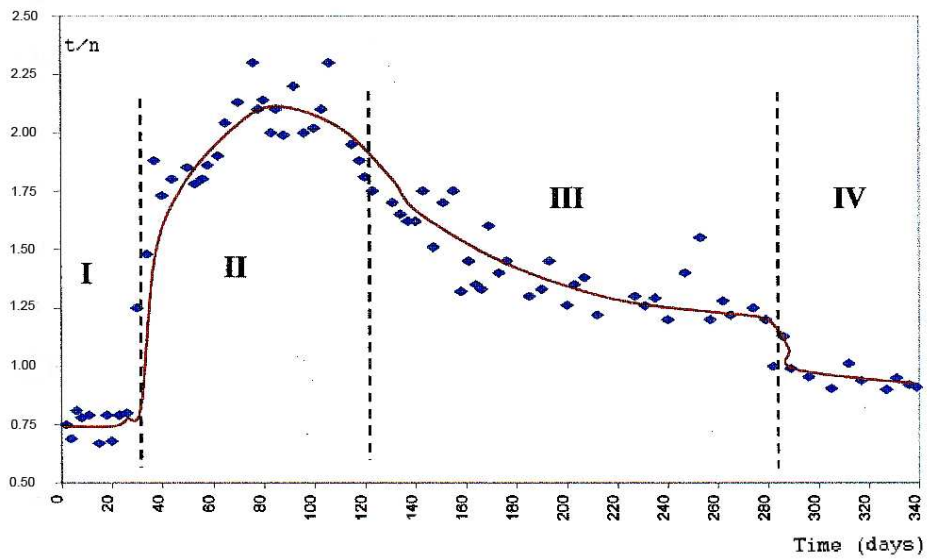


Fig. 2. Variations of the t/n ratio during the application of ammonium sulfate in the Cold Store *Lacpol* installation in Gdynia

DISCUSSION

In Fig.2, a one-month period when the preparation has not been applied is denoted as I. The ratio $t/n \approx 0.75$ indicates scale deposition in the installation.

During the second two-month period (II) the preparation dose of 1.7 of the stoichiometric value has been applied. The t/n has increased even up to 2, but low pH (close to 6.2) has made authors reduce the preparation dose. Scale has kept softening and dropping off metal surfaces in great quantities.

Over the third period (III) a dose equal to 1.5 of the stoichiometric value has been applied and the recycled water pH has increased up to $6.5 \div 6.8$. The mentioned procedures have been applied for four months and then it has been decided to stop the installation for a short time to remove sludge and pieces of dropped-off scale from trays under coolers and condensers.

After 330 days of the preparation application, in the fourth period (IV) it has been decided to reduce the preparation dose down to 1.2 of the stoichiometric value because the scale has practically been removed from the installation. The t/n ratio has been close to 1, and the carbonate hardness (alkalinity m) has been of fractional value, which confirmed decarbonization of the water.

The water treatment process in the discussed installation has been controlled for the next 10 years. By that time the recycled water pH has been maintained within the range of $6.5 \div 7.5$. When the pH has been getting lower than 6.5 the dose of ammonium salts has been reduced by 10%, and when it has reached values higher than 7.5 - the dose has been increased by 10%. The installation has operated according to the expectations - scale deposit has not grown.

At the same time, a research into the corrosive effect of water on ST3 steel has been carried out as well as microbiological tests. Results of those investigations will be the subject of separate reports.

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W pracy przedyskutowano zjawiska, które powodują tworzenie się kamienia kotłowego oraz osadów w układach z użyciem wody chłodzącej. Zaprezentowano wyniki badań dotyczących modyfikowania wody chłodzącej w instalacjach przemysłowych z zastosowaniem soli amonowych silnych kwasów. Stwierdzono, że stechiometryczna dawka powoduje usuwanie twardości węglanowej. Odpowiednio wyższa dawka powoduje rozpad kamienia i niewystarczające się jego rozpuszczanie. Jednoczesne zastosowanie inhibitora korozji i inkrustacji zapobiega stratom korozji i dodatnio wpływa na przeróbkę wody.

słowa kluczowe: kamień kotłowy, chłodzenie, przeróbka wód, korozja, twardość wody, sole amonowe, inhibitory korozji