



Anna TURLEJ ORCID 0000-0002-9405-9753, anna.turlej@itwl.pl – corresponding author
Bolesław GIEMZA ORCID 0000-0001-5135-8860, boleslaw.giemza@itwl.pl
Marta SKOLNIAK ORCID 0000-0002-0850-6781, marta.skolniak@itwl.pl
Air Force Institute of Technology (Instytut Techniczny Wojsk Lotniczych)

IMPACT OF THE ANTIFREEZE COMPOSITION ON THE RISK OF CORROSION OCCURRENCE IN COPPER STRUCTURE ELEMENTS OF THE HVAC SYSTEMS

Wpływ składu komponentowego płynu niskokrzepnącego na ryzyko wystąpienia korozji miedzianych elementów konstrukcji systemów ogrzewania i chłodzenia

Abstract: *The operation time of HVAC systems in industry and construction engineering is counted in decades. Corrosion protection of these systems is crucial for their long-term and failure-free operation. In the case of working mediums based on glycols, corrosion protection is provided by anti-corrosion additives, which are the component of antifreeze. The defence mechanism consists in the interaction of these additives with metal surfaces, with whom they contact by creating durable and efficient layers separating their surfaces from aggressive environmental factors. Observation of the structure of protective layers and corrosion micro changes was possible due to the application of microscopic imaging. The main building material in heat exchangers is copper. Studies have shown that the dilution of antifreeze may result in the formation of insufficiently clear protective layers on the copper surface, which may intensify the negative effects of fluids on copper elements of infrastructure HVAC systems.*

Keywords: copper corrosion, corrosion of heat exchangers, corrosion studies, corrosion protection, anti-corrosive additives, antifreeze, micro-imaging, microscopic examination

Streszczenie: *Czas pracy systemów grzania i chłodzenia w przemyśle i budownictwie jest liczony w dziesięcioleciach. Ochrona przeciwkorozyjna tych systemów ma kluczowe znaczenie dla zapewnienia ich długotrwałej i bezawaryjnej pracy. W przypadku czynników roboczych na bazie glikoli ochronę przed korozją zapewniają przeważnie dodatki przeciwkorozyjne znajdujące się w składzie płynów niskokrzepnących. Mechanizm*



ochronny polega na oddziaływaniu tych dodatków z powierzchniami metali, z którymi mają kontakt poprzez wytworzenie trwałych i skutecznych warstw separujących ich powierzchnie od agresywnych czynników środowiska. Obserwacja struktury warstw ochronnych oraz mikrozmiian korozyjnych była możliwa dzięki zastosowaniu metod obrazowania mikroskopowego. W konstrukcjach wymienników ciepła głównym budulcem jest miedź. W badaniach wykazano, że skutkiem rozcieńczenia płynów niskokrzepnących może być uformowanie się niedostatecznie wyraźnych warstw ochronnych na powierzchni miedzi, co w konsekwencji może prowadzić do nasilenia negatywnych skutków oddziaływania płynów na miedziane elementy konstrukcji infrastrukturalnych systemów wymiany ciepła.

Słowa kluczowe: korozja miedzi, korozja wymienników ciepła, badania korozji, ochrona przeciwkorozyjna, dodatki przeciwkorozyjne, płyny niskokrzepnące, mikroobrazowanie, badania mikroskopowe

Received: November 7, 2023/ Revised: November 21, 2023/ Accepted: December 12, 2023/ Published: December 28, 2023

1. Introduction and purpose of the study

One of the most common causes of breakdowns in HVAC systems, where glycol antifreeze is used as the working fluid, is the corrosion of metal elements. Copper elements find wide application in heating/cooling structures. Copper, a relatively easy metal to work and assemble, is characterized by a high thermal conductivity coefficient, desirable in area where heat exchange occurs.

In infrastructure HVAC systems, metal elements and a working fluid create an electrochemical cell. In many environments, copper is indicative of high chemical resistance. However, in real working conditions of HVAC systems, this metal can suffer from corrosion, mainly electrochemical corrosion.

Copper corrosion, including also in the context of copper corrosion of heat exchangers, is the subject of many studies in Poland and abroad [1-7]. Effects of copper corrosion are not always evident and easily detected. Moreover, copper corrosion can manifest, e.g. by the change in metal colour, or increased metal ions in the system. The presence of copper ions in the HVAC system can additionally result in the corrosion of other metals, such as steel, zinc or aluminium, when they are not connected by a common working fluid cycle.

For electrochemical systems, it is possible to plot an equilibrium diagram that facilitates the delineation of corrosion zones, passivation zone and thermodynamic durability. Corrosion zones are related to the formation of copper compounds soluble in water. The release of copper ions depends, inter alia, upon the pH of the examined solution. Copper forms compounds soluble in water consisting of Cu^{2+} ions at low pH values and CuO_2^{2-} ions at high pH values. In the passivation area, copper forms oxides that are insoluble in water (CuO and Cu_2O), which can decelerate the corrosion process. However, they do

not form an impermeable coating and, therefore, do not protect the surface of this metal from exposure to further external factors.

The impact of the pH value on copper corrosion in simulated conditions was studied by N. Mora et al. [8]. Copper corrosion phenomena were studied using solution absorbance. It was demonstrated that copper corrosion occurs most rapidly in the solution with pH 8.0.

