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Research paper

Corrosion monitoring as a factor increasing the safety of hydrotechnical infrastructure

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Abstract: Water distribution systems at KGHM S.A. are of great importance for the efficient production of copper and environmental protection. For failures leading to perforation and leakage, the corrosion processes are responsible. This paper aims to assess corrosion on the basis of the analysis of the exposure of the Hydrotechnical Plant pipelines. To this end, the system of transfer and deposition of post-flotation waste as well as the circulation of industrial water in the process of copper ore enrichment are described. Water sources as well as inflows and outflows in the water system are indicated; corrosion hazards are determined. Water is obtained from mines; it is often contaminated during the copper ore mining process. The chemical analysis of industrial (technological) water and sludge water resulting from the sedimentation of post-flotation waste showed a high concentration of inorganic salts which are responsible for the corrosive processes. Furthermore, tests were carried out to determine the corrosion rate. Additionally, possible methods to reduce corrosion have been proposed, i.e., a corrosion monitoring system has been described as a tool for reducing production interruptions and environmental pollution.

Keywords: corrosion monitoring, hydrotechnical infrastructure, industrial (technological) water

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1. Introduction

The tailings storage facility (OUOW) Żelazny Most is one of the largest facilities of this type in the world. It is located in Poland in the Dolnośląskie Voivodeship in the town of Rudna (approx. 100 km from Wrocław), between Głogów and Lubin. OUOW Żelazny Most is a key element of the water and sludge management for KGHM Polska Miedź S.A. It covers an area of over 1,600 hectares, and annually receives about 30 million tons (Mg) of post-flotation waste. Currently, the facility is being expanded with the Southern Quarter, which covers a further 600 ha. In total, after the expansion, the dam will be over 20 km long; currently, it is 14 km. The Żelazny Most facility is the only waste storage site for all mines and Ore Enrichment Plants owned by KGHM Polska Miedź S.A. The Hydrotechnical Plant, also a part of the technological line of KGHM Polska Miedź S.A., is responsible for the maintenance, operation and expansion of Żelazny Most. As of 01/04/2021, almost 1.1 billion tons (Mg) of dry mass of post-flotation waste was deposited, which gives 669 million m^3 of this waste. On the other hand, the water body contains over 5 million m^3 of water, which covers an area of 450 ha with a circumference of 10 km.

Figure 1 shows the Żelazny Most tailings storage facility (OUOW) with the South Quarter which is currently under construction.

Fig. 1. The Żelazny Most tailings storage facility (OUOW) with the South Headquarters under construction – the main building of the Hydrotechnical Department

2. The industrial (technological) water cycle

The extracted copper ore from the mines is directed to the Ore Enrichment Plant, where two products are the results of the enrichment process, i.e. copper concentrate and flotation tailings. The copper concentrate is directed to the KGHM smelters where it is further processed into pure copper and silver. The post-flotation tailings are transported via a pipeline system from the Ore Enrichment Plant to the Żelazny Most tailings pond. Flotation waste is a mixture of water and ground rock. There is 5 m^3 of water per 1 ton of solid waste. Solid waste sediments and remains on the site, and the water flows to the reservoir in the central part of the OUOW. Tower intakes equipped with siphons are used to collect water from the reservoir in the central part of the facility, from which water is supplied to the pumping station through pipelines at the bottom of the OUOW. The pumping stations pump water to the Ore Enrichment Plant in order to reuse it in the process of enriching copper ore. After treatment, the excess water is periodically discharged to the Odra River near Głogów.

Primary water inflows to the water and flotation waste management system are mainly represented by mine waters, which enter the system in the amount of approximately 26.35 million m^3/year. The second primary inflow with a much lower flow rate estimated at about 1.87 million m^3/year are mixed waters, i.e. pre-treated rainwater and process waters from shaft sites, sanitary sewage and water from cooling system renewal. The smallest inflow is the deposit water contained in the processed ore, in the form of moisture. In all mines, the processed ore does not exceed 5% humidity, therefore, with the total processing amounting to 30 million Mg of ore/year, the mass of water supplied in this way does not exceed 1.5 million Mg/year. The last source of inflow is rainwater, the amount of which per year is estimated at approx. 5.6–8.0 million m^3. Besides those mentioned above, there are no other sources of water drainage.

