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Properties of the aggressiveness of geothermal and marine water and their negative impact on hydromechanical fittings

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Abstract

This article concerns the issue of the long-term operation of hydromechanical fittings during their contact with aggressive water. The aim of this analysis was to investigate the significance of the quality of water during the operation of wind power farms and geothermal power stations, especially hydromechanical fittings during long-term operation at the base of the Baltic Sea and geothermal power stations. This article presents the properties of water and their impact on hydromechanical equipment during long-term operation in marine and geothermal waters. The paper includes the analysis and evaluation of their impact. Additionally, the article describes important problems with the operation of wind power farms and geothermal power stations. The results of periodical analyses of southern Baltic marine water and thermal groundwater from "Geotermia Podhalańska" were evaluated and used as the basis for future research. Every negative parameter of water, known as its aggressiveness, adversely affects the basic materials of wind masts and pipelines, as well as the hydromechanical equipment in contact with marine and thermal water. The presented results show the necessity of controlling the water quality prior to the operation of geothermal water and building wind power masts in coastal marine water. Attention was paid to corrosion during contact with aggressive water with unprotected materials. This issue is rarely seen in the literature but is very important.

Introduction

Water aggressiveness, also known as corrosiveness, is a characteristic resulting from its chemical composition. In general, it damages rocks, concrete, metal structures, and control equipment that are in direct and prolonged contact with water. Water aggressiveness causes irreversible damage such as the loss of basic materials. Therefore, in view of the necessity to immerse or wash the surfaces of hydromechanical equipment, which can be subject to intense corrosion and leaching, the water quality should be monitored. The second aspect is the need to provide chemical or mechanical protection and select appropriate homogeneous or mixed materials that are resistant to corrosion. This issue is presented using the example of the Polish Economic Zone of the Southern Baltic Sea and the Podhale Geothermal Park. The article draws attention to the quality of the geothermal waters from underground intakes, as well as marine waters using the example of the Polish Economic Zone of the Baltic Sea. The evaluated quality parameters of geothermal waters did not differ significantly from those of marine water, except for the temperature. Basically, the difference consists in the occurrence of fluctuations of the parameter values in marine waters, whereas in groundwater from a particular intake, those parameters can be regarded as stable.

The available literature and Internet resources do not link the aggressiveness of geothermal and marine waters to the corrosion of hydromechanical fittings, despite clear links between the phenomena. Publications only consider the occurrence of different kinds of corrosion as the effect of electrochemical phenomena, and the causes are presented in a simplified way.

Materials and methods

The main objective of this article was to demonstrate the existence of aggressive characteristics in marine and geothermal waters and how they affect hydromechanical fittings when in direct contact with them. This goal was realized in several stages in the paper.

1. A review of the available specialist literature, legal acts, and standards connected with the subject of the research was carried out. This provided the basis for finding the physical and chemical phenomena occurring in marine and geothermal waters. The principles of design and operation of wind power masts and geothermal water intakes were analyzed.
2. A detailed analysis of archival documentation was performed, concerning changes in the water environment in the Southern Baltic Sea and representative geothermal water intakes in Poland. The review enabled us to conclude that there are issues with the operation of hydromechanical devices in permanent contact with water.
3. The studies on the predicted effects resulting from the aggressiveness of the marine water of the Baltic Sea and data from the current operation of geothermal intakes were analyzed. Due to the predicted and confirmed material damages, monitoring the water quality parameters and controlling the quality status of the surfaces exposed to aggressive factors, i.e., corrosion and erosion, were considered important. The author made trips to wind farm sites in the south-western Baltic Sea (near Wolin Island), as well as geothermal energy sites in Bańska Niżna (southern Poland) and Iceland (Hellisheidi power plant).
4. The above-mentioned stages allowed conclusions to be drawn from the conducted research and to outline the directions for follow-up studies.