The products of copper corrosion can precipitate on its surface, affecting, more or less, the metal's appearance. T. Wang team [9] characterized corrosion products of copper coil pipes applied in water generation systems with low oxygen content in a nuclear plant. The surface morphology of the corroded coil was characterized, and products originating from dissolving of the passive layer were identified. The tough corrosion layer, a few micrometers thick, consisted mainly of locally accumulated loose corrosion products and substances in the form of needle-shaped crystals located randomly. In the passive layer, three main copper oxidation products were identified: CuO, Cu(OH)₂ and Cu₂O. The unintentional presence of O₂ and CO₂ in the system resulted in the destabilization of the passive layer of copper. In the water chamber, the following substances were identified: CuO, Cu(OH)₂, Cu₂O and CuCO₃·Cu(OH)₂.

In copper installations with the closed cycle of the working fluid, corrosion is mostly visible on irregularly shaped parts - valves, elbows, connections, pressure gauges, etc. exposed to turbulent fluid flow. Intensity conditions of fluid flow have a substantial impact on the durability of protective layers of copper oxides on the outer layer of pipes made of copper and its alloys. Prof. K. Kida and K. Mizobe [10] demonstrated that protective surface layer of copper oxide cannot withstand the initial phase of the turbulent flow. At this point, corrosion processes proceed most rapidly.

Corrosion occurring in infrastructure heating and cooling systems on copper elements can be due to a wide variety of factors, including the presence of micro-organisms. When propylene glycol-based fluid is used as a working medium, it can be relatively easy for microflora to proliferate because propylene glycol-based fluids are characterized by low harmfulness for organisms and the environment.

The presence of bacterial flora in heat exchangers can decrease the system efficiency and accelerate corrosion processes inside the metal pipes. Copper has antibacterial properties, which can effectively prevent the adhesion of bacterial biofilm; however, studies with *Pseudoalteromonas lipolytica* conducted by N. Guo et al. [11] showed the most severe effects of copper corrosion in a solution consisting of inactivated bacterial strains in surface and electrochemical evaluation. The abiotic solution contained brown-black dyes with high molecular mass made from amorphous bacteria. These dyes were still involved in the Cu to Cu(I) oxidation process.

Bacterial strains prevalent in HVAC systems generate many substances that exhibit undesirable chemical activity. In the work of the team Z. Chen et al. [12] strains of gram-negative anaerobic *Desulfovibrio vulgaris* bacteria were used to describe their impact on

copper corrosion. It was demonstrated that the propagation of micro-organisms intensified copper corrosion. These bacteria produced hydrogen sulfide, which, especially in the presence of water, is a strong corrosion factor for elements made of copper.

In the HVAC systems, glycol-based antifreeze is used as a liquid working medium since these liquid types most broadly meet the criteria for assessing the physicochemical parameters and functional properties required for working media for these systems. The typical antifreeze concentrate consists of ethylene or propylene glycol and an improver package, including anti-corrosion additives. To obtain a ready-to-use liquid, the concentrate is diluted with water. The ratio of glycol to water determines the crystallization temperature value of the ready-to-use liquid. The dependence between the glycol concentration in water and crystallization temperature of the liquid is not linear, but up to a certain concentration, glycol concentration in water results in decreased crystallization temperature of the liquid.

The dilution rate of the concentrate with water has an impact on the crystallization temperature value of the ready-to-use liquid. Low-temperature requirements for working media in infrastructure HVAC systems are less stringent than the criteria that should be fulfilled by the liquids in the combustion engine cooling systems. For the cooling systems of combustion engines, it is usual to dilute the concentrate with distilled water at a volume or mass ratio of 1:1, which ensures that the coolant remains fluid down to temperatures below -35°C . The low-temperature criteria to be met by the working medium in an infrastructure HVAC system are typically -20°C or -15°C . Hence, the proportion of water relative to the concentrate can be correspondingly higher. Economic considerations, therefore, determine that some investors and HVAC contractors choose to dilute the concentrate to a greater extent than the manufacturer recommends. However, the concentration of improvers, including anti-corrosion additives, is decreased by higher dilution. According to the manufacturers of liquids, excessive dilution of concentrate can contribute to increased corrosion.

The manuscript aimed to identify changes on the copper surface due to the activity of antifreeze with different concentrations of propylene glycol and improvers. The study aimed to verify the thesis that increasing the dilution of glycol antifreeze concentrates by the above-mentioned manufacturers intensifies corrosion in copper elements of infrastructure heat exchange systems and increases the risk of system breakdown.

2. Study objects

To implement the objective described in this article, propylene glycol-based antifreeze samples, consisting of a mixed package of additives (inorganic and organic), prepared on the basis of the antifreeze concentrate for use in combustion cooling systems, were

examined. The fluids tested were of a complex, multi-component chemical composition forming a buffer of pH ~8.

Sample 1 had a crystallization temperature of $-47,7^{\circ}\text{C}$.

The original propylene-based glycol consisted of a mixed additive package. Glycol content in a liquid with crystallization temperature below -35°C is usually approx. (40-50) % (m/m), the participation of additives is between 5 % and 10 %.

Sample 2 had a crystallization temperature of $-18,0^{\circ}\text{C}$.

The original liquid was diluted with distilled water at a volume ratio of 2:1 (two parts of fluid, one part of distilled water). Assuming that the original fluid contained 50 % of glycol, an indicative glycol content in sample 2 was 33,3 % (m/m), and the participation of additives decreased between 3,3 % and 6,7 %.

Sample 3 had a crystallization temperature of $-32,7^{\circ}\text{C}$. Sample 3 is the original fluid diluted with distilled water at a volume ratio of 3:1 (three parts of fluid, one part of distilled water). Assuming that the original fluid contained 50 % of glycol, an indicative glycol content in sample 2 was 37,5 % (m/m), and the participation of additives decreased between 3,8 % and 7,5 %.

