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INNOVATIONS IN INDUSTRIAL WATER PREPARATION IN A METALLURGICAL PLANT

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The purpose of the research was to determine the effectiveness of nano-silver biocide on cooling water biological stability which should lead to attempt to optimise the operation of the cooling towers functioning in metallurgical plants. As shown by the study results, the nano-silver agents allowing for reduction/elimination of biological threats in the cooling systems.

Key words: metallurgical plant, industrial water, cooling tower, nano-silver, microorganism-deactivation

INTRODUCTION

Thousands of metallurgical facilities use large volumes of water from lakes, rivers, estuaries or oceans to cool their plants [1]. Due to the huge water consumption in each metallurgical plant, cooling water is generally reused in order to reduce costs and the natural water resource [2, 3].

Table 1 **Consumption of make-up water and recycled water by metallurgy industry [1]**

Industry	Make-up water / 1 000 m^3/day	Recycled water / 1 000 m^3/day	Recycling rate %
Steel	3 744	34 450	90,2
Non ferrous metals	733	2 453	77,0
Metal products	545	498	47,7

As show the data in Table 1, the recycling rate in the steel industry ranges to 90 % while in metal production industry the rate does not reach the level of 50 % [1]. Admittedly, the biggest water consumer is the steel industry, in which water is use in many processes like: iron ore sinter, blast furnace, lime production, basic oxygen furnace, continuous casting plant and hot rolling. In some of this process like blast furnace or continuous casting line, circulating cooling water play most important role [3]. Table 2 shows calculation of circulating cooling water consumption in diverse unit processes of steel production. Presented data come from integrated steel plants in Poland, and summarised values were converted to functional unit (FU). FU in this table was one ton of cast steel produced in the integrated steel plants.

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Table 2 **Volume of circulating cooling water consumption in integrated steel plants in Poland [3]**

Unit processes	Circulating cooling water / m^3/FU
Iron ore sinter plant	0,43
Blast furnace	23,08
Lime production plant	0
Basic oxygen furnace	0
Continuous casting plant	9,78
Hot rolling	1,40

As results from the data each ton of cast steel requires about 35 m^3 of water for cooling and many steel plants in Poland use cooling tower for this process. The cooling system must address five major challenges for cooling tower maintenance. They include traditional issues such as: controlling inorganic scale deposition on cooling surfaces, providing corrosion protection for steel, copper, copper/nickel tubing, and cooper alloys, controlling microbiologic growth, including biofilms on cooling surfaces and bacterial counts in the cooling tower basin water, preventing fouling in heat exchangers and condensers and controlling airborne impurities and contaminants that enter external to the water source [4, 5]. But, it should recognized that there is no universal program capable of treatment of all the varieties of makeup water sources [5]. Meanwhile, the quality of water circulating in the cooling tower cycle will have a significant impact on its operation, and the cooling system operation can directly affect reliability, efficiency, and costs of many industrial processes [6]. One of the most important problems in the cooling water treatment process is biological stability of water. Cooling towers are specific heat exchangers, providing perfect conditions for microorganism growth. High humidity, contact with the external environment and relatively stable temperature foster the growth of microorganisms that agglomerate at the boundary of the solid body–liquid phase to form the bacterial jelly (biofilm) [6, 7]. While analysing the hazard involved in biofilm development in technological systems of cooling towers, one should note that microorganisms, i.e. algae, bacteria and fungi, may significantly reduce heat transmission due to the formation of biofilm layers and make equipment operation difficult as a result of reduced conduit cross-sections [8, 9]. Reduction of heat transmission through biofilm layers is four times higher than it is in the case of lime deposits [10, 11]. Additionally, metabolism processes occurring in microorganisms cause corrosion resulting in system damage. Moreover cooling tower is an ideal incubators. The prolonged persistence of pathogen bacteria in aquatic biofilms serves as a reservoir and detachment through shear forces or another mechanisms permits continuous pathogen intrusion into bulk water [12, 13]. More recently, disease outbreaks caused by the aerosolization of waterborne bacteria from inadequately managed cooling towers have caused concern and, in some cases, legal action [14]. The search for solution to this problem is nowadays a part of significant business sector. What clearly makes more sense is putting more effort in the prevention of biofilm by means of advanced strategies. The most common form of prevention is dosing of biocides into water. Biocides are substances that inhibit the microbiological growth in the cooling water, reduce the number of microorganisms in the feeding water and impair the stability and structure of the biofilm ground, thus minimising the organic contamination level in the cooling system. In general, biocides are divided into oxidising biocides and non-oxidising biocides containing nano-silver. Summarizing it must be, clearly emphasised that nano-silver is an innovative technology and the potential hazards for the environment and people are not fully known yet.

