

Article

Chemical Composition and Corrosion—Contributions to a Sustainable Use of Geothermal Water

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Abstract

The utilization of geothermal resources as renewable energy is a subject of interest for the regions that possess these resources. The exploitation of geothermal energy must consider local geological conditions and an integrated approach, which should include practical studies on the chemistry of geothermal waters and their effect on thermal installations. Geothermal waters from Bihor County, Romania, have a variable composition, depending on the crossed geological layers, but also on pressure and temperature. Obviously, water transport and heat transfer are involved in all applications of geothermal waters. This article aims to characterize certain geothermal waters from the point of view of composition and corrosion if used as a thermal agent. Atomic absorption spectroscopy (AAS) and UV–Vis spectroscopy were employed to analyze water specimens. Chemical composition includes calcite (CaCO_3), chalcedony (SiO_2), goethite ($\text{FeO}(\text{OH})$), and magnetite (Fe_3O_4), which confirms the corrosion and scale potential of these waters. Corrosion resistance of mild carbon steel, commonly used as pipe material, was studied by the gravimetric method and through electrochemical methodologies, including chronoamperometry, electrochemical impedance spectroscopy (EIS), potentiodynamic polarization method, and open circuit potential measurement (OCP). Statistical analysis shows that the medium corrosion rate of S235 steel, expressed as penetration rate, is between 0.136 mm/year to 0.615 mm/year. The OCP, EIS, and chronoamperometry experiments explain corrosion resistance through the formation of a passive layer on the surface of the metal. This study proposes an innovative methodology and a systematic algorithm for analyzing chemical processes and corrosion phenomena in geothermal installations, emphasizing the necessity of individualized assessments for each aquifer to optimize operational parameters and ensure sustainable resource utilization.

Keywords: renewable energy; geothermal water; chemical analysis; steel corrosion and scales; methodology



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1. Introduction

At present, dominated by the rewriting of political, economic, and social alliances, the energy crisis of the last decades, determined by the reduction in fossil fuels and the

negative effect on the environment, has intensified. Decarbonization becomes an interesting issue, especially in megacities [1]. Education and politics could work together for a new level of civilization [2,3]. Globalization has brought both benefits and vulnerability under the conditions of a paradigm shift. If in the last 20 years, economic and environmental factors have dictated the finding and development of alternative solutions to classic fuels, currently the priorities have become others, such as energy safety and security [4,5]. Thus, renewable energy sources with local potential are starting to become important, sometimes paying a higher price, in order to no longer be energetically dependent on a foreign energy producer. In this context, the sustainable use of renewable energy sources [6–8]—solar, wind, and geothermal—becomes an energy security and environmental objective, which each country can develop. The main problem of the geographical and temporal variability of renewable energy resources is well known, therefore each country must analyze its local resources and capitalize on them. Even if they seem of local interest, studies and research into the development of renewable resources are applications of knowledge acquired in the use of energy sources.

Like any renewable energy source, geothermal energy is only available in geographical areas where there are geothermal water reservoirs, such as in Europe and other developed countries [6,9–13]. This concern for the valorization of local resources is increasingly becoming a topic addressed by specialists from all over the world [4–6,8,14,15].

The main way to exploit geothermal energy is to use it in thermal applications. While geothermal energy that directly utilizes geothermal water is indeed limited to such locations, geothermal energy as a broader concept can be harnessed virtually anywhere through the use of geothermal heat pumps. These systems exploit the stable temperatures of the Earth's subsurface to provide heating and cooling solutions, demonstrating that geothermal energy is not strictly dependent on the presence of geothermal water reservoirs. The variability of waters and the concentration of ionic species, with corrosive potential, makes it necessary to study each case separately, depending not only on the origin but also on the field of application—the production and transport of thermal energy [16–18], heating of houses and heat pumps [6,19–22], heating of greenhouses [23], and balneology [14]—as well as on the mode of use of geothermal waters: direct [14,24] and/or indirect [16]. However, the variability of the concentration of ionic species with corrosive potential can significantly affect the longevity and efficiency of geothermal systems. In geothermal waters, corrosion is primarily caused by species such as chloride, sulfate, and hydrogen sulfide, which can accelerate the deterioration of metal components within heat exchangers and piping infrastructure. A second cause of deterioration in geothermal systems is the formation of mineral deposits or scale, such as calcite, magnetite, goethite, and chalcedony. These mineral precipitations occur due to changes in temperature, pressure, and chemical composition of the geothermal fluid, leading to the accumulation of solid layers that reduce heat transfer efficiency and obstruct fluid flow in pipes and heat exchangers.

An important aspect in exploiting this local resource, geothermal energy, is the interdisciplinary approach of engineering aspects and the integration of physical, chemical, and biological studies, through a better understanding of theoretical and practical principles [15,20–22,25,26]. Physics-based neuronal networks or computer-based analytical optimization or statistics were also proposed as tools for an efficient utilization of geothermal waters, in order to identify the corrosion of infrastructure materials [10,21,27–29].

The chemical composition characterization of water and metal surface scales usually involves spectroscopy analytical methods such as FTIR, IR or ATR-IR [8,25], XRD [18,25,26,30–32], SEM [25,30,32,33], FEM [31,34], EDS [30,33], and Raman [32]. Visual, optical, and metallographic microscopy for surface studies has been used to describe the metallic materials used for geothermal installations [25,30,34]. Water geochemistry is focused on mineral

composition and scale formation [18]. Recent studies regarding corrosion and scales in geothermal environments include discussions on calcite [13,26,32,35–37], magnetite [25,37], goethite [11,25], hydrogen sulfide [36,38], and other compounds [15,39].

The corrosion behavior of working metals and alloys involved in geothermal plants, pipes, or other thermal equipment is described by electrochemical techniques as the weight loss method (gravimetry) [30,32,39], open circuit potential measurement (OCP) [34,40], electrochemical impedance spectroscopy (EIS) [33,40], potentiodynamic polarization (Tafel) method [33,41], and chronopotentiometry [34]. Important information for corrosion is gained by measuring the pH value [13,24,28,29,39–42] and redox potential in some studies [26,39]. Mild carbon steel [15,30,35,40,43,44], stainless steel [31,45], and other metals, such as Al, Cu, and Cu-Ni alloys [30,39,43], have been studied as working metals in geothermal waters.

Studies from the last decade describe the forms of corrosion in geothermal waters as general [18,30,42], uniform [39], or localized, which is the most dangerous, including types such as stress corrosion [30,34], cracking [29,30], pitting [30,34,45], selective [34], or galvanic [39]. In the case of intense localized corrosion, manifested on small surfaces, the damage is hard to recognize, acts very rapidly, and the occurrence of installation failures is imminent. Knowledge of the corrosion behavior (attack rate, uniform or localized corrosion, passivity, pitting, stress corrosion cracking) of metals or alloys, under different environmental conditions, is a prerequisite for applying a protection method or for selecting a metal or alloy suitable for specific environmental conditions. For anticorrosion protection of geothermal installations and pipes, corrosion inhibitors [32,35,41,46] and scale inhibitors [44] have a large application.

The water specimens were collected from geothermal wells within Oradea city, well 4767 and well 1717, which are in the Ioșia district, and from two geothermal wells from Săcuieni village, well 1704 and well 4691. The techniques employed in the analysis of water have been used based on the particular characteristics of the constituents [23], also including chromatography (IC).

To investigate the corrosion phenomenon, two types of solutions were used for comparison: a 3.5% NaCl solution, similar in composition to seawater with known high corrosive potential, and industrial water, from the local heating network.

The corrosion investigation methods include both classical and modern methods of corrosion evaluation: the gravimetric method, open circuit potential measurement, electrochemical impedance spectroscopy, Tafel curves, and chronoamperometry. The electrochemical results were interpreted in consideration of the pH, conductivity, and mineral composition of geothermal waters.

The distinctive aspect of this study is derived from the establishment of an innovative methodology and a systematic algorithm for investigating chemical processes and corrosion phenomena, essential aspects in the design of an efficient geothermal installation. The study highlights that, although preliminary solutions have been identified for managing these challenges, it is imperative to analyze each aquifer individually. This tailored approach ensures the optimization of operational parameters, mitigating the risks associated with corrosion and contributing to the sustainable and safe utilization of geothermal resources. Thus, the proposed research provides a methodological framework, indispensable for the design and implementation of geothermal installations under conditions of maximum efficiency and safety.

2. Materials and Methods

2.1. Analytical Methods for Geothermal Water

The anions that were found in the wells' fluids were determined via ion chromatography (IC) using the IC DIONEX AQUION equipment (Thermo Fisher Scientific, Waltham, MA, USA) [47], except bicarbonate content, which was analyzed by potentiometric titration with TitroLine 7750 equipment (SI Analytics, Mainz, Germany). In order to perform the chromatographic analysis, the eluent was initially prepared with a solution consisting of 4.5 mM Na_2CO_3 and 1.4 mM NaHCO_3 , as well as the standard solutions for the calibration curves for the anions. The ion chromatography standard solutions were initially prepared at a concentration of 1000 mg/L from SIGMA-ALDRICH (MilliporeSigma, Darmstadt, Germany).

Atomic absorption spectroscopy (AAS: PinAAcle 900T) (PerkinElmer Inc., Waltham, MA, USA) [48] was employed after the filtration and acidification of water specimens to analyze for sodium, potassium, magnesium, and calcium. The samples were directly aspirated into an oxidizing air-acetylene flame. The absorption was measured at 589.6 nm, 766.5 nm, 285.2 nm, and 422.7 nm, respectively. Iron was measured by AAS—graphite furnace method: dried 30 s at 140 °C, ached 30 s at 1200 °C, atomized 3 s at 2100 °C. Absorption was read at 248.3 nm. The curves used for calibration were obtained from standard solutions for every cation by successive dilutions from the starting solution of 1000 mg/L Certipur® (Merck KGaA, Darmstadt, Germany), in accordance with the advised utmost concentration to ensure the linearity of the Lambert–Beer law.