The dilution of the original fluid changed the concentration of improvers, including the decreased concentration of corrosion inhibitors. The dilutions were planned in such a way that the solution would reach a certain value of the crystallization temperature, respectively below -15°C but not below -20°C required, inter alia., for heat pumps (sample 2) and below -20°C but not below -35°C , i.e. the criterion used, inter alia., in solar collectors (sample 3).

3. Methodology and test

Impact studies of the prepared fluids on the copper plate material were conducted on a bench equipped with analogue-controlled laboratory heating blocks, which maintain the temperature with an accuracy of $\pm 2^{\circ}\text{C}$. The bench has an adjustable air dosing system.

The copper plate was embedded in an electrochemical cell built from three metal types. The copper plate with the following approx. dimensions (50*25*1,6) mm (element composition: Cu – 99,9 %; Zn – 0,05 %; Fe – 0,02 %; Ni – 0,01 %) acted as a fire cathode and antifreeze samples as electrolytes. Two metal plates with lower potential standards than copper, i.e. steel and aluminium, functioned as an anode.

Three identical cells with three identical glass vessels with the capacity of 1 dm³ containing 0,5 dm³ each of the three prepared samples. Test sets were maintained at a temperature (86–90)^oC for 672 hours. Throughout the test, the fluids were aerated continuously with air at a flow rate of (90 – 110) cm³/min.

After the test, the copper plate was disassembled from the test unit, rinsed with distilled water, dried in a stream of cool air and subjected to weight and optical evaluation.

The weight evaluation included a change in the plate mass after the test relative to the same place before the test. Mass decrement was recorded when the plate after the test was of lower mass than the plate before the test. The weight evaluation in corrosion tests enabled the identification of changes which are the effects of general corrosion characterized by an even or uneven loss of the material surface layer. Building upon the normative requirements for antifreeze [13], the general corrosion was defined as the change in the plate mass higher than 10 mg, assuming that the initial plate mass with the adopted dimensions was (14-17) g.

The visual inspection was made with optical methods: a macroscopic and microscopic technique. Macroscopic visual assessment allows the observation of surface effects such as colour changes, tarnish, and pitting corrosion with a minimum diameter of ~0,1 mm. The application of the microscopic imaging enables to determine effects and distinguish objects formed on surfaces and changes in the structure.

Macro-photographies were made with Nikon D7200 with Nikkor AF-S Micro Nikkor 105 lens. LOM (Laser Optical Microscopy) microscopic evaluation was performed using a Nikon LV100ND microscope equipped with a Nikon DS-Ri2 digital camera and NIS BR software, using bright field (BF), polarised light (POL) and fluorescence (FLUO A – UV-2A filter) techniques.

The bright field technique enables to observe a magnified image with true colours. The polarised light technique enables us to distinguish between isotropic objects and anisotropic objects. Isotropic objects are visible as dark, while anisotropic objects shine in polarised light. Fluorescence methods use the ability of certain substances to absorb a beam of light of a certain wavelength and then emit a lower energy and longer wavelength.

SEM microscopic evaluation was performed using a Quanta 3D FEG microscope with an EDX (Energy Dispersive X-ray Spectroscopy) attachment. Feret diameter - the distance between two conventional parallel planes bounding the object perpendicular to this direction - was used to assess the magnitude of the observed changes.

4. Test results

The research carried out with the proposed methods was alternative and progressive to the methods usually used to study the corrosive effects of the antifreeze. The methodology was initially developed in-house for a cell constructed from three metals commonly used for heat exchangers in heating and cooling systems. The project was exploratory. It aimed to confirm that by microscopic methods can detect the onset of corrosion at the early stage, when the weight or macroscopic evaluation does not provide information on corrosion changes.

4.1. Visual macro- and microscopic assessment

Tests of the effects of the prepared fluids on the copper plate material were carried out in triplicate for each type of fluid. The average value of the difference between the copper plate mass after the test and before the test was presented in Table 1.

Table 1

Change in the mass of the copper plate after 672 hours of testing at (86–90) °C, with an air flow of (90–110) ml/min.

Copper ¹⁾	
Liquid designation	Change in mass of the copper plate ²⁾ [g]
Sample 1 (original liquid)	-0.0030
Sample 2 (liquid diluted in ratio 2:1 (v/v))	-0.0006
Sample 3 (liquid diluted in ratio 3:1 (v/v))	-0.0011

¹⁾ copper M1E according to PN-77/H-82120
²⁾ the average change in the mass of the plate was calculated based on the results obtained from weighing 3 copper plates tested in the same liquid.

In the case of copper plates tested in the original liquid based on propylene glycol containing a mixed package of additives, a mass decrement with the value of 3,0 mg was recorded; however, in the case of its dilutions, the mass decrement was less and amounted to 1,1 mg for the liquid diluted at a volume ratio fluid-water 3:1 (sample 3) and 0.6 for the fluid diluted at a volume ratio fluid-water 2:1 (sample 2).

For studies conducted by a gravimetric method, potential uncertainty sources related to the measurement system were identified. Random errors can be caused by environmental factors. The initial mass of the test metal plate is relatively sensitive to the human factor associated with the pre-treatment of the material. The test consisted of assessing the change in mass rather than accurately and precisely determining it against a standard value. Due to this, the main uncertainty component affecting the accuracy of the obtained results was the precision of the measuring instrument. The study used an analytical balance calibrated in the measurement range from 0.01 g to 200 g, for which the indication error at a load of 0.01 g was $9.2 \cdot 10^{-6}$ g. The measurement uncertainty associated with the instrument was, therefore, at least two orders of magnitude lower than the results obtained.