The final outflows from the water management system and post-flotation waste are mainly represented by the amount of technological water discharged into the Odra river of about 18–20 million m^3/year. Another, much smaller outflow is:

a) water remaining as humidity in the deposited waste, up to about 10 million m^3/year,
b) losses by evaporation from the body of water reservoir and infiltration, up to about 12.6 million m^3/year,
c) water discharged to the atmosphere while drying of the final concentrate as steam and as moisture (about 8.5%) of the concentrate supplied to the smelters. Assuming roughly that after the filtration process the moisture content of the concentrate is on average 12.5%, the moisture content of the concentrate supplied to the smelters 8.5%, and the average yield of the concentrate from all enrichment plants is around 6%, the mass of water lost in this way does not exceed about 260 thousand m^3/year [3].

3. Identification of potential causes of pipeline damage

Industrial (technological) water pipelines and flotation waste hydro transport pipelines are very important elements of the technical infrastructure from the point of view of production and safety for the environment and people. Their total length is about 250 km. The industrial water network ensures the supply of water to the treatment process for all three enrichment plants in the amount appropriate to the processing size of the given plant and the discharge of excess water to the Odra River. On the other hand, the hydro-transport network of post-flotation waste ensures the collection of waste from all three enrichment plants and their storage at the Żelazny Most tailings pond. In addition, these networks provide the collection of mine water, treated rainwater and process water and sanitary sewage from all three mines and three enrichment plants.

Failures of pipelines for transporting technological water and pipelines for transporting post-flotation waste were analyzed. The distinguished types of pipelines are characterized by different properties, despite the use of the same materials. Pipelines for transporting water are not subject to intense abrasive wear. The most important cause of failure is corrosion, especially local corrosion of longitudinal seams. These pipelines are covered from the inside with a dense, absorbent, permeable layer of corrosion products. It is extremely difficult to diagnose their condition due to the precipitation and deposition of sediments, the lack of free access and the required availability. Figure 2 shows the corroded section of the longitudinal seam and the circumferential weld connecting the DN 800 water pipelines.

Fig. 2. DN 800 water pipeline – corroded section of the longitudinal seam and butt circumferential weld above

In the case of pipelines for the transport of flotation waste, corrosion is not the dominant destruction mechanism. The main evaluation criterion is the wall thickness, potentially significant is the radius of elastic deformation of the pipeline – susceptibility to wall buckling, coating imperfections leading to local turbulence and faster local wall wear [4].

4. Identification of aggressive corrosive factors of industrial (technological) water

The most important aggressive corrosive factor causing the degradation of technical infrastructure (hydrotechnical infrastructure) is the high chloride content in the process water (currently 39,000 mg/l). These chlorides are found mainly in mine waters (mine dewatering) and are released in the process of copper ore flotation.

On the other hand, on the basis of the studies into salt leaching from the ore extracted in mines carried out by KGHM Cuprum, Research and Development Center, average unit ore leaching rates were determined:

a) Rudna Mining Plant – 0.00689 Mg/Mg of ore,
b) Polkowice – Sieroszowice Mining Plant – 0.00350 Mg/Mg of ore,
c) Lubin Mining Plant – 0.00237 Mg/Mg of ore. It has been calculated that, in total, of the entire mass mined by KGHM Polska Miedź S.A. in the years 2014–2018, about 135.3–145.2 thousand Mg of chlorides per year were leached [2].

Due to the fact that industrial water is highly corrosive water, electrochemical tests were carried out to determine the corrosion rate of steel, and coupon corrosion tests were started, i.e. corrosion coupons of various types of steel were installed in the Hydrotechnical Plant for the purpose of appropriate and optimal selection of construction materials. Additionally, the presented results confirm the legitimacy of building a corrosion monitoring system in technical water installations belonging to the Hydrotechnical Plant. The purpose of corrosion monitoring will be to determine the rate of corrosion of steel in water on-line, which will allow the determination of the real hazard over time and will allow to determine changes in the composition of the water due to various sources. Corrosion monitoring techniques will be reviewed later in this article.

5. Electrochemical tests – laboratory determination of the corrosion rate

Electrochemical tests were performed to determine the corrosion rate of S235JR unalloyed steel in the process water environment from the Hydrotechnical Department (ZH – abbreviation in Polish). The research aimed to determine how the corrosive aggressiveness of water will change in the future, when the concentration of soluble salts will continue to increase. For this purpose, the concentration of the samples of technological water was changed by water evaporation. Comparative dilution water tests were also performed to evaluate what the corrosion rate was in the past when the soluble salt concentration was lower. Table 1 shows the salt concentrations in the tested water samples.