Silica and boron were determined by the spectrophotometric method using a UV–Vis Specord 210 Plus (Analytik Jena GmbH & Co. KG, Jena, Germany). Absorption was determined at 410 nm and 420 nm, respectively. The analytical procedure for silica is based on the yellow silico-molybdate complex formed, and for boron, the method is based on the complex formed when boron reacts with azomethine reagent in a buffer solution of pH 5.0 to 5.5.

In order to determine pH values and hydrogen sulfide content, water samples were collected and measured in situ. H_2S was determined by titration with $\text{Hg}(\text{CH}_3\text{COO})_2$ solution using a Gilmont micrometer burette (Cole-Parmer Instrument Company, Vernon Hills, IL, USA).

The total dissolved solids were gravimetrically analyzed using a Kern ABT 220-5DNM analytical balance.

In this paper, the analytical results for the determination of the chemistry of the geothermal fluids are presented, classified, and explained using traditional methods and classification diagrams [12,49,50].

The WATCH speciation program [51] was used to model what happens to geothermal fluids under different conditions, initially at the temperature of the wellhead and then followed by the reduced temperatures found in the distribution system during production. This is particularly useful in the study of scaling [52,53]. The scaling potential was estimated by calculating the saturation indexes for various minerals.

2.2. Electrochemical Methods for Corrosion Evaluation

Electrochemical measurements were carried out using different electrochemical methods: weight loss (gravimetric) investigations, OCP measurement, EIS investigations, Tafel potentiodynamic plots (PP), and chronoamperometry.

2.2.1. Preparation of Metallic Specimens for Corrosion Assessment

All the experimental investigations were performed on S235 carbon steel samples with the following chemical composition (% wt.): C 0.22, Si 0.05, Mn 0.60, Ni 0.30, S 0.04, P 0.04, Cr 0.30, N 0.012, Cu 0.30.

All steel samples were mechanically polished with emery papers of different grades (320, 400, 600, and 1200) and then cleaned with deionized water, degreased with alcohol and acetone (AR grade), and lastly dried in warm air.

Carbon steel coupons measuring $50 \times 20 \times 2$ mm (exposed surface area 2280 mm^2) were used for the gravimetric measurements. For electrochemical methods, S235 steel samples with an exposed surface area of 1 cm^2 were used.

2.2.2. Test Solution Preparation

The standard corrosion solution of 3.5% NaCl was prepared by dissolving solid sodium chloride (AR grade) in deionized water. All other investigated corrosive media were used as such: geothermal water and district heating water samples.

The geothermal water samples were collected from 4 wells in 2 different areas, the Oradea and Săcuieni reservoirs, respectively. For water sample wells, the abbreviations used to designate sources, wellhead temperature, and pH values measured in situ and in the laboratory are given in Table 1.

Table 1. Wellhead temperature and pH values of the water from wells 1717, 4767, 1704, and 4691.

Geothermal Reservoir	Well No.	Abbreviations	Wellhead Temperature, °C	Ph In Situ	pH in Laboratory
Oradea-Ioșia	1717	I 1717	72	7.54	7.87
Oradea-Ioșia	4767	I 4767	94	7.62	7.96
Săcuieni	1704	S 1704	84	7.52	8.75
Săcuieni	4691	S 4691	82	7.67	8.69

2.2.3. Gravimetric Measurements

The initial and final weights of the prepared polished coupons were recorded using an analytical balance, Kern ABT 220-5DNM (KERN & SOHN GmbH, Balingen, Germany). The coupons were dipped in 250 mL test solution (geothermal water samples from 4 wells) for various duration times of exposure (5, 24, 48, 72, and 96 h), maintaining a constant temperature of 80 ± 2 °C. After the exposure time expired, the S235 steel samples were taken out, and corrosion products formed on the metal surface were chemically cleared following standard procedure. The coupons were then washed with deionized water and ethanol/acetone mixture and dried to record their final weight loss. A set of 5 samples was used for every test.

The estimation of the corrosion rate (expressed as the penetration index p , in mm/y) was based on the weight loss of each specimen, according to the following relation:

$$p = \frac{\Delta m \cdot 8.76}{S \cdot t \cdot \rho}, \text{ in [mm/y]} \quad (1)$$

where p is the corrosion rate expressed as the penetration index [mm/year], Δm is the weight loss calculated by subtraction between the initial and final weights of metal coupons [mg], 8.76 is a correction factor to convert measurement units of time and surface, S is the area of the specimen surface exposed to the working solution [m^2], t is the duration of the experiment [hours], and ρ refers to the density of the specific carbon steel [g/cm^3].

The conductivity values of water samples were determined with a PEAKTECH P 5125 conductivity meter (PeakTech Prüf- und Messtechnik GmbH, Ahrensburg, Germany), and the pH values were measured with a Voltcraft PH-100 ATC pH meter (Conrad Electronic SE, Hirschau, Germany).

2.2.4. Electrochemical Techniques

The electrochemical measurements were performed using a VoltaLab PGZ40 potentiostat/galvanostat (Radiometer Analytical, Villeurbanne, France), coupled with VoltaMaster 4.0 software for data acquisition and processing. The used electrochemical system was a three-electrode cell arrangement with carbon steel S235 (1 cm²) as the working electrode, platinum gauze as the counter electrode (5 cm² active area) and an Ag/AgCl saturated electrode (SSCE) as the reference electrode, in a thermostated electrochemical cell for temperature control. In addition, all the electrochemical measurements were performed in aerated geothermal water at 80 ± 2 °C temperature. The measurements were performed at the open circuit potential value. Prior to the electrochemical measurements, 15 min of immersion time was allowed to ensure steady-state conditions. The working electrode was polished with alumina paste, rinsed, and dried prior to all measurements. All the electrochemical potentials were recorded with respect to the reference electrode SSCE.

For the potentiodynamic polarization measurements, the potential was scanned from -1.5 V to 1.0 V with a sweep rate of 20 mV/min, starting from the cathodic potential toward the anodic region.

The electrochemical impedance spectroscopy (EIS) measurements were performed over a frequency range of 100 kHz to 50 mHz, with 10 mV amplitude sinusoidal voltage.

The chronoamperometry spectra were recorded for a period between 140 and 240 min, at a constant negative potential value (-950 mV versus SSCE), corresponding to the limiting current of the reduction reaction of the dissolved oxygen.

3. Results and Discussions

3.1. Short Description of Studied Geothermal Bihor County Reservoirs

Geothermal exploration started in Romania in 1962. The main geothermal areas discovered in Romanian territory are near the border with Hungary, in the Pannonian Basin. The geothermal water is mainly used for heating, greenhouses, industrial uses, and swimming pools.

The Oradea geothermal reservoir is located in fractured Triassic limestones and dolomites in an area of about 75 km² [17]. The Inferior Pontian geothermal reservoir of Săcuieni [54,55] has a small surface area of about 25 km² and is also situated in Romania in the West Plain, north of Oradea. The Săcuieni aquifer consists of gritstones at an average depth of 1600 m. Water samples were taken for chemical analysis from four geothermal wells, two within the city of Oradea and two from the neighboring area, Săcuieni, in Romania (Figure 1).

The purpose of the investigations was to evaluate their production properties, with emphasis on the danger of corrosion and/or scaling potential. Within Oradea city's Ioșia district, two production wells, 4767 and 1717, used in a swimming pool and for district heating, respectively, were selected.

The Săcuieni geothermal area is exploited for greenhouse heating and district heating [19,54,55]. Within this reservoir, two wells, 1704 and 4691, were selected for the study. The geothermal water from these drilled wells is available in artesian flow.

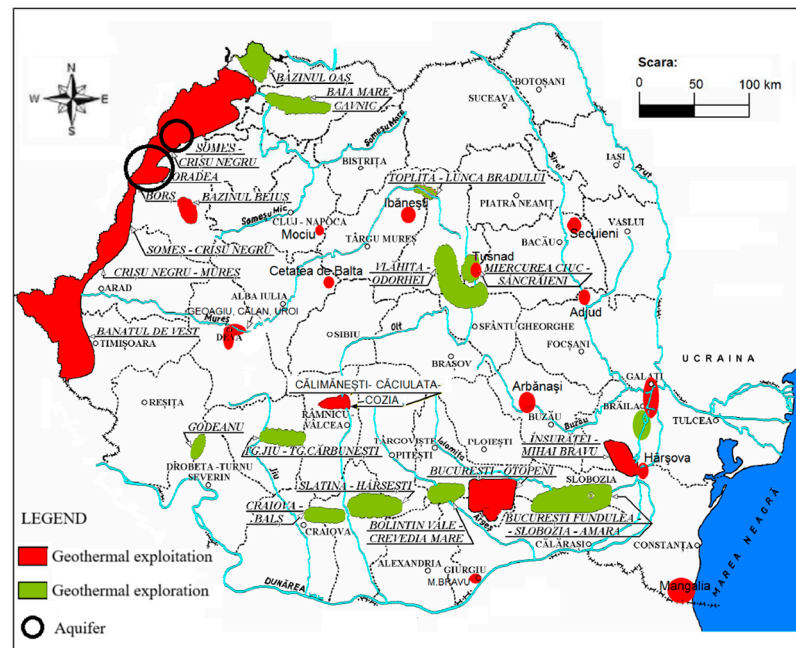


Figure 1. Romania geothermal map with marked localization of Oradea and Săcuieni aquifers [55].

3.2. Geothermal Water Characterization

The outcomes of the chemical studies conducted on the specimens obtained from Ioșia, Oradea, and from Săcuieni were processed for the chemical characterization of the waters from these reservoirs.

3.2.1. Temperature and pH Measurements

The temperature at the wellhead and the values of pH determined in situ and in the lab of the water samples from the studied wells are given in Table 1. The temperature is 10–15 °C higher in the well. The strong geothermal anomaly of the Pannonian Basin, which reaches its highest levels along the Tisza Valley, is linked to the origin of the high temperature of the thermal waters in the lower Pontic system [55]. The pH initial values measured in the lab presented no significant modifications to those measured in situ. In Table 1, you may notice that the pH of the studied waters is slightly more basic for the two wells from Ioșia, while the geothermal waters from Săcuieni exhibit a rather high alkalinity, more than 8.6 [54,55].