Based on the small number of results obtained from preliminary experiments, the type of statistical distribution they are subjected to cannot be clearly established. Therefore, estimating the uncertainty associated with the research process was impossible at this work stage.

Macro- and microphotography of the copper plate before the test was shown in Figure 1.

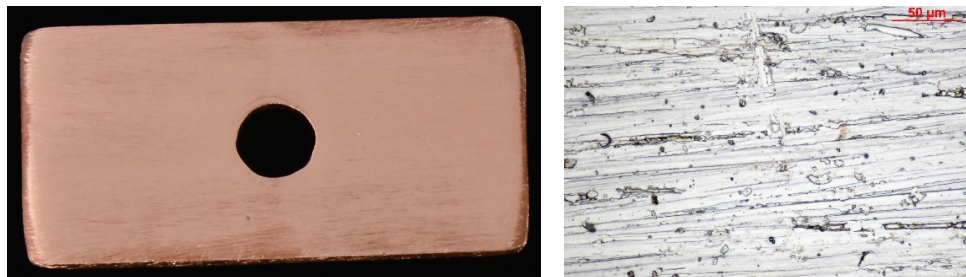


Fig. 1. Plate before the test; on the left- macro photography - copper plate; on the right – microphotography - copper plate, BF technique, 10x50 BF

4.1.1. Macroscopic assessment of plates after testing



Fig. 2. Macrophotography of plates – on the left - copper plate tested in the original liquid (sample 1), in the middle, the plate tested in sample 3, on the right, the plate tested in sample 2.

Points and scratches on plates visible in Figure 2 plates were not treated as corrosion changes.

No morphology changes were observed on the copper plate tested in the original fluid (sample 1). The plate shows a light tarnish and change in colour to orange.

Tarnish and uneven discoloration of the surface (orange) was observed on the copper plate tested in liquid 2.

Surface tarnish and even discoloration (dark orange) were observed in cavities on the surface created by the machining of the plate, as well as a grey tarnish was observed on the plate tested in liquid 3.

4.1.2. Microscopic evaluation of plates after testing

Microscopic test results were presented for copper plates subjected to the impact of the original liquid (sample 1), sample 3, i.e. the mixture of the original fluid with water in ratio 3:1 in sample 2, i.e. the mixture of the original fluid with water in ratio 2:1.

The following was found on the surface of the plates:

Original fluid (Sample 1)

- The presence of numerous objects, probably flake-shaped precipitates (Fig. 3, a, b, red arrows) and fibre-shaped precipitates (Fig. 3, a, b, Fig. 4b, c black arrows).
- Flake-shaped objects are characterized by high concentration of sodium (Na), oxygen (O) and nitrogen (Fig. 3, d, e, g).
- Fibre-shaped objects are characterized by high concentration of oxygen (O) and calcium (Ca) (Fig. 3, e, f).
- For flake-shaped objects, MaxFeret $< 50 \mu\text{m}$, and for fibre-shaped objects, the width (diameter) of fibres amounts to $< 1 \mu\text{m}$.
- Precipitates occur in high density in cavities on the plate surface (Fig. 3 c).

Sample 2

- Sparse yellow-brown (black area) discolouration, tarnish-like (Fig. 4 g).
- In Fig. 4 h, and it is observed additionally, point blue spots (MaxFeret $< 10 \mu\text{m}$) are visible.

Sample 3

- Sparse yellow-brown discolouration (red and black arrows), looking like tarnish (Fig. 4 d, e).
- In Fig. 4e, there are numerous, very fine (MaxFeret $< 1 \mu\text{m}$) point spots (yellow area).
- In Fig. 4f, it was demonstrated that the observed spots can be the source of deeper changes on the surface (black and red arrows).

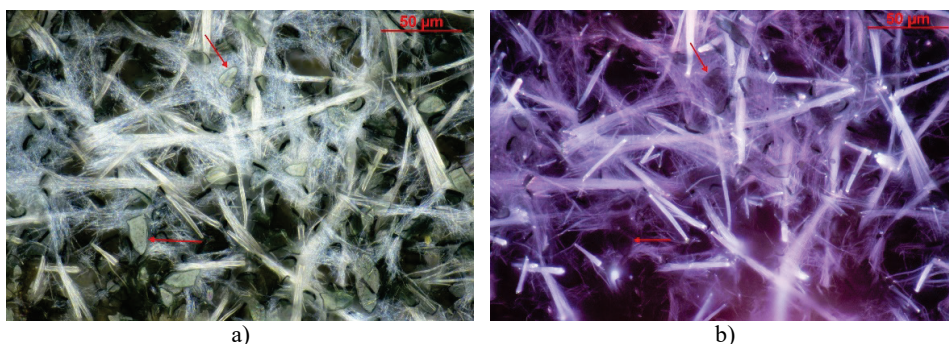


Fig. 3. The plate examined in the original fluid - sample 1 - red arrows indicate flaky structure: a) LOM 10x50 BF, b) 10x50 FLUO A