During the course of the experiment, the magnitude of the polarization usually does not exceed 10 mV. The value of the Tafel's coefficients is determined in an independent measurement using the method of extrapolation of Tafel'a curves (the slope coefficient of the anodic and cathode polarization curves in the area where these curves have a rectilinear path in the E vs log I coordinate system), or literature value are accepted.

It follows from basic physical laws that the corrosion rate is inversely proportional to the magnitude of the polarization resistance (5.1).

$$V_{\text{kor}} = k \times \frac{1}{R_p} = k \times \frac{\Delta I}{\Delta E} \tag{5.1}$$

where: k – proportionality coefficient [V·kg·C^{-2}], R_p – polarization resistance [Ω·cm^2], ΔI – polarization current [mA], ΔE – potential [mV].

Table 1. Concentrations of chloride ions in the tested water samples

No.	Description of the water sample	Ion content Cl^- (mg/dm^3)
1	The water sample 3-fold concentrated	111 894
2	The water sample 2-fold concentrated	74 596
3	The water sample 1.5-fold concentrated	55 947
4	The water sample from Hydrotechnical Plant	37 298
5	The water sample diluted 2 times	18 649
6	The water sample diluted 4 times	9 325
7	The water sample diluted 8 times	4 662
8	The water sample diluted 16 times	2 331

The value of the k coefficient can be determined experimentally for a given system as a result of parallel measurements of the corrosion rate using the gravimetric method and measurements of polarization resistances. It can also be calculated using the Tafel's coefficients.

The results of the corrosion rate measurements are shown in Figure 3. The orange diagram shows the corrosive aggressiveness of water mixed with a magnetic stirrer, the blue diagram shows the correlation for a water sample without mixing. The vertical red line corresponds to the concentration of chloride ions in the Żelazny Most reservoir in 2018, while the green one in 2021. The results of the research indicate that currently (in 2021) the corrosion rate of the alloy steel is at the lowest level. The corrosion rate of steel in mixed water is 0.648 mm/year, and 0.372 mm/year in unmixed water. The difference in the corrosion rate results from the partial erosive effect of the water flow, which contributes

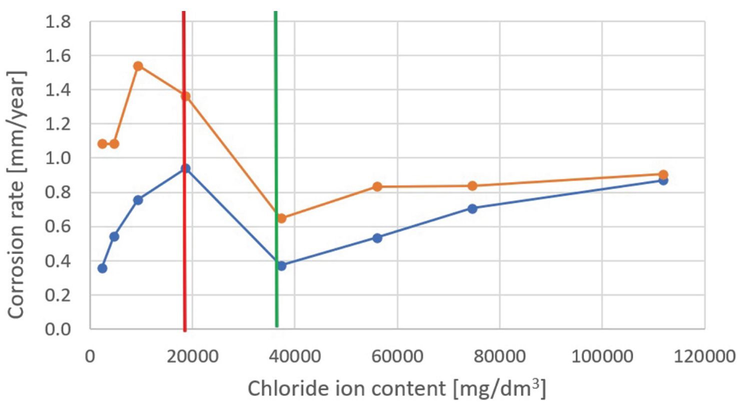

Fig. 3. Diagram of the corrosion rate of unalloyed steel as a function of chloride ions content in water

to the rupture of the layers of corrosion products, increasing the water oxygenation and eliminating the diffusion effects. The corrosion rate decreased twice in comparison to 2018. The reason results from the effect of lowering the oxygen content in water with the increase of corrosion rate, moreover, the difference in the corrosion rate of steel in mixed water as compared to stagnant water related to achieving the solubility of oxygen in water without mixing will decrease.

6. Corrosion monitoring

Corrosion monitoring is the most economical way to apply countermeasures and extend the service life of facilities and equipment, as well as a way to control and protect the environment and human safety. By monitoring corrosion, you can avoid dangerous breakdowns and the high cost of their elimination. The main goals of corrosion monitoring are as follows:

1. Determining the corrosion rate of metallic construction materials both temporarily and as an average value over an extended period of time. On the basis of the conducted research, it is possible to determine:
   – time of safe operation of equipment, pipelines and apparatuses as well as repair periods, definition of an inspection and maintenance plan,
   – corrosion hazards related to the corrosive properties of the streams,
   – information on disturbances in technological parameters due to corrosion.
2. Selection of methods and conditions of corrosion protection.
3. Testing the effectiveness of corrosion protection based on the following methods:
   – assessment of inhibitory protection, analysis of the amount of inhibitor dose,
   – cathodic protection assessment,
   – testing of organic protective coatings.
4. Selection of construction materials, enabling the selection of materials, taking into account corrosion resistance and economic calculation.