The measurements of pH obtained both in situ and in the lab present slightly alkaline values, higher in the Oradea reservoir due to the presence of limestone and dolomite [53].

A set of pH and conductivity measurements were performed in the solutions used for the gravimetric corrosion tests, after 96 h, at room temperature. The increase in the pH and conductivity values of water over time indicates an increased number of ionic species in the water (Table 2).

Higher pH values can favor the formation of mineral deposits which can affect the efficiency of thermal energy systems. Some authors have shown that pH can determine significant changes over time, with variations in temperature, due to the re-establishment of equilibrium reactions of species present in geothermal water [40]. An increase in pH toward more alkaline values is common in corrosive environments, where anodic and cathodic reactions generate alkaline compounds.

An increase in conductivity suggests the accumulation of ions in solutions, such as metal ions and by-products of corrosion reactions, thus signaling an intensification of electrochemical processes, which may reflect active corrosion. Corrosion reactions generate soluble products and alter the chemical equilibrium of solutions.

Table 2. Initial and final pH and conductivity values of geothermal water measured in lab conditions, at room temperature.

Well	Initial		After 96 h	
	pH	Conductivity λ , mS/cm	pH	Conductivity λ , mS/cm
I 1717	7.87	7.58	8.99	8.78
I 4767	7.96	8.04	9.01	9.23
S 4691	8.69	5.48	9.81	6.30
S 1704	8.75	5.17	9.80	6.55

3.2.2. Chemistry of Geothermal Fluids

Analytical studies established the comparative content of anions, cations, mineralization, and H₂S in the analyzed waters (Table 3).

Table 3. Chemical composition of investigated geothermal water samples.

Chemical Composition, (mg/L)	Săcuieni Reservoir		Oradea Reservoir	
	Well 1704	Well 4691	Well 1717	Well 4767
Na ⁺	1155.2	1294.2	65.3	48.2
K ⁺	145.1	185.5	16.4	9.4
Ca ²⁺	32.8	18.2	132.6	138.7
Mg ²⁺	9.6	7.9	15.9	18.4
Cl [−]	668.6	726.7	31.2	61.6
SO ₄ ^{2−}	14.6	21.3	129.0	254.0
HCO ₃ [−]	2247.3	2410.2	455.7	289.0
NO ₃ [−]	1.1	0.85	0.05	0.42
SiO ₂	38.4	64.2	28.8	32.5
BO ₂ [−]	8.4	9.1	0.213	0.44
Fe ³⁺	0.14	0.19	0.45	0.56
TDS	2790	2880	669	740
H ₂ S	0.008	0.016	0.156	0.121

The predominant anions found in the geothermal waters were bicarbonate (289–455.7 mg/L) and sulfate (129–254 mg/L) for Oradea, and bicarbonate (2247.3–2410.2 mg/L) and chloride (668.6–726.7 mg/L) for Săcuieni. The main cations were calcium, magnesium, sodium, potassium, and small amounts of iron. The predominant cation for the Oradea reservoir was calcium (132.6–138.7 mg/L), and for the Săcuieni reservoir, sodium (1155.2–1294.2 g/mL). The elevated calcium and magnesium levels in the Oradea aquifer signify greater hardness than in the Săcuieni aquifer, attributable to the occurrence of limestone and dolomite, which are rich in calcium and magnesium salts, in contrast to the predominantly sandy composition of the Săcuieni aquifer. Reduced calcium and magnesium ion content for the Săcuieni aquifer may be a result of a change in alkaline substance, favored by the presence of sodium clays in the area, which extract calcium and magnesium ions from water, releasing sodium cations.

The high sodium concentration in the Săcuieni wells can be attributed to its presence in an area of clay strata. High levels of sodium and chloride from the pontine thermal water may be the result of extended contact between the water and collector rocks, and also because of the coastal or littoral nature of these rocks. In these areas, it is possible

for chloride, sulphate, or carbonate rocks to accumulate, which are easily dissolved in a liquid with a high constant dielectric, like water under high temperatures. The chloride presence comes from external sources, such as sedimentary minerals like sylvite, sodium chloride, carnallite, and chlorothionite, which are found in small amounts in syngenetic saline waters [55].

Mineralization, expressed by TDS (total dissolved solids), is high for samples from Săcuieni (1704, 4691), being almost 3 g/L, whereas in samples from Ioşia-Oradea (1717, 4767), the mineralization is close to 0.7 g/L.

The Schoeller diagram plots the equivalent concentration of sulfate, carbonate, chloride, magnesium, and calcium, and the aggregate of alkali ions, sodium and potassium, on the Y-axis, while these elements are arranged in this sequence on the X-axis (Figure 2). Each specimen of water is depicted in the picture by a line. Water specimens from identical or analogous water groups exhibit a consistent pattern on the chart.

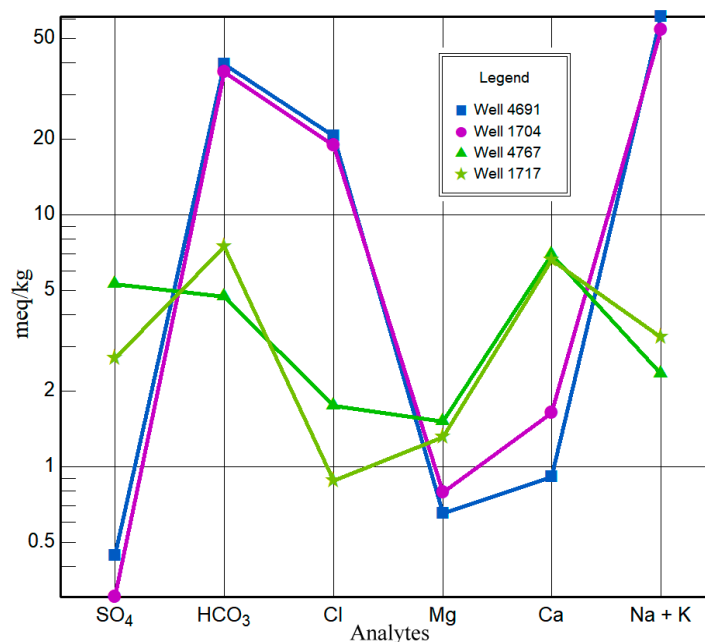


Figure 2. Schoeller diagram for the water samples of the wells 1717 and 4767 (Oradea-Ioşia) and 1704 and 4691 (Săcuieni).

As demonstrated in the Schoeller classification diagram, shown in Figure 2, the waters from Săcuieni can be classified as bicarbonate–sodium–chloride, and the waters from Ioşia, Oradea, as bicarbonate–calcium–sulfate. Hydrogen sulfide is very low at wells 1704 and 4691, while in wells 1717 and 4767, it is 0.156 mg/L and 0.121 mg/L, respectively, but high enough to give some inbuilt corrosion defense. While hydrogen sulfide (H₂S) is generally known for its corrosive effects, some studies discuss methods for mitigating its impact. For example, research on H₂S removal from geothermal fluids using Fe(III)-based additives suggests that certain treatments can help prevent H₂S-induced corrosion [38].

The calculated saturation index vs. temperature values for waters from the selected wells are shown in Figure 3.

Decreasing the temperature increases the solubility of calcite. The computer software shows the precipitation of calcite has to be expected at the wellhead temperatures and the lower temperatures reached during the exploitation of these geothermal wells. The supersaturation in respect to calcite is higher in wells 1704 and 4691. The equilibrium temperature for chalcedony corresponds to the measured temperatures. The chemical analysis from Săcuieni wells calculated in the WATCH program at production temperature and by cooling in steps indicated a supersaturation for goethite, with the saturation index

(SI) being more than 2, and a very high supersaturation in respect to magnetite, with the SI being 10.89 at well 4691 and 10.28 at well 1704 at wellhead temperatures (Figure 3a,b). This means that there might be severe corrosion problems. According to the mineral saturation diagrams (Figure 3c,d), for the wells from Ioşia-Oradea, the saturation index of goethite indicates oversaturation both at the temperatures at the wellhead and the lower temperatures reached on cooling during utilization, together with a high supersaturation with respect to magnetite. These simulation results suggested that most of the scales are due to corrosion processes and are related to calcite, magnetite, goethite, and chalcedony.