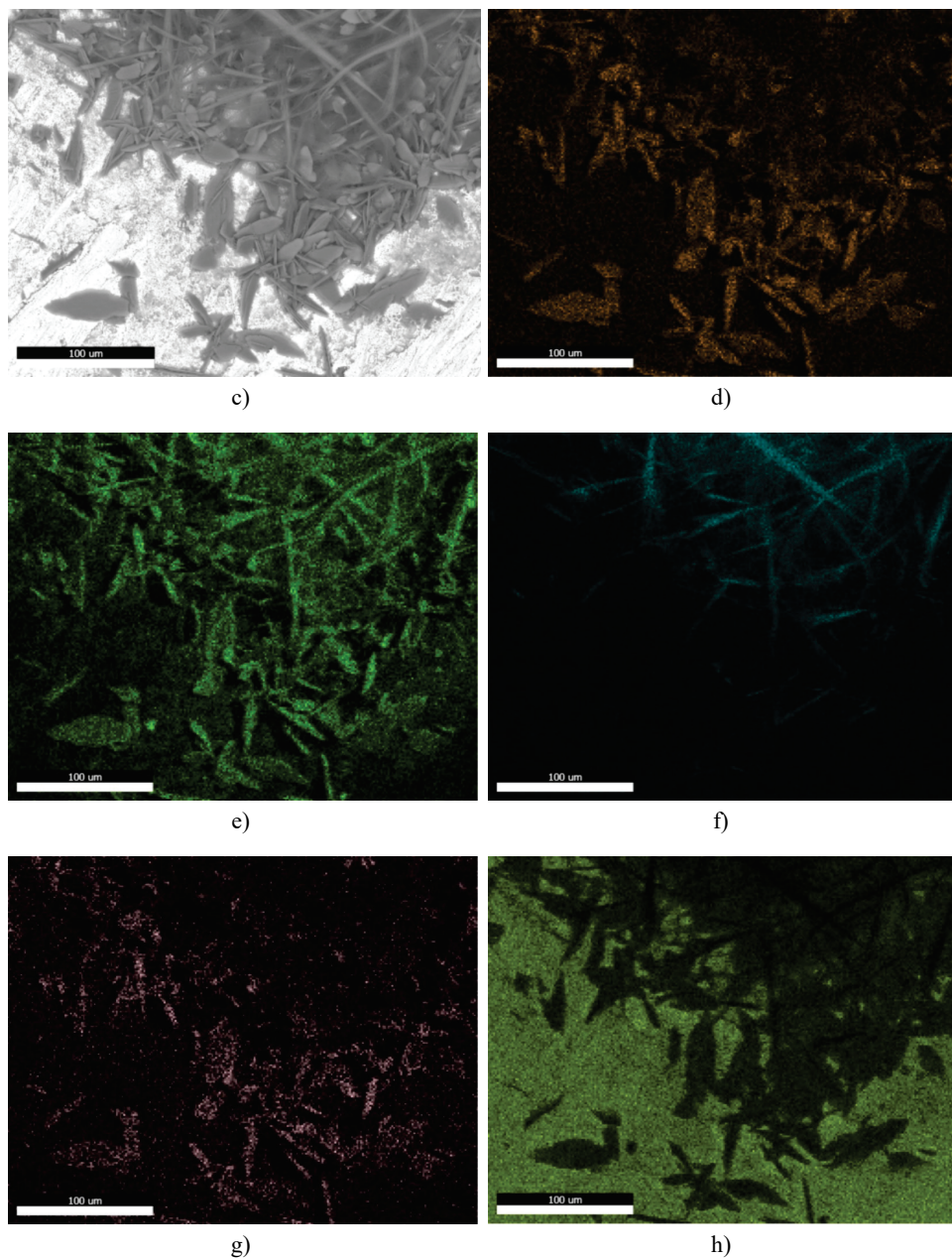


Fig. 3. cont. The plate examined in the original fluid - sample 1 - red arrows indicate flaky structure:
c) SEM, d) SEM – Na, e) SEM – O, f) SEM – Ca, g) SEM – N, h) SEM – Cu