The role of monitoring is to test and determine the rate of atmospheric corrosion and the rate of corrosion in various types of industrial and municipal installations, chemically aggressive media and biological environments.

Monitoring mainly covers critical places which are most at risk of corrosion or are of key importance for the efficient and safe functioning of the device. Safe operation is understood as the possible complete elimination of risk to people and the environment. The key element in monitoring systems is placing coupons or measurement probes in selected, representative places of the installation. The site is selected on the basis of an analysis of the structure and technological process, taking into account the following elements:

– particularly vulnerable places (kinks, elbows, clarifiers),
– type of corrosion contamination,
– availability and the ability to monitor technological parameters [7].

Continuous corrosion monitoring in industrial plants and technical installations with a concentration of aggressive corrosive media is of great importance. Such a significant threat is faced in the Hydrotechnical Plant which is one of the divisions belonging to KGHM Polska Miedź S.A. In this plant, there is a highly aggressive water environment, which intensely affects the corrosion processes of pipelines, fittings, machines, devices as well as steel structures and concrete structures.

7. Corrosion monitoring techniques

Determining the corrosion rate is important for assessing the condition of all types of structures, forecasting their durability and diagnosing the corrosion process. The following methods are used for monitoring:

– non-disturbance – only the own signal is measured, which can be the corrosive potential, electrochemical noise, monitoring with the resistance metric method (ER),
– disturbance – the response of the system to a disturbance with an external signal is measured, this group includes the method of monitoring the impedance spectroscopy (EIS) measurements using the linear polarization method (LPR).

7.1. ER resistance method

The resistance method consists in placing a corrosimetric probe in the corrosive environment, equipped with a sensor made of the metal being the subject of the research. This sensor has specific dimensions (length and diameter). The corrosion rate is calculated on the basis of measurements of changes in the electrical resistance of the sensor due to the corrosion process. The dissolution of the material leads to a decrease in the cross-section of the sensor, related to an increase in the electrical resistance measured by the meter using the formula (7.1):

$$R = \frac{\rho l}{S} \tag{7.1}$$

where: R – measured electrical resistance of the sensor [Ω], ρ – metal resistivity [Ω m], l – length of the corrosimetric sensor [m], S – cross-sectional area of the corrosimetric sensor [m^2].

The measurement of the corrosion rate consists in testing the electrical resistance of the sensor element placed in the media environment under test. Measurements can be carried out off-line using a corosimeter or on-line methods using automatic corrosion monitoring systems.

7.2. LPR linear polarization method

Corrosion monitoring using the linear polarization method (LPR) is based on the assumption that if there is an equilibrium between the cathode and the anode processes near the corrosion potential, then there is a linear correlation between the current and the potential with low polarization. Under such conditions, the corrosion rate is determined using the Stern and Geary equation (7.2), [9]:

$$i_{\text{kor}} = \frac{b_a \times b_k}{2.3\,(b_a + b_k)\,R_p} \tag{7.2}$$

where: i_{kor} – corrosion current density [A/cm^2], b_a, b_k – anodic and cathodic Tafel'a coefficients [V], R_p – polarization resistance [Ω·cm^2].

The corrosion rate is determined on the basis of the knowledge of the corrosion current based on Faradays law (7.3):

$$V_{\text{kor}} = \frac{0.13 I_{\text{kor}(E.W.)}}{d} \tag{7.3}$$

where: d – density of the tested material [g/cm^3], $(E.W.)$ – gram equivalent [g].

The intensity of the current is entered in the unit [μA/cm^2]. The polarization resistance is defined as the quotient of the potential and the current flowing in the circuit due to the polarization.

Due to the specificity of the measurement technique, its implementation requires an electrolytic environment characterized by a specific ionic conductivity. As in the case of the ER method, it is possible to perform measurements periodically with the use of corrosimeters or with the use of automatic systems.

The advantage of the linear polarization method is its non-destructive nature and short measurement time. There is a possibility of online monitoring of very low corrosion rate values, elusive with the methods presented so far. The main disadvantage of this method is that it can only be used in electrolytic environments and that there is a need to ensure high measurement accuracy, low current and potential values. Difficulties in the implementation of measurements can also be noticed in the case of unstable systems [1, 5, 6].