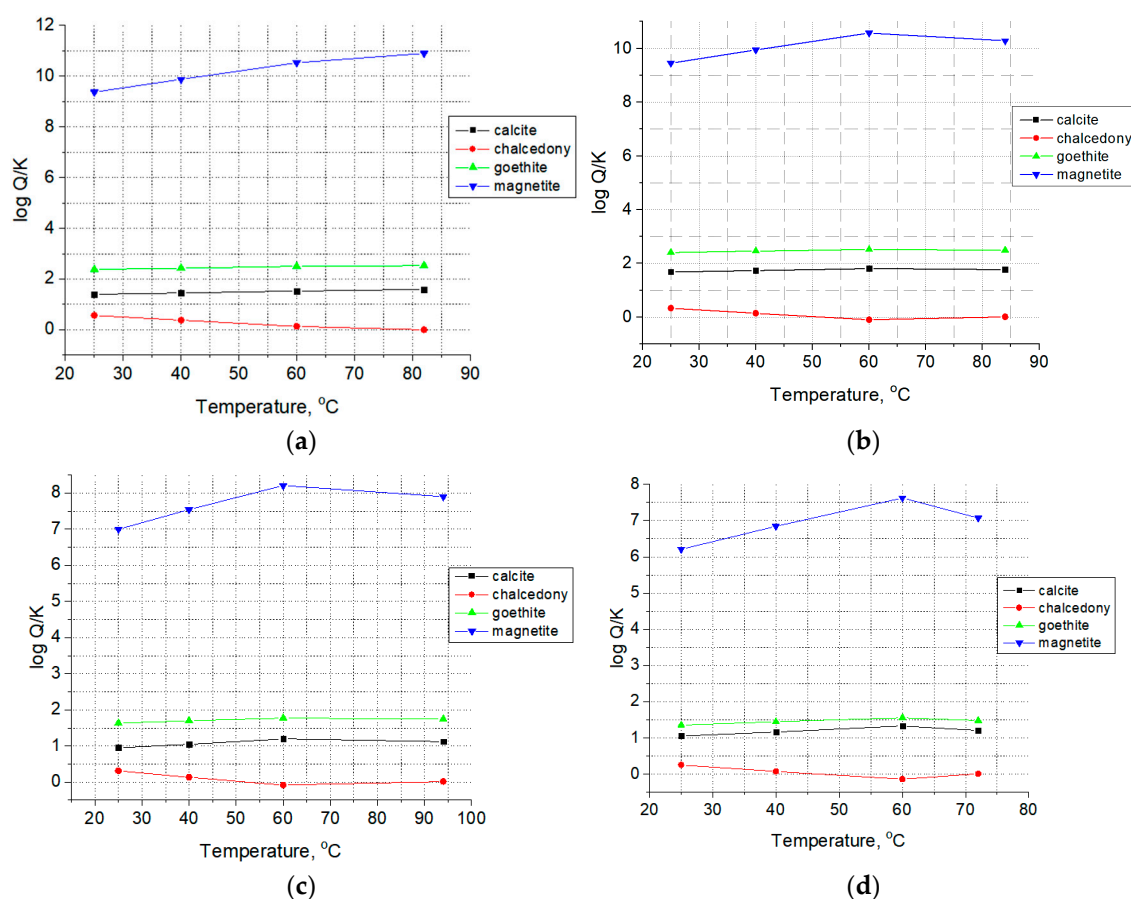


Figure 3. The $\log Q/K$ vs. temperature diagram for water from (a) well 4691-Săcuieni, (b) well 1704-Săcuieni, (c) well 4767-Oradea-Ioşia, and (d) well 1717-Oradea-Ioşia.

The Piper diagram, which can be found in Figure 4, is composed of two triangle diagrams. The first figure is used to depict the proportions (in equivalent concentrations) of the important cations, while the second diagram is used to plot the equivalent concentrations of the important anions. Using the triangular shapes as a starting point, parallel lines are created into a diamond shape at the point where the lines intersect.

The Piper diagram (Figure 4) was used to classify water samples from wells 4691 and 1704 from Săcuieni as sodium–bicarbonate waters, while water samples from wells 4767 and 1717 from Ioşia-Oradea were classified as bicarbonate–sulfate–calcite and bicarbonate–calcium–sulfate waters, respectively.

The Durov diagram, which is shown in Figure 5, makes use of the same triangular diagram as the Piper diagram. These triangles are combined into a square, and the total dissolved solids plus pH of the water specimens are added in the connecting rectangles.

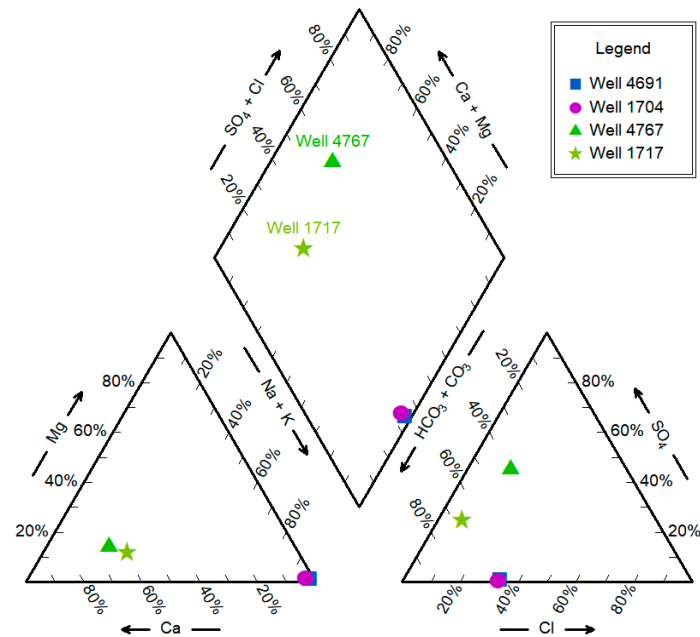


Figure 4. Piper diagram for classification of the water samples.

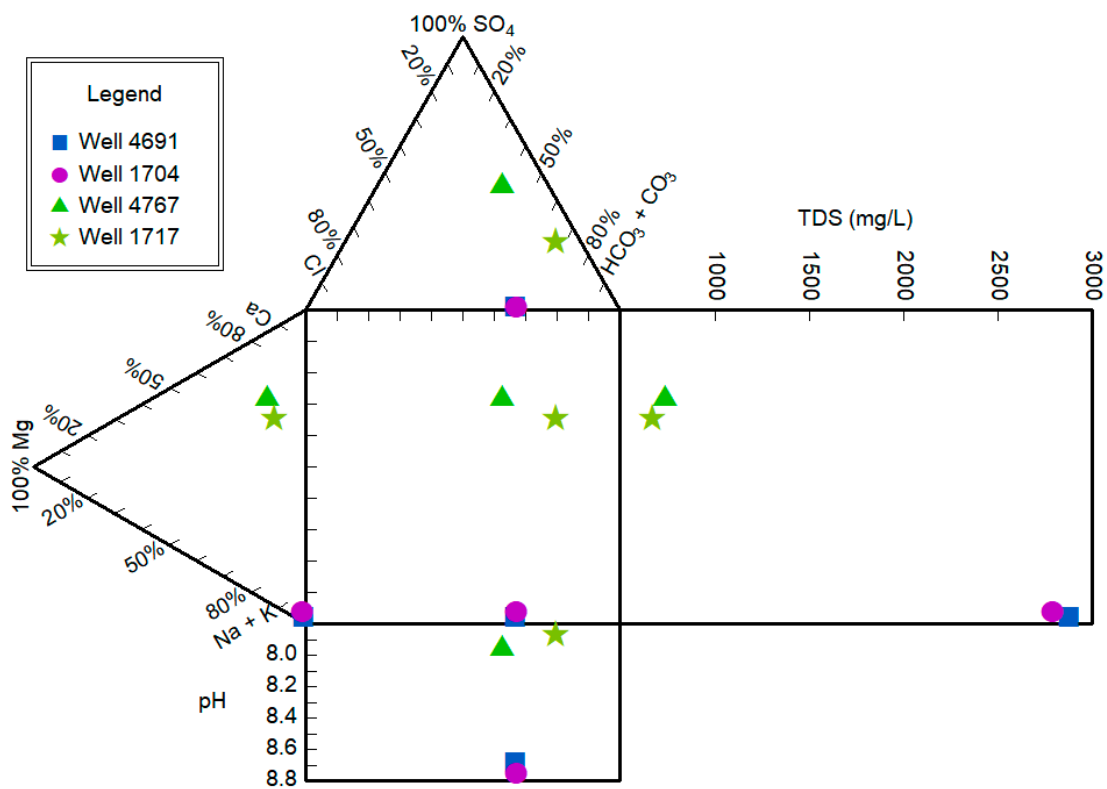


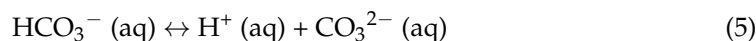
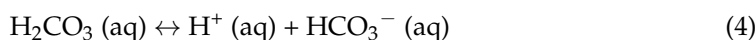
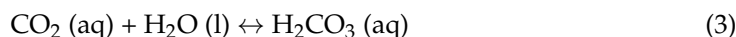
Figure 5. Durov diagram for classification of the water samples.

3.3. Corrosion Process Investigations

3.3.1. Corrosion and Scale Formation Mechanism

The chemicals analyses and simulation suggest that most of the scales are due to corrosion processes and are related to calcite, magnetite, goethite, and chalcedony. The following mechanisms of corrosion products are described.

When scales based on calcium carbonate appear, the mechanism [35] depicted in Figure 6 is involved:



The appearance of calcium carbonate scaling is determined by pH and pressure modifications. An alkaline shift of pH, over 8.8, determines the precipitation of carbonates, which grow with the increased temperatures of geothermal waters [35].

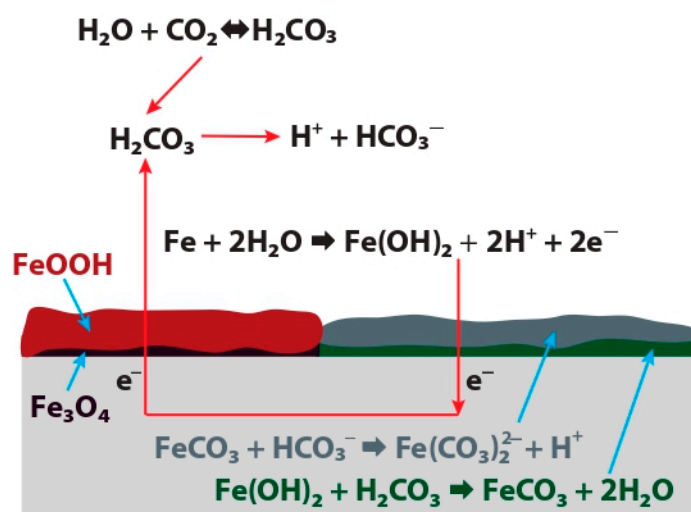
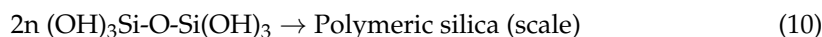
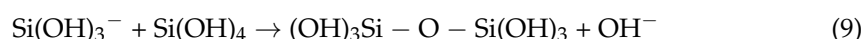
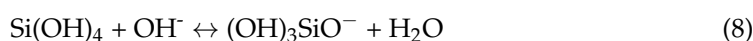


Figure 6. Mechanism of scale formation on mild steel in geothermal water.