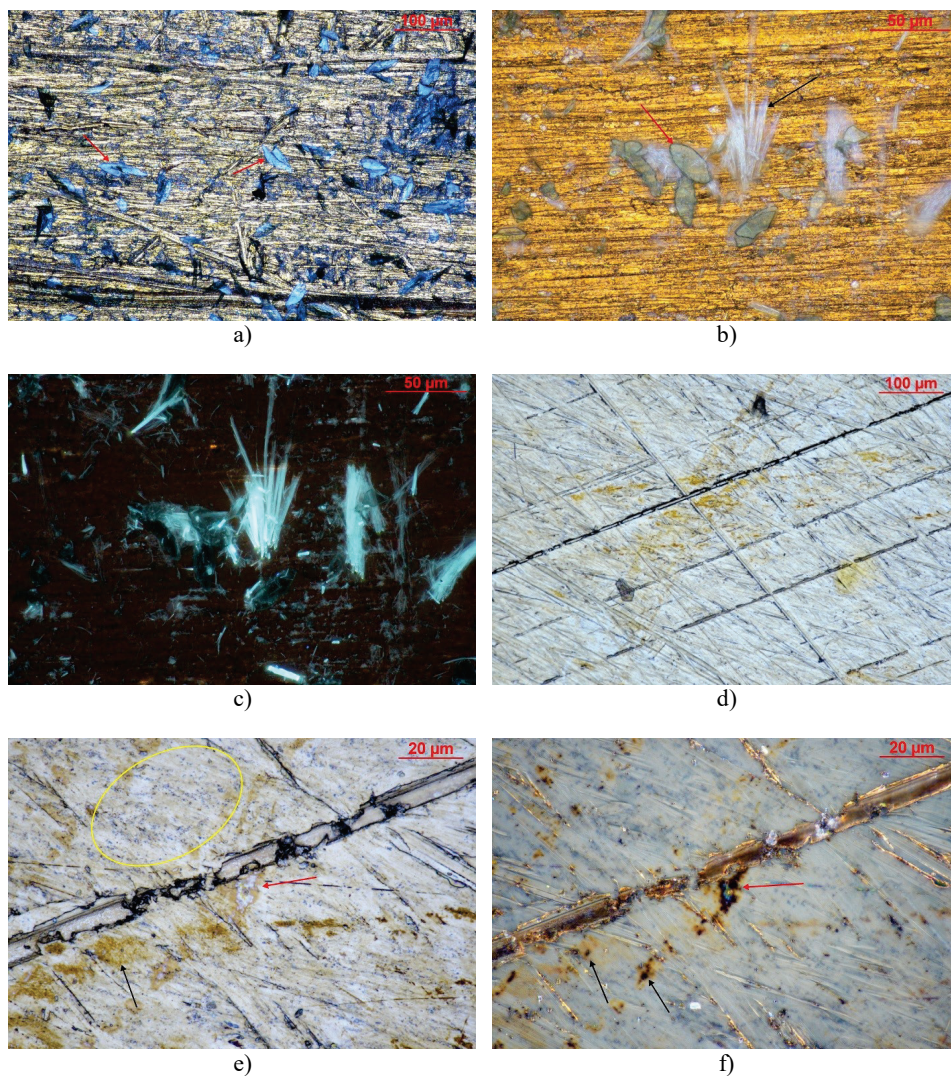


Fig. 4. Copper plates: a) plate tested in the original fluid, BF 10x20 – red arrows indicate a flaky structure, b) plate tested in the original fluid, BF, 10x50 red arrows indicate a flaky structure, black arrows indicate a fibre structure, c) plate tested in the original fluid, FLUO A, 10x50, d) plate tested in sample 3, BF, 10x20, e) plate tested in sample 3, BF, 10x100 – area covered with very fine, point spots marked in yellow, red and black arrows indicate bigger discoloration, f) plate tested in sample 3, POL, 10x100 – red and black arrows indicate potential sources of deeper changes on the surface

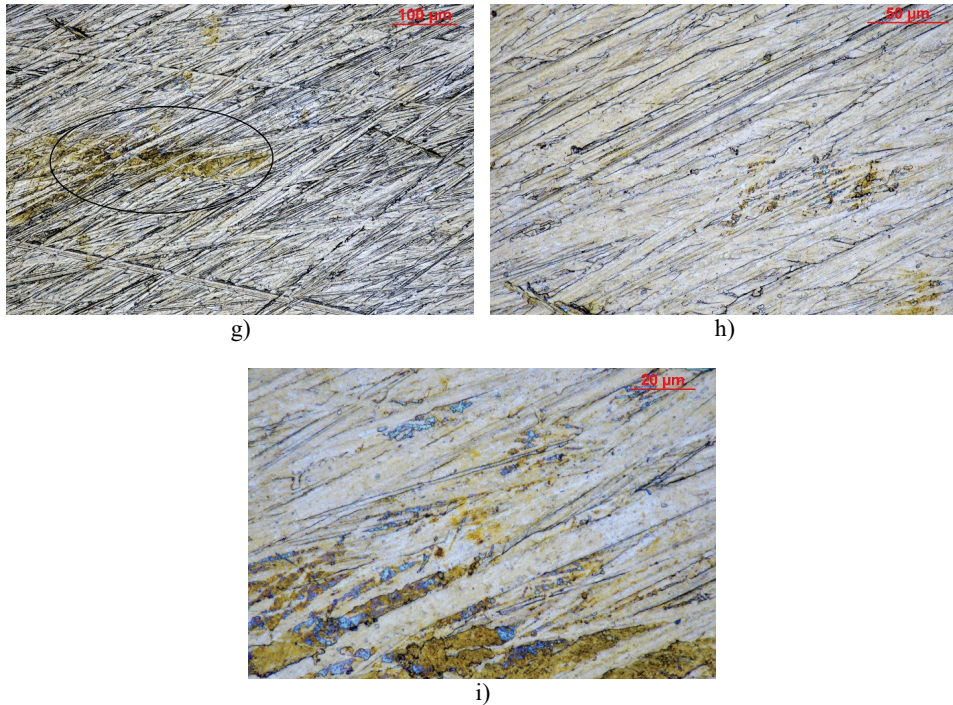


Fig. 4. cont. Copper plates: g) plate tested in sample 2, BF, 10x20 – black area indicates tarnish-like h) plate tested in sample 2, BF, 10x50, i) plate tested in sample 2, BF, 10x100

5. Discussion of results

The objective of the manuscript was to verify changes on the copper surface under the influence of antifreeze with different concentrations. The variation in changes on the test plates provided the basis for assessing whether increasing the dilution of glycol-based antifreeze concentrates above the degree recommended by the manufacturers could exacerbate the corrosion phenomena occurring on the copper structural components of the infrastructural heat exchange systems. The excessive dilution of antifreeze concentrate leads to reduced concentration of improvers, including corrosion inhibitors. The essence of the conducted test was to verify the thesis that excessive dilution of antifreeze leads to an increase in the negative effects on copper elements of infrastructure heat exchange systems.

Samples based on propylene glycol were prepared and tested. One of the testing samples was the original fluid ready for use in the combustion engine cooling system. The original antifreeze used in the experiment contained a mixed package of additives, i.e. both organic and inorganic additives, including silicates. Two remaining samples were prepared

by diluting the original fluid with distilled water. In this way, samples were obtained at three different concentrations of glycol in water and additives, respectively.