7.3. Coupon method for corrosion monitoring

In cases where it is not possible to carry out monitoring based on the ER resistance technique or linear LPR polarization, or where a detailed determination of the corrosion rate is required in order to establish the preconditions for the implementation of the above-mentioned monitoring methods, it is proposed to use the coupon corrosion technique. Coupon testing is also the most appropriate form of testing susceptibility to local corrosion and hydrogen ingress. Coupon corrosimetry consists in the exposure of metal samples, the corrosion resistance of which is the subject of the monitoring system, under real conditions and periodic inspection. Due to the nature of monitoring, it is a technique that allows the most accurate assessment of the real corrosion risk, the rate of uniform corrosion and the susceptibility of materials to local corrosion. Its main disadvantage is the inability to detect rapid changes in the corrosion process and the lack of automation. Therefore, Coupon corrosimetry is used as an adjunct to other forms of corrosion monitoring.

7.4. Physicochemical tests of water environments

Corrosion monitoring is supplemented by physicochemical measurements of aquatic environments. Corrosive processes in water environments depend on their chemical composition and physical properties. Significant factors influencing the intensity of the corrosion process are:

- **Conductivity of water.** Conductivity of water depends on the content of organic compounds soluble in it. Changes in water conductivity may be a derivative of the ongoing technological processes (washing, absorption, dosing corrosion inhibitors). It is possible to monitor the side effects associated with the change in the water composition as a result of the ongoing technological process. Conductivity measurements of water can be used to determine the cause of changes in the corrosive aggressiveness of water.
- **Oxygen content.** Oxygen dissolved in water is a depolarizer. In general, as the oxygen content increases, the corrosion rate may increase. Monitoring the oxygen content can be a method of assessing the tightness of the installation.
- **pH measurement.** The pH value indicates the mechanism of the corrosion process taking place. In the case of a pH lower than 4, processes based on hydrogen depolarization take place. The speed of the corrosion process is a function of the pH of the water. In the case of a water pH higher than 4, the corrosive processes occur on the basis of oxygen depolarization.
- **Temperature measurement.** Water temperature affects the speed of corrosive processes and the solubility of chemical compounds and gases. It allows the assessment of changes in the properties of individual water parameters.

7.5. Automatic corrosion monitoring systems

The computer corrosion monitoring system consists of the following components:

- Corrosion sensors – enabling the measurement of corrosion monitoring by LPR and ER methods.
- Physicochemical sensors – enabling the measurement of conductivity, water temperature and pH.
- Signal conditioning system – also known as a measurement module, enabling the change of a current signal to a voltage one and control of the measurement procedure for individual sensors.
- Software installed in the measuring computer – performing the measurements of the corrosion rate and the data transmission system.

8. Coupon corrosimetry in the Hydrotechnical Plant

Due to the difficult and unusual operating conditions of the technical (hydrotechnical) infrastructure, corrosion coupons made of various steels were installed on the premises of the Hydrotechnical Plant. Twenty-four exhibition locations were established at the facilities and technical infrastructure belonging to the Hydrotechnical Plant. It was decided that the coupons should be exposed to water, flotation tailings and air. Single steel coupons: 1.4301, 1.4462, 1.4404, 1.4307, 1.4571 and S235JR were installed in January 2021. In May 2021, single steel coupons were installed: 1.4410, 1.4539, Inconel 600 (Alloy 600) and double coupons, tightly adjoining (bolted) steel: 1.4539, Inconel 600, 1.4410, 1.4301, 1.4462, 1.4307, 1.4404 in order to investigate the occurrence of crevice corrosion. In addition, single corrosion coupons with a zinc metallization coating were installed, applied to the metal substrate using the spray metallization method. The minimum layer thickness is 150 µm. Figure 4a shows the exposure of corrosion coupons installed in the Żelazny Most tailings pond (western dam) – exposure in post-flotation tailings and exposure in the air. On the other hand, Figure 4b shows the corrosion coupon made of S235JR steel after four months of exposure to air. The place of exposure was the filtration water tank of the Tarnówek pumping station The aim of the study is to answer the question of how the selected types of steel behave in the conditions of the Hydrotechnical Plant, and ultimately the appropriate and optimal selection of construction materials.