Silica scale in geothermal water is formed according to the following mechanism [35]:



Silica scaling could be a very important issue, comparative with the corrosion of metal materials working in geothermal waters.

Iron oxides and silica form amorphous silicates, which are harder to eliminate than carbonate scales:



The scales of hematite deposits (Fe_2O_3), through oxidation, usually form protective films of magnetite (Fe_3O_4) that can be deposited inside tubing, thus mitigating corrosion.

A significant content of humic acids, phenolic compounds, and oil hydrocarbons has also been reported in geothermal waters from the Săcuieni aquifer, their presence being due to local geological and hydrogeological characteristics, such as coal seams and oil deposits [54,55]. Although they are not the subject of this study, their existence was not highlighted as one of the causes of a certain corrosion behavior of the studied steel.

Corrosion in geothermal waters may also be due to the presence of hydrogen sulfide [36,38]. While this study did not directly investigate H₂S-induced corrosion, it identified small amounts of H₂S in the geothermal waters of the Oradea and Săcuieni aquifers. The corrosion mechanism related to H₂S has been analyzed by other researchers [31,32,36,38], and it is presented in Figure 7.

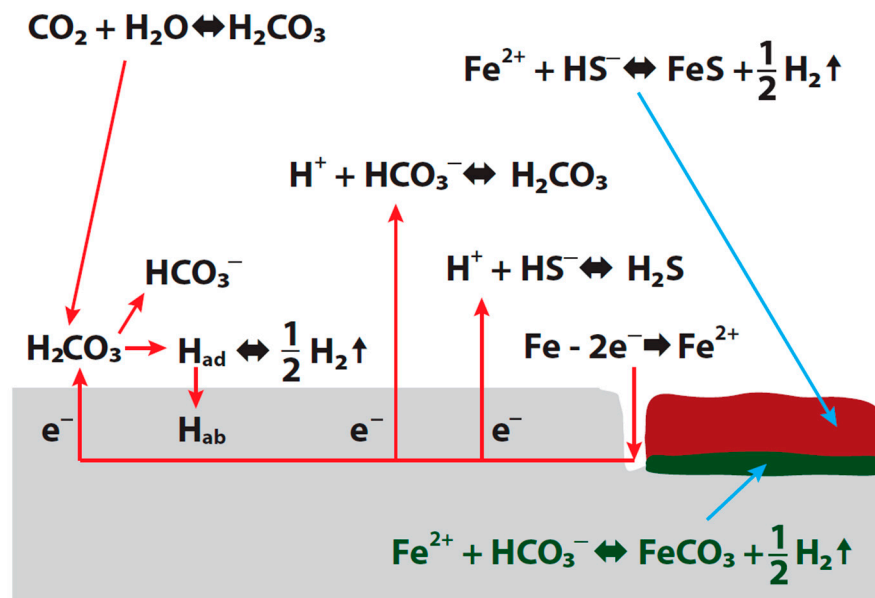


Figure 7. Mechanism of scale formation on mild steel in geothermal water with H₂S content.

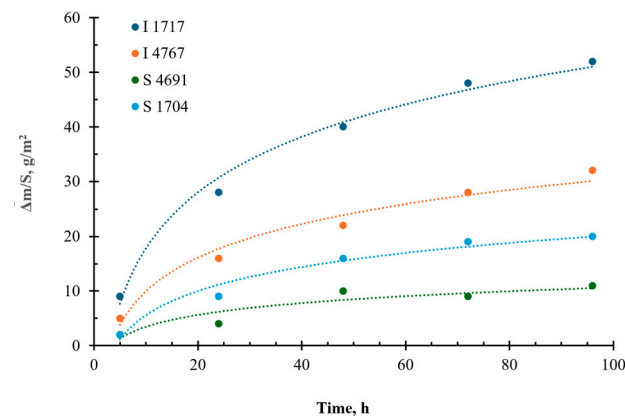
The mechanism of iron corrosion in the H₂O–CO₂ system is altered by rather modest concentrations of H₂S in thermal water, through the high adsorption of sulfide anions, which prevents the formation of the iron oxide coating [31,32,36,38]. As a result, according to the scheme in Figure 7, the evolution of sulfide and carbonate layers takes place. The hydrogen sulfide particles, soluble in water, participate in autocatalytic cathodic reactions, analogous with the particles of carbonic acid, stimulating the process of steel corrosion and covering the metal surface with an iron sulfide layer. The adsorption of H₂S onto metal surfaces is so intense that it rapidly forms a black layer of sulfides, even in geothermal fluids with negligible hydrogen sulfide content. Regardless of the level of metal surface supersaturation, iron sulfides, mainly in the form of mackinawite, are the end product of the solid-state reaction [31,32,36,38].

3.3.2. Estimation of Corrosion Using Gravimetric, Visual, and Statistical Methods

The results of the corrosion studies using the gravimetric method, expressed in terms of the corrosion rate as penetration index, are presented in Table 4 and Figure 8, measured at different times of exposure: 5, 24, 48, 72, and 96 h. The penetration rate values of mild carbon steel, between 0.136 mm/year and 0.615 mm/year, indicate its classification in the category of medium to low stable metals. If the penetration rate is beyond 0.1 mm/year, the studied metal is safe in use.

Table 4. Corrosion rate expressed as penetration index for carbon steel in geothermal water at different exposure times (5, 24, 48, 72, and 96 h).

Well	Penetration Index p, mm/Year				
	5	24	48	72	96
I 1707	2.093	1.337	0.949	0.754	0.615
I 4767	1.265	0.788	0.521	0.435	0.376
S 4691	0.466	0.225	0.241	0.154	0.136
S 1704	0.408	0.385	0.299	0.253	0.203

**Figure 8.** Specific mass loss for carbon steel in time measured in geothermal waters from wells 1717 and 4767 (Iloșia-Oradea) and 1704 and 4691 (Săcuieni), respectively.

At first, an increase in corrosion appears, but in time, stabilization of the corrosion rate is observed. This occurs because a protective coating forms on the surface of the metal.

Corrosion rate values do not provide absolute information; therefore, visual or optical evaluation of metal samples is essential. A low corrosion rate may indicate a mild or moderate corrosive attack, but it is a general value; it says nothing about the existence of localized forms of corrosion and implicitly about their danger of perforating the metal.

In Figure 9, a box chart is presented illustrating the evolution over time of the penetration rate of carbon steel in different geothermal wells, as determined by gravimetric investigation.

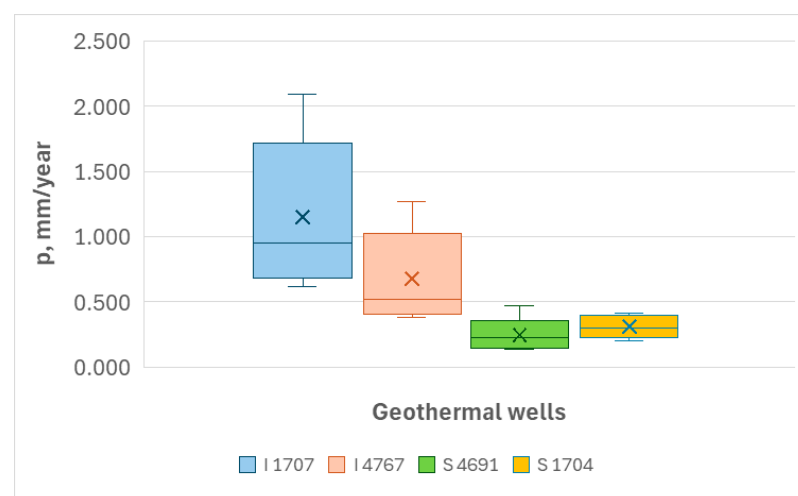
**Figure 9.** Box chart for the comparative characterization of penetration rate for different geothermal wells via gravimetric investigation.

Table 5 provides a thorough overview of the examined dataset by displaying important statistical data like mean values, SD, and COV. From the COV outcomes, it can be noticed that the lowest value is 27.99%, corresponding to the Săcuieni well 1704, whose water is less corrosive for carbon steel S235. The close VOC values for the other wells, over 50%, show that the analyzed waters are quite corrosive for the chosen metallic material. One of the main ways to limit corrosion is to choose a more resistant material and, obviously, repeat the corrosion tests.

Table 5. Statistical data for the evolution of the penetration rate of carbon steel in different geothermal waters.

Well	I 1707	I 4767	S 4691	S 1704
Mean	1.15	0.68	0.24	0.31
SD	0.59	0.36	0.13	0.09
COV	51.60	53.85	53.90	27.99

In Figure 10, a visual evaluation of the carbon steel samples from wells 4767 and 4691 is presented. The first observation is that waters from Săcuieni (well 4691) produced more localized corrosion attacks, in the form of pitting corrosion, than waters from Oradea (well 4767), where the attacks look more uniform.

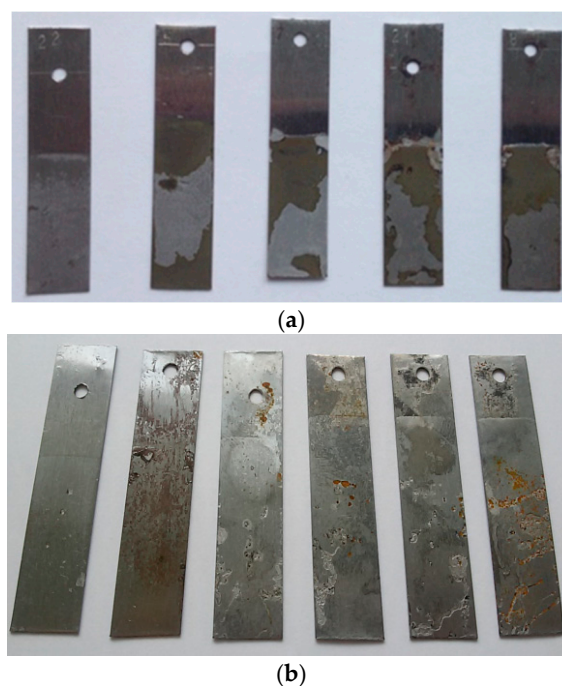


Figure 10. Visual evaluation of carbon steel samples exposed to geothermal waters in gravimetric experiments: (a) I 4767, (b) S 4691.