The object of analysis was copper plates embedded in the structure of the electrochemical cell. Copper is the most common structural material in heat exchange systems, often in direct contact with the working medium. Thus, this material type was the focus of this study. In addition to copper, the cell included two other types of metal, steel and aluminium, both of which have a higher electrochemical activity (lower standard potential) than copper. Plates made of metals with higher electrochemical activity functioned as an anode - negative electrode on which oxidation processes took place. As a result of these processes, metal from the anode can pass into the solution in the form of ions, thus releasing electrons. The copper plate acted as a positively charged cathode, inducing reduction processes. It is impossible to analyse individual cathodic processes when using such a chemically complex electrolyte as the antifreeze with an incompletely identified composition. However, these processes produced some observable effects on the surface of the copper cathode.

Building upon the gravimetric analysis, it was demonstrated that the greatest change in the mass of the copper plate was after testing in the original fluid (with the highest concentration of glycol and additives) and was gradually decreased parallel with the increasing dilution rate. However, the recorded weight decrement of the copper plates tested in the original fluid and the diluted samples were at least an order of magnitude smaller than the weight changes defining corrosion according to the adopted criteria. With small differences in masses, an attempt to compare them could lead to conclusions subject to significant error due to the measurement uncertainty. It was therefore considered that based on the conducted gravimetric analyses and the assumed assessment criteria, it is impossible to conclusively state that changes in the form of general corrosion had occurred due to the performed test. Moreover, based solely on the gravimetric assessment, it is impossible to conclude that no corrosion changes occurred due to the conducted testing process.

Macroscopic optical methods were applied to observe surface effects, such as changes in colour, tarnish, and bigger corrosion pits a minimum diameter above 0.1 mm. The visual macroscopic assessment noted that impact of original fluids and their dilutions on copper plates resulted in a slight tarnish of plate surfaces and a change in their colour to a more intense orange. However, the macroscopic observation did not allow for clear differentiation of colour changes depending on fluid concentration. To a limited degree, it enabled us to distinguish slight differences in colour or saturation rate of colour. The change in colour with a more intense saturation was observed in the case of the plate tested in the original fluid. The copper plate tested in the diluted fluid was characterized by a less intense colour than the plate tested in the original fluid with a higher concentration of glycol.

The colour of copper changes due to oxidation. Energy differences between valence shells of copper - fully filled 3d shell and partially filled 4s shell, correspond to the energy

of orange light. Copper does not react with water, but in air, it becomes covered with a thin layer of copper (II) oxide, due to which it darkens and takes on a red to reddish-brown colour. The produced oxide layer prevents further copper oxidation. Copper in the 1st and 2nd oxidation state forms a wide range of colourful compounds in the form of salts.

Bigger surface changes can be identified solely with optical macroscopic methods. Substantial changes between plates tested in a diluted and the original fluid were best visible during microscopic observation. Thanks to applying microscopic imaging, it was possible to note smaller effects formed on the surface and distinguish changes in their structure.

Both in bright-field microscopy and fluorescence technique, the copper plate surface tested in the original fluid, the plate of which was fully covered with numerous objects in the form of flake- and fibre-like crystallites. No crystalline forms were observed on the surfaces of tested plated in diluted fluids. The plate surfaces tested in diluted fluids were covered with discontinuous tarnish layers, in which thicker areas are brittle (in morphologic assessment, cracks and chipping of the thicker tarnish layer were found). In the bright field technique, point blue changes were observed on copper plates. Using the polarisation technique, it was captured in the case of plates tested in diluted fluids that these stains could be the source of deeper surface changes.

6. Conclusions

The research presented here aimed to to verify the thesis that increasing the dilution of glycol-based antifreeze concentrates beyond that recommended by the manufacturers increases corrosion on copper. By exacerbating corrosion phenomena, the risk of failure of the entire system increases.

In the structures of heating and cooling systems, where liquid based on glycol is a working medium, elements made of copper find a wide application. Copper components in heating and cooling systems are not isolated units but can contact other metals such as steel or aluminium to form electrochemical cells locally. Therefore, the experimental work was planned so that the copper plate is part of an electrochemical cell developed and constructed for the present study.

Copper is a basic material for constructing infrastructural heat exchange systems, so this manuscript discusses the changes occurring in copper.

The copper study used several methods to identify metal surface corrosion changes. The gravimetric method is commonly used to identify general corrosion made visible in the form of more or less even decrements of the surface layer. According to the adopted criteria, no changes in copper of a general corrosion nature were identified.

Analysis for the presence of corrosion pits was carried out using optical methods: visual macroscopic and microscopic methods. Identification of corrosion pits by visual

macroscopic methods is possible when corrosion pits of significant size are present. Such significant changes were not observed in the test material. The identification of changes occurring on the copper surface as a result of antifreeze liquids with different concentrations of propylene glycol and additives was enabled by the use of microscopic imaging methods. Using microscopic methods, the changes on the copper surface produced by the original fluid containing the mixed additive package and the two diluted samples were differentiated. Through the use of microscopic imaging techniques, it was observed that the formation of a uniform layer covering the copper surface is related to the concentration of the sample. Under the influence of the original fluid, a uniform layer of tarnish has formed on the copper surface, covering uniformly the entire surface of the copper plate. Moreover, deposits with various structures were identified on the copper surface, the elemental composition of which, determined using a scanning electron microscope, made it probable that they were the result of the action of at least one type of anti-corrosion additives contained in the original antifreeze fluid. It can be assumed that the uniform layers covering the surface of the test plate in the original fluid and the point-like deposits represent a form of corrosion protection for copper.