Theoretical basis for studying the surface and groundwater quality parameters in terms of aggressiveness

Objects that are wetted or permanently immersed in water show surface and internal changes after a certain period of direct contact. The observed changes are caused by the formation of corrosion micro-cells. Water containing dissolved and suspended compounds acts as an electrolyte (Łaskawiec, 2000; Blicharski, 2009). Several types of water aggressiveness can occur in the analyzed cases. Alkaline aggressiveness takes place when water contains less than 90 mg $CaCO_3/dm^3$. The second type is carbonate aggressiveness, which occurs when the water contains more than 4 mg CO_2/dm^3. In turn, magnesium aggressiveness occurs if the water quality analysis shows a magnesium ion concentration of more than 1000 mg Mg^{2+}/dm^3. A sulfate ion content exceeding 250 mg SO_4^{2-}/dm^3 is also considered corrosive. Ammonium aggressiveness, which occurs when the concentration of $N\text{-}NH_4/dm^3$ ions is greater than 15 mg, is another type of water aggressiveness. Water with a pH less than 7.0 and chloride content exceeding 1000 mg/dm^3 is also characterized as aggressive (Dowgiałło et al., 2002). In addition, the presence of dissolved hydrogen sulfide in water threatens the equipment and structures in contact with it. The concentration of gaseous oxygen dissolved in water is also significant, especially in relation to the elements of hydromechanical equipment made of cast iron (Łaskawiec, 2000).

The samples of marine water were taken at permanent monitoring points of the South Baltic Sea's water quality (Figure 1). The samples of geothermal waters were collected from the outflow in the IG-1 research well of the Polish Academy of Sciences and also from the PGP-2 and PGP-3 wells of Geotermia Podhalańska in Bańska Niżna. The analyses were carried out in authorized laboratories, and each water characteristic was analyzed according to the EU procedures. Due to the specificity of the water environment, different numbers of samples were taken to study the quality parameters. Marine water is characterized by highly variable parameters due to the seasonality of phenomena; hence, the frequency of sampling was 24 times a day. Underground thermal water environments, especially those from deep wells, i.e., lower than 3000 m below ground level (bgl), exhibit stable parameters formed over millions of years. In the beginning, immediately after drilling the IG-1, PGP-2, and PGP-3 wells, a full analysis of the water quality was carried out. In the following

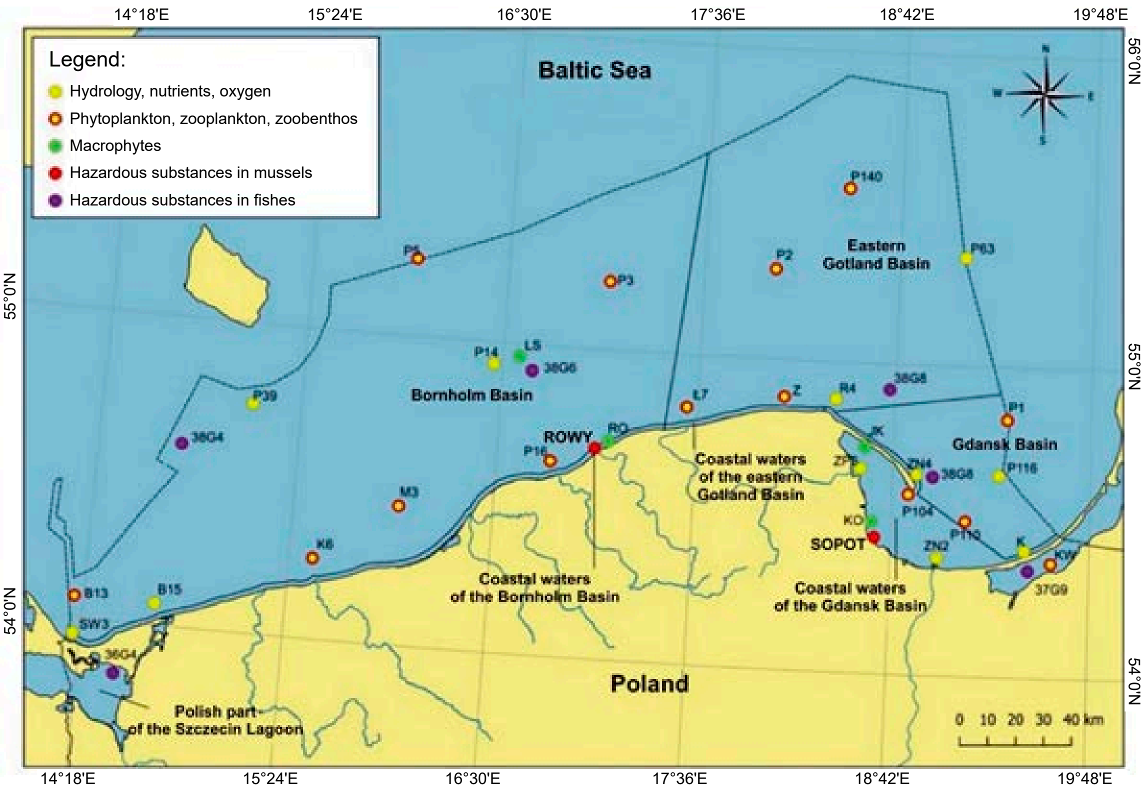

Figure 1. Distribution of Baltic Sea water quality monitoring points in the Polish coastal zone (Bakierowska, Wojtaszek & Kopiec, 2020)