Two synergetic mechanisms can explain the appearance of pitting corrosion: first, the presence of chloride ions, which destroy the passive layer of steel, and second, the presence of oxygen, which accelerates corrosion. Previous studies [55] indicate high amounts of chloride and ammonium ions in the discharged waters of the Săcuieni wells 1704 and 4691. Chlorides in geothermal water are a significant factor in the occurrence of corrosion, especially for metal systems used in the exploitation of geothermal resources. The effect of these ions in conditions of high temperatures and increased pressure can have the following effects: the occurrence of localized pitting corrosion that affects the structural integrity of the metallic material of an installation, which can quickly lead to its perforation. In the case

of stainless steels, chloride ions can destroy the passive protective layer. The presence of dissolved oxygen, through the mechanism of corrosion with differential aeration, can attack the passivated areas, amplifying the corrosion process and implicitly the degradation of the metal or alloy.

Among the primary elements that contribute to the corrosion of metals in heating systems, dissolved oxygen constitutes one of the most important contributors. In the presence of oxygen, ferrous metals corrode, which leads to damage to pipes and other components of heating systems. Oxygen also contributes to the formation of deposits that reduce the efficiency of heat exchangers and can block pipelines. To prevent the action of oxygen, water can be treated by degassing, the use of corrosion inhibitors, or the proper sealing of systems to prevent air from entering, which is crucial.

Some authors have reported a fivefold increase in corrosion rate if water temperature decreased because oxygen is dissolving in the geothermal fluid [40]. A temperature above 80 °C will prevent oxygen dissolution in water.

The values of the gravimetric penetration rate are between 0.203 and 0.615 mm/year, which are close to other reports obtained for mild carbon steel: 1.6 mm/year [35]. Of course, these values are higher comparatively to austenitic stainless steels, around 0.02–0.07 mm/year [40].

3.3.3. Estimation of Corrosion Using Electrochemical Methods

The values of OCP for the investigated steel specimens over time are displayed in Figure 11, for geothermal water samples and the NaCl 3.5% solution. In all electrochemical process techniques, 3.5% NaCl is like seawater, known to be an extremely aggressive environment for most metallic materials. Experiments in 3.5% NaCl solution are used for comparative purposes to evaluate corrosion behavior in severe environments. Another reason for this choice was the fact that the geothermal waters from Săcuieni have a high content of chloride ions.

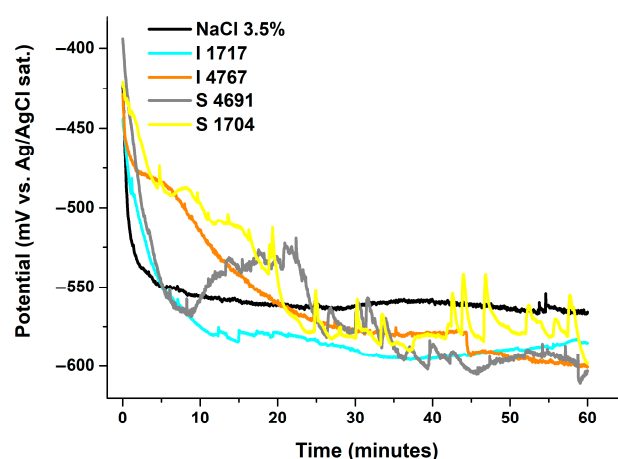


Figure 11. OCP curves for S235 carbon steel in geothermal water samples and NaCl 3.5% solution.

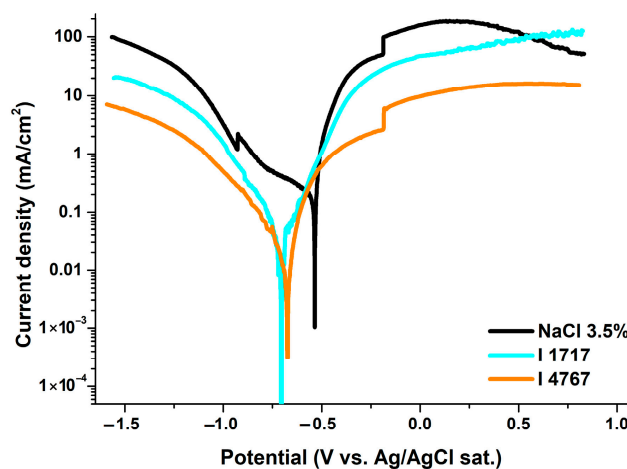
During the experiment, the OCP of the metal coupons fluctuated, due to the formation\ dissolution of the corrosion products' film and mineral scale. After 1 h, a trend toward more stable values is observed, decreasing by approximately 200 mV.

The increase toward more negative values of OCP occurs in conjunction with the development of a passive layer on the surface of the metal material. As the layer of passivity forms and becomes denser, the corrosion current decreases rapidly. This phenomenon is commonly encountered in stainless steel. The concentration of aggressive chloride

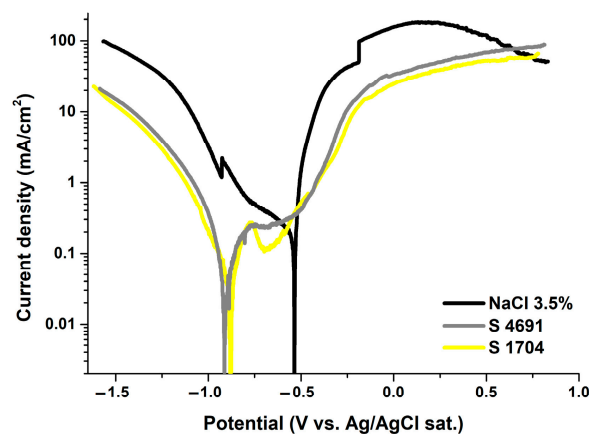
ions, such as chlorides, and the pH and temperature of the solution influence the rate of formation and stability of the passive layer.

The presence of oscillations can be attributed to complex processes, such as the intermittent formation and dissolution of the passive layer or corrosion products. Oscillations can occur due to the instability of the protective layer, local variations in ion concentration, or secondary electrochemical reactions. This action is commonly seen in hostile, corrosive settings or when contaminants prevent the passive layer from forming.

The potentiodynamic polarization curves for carbon steel corrosion in geothermal waters and NaCl 3.5% solution are presented in Figure 12. Changes in corrosion potential values that are less positive indicate an increased corrosion tendency which may be the effect of several causes: the presence of aggressive ions that intensify anodic reactions, such as chloride ions, the composition of the mild carbon steel, which is susceptible to corrosion, and of course a higher temperature value.



(a)



(b)

Figure 12. Tafel potentiodynamic plots for carbon steel corrosion in geothermal waters and NaCl 3.5% solution: (a) I 1717, I 4767; (b) S 4691, S 1704.

Table 6 gives the values of electrochemical parameters calculated from the potentiodynamic polarization curves for carbon steel in geothermal waters, in comparison to 3.5% NaCl. These parameters include the potential of corrosion, E_{corr} (mV); the polarization resistance, R_p ($\Omega \cdot \text{cm}^2$); the density of the corrosion current, i_{corr} ($\mu\text{A}/\text{cm}^2$); the anodic and cathodic Tafel slopes, b_a and b_c (mV/dec); and the corrosion rate, under the form of penetration rate, p (mm/year).

Table 6. Electrochemical parameters calculated from Tafel potentiodynamic plots for carbon steel in geothermal waters and NaCl 3.5% solution.

Water Samples	E_{corr} , mV	R_p , $\Omega \cdot \text{cm}^2$	i_{corr} , $\mu\text{A}/\text{cm}^2$	b_a , mV/dec	$-b_c$, mV/dec	p , mm/Year
NaCl 3.5%	−541	87.14	118.8	29	116	1.389
I 1717	−709	825.58	13.1	46	72	0.152
I 4767	−679	1570	6.4	48	80	0.075
S 4691	−915	443.35	9.23	28	22	0.108
S 1704	−883	459.64	20.54	54	74	0.240

The differences between the corrosion rate values calculated by the two methods, gravimetry and potentiodynamic polarization, lie in their very basic principles. The gravimetric method provides a direct measurement of the mass loss of the corroded material over a period of time, being a more global and slower method. In contrast, the potentiodynamic polarization method is faster and allows for the instantaneous evaluation of the corrosion rate by measuring the electrochemical current associated with the corrosion process. In general, the corrosion rate determined by the gravimetric method can be in the order of 2–10 times lower than that calculated by potentiodynamic polarization, because the electrochemical method can include secondary processes and local reactions that are not reflected in the global mass loss.

In order to find more information about the scaling characteristics and electrochemical corrosion properties of various geothermal water sources, the electrochemical impedances of an S235 electrode in aerated geothermal water were investigated at 80 ± 2 °C temperature. The electrochemical impedance investigation was accomplished in an open circuit potential condition. The results of the EIS studies are presented in Figure 13 and Table 7.