In the diluted samples, the deposit layers were locally present and did not evenly cover the plate surface. No deposit structures were visible on the copper surface treated with diluted fluids. In addition, points have been identified on the surface of copper tested in diluted fluids that may represent the source of deeper surface alteration. Microscopic observation of the material tested in diluted liquids therefore leads to the conclusion that diluting them to a higher degree than recommended by the manufacturers results in incomplete protection of the copper surface and may be the cause of exacerbating the negative effects on the structural components of infrastructural heat exchange systems made of this material.

The use of microscopic imaging to study changes in the copper surface under the influence of various antifreeze is an interesting research direction. The results obtained show that this method can be of particular relevance in the context of identifying micro variations relevant to the long-term operation of heating and cooling systems.

In conclusion, it can be said that the aim of the research has been achieved. The thesis that increasing the dilution of glycol-based antifreeze concentrates beyond that recommended by the manufacturers exacerbates the corrosion phenomena occurring on the copper and consequently increases the risk of failure of the entire system has been confirmed.

7. References

1. M.F. Martinez-Moreno, C. Povedano-Priego and M.L. Merroun, "Impact of compacted bentonite microbial community on the clay mineralogy and copper canister corrosion: a multidisciplinary approach in view of a safe Deep Geological Repository of nuclear wastes," *Journal of Hazardous Materials*, Volume 458, 15 September, 2023.
2. S. Rai and G. Ji, "Corrosion inhibition of copper in NaCl solution by water extract of mint leaves," *Materials today: Proceedings*. Oct. 28, 2023, Available: <https://www.sciencedirect.com/science/article/abs/pii/S2214785323050393>, DOI 10.1016/j.matpr.2023.10.134.
3. H. Zhao, Q. Yue, D. Wang, D. Sun, M. Wu, Y. Pan and S. Yang, "Analysis of heat exchanger corrosion failure in 800,000 light hydrocarbon plant in Liaohe Oilfield," *Engineering Failure Analysis*, Volume 151, September 2023. Available: <https://www.sciencedirect.com/science/article/pii/S1350630723003023?via%3Dihub>, DOI 10.1016/j.engfailanal.2023.107348.
4. M.M. Lachowicz, "A metallographic case study of formicary corrosion in heat exchanger copper tubes," *Engineering Failure Analysis*, Volume 111, April 2020. Available: <https://www.sciencedirect.com/science/article/pii/S1350630720300443>, DOI 10.1016/j.engfailanal.2020.104502.
5. L. Cozzarini, L. Marsich and C. Schmid, "Ant-nest corrosion failure of heat exchangers copper pipes," *Engineering Failure Analysis*, Volume 109, January 2020. Available: <https://www.sciencedirect.com/science/article/pii/S1350630719302985>, DOI 10.1016/j.engfailanal.2020.104387.
6. N. Katagiri, A. Kioka, M. Nonoyama and Y. Hayashi, "Inhibiting flow-accelerated copper corrosion under liquid jet impingement by utilizing nanobubbles," *Surfaces and Interfaces*, Volume 40, August 2023. Available: <https://www.sciencedirect.com/science/article/pii/S2468023023004376>, DOI 10.1016/j.surfin.2023.103067.
7. W. Wang, K. Cheng, B. Wang, M. Zhang and R. Tian, "Sensitivity study of thermal hydraulics to corrosion of heat exchange tubes in steam generator," *Nuclear Engineering and Design*, Volume 402, February 2023. Available: <https://www.sciencedirect.com/science/article/pii/S0029549322004320>, DOI 10.1016/j.nucengdes.2022.112081.
8. N. Mora, E. Cano, E.M. Mora and J.M. Bastidas, "Influence of pH and oxygen on copper corrosion in simulated uterine fluid," *Biomaterials*, Volume 23, Issue 3, February 2002. Available: <https://www.sciencedirect.com/science/article/pii/S0142961201001545?via%3Dihub>, DOI 10.1016/S0142-9612(01)00154-5.

9. T. Wang, Y. Wang, X. Jia and C. Ye, "Corrosion failure analysis of hollow copper coil used in generator internal cooling water system operated at low-oxygen/neutral water chemistry," *Engineering Failure Analysis*, Volume 141, November 2022. Available: <https://www.sciencedirect.com/science/article/pii/S135063072200615X>, DOI 10.1016/j.engfailanal.2022.106642.
10. M.H. Mahmood, Suryanto, Muataz Hazza Faizi Al Hazza, "The Effects of Water Flow Rate on Copper Corrosion," *Key Engineering Materials*, Vol. 748, August 2017. DOI 10.4028/www.scientific.net/KEM.748.235.
11. N. Guo, X. Mao, T. Liu, X. Hui, Z. Guo, B. Tan, K. Shao, X. Feng Li and Z. Zeng, "Corrosion mechanism of copper in seawater containing the bacterial pyomelanin with redox activity," *Corrosion Science*, Volume 204, 1 August 2022. Available: <https://www.sciencedirect.com/science/article/abs/pii/S0010938X22003250>, DOI 10.1016/j.corsci.2022.110407.
12. Z. Chen, W. Dou, S. Chen, Y. Pu and Z. Xu, "Influence of nutrition on Cu corrosion by *Desulfovibrio vulgaris* in anaerobic environment," *Bioelectrochemistry*, Volume 144, April 2022. Available: <https://www.sciencedirect.com/science/article/pii/S1567539421003030>, DOI 10.1016/j.bioelechem.2021.108040.
13. Polish Standard, PN-C-40007:2000 Płyiny niskokrzepnące do układów chłodzenia silników spalinowych – Wymagania i badania.