years, only the main quality parameters were examined, excluding those at the detection limit. The full analysis was repeated before the decision was made to drill a deeper hole, reaching approximately 5300 m bgl (to be drilled in the near future) (GP documentation, 2006; 2018; 2020).

Characteristics of the marine water quality of the South Baltic in terms of its negative impact on materials

On the basis of the existing national and European Union legal acts, especially those relating to the water quality of the Baltic Sea, 11 indicator parameters were determined. Not all are related to water aggressiveness; however, fluctuations in their values may indicate that changes were caused by the interference in the marine water due to natural or anthropogenic reasons. Attention should be paid to these changes and whether they stem from natural seasonal phenomena. The indicators of the environmental state of the Baltic waters are: D1 – Biodiversity, D2 – Alien species, D3 – Commercially exploited fish and shellfish, D4 – Trophic chain, D5 – Eutrophication, D6 – Seabed integrity, D7 – Changes in hydrographic conditions, D8 – Pollutants, D9 – Pollutants in fish for consumption, D10 – Waste, D11 – Underwater noise (Bolałek & Falkowska, 1999; Bakierowska, Wojtaszek & Kopiec, 2020).

Each listed indicator comprises the parameters that describe the water quality. It would seem that – with regard to aggressiveness – temperature should not be a significant marine water quality parameter. However, it is important since the greater its value, the higher the rate of physicochemical processes and, consequently, the intensity of material corrosion (Surowska, 2002). The average temperatures of the Baltic Sea waters are provided below, according to the report of the Chief Inspectorate of Environmental Protection (Bolałek & Falkowska, 1999). In the surface layer (0–10 m), the average temperatures for the entire coastal zone were: 3.2 – 20.8°C in the Bornholm Basin; 3.2 – 19.8°C in the eastern zone of the Gotland Basin; 3.8 – 20.3°C in the Gdańsk Basin (Wieteska & Szymańska, 2017; Bakierowska, Wojtaszek & Kopiec, 2020).

In the vertical profile, fluctuations in temperature decreased as the depth increased, being less dependent on seasonal changes. Shallows and shelf zones, which are more exposed to both natural and anthropogenic processes, may constitute exceptions. Salinity is another relevant parameter, which is the sum of substances dissolved in water, expressed in g/dm^3. This group includes chloride ions, sulfate ions, and ammonium ions, which contribute to water aggressiveness. The near-surface layers comprise dissolved oxygen and carbon dioxide, whereas hydrogen sulfide – connected to the decay of organic matter – is present in the bottom layers (Dowgiałło et al., 2002). Therefore, the location of hydromechanical elements in the vertical profile is important. The salinity of the Baltic Sea in the considered area, according to the averaged data, is as follows: 7.43–7.95 in the Bornholm Basin; 7.37–7.66 in the eastern zone of the Gotland Basin; 7.13–7.57 in the near-surface layers of the Gdańsk Basin; 6.88–7.62 in the coastal waters of the Gdańsk Basin. The highest fluctuations occurred from March to June, whereas the lowest occurred in the second half of the year, i.e., in late autumn and in winter (Wieteska & Szymańska, 2017; Bakierowska, Wojtaszek & Kopiec, 2020). Attention should be drawn to the Bornholm Deep, where salinity values of 16.58–16.88 were observed at the depth of 80 m.

The pH is another studied parameter and is considered the main indicator of marine water pollution. Changes in its value are influenced by natural (geological, hydrodynamic, and climatic/weather) and anthropogenic phenomena, resulting from various human activities (Chałacińska et al., 2014).

In recent years, the pH has been weakly alkaline, with a tendency to decrease slightly (Table 1). Highly alkaline or acidic pH threaten the materials with a low resistance to corrosive conditions.