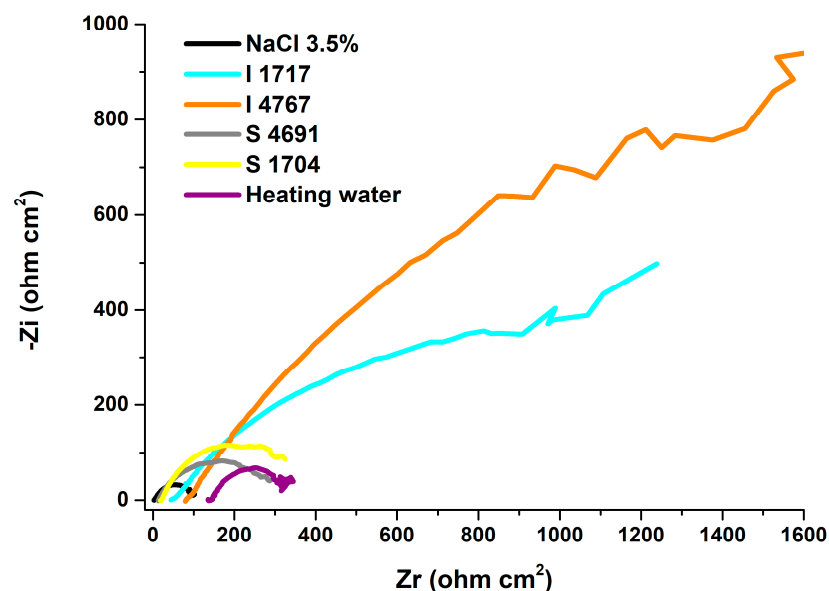
**Figure 13.** Nyquist plots for carbon steel in geothermal water samples, NaCl 3.5% solution, and secondary heating waters.

Table 7. Electrochemical parameters calculated from electrochemical impedance spectroscopy plots for carbon steel in geothermal water samples, NaCl 3.5% solution, and secondary heating waters.

Water Samples	$R_s, \Omega \cdot \text{cm}^2$	$R_{ct}, \Omega \cdot \text{cm}^2$	$C_{dl}, \mu\text{F}/\text{cm}^2$
NaCl 3.5%	2.88	109.2	1036.0
I 1717	47.95	1633.0	872.7
I 4767	83.98	3421.0	130.2
S 4691	12.76	292.4	487.5
S 1704	16.07	349.2	574.2
Heating water	144.60	209.5	304.1

In each and every Nyquist diagram, there is a single capacitive loop that has been flattened, most likely as a result of the absence of surface uniformity, irregularities, and imperfections. The increasing diameter of the semicircle, which is explained by the formation of mineral scales shielding the metal surface from corrosion, is the cause of the higher charge transfer resistance R_{ct} values that are seen.

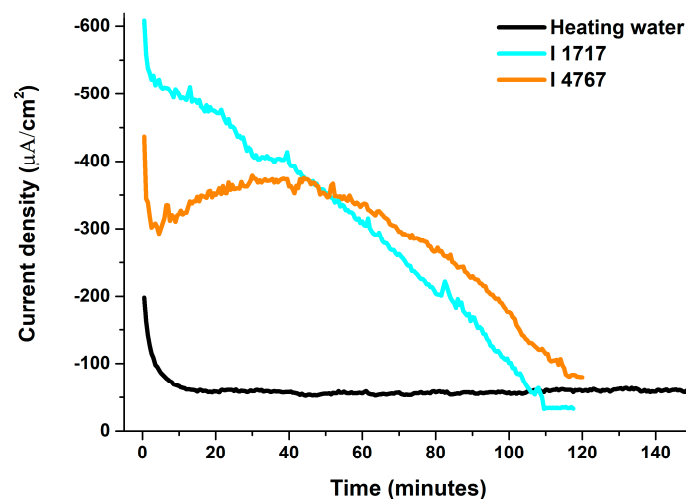
As can be observed from the Nyquist plots, the diameter of the capacitive loop along with the values of the impedance magnitude (Table 7) significantly rise for wells I 1717 and I 4767 compared with all other investigated samples, representing a higher protection efficiency performed by the scale film formation on the steel surface.

The electrochemical parameters that were computed based on the impedance data are presented in Table 7. The solution resistance, charge transfer resistance, and double-layer capacitance are represented by R_s , R_{ct} , and C_{dl} , respectively. In the interface between the electrolyte, the porous corrosion product layer, and the metal, each of these characteristics represents a different component of the interface. The resistance R_s of the solution is determined by the electrolyte conductivity as well as the shape of the working electrode. This resistance is noticeable at high frequencies. There is a connection between the first time constant, which is predominant at high frequencies, and the corrosion product layer that develops at the surface of the metal. Important at low frequencies, the second time constant represents both the double-layer capacitance (C_{dl}) and the charge transfer resistance (R_{ct}).

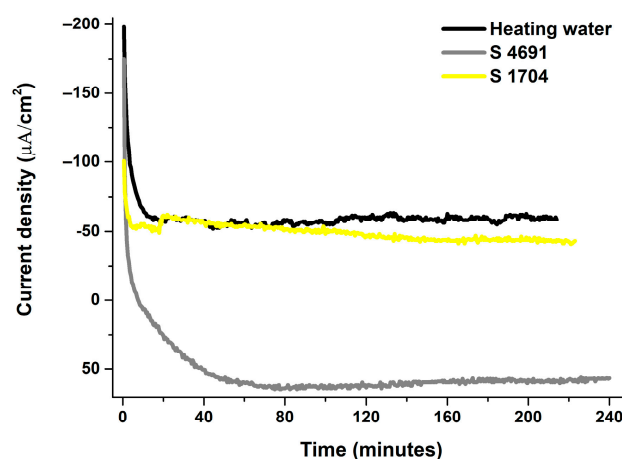
The elevated R_{ct} values signify a greater hindrance of the active area at the metal surface, resulting from the adsorption of intermediate/product molecules and the displacement of H_2O molecules from the surface. A reduction in the local dielectric constant and/or an augmentation in the thickness of the electrical double layer may lead to a decline in the C_{dl} values. The C_{dl} values decrease when additional intermediate or product molecules adsorb onto the metal surface, therefore limiting the exterior layer area.

As an additional point of interest, the intersection of the real impedance axis and the Nyquist semicircles, which is situated in the high-frequency zone and is close to the origin of the coordinates, demonstrates that all of the geothermal water types have small solution resistance values. It can be noted that the solution resistance R_s values are very low for all investigated water samples (2–145 $\Omega \cdot \text{cm}^2$), whereas the charge transfer resistance R_{ct} is in the range of 110–3400 $\Omega \cdot \text{cm}^2$.

The chronoamperometric curves on carbon steel were recorded at a constant potential of -950 mV and are shown in Figure 14, this time compared to the heating water in the secondary circuit. Carbon steel does not have a well-defined passivation potential, since it does not form a stable passive layer, like stainless steels. However, under certain conditions, a temporary reduction in the corrosion rate may occur. Chronoamperometric studies should cover the range in which the anodic and cathodic processes occur, i.e., approximately -1.0 V to $+0.5$ V, with respect to the reference electrode.



(a)



(b)

Figure 14. Chronoamperograms plotted at a potential of -950 mV on carbon steel in geothermal and secondary heating waters: (a) I 1717, I 4767, (b) S 4691, S 1704.

In the case of the waters from wells 1704 and 4691 of Săcuieni, a decrease in corrosion currents toward a limited value is observed, to values even lower (more positive) in the case of district heating water, which can only be explained by the appearance of passivity layers that prevent the advancement of corrosion. Over the 120 min interval, it is observed that, in the case of waters from Oradea wells 1717 and 4797, although the corrosion currents decrease over time, corrosion is initially much more active due to the development of cathodic reduction reactions and does not reach a stable level. It is evident from all examined water samples that the current density value drops as the deposition of mineral scales gradually blocks the active electrode surface. When this layer of scale covers the entire metal surface, the scaling time is reached.

This apparently contradictory behavior can be explained by the differences in corrosion mechanisms and the way each analysis method reflects these processes. Gravimetric and potentiodynamic polarization methods measure mass loss and electrochemical currents associated with active corrosion. If corrosion rates are higher in the geothermal waters of Săcuieni, this indicates intense corrosion activity, with rapid electrochemical reactions and significant material losses.

Electrochemical impedance spectroscopy studies provide information on the stability of the passive layer and long-term corrosion resistance. The higher stability indicated by EIS of the Săcuieni waters is determined because a more uniform passive layer appears. This protects the metal from continued corrosion, even if the initial corrosion rate is high. Chronoamperometry reflects the processes of stabilization of the passive layer. Oscillations or slow decreases in the current may indicate a higher stability of the protective layer in the 1704 and 4691 waters from Săcuieni. A water with a more intense initial corrosive activity but which subsequently undergoes the appearance of a stable film of passivity, may confer higher corrosion resistance in the long term. This emphasizes the importance of using several complementary methods to obtain a complete picture of corrosion behavior.

There was a correlation between the parameters R_{ct} and p and the characteristics of the geothermal water. The results are presented in Figure 15. Some studies [33] have shown that the solution resistance R_s is influenced by the total mineralization of aerated geothermal water at room temperature, due to the crucial influence of total mineralization (TDS) on the ionic activity of the solution. Though, this dependency relationship cannot be applied in case of the charge transfer resistance R_{ct} .