MATERIALS AND METHODS

The purpose of the research was to determine the effectiveness of nano-silver biocide on cooling water biological stability.. The biocide (the patent for its formula is currently pending) was proportioned into water taken from the circulating cooling water. Water taken from the system (1 dm^3) was subject to a disinfection process at a laboratory site by way of adding liquid nano-silver solution in the dose of 0,1 g/m^3. Selection of the dose was preceded by multiple literature studies and a number of tests carried out on model water (pure distilled water with injected bacterial colonies). After adding the biocide, samples were mixed and left in laboratory conditions in order to ensure appropriate contact time. It was assumed that contact duration for water and biocide should be at least 1 hour. After that time, 1 cm^3 of water was taken from each sample in order to carry out microbiological analyses. At the same time, microbiological tests were performed for check samples containing pure circulating water. In order to reduce errors and to make it possible to perform statistical evaluation of obtained results, the tests were repeated six times. Microbiological analyses were carried out according to the standard EN ISO 6222:1999. The effectiveness of produced biocide was determined according to the following relation:

$$S = (1 - N / N0) \times 100 \% \qquad (1)$$

where:
S − biocide effectiveness/ %;
N − number of bacteria after disinfection/ cfu/cm^3;
N_0 − number of bacteria before disinfection/ cfu/cm^3;
cfu − colony forming unit.

Based on the achieved results, the potential demands of steel industry market in Poland for nano-silver application has been calculated.

DISCUSSION OF RESEARCH RESULTS

The water used for the purpose of research regarding biocidal effectiveness of nano-silver was collected directly from the cooling tower circuit. The quality of water used in the tests corresponded to the parameters specified in standard VDI 3802 regarding water quality in cooling systems. The reaction of the applied water was 8,3±1, with alkalinity from 1,4 val/m^3 and carbonate hardness maintained at the level not exceeding the value of 0,7 mol/m^3. Electric conductivity, strictly connected with water salinity, oscillated at the level of 600 μS/cm, which is a safe value since high conductivity water manifests corrosive properties. The population of the particular microorganism groups in the tested water − the most important parameter from the point of view of conducted tests, is presented in Figure 1.

The Figure 1 depicts also the population of the particular bacteria groups upon application of nano-silver. As indicated by the obtained test results, application of nano-silver in the dose of 0,1 mg/dm^3 had a significant impact on the decrease in the population of microorganisms in the controlled system, and in case of coli group bacteria − their complete deactivation.

Since the objective of the study was an attempt to optimise the operation of the cooling towers functioning in metallurgical plants, the most significant issue is determination of effectiveness of deactivation of the particular groups of microorganisms by means of application of nano-silver. This parameter is presented in Figure 2.

As can be seen in the Figure 2, the highest effectiveness of nano-silver deactivation was observed in relation to coli group bacteria – 100 % of bacteria were destroyed. The biocide proved to be less effective in relation to the group mesophilic microorganisms - the deactivation effectiveness was only 45 %. Nevertheless, it must be noted that the tests were carried out for a very low dose of nano-silver and, most probably, an increase in the dosage will result in improvement of these very satisfying effects. However, further increase in the nano-silver dosage must be combined with calculation of potential costs of the undertaking since the nano-silver

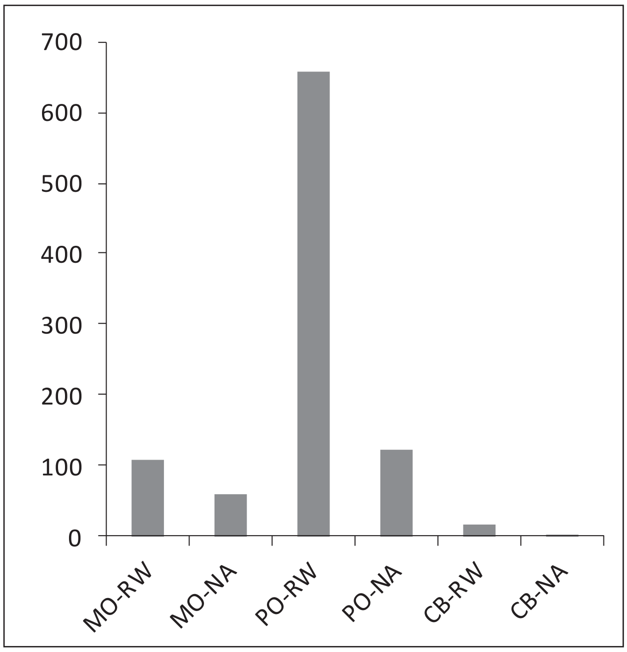

Figure 1 Population of selected bacteria groups in water (cfu/cm^3) prior to and upon application of nano-silver in the dose of 0,1 mg/dm^3

MO-RW mesophilous organisms in raw water;
MO-NA mesophilous organisms in water after nano-silver application;
PO-RW psychrophilic organisms in raw water;
PO-NA psychrophilic organisms in water after nano-silver application;
CB-RW coliforms bacteria in raw water;
CB-NA coliforms bacteria in water after nanosilver application.