Table 1. The pH values of Baltic waters according to monitoring measurements conducted in 2018–2019 (Bakierowska, Wojtaszek & Kopiec, 2020)

Area	pH					
	Minimum		Maximum		Mean	
	2018	2019	2018	2019	2018	2019
Gdańsk Basin	7.02	6.88↓	9.22	8.97↓	7.98	7.91↓
Eastern Gotland Basin	7.05	7.04↓	9.27	8.04↓	8.04	7.98↓
Bornholm Basin	7.06	7.04↓	8.99	8.58↓	7.99	7.98↓

Detailed analysis of the monitoring data confirmed that the water layers at the depth of 60–80 m provided the most favorable conditions in terms of the durability of materials from which hydrotechnical regulatory fittings are made.

The presence of dissolved gases constitutes the next group of the studied parameters describing the marine water quality. They may originate both from natural sources and anthropogenic processes. Three gases that are most characteristic of the processes occurring in Baltic waters were selected. They included gaseous oxygen, carbon dioxide, and hydrogen sulfide. The partial pressure describes the presence of oxygen and carbon dioxide. These gases are found both in the water and in the air above its surface. They are the major components of air and dissolve well in water, although the mechanism of their effect on materials in contact with them is different. Because of the solubility characteristics, marine and ocean waters and – to a small extent – standing and flowing inland waters regulate the presence of these gases in the air. If the partial pressure in the water is greater than that in the air, to equalize the pressures, the water releases dissolved gas into the air (WSC Regulation, 2011; 2016). The reverse process also occurs. In 2019, CO_2 measurements were performed in three basins of the Polish economic zone of Baltic waters. The average pCO_2 values from the measurements were as follows: 195–813 µatm in the Bornholm Basin, 119–836 µatm in the Gotland Basin, and 121–913 µatm in the Gdańsk Basin. It is important that during the warm months, the dissolved carbon dioxide content in the water decreased due to the intense metabolic processes of phytoplankton. Its high content lowered the water pH, which was unfavorable for non-resistant materials exposed to corrosion (Kozłowska, 2002).

In surface waters, as in marine waters, the presence of CO_2 is mainly related to the infiltration of atmospheric air into the near-surface layers. The intensity depends on the state of the water surface. When the surface is calm, the process is slow, but waves accelerate infiltration (dissolution). The degradation of organic matter sediments constitutes the second source of CO_2. Their accumulation contributes to elevated concentrations in the bottom zone. During the season characterized by the formation of vertical sea currents, the CO_2 contents may be displaced from the bottom zone towards the surface, which may be the reason for the lower pH of water in these layers: $H_2O + CO_2 \rightarrow H_2CO_3$ (hence the acidic pH value) (Ulfsbo, Hulth & Anderson, 2011; Chałacińska et al., 2014; Świderski, 2015; Wieteska & Szymanska, 2017).

From the point of view of aggressive water properties, the gases present in the South Baltic waters include oxygen and hydrogen sulfide. The oxygen present in the near-surface layers, studied by the classical Winkler method, is derived from atmospheric air. The study confirmed that the oxygen concentration decreases with depth, which is a natural process. Small amounts may move downward during emerging vertical currents and storm surges. This is related to seasonal weather events (Szelangiewicz & Żelazny, 2015). Similarly, decreasing CO_2 and slightly increasing O_2 concentrations have

Table 2. Physicochemical parameters of the South Baltic waters contributing to their aggressiveness

Area	Parameter					
	pH	O_2	H_2S	CO_2	Temperature	Salinity Cl–
Bornholm Basin	7.98	122%	–	195÷813 µatm	3.2÷20.1°C	7.43÷7.8 g/dm^3
Gdańsk Basin	7.91	129%	Not studied –89÷–100 m	121÷913 µatm	3.8÷20.3°C	6.81÷7.3 g/dm^3
Gotland Basin	7.98	127%	–	119÷836 µatm	3.2÷19.6°C	7.39÷7.7 g/dm^3

been observed during the summer months as a result of phytoplankton metabolism. As far as the presence of hydrogen sulfide is concerned, its elevated concentrations in the bottom zone – determined via the iodometric method – were confirmed as a result of the degradation of decomposable organic matter (Behrendt, 2005; Souissi & Triki, 2007; Ulfsbo, Hulth & Anderson, 2011; Wieteska & Szymańska, 2017). Some amounts may have originated from river runoff of municipal wastewater and organic particles washed by heavy rains along the river channels.

It was found that in the waters of the South Baltic, the following quality parameters, presented in Table 2, contributed to the corrosive properties of water: pH, dissolved oxygen, hydrogen sulfide, carbon dioxide, chloride content (expressed as salinity), and temperature.