(a)

(b)

Fig. 4. Exposure of corrosion coupons: a) corrosion coupons, various types of steel – exposure in air and in post-flotation tailings – OUOW Żelazny Most, Western Dam, b) corrosion coupon made of S235JR steel after four months of exposure to air – filtration water reservoir, Tarnówek pumping station

9. Summary

Modern measurement techniques allow corrosion monitoring at KGHM Polska Miedź S.A. Department of Hydrotechnical Plant. Continuous testing of the corrosive aggressiveness of industrial water along with the analysis of its physicochemical properties will enable a comprehensive determination of the corrosion risks associated with its impact on the technical (technological) installations operated, e.g. industrial water and hydro transport of post-flotation waste. The use of monitoring systems for water systems and monitoring of technical (technological) installations will contribute to the improvement of the repair management and maintenance process, which may reduce the cost of repairs and operating costs and will contribute to reducing the failure rate of installations, fittings, equipment machines and steel structures and concrete structure. All the described activities related to the protection against corrosion will reduce the number of failures and reduce the risk of their occurrence, which will significantly increase the safety of technical (hydrotechnical) infrastructure related to its operation – the safety of employees and the natural environment.

Thanks to the use of optimal methods of managing corrosion problems, it is possible to reduce the annual corrosion cost level from 25% to 30% [8].

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Monitorowanie korozji jako czynnik zwiększający bezpieczeństwo infrastruktury hydrotechnicznej

Słowa kluczowe: monitorowanie korozji, infrastruktura hydrotechniczna, woda przemysłowa (technologiczna)

Streszczenie:

Systemy dystrybucji wody w KGHM S.A. mają duże znaczenie dla efektywnej produkcji miedzi i ochrony środowiska. Procesy korozyjne są odpowiedzialne za wiele awarii prowadzących do perforacji i wycieków. Ocena korozji oparta jest na ocenie ekspozycji rurociągów należących do Zakładu Hydrotechnicznego. Opisano system przesyłania i deponowania odpadów poflotacyjnych oraz obieg wody przemysłowej w procesie wzbogacania rud miedzi. Wskazano źródła wody oraz dopływy i odpływy w systemie wodnym. Określono zagrożenia korozyjne. Woda jest pozyskiwana z kopalń i często jest zanieczyszczana podczas procesu wydobycia rudy miedzi. Analiza chemiczna wody przemysłowej (technologicznej) i wody nadosadowej powstałej w wyniku sedymentacji odpadów poflotacyjnych wykazała wysokie stężenie soli nieorganicznych, które są odpowiedzialne za procesy korozyjne. Wykonano badania elektrochemiczne polegające na wyznaczeniu szybkości korozji stali niestopowej typu S235JR w środowisku wody technologicznej z Zakładu Hydrotechnicznego. Dodatkowo opisano techniki monitorowania korozji tj. metodę rezystometryczną ER, metodę polaryzacji liniowej LPR, metodę kuponową oraz badania fizykochemiczne środowisk wodnych i automatyczny system monitorowania korozji. Natomiast ze względu na trudne i nietypowe warunki eksploatacji infrastruktury technicznej (hydrotechnicznej) zamontowano na terenie Zakładu Hydrotechnicznego kupony korozyjne wykonane z różnych stali oraz stopów niklu. Ustalono dwadzieścia cztery miejsca ekspozycji na obiektach i infrastrukturze technicznej należącej do Zakładu Hydrotechnicznego. Zdecydowano się na ekspozycję w wodzie przemysłowej, odpadach poflotacyjnych i powietrzu. Celem badania jest uzyskanie odpowiedzi na pytanie, jak wybrane rodzaje stali zachowują się w warunkach Zakładu Hydrotechnicznego, a ostatecznie odpowiedni i optymalny dobór materiałów konstrukcyjnych. Dotychczasowe działania, obserwacje i badania potwierdzają zasadność budowy systemu monitorowania korozji w wodnych instalacjach technicznych należących do Zakładu Hydrotechnicznego. Ciągłe badanie agresywności korozyjnej wody przemysłowej wraz z analizą jej właściwości fizykochemicznych pozwoli na kompleksowe określenie zagrożeń korozyjnych związanych z jej wpływem na eksploatowane instalacje techniczne (technologiczne) np. wody przemysłowej, hydrotransportu odpadów poflotacyjnych. Ponadto dzięki zastosowaniu optymalnych sposobów zarządzania problemami korozyjnymi, możliwie jest obniżenie rocznego poziomu kosztów korozji od 25% do 30%.

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