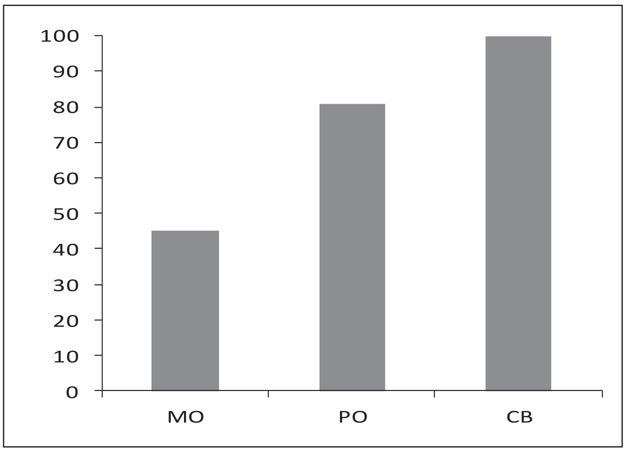

Figure 2 The effectiveness of biocide in % on mesophilic organisms (MO), psychrophilic organisms (PO) and coliforms bacteria (CB)

based agents are still very expensive and the volumes of water used in the metallurgy industry are tremendous. Assuming that the use of nano-silver in technical conditions in the dose of 0,1g/m^3, will result in improvement of functioning of the cooling tower in the steel industry facilities, the potential market of biocide application in Poland has been determined. The data analysis shows that the biggest demand for cooling water is manifested by the steelworks furnaces. Therefore, these furnaces are also characterised with the highest demand for corrective agents. The potential demand for the biocide for this process is 2,31 g per each ton of manufactured steel. Whereas, the total demand for biocide for the entire process of steel production, in relations to one ton of manufactured product, is 3,47 g. Taking into account the steel production volume in Poland in 2013, the potential market for the new cooling water conditioning agent is ca. 30 Mg/year. However, in order to induce interest in the new product, it is necessary to conduct further research, this time at the technical scale, taking into consideration the full rotation of the seasons since, as can be seen in the Polish conditions, the biggest problem with biological stabilisation of water in the cooling circuits is observed in the summer months. It might be also necessary to apply higher doses of biocide in this case. Another aspect requiring an analysis is the potential impact of nano-silver on the water environment since bottom and surface blowdowns from most cooling facilities are discharged to the environment without treatment.

CONCLUSIONS

In a significant number of processes, water or aqueous solutions are used either as process or as auxiliary liquids. Most devices in which water or aqueous solutions are used offer a set of optimal conditions for the development of microbiological films. In heat exchangers like cooling towers, biofilms are predominantly formed by bacteria. Biofilm has been for many decades mainly associated with the problem of device corrosion. Gradually, scientists and engineers became fully aware of the much wider effects of unwanted biofilm formation on the cooling tower operation process, e.g. reduction of heat transfer efficiency, increase in the pressure drop across the heat exchanger, contamination of the fluids flowing through the devices as a result of biofilm detachment. In order to provide reliable technological conditions of cooling tower operation, it is necessary to provide proper microbiological cleanliness of the circulating water. As shown by the study results, the agents allowing for reduction/elimination of biological threats in the cooling systems are biocides, benefiting from biocidal properties of nano-silver. The selection of proper protection program for the operated system requires, however, definition of all hazards. Thus, each selection of the biocide should be preceded with laboratory analysis of the deposit composition, determination of their place of occurrence, development rate and hazard scale. The presented study results may be a valuable guidance for the operators of cooling towers, considering optimisation of their systems. Summarizing, microbiological growth is a major concern in cooling tower operation, which affecting in a variety of operational and system problems including corrosion, reduction in process efficiency, system cleanliness and potential health concerns. Extensive growth of microorganisms in industrial cooling systems, in that in metallurgy industry systems, may shorten equipment life significantly [3, 12]. It shout be recognized that a good biocide program is an important part of cooling systems maintenance program. Biocides using in cooling process have to work together with scale and corrosion inhibitors to optimize cooling system performance.

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