Aggressiveness of thermal water from underground intakes

The research was based on the data obtained from Przedsiębiorstwo Energetyki Cieplnej Geotermia Podhalańska S.A. Geotermia Podhalańska as the representative, oldest geothermal operator in Poland. It has identified the problems connected with the exploitation of thermal water intakes.

Usually, thermal waters are extracted from deep aquifers, e.g., PAN-1 Biały Dunajec – 2394 m bgl, PGP-2 Biały Dunajec – 2450 m bgl, Bańska PGP-1 – 3242 m bgl, and Bańska IG-1 – 5261 m bgl (Figure 2). In addition to their high temperature, the waters contain many anions and cations, as well as dissolved gases resulting from geodynamic processes. Among the ions, those mentioned in the Introduction are very common. The water from Bańska PGP-3 thermal well contains the following aggressive ions: sulfate SO_4^{2-} – 785.8 mg/dm^3, and chloride Cl^- – 497.9 mg/dm^3. An in-depth physicochemical analysis showed that the concentration of magnesium ions was low, amounting to 42.7 mg Mg^{2+}/dm^3. This precludes the phenomenon of magnesium aggressiveness, which is caused by a concentration

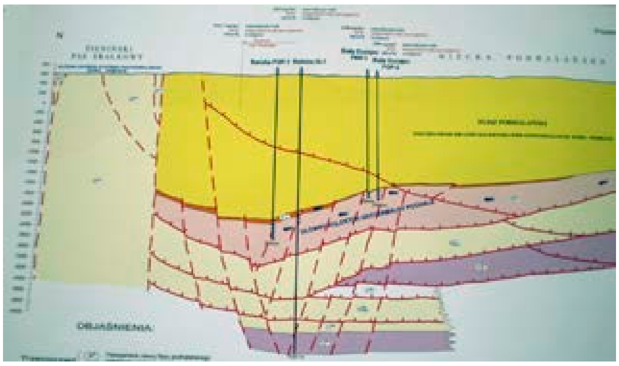

Figure 2. Hydrogeological profile of geothermal structures with indicated exploitation, injection, and research wells of Geotermia Podhalańska (GP Documentation, 2006)

of at least 1000 mg Mg^{2+}/dm^3. Similarly, the content of calcium carbonate reached the minimum values, below 300 mg $CaCO_3$/dm^3. During the research, hydrogen sulfide was also observed in the thermal water, which was perceptible by human smell. The pH was slightly alkaline, which was confirmed by the physicochemical analyses conducted regularly by the services operating the intakes (PGP-3 pH = 7.21 in 2018, pH = 7.6 in 2020) (Kleczkowski, 1984; Ozga-Zielińska & Brzeziński, 1994; GP documentation, 2006; 2018; 2020).

Table 3. Physicochemical parameters of the geothermal water from the Geotermia Podhalańska intakes that contributed to their aggressiveness

Water parameter	Unit	Geothermal well	
		PGP-2	PGP-3
pH	–	7.15	7.6
Temperature	°C	83	85
Electrical conductivity γ_{25}	mS/cm	3.53	3.53
COD_{Mn}	mgO_2/dm^3	0.9	1.1
Mg^{2+}	mg/dm^3	43.4	42.7
Cl^-	mg/dm^3	510.7	493
SO_4^{2-}	mg/dm^3	820.5	971
HCO_3^-	mg/dm^3	291.6	352.9
H_2S	mg/dm^3	0.21	0.23
CO_3^{2-}	mg/dm^3	< 0.5	< 0.5

Figure 3. Corrosion damage of a hydromechanical valve component resulting from geothermal water aggressiveness after 5 years of operation in the PGP-1 well

Analysis of the design and exploitation documentation of geothermal wells showed that in terms of the groundwater used for energy purposes, the following quality parameters contributed to their corrosiveness (aggressiveness): pH, temperature, electrical conductivity, COD, magnesium ions, chloride ions, sulfate ions, bicarbonate ions, carbonate ions, and the presence of dissolved hydrogen sulfide (Table 3).

The collected research material concerning the water quality parameters was confirmed both by the planned dismantling of the control fittings and by the leaks noticed. The first signs of damage already appeared after the first five years of exploitation of the Podhale geothermal waters. The fittings were disassembled, which permitted a visual assessment of the effects of exposure of the material to water aggressiveness (Figure 3). Then, the stability of the quality parameters was evaluated. It was found that in all wells, the water parameters were considered to be stable. The assessment was based on the thorough water analyses carried out by certified laboratories (Hydrogeochemical Laboratory of AGH University of Science and Technology in Cracow and Environmental Laboratory of SGS in Pszczyna) on wells since the beginning of their operation.

Types of damage resulting from the exposure of control fittings to aggressive water during the operation of hydromechanical equipment

The components of hydromechanical fittings, whether directly in contact with marine water or geothermal water, are manufactured using multiple materials. Each homogeneous material, as well as mixed materials, is then exposed to corrosion. The type, intensity, and extent of corrosion and its effects depend on numerous factors. The results of the conducted research showed that significant pitting and surface corrosion (combined with erosion) were found on the dismantled elements (Table 4). The erosion during the water flow caused detachment and lifting of corrosion products, which re-exposed the raw material to water corrosion.

Table 4. Elements exposed to water aggressiveness and types of material damage

Fitting component	Material	Type of damage
Gate valve flange	Ductile Iron	Surface and pitting corrosion combined with erosion
Gate valve body	Ductile iron	Surface and pitting corrosion
Screws	Steel	Surface corrosion
Gaskets	NBR	Chemical corrosion
Gaskets	EPDM	Chemical corrosion
Slider wedges	Ductile cast iron with EPDM coating	Point or linear penetration in single cases; pitting corrosion
Nuts	Steel	Surface corrosion; mechanical corrosion with erosion

In the article, the theoretical issues concerning the water quality parameters, especially those that contribute to the aggressiveness of marine and geothermal water, were juxtaposed with the investigations concerning the effects of exposing the components of hydro-mechanical fittings to their adverse properties. It was found that after several years of intense operation, corrosive cavities appeared on the surfaces of the masts of wind power plants and geothermal heat plants that contacted water. The types of cavities and their size depended on the kind of material and its resistance to external factors. The components of hydromechanical fittings made of ductile iron were subject to surface and pitting corrosion, combined with erosion. Erosion is a result of water movement, i.e., waves in the case of marine water and flow in pipes in the case of geothermal water. The components made of NBR have a low resistance to acidic and alkaline environments, which are found in both types of water. In turn, EPDM exhibited structural punctures, which were likely the result of imperfect surface anti-corrosion coatings, erosion, or the improper selection of materials for the operating conditions of the device. While EPDM is chemically resistant, it degrades and shrinks at low temperatures, which can cause cracking. The surfaces of valve components that are exposed during operation and have not been protected since the beginning of operation are subject to damage, causing failures and adversely affecting the stability of the wind masts. This also affects the safety of operating thermal equipment under high pressures and high temperatures.

Conclusions

Marine and geothermal waters have similar quality parameters, especially those contributing to aggressiveness towards the materials they come in contact with. In the South Baltic waters, the near-surface layers containing dissolved oxygen are the first place where the base of wind turbine masts is exposed. The second is the bottom zone, especially in the deepest parts of the basin, due to the presence of hydrogen sulfide. This requires both constant observation of occurring phenomena and the selection of appropriate materials, as in the presence of dissolved oxygen. Such materials should not only be chemically resistant but also characterized by high strength against mechanical stimuli, which detach the corrosion products from the material and thus expose the surface to further effects of water aggressiveness. Corrosion is also accompanied by erosion, as well as wave action that detaches corrosion products and exposes the raw material to the negative effects of marine water; however, these conditions may change seasonally or as a result of wastewater introduction.

The chemical parameters of marine water, such as pH, the presence of dissolved oxygen, hydrogen sulfide, carbon dioxide, and chlorides, contributing to the salinity effect, are responsible for the corrosion damage to hydromechanical fittings.

The physical parameters of marine water, such as low temperature and wave action, can aggravate the chemical parameters that corrode exposed components.

The chemical parameters of geothermal waters, such as pH, the presence of dissolved hydrogen sulfide, chloride ions, sulfate ions, magnesium ions, carbonate ions, and bicarbonate ions (at appropriate concentrations), contribute to the corrosion of hydromechanical equipment in contact with these waters.

The physical parameters of geothermal waters, such as high temperature and electrical conductivity, may increase the corrosion rate of exposed elements.

It is necessary to continue periodic research on marine and geothermal water quality in the context of the corrosive impact on materials they contact.

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