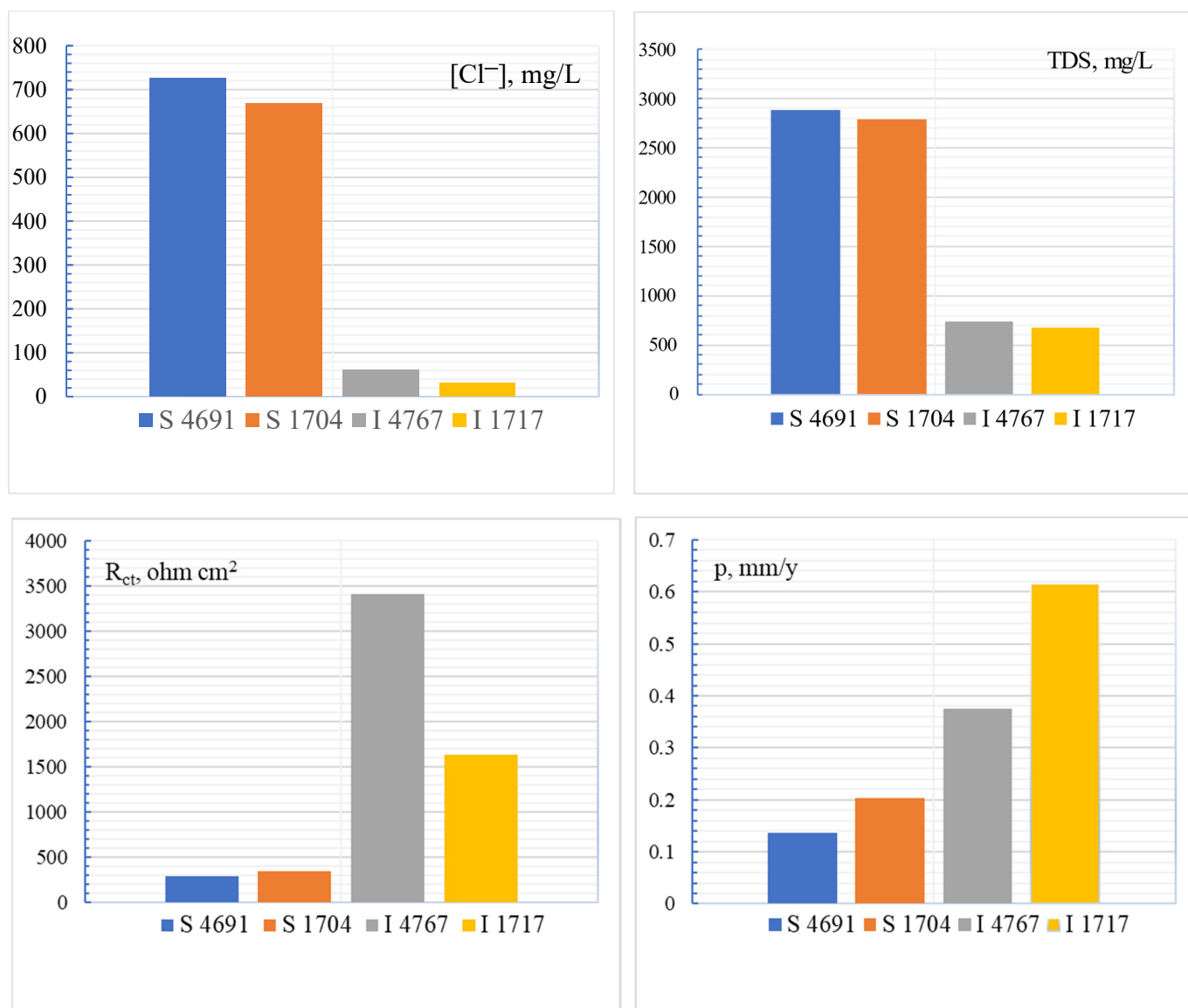


Figure 15. Relationship between electrochemical parameters from EIS and the chemical composition of different aerated geothermal water wells.

As the overall mineralization decreases across the mineralization range, the aerated geothermal water's corrosivity progressively rises.

For every tested water sample, the charge transfer resistance and the change tendency of the chloride ion concentration are inversely proportional. Therefore, based on the extreme permeability and advantageous charge transfer property of chloride ions, it can be assumed that the corrosion rate is mostly influenced by the concentration of chloride ions as well as the overall mineralization of the geothermal water.

Nevertheless, for the promise of geothermal energy, operational problems in geothermal installations could stand in the way of dependable and secure energy generation. One of these operational problems is corrosion, which is mostly caused by geothermal fluids that are abundant in dissolved particles and gases and is a major factor in the deterioration of metallic materials. The architecture of a geothermal energy facility is frequently planned in such a way that it may continue to run correctly for more than 25 years without requiring extensive maintenance. Exploratory studies that primarily describe the reservoir's geological and chemical characteristics have been customarily utilized in the process of selecting building components. To prevent significant material deterioration and additional expenses, the power plant's operating and maintenance protocols must be modified and optimized when the geothermal system's characteristics change. Additionally, this calls for the constant observation of physico-chemical variables such as fluid chemistry, temperature, and pressure [40].

3.4. Challenges and Methodology in Geothermal Corrosion Research

In this work, the corrosion reaction of carbon steel in geothermal water was the primary target of investigation. Laboratory-based techniques, including gravimetry, potentiodynamic polarization, and chronoamperometry have been used. However, the research has certain limitations. The laboratory conditions may not fully replicate the complex environmental factors present in operational geothermal systems, such as variations in temperature, pressure, and fluid dynamics. Additionally, the interaction between dissolved gases, mineral precipitations, and microbial activity was not extensively examined, which could influence long-term corrosion mechanisms.

Another study limitation could be the unique chemistry of each aquifer, which means that specific assessments are required for each type of geothermal exploitation. The present study, without being exhaustive, aims to propose a research approach algorithm (Figure 16) that can guide future investigations in adapting methodologies to different geothermal water compositions.

This flowchart outlines the structured approach used in this study to investigate corrosion in geothermal waters. It visually represents the sequential stages, from chemical and physical measurements to corrosion testing and the determination of optimal operational conditions. By integrating laboratory and in situ analyses, this framework provides a systematic methodology for evaluating material performance and corrosion mitigation strategies.

Further studies incorporating real field conditions and extended exposure periods are necessary to validate and expand upon these findings. This study focused exclusively on the characteristics of carbon steel corrosion. Future research should extend the investigation to other steel types commonly used in thermal installations. Additionally, the applied methods primarily captured general corrosion processes, without specifically assessing localized corrosion phenomena such as pitting and crevice corrosion, which are often more detrimental to thermal system integrity.

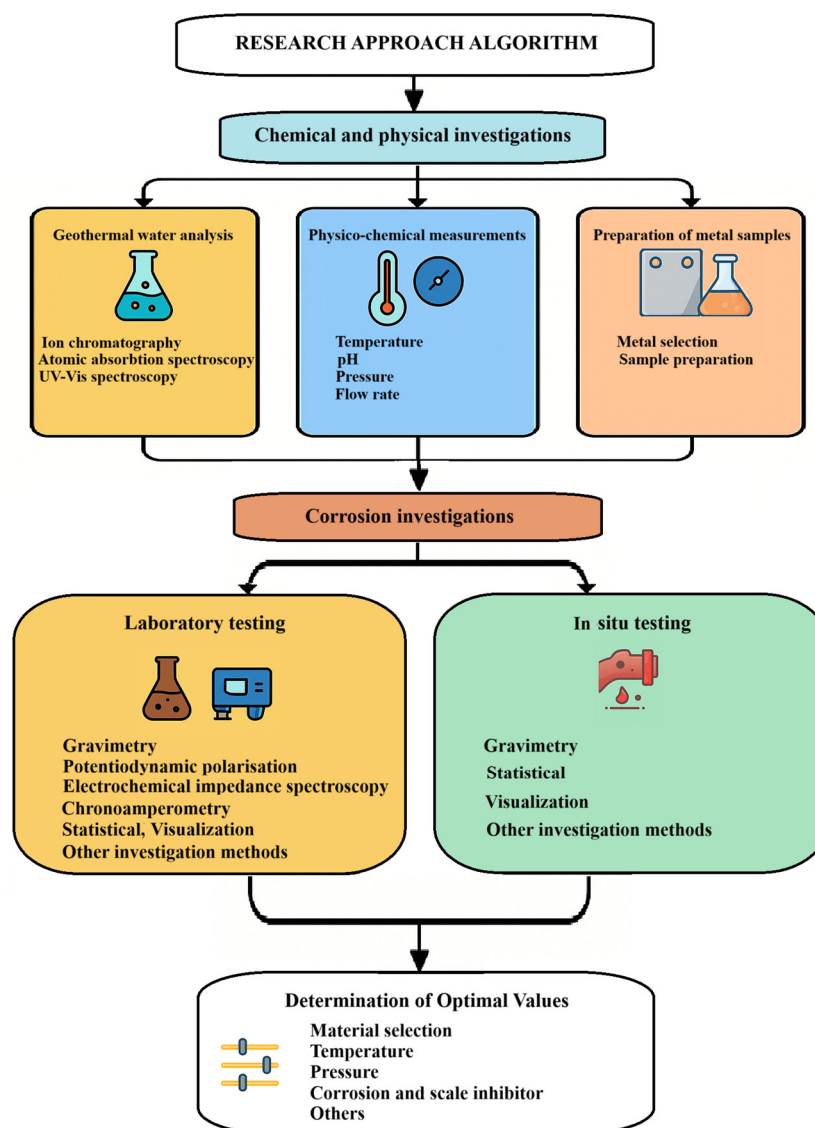


Figure 16. Flowchart of the Structured Methodology for Geothermal Corrosion Analysis.

4. Conclusions

Chemical analyses demonstrated a great similarity in the chemical composition of waters having a similar aquifer provenience, which indicates the identical origin and a unitary recharge of the aquifer. It has been demonstrated that in recent decades, different changes including weather-related have had a little influence on the thermal aquifers that are situated at considerable depths. This is demonstrated by the fact that analyses conducted on the collected water samples have not indicated substantial variations when compared to prior measurements [19,54,55].

Considering the chemical content, namely, the majority ions present in the two thermal aquifers and its correlation with the hydrogeological particularities, it can be concluded that in the Triassic Oradea aquifer (wells 1717 and 4797), the waters are bicarbonate–sulfate–calcium, and for the Pontian Săcuieni aquifer (wells 1704 and 4691), the waters are bicarbonate–sodium chloride. The main minerals found to be responsible for scaling and corrosion are calcite, magnetite, goethite, and chalcedony. Alkaline values of measured pH indicate that geothermal waters can lead to corrosion and scale formation.

This study confirms that the accidental appearance of oxygen together with decreasing temperature, a situation which may appear in the installation or maintenance of a geothermal plant, are important factors to be valued in design and operation. Because of the variability of physical and chemical parameters, corrosion becomes a certitude.

Increasing pH and conductivity over the experiment indicate an active corrosion process of the mild carbon steel in the studied waters. The electrochemical studies (OCP, PP, and EIS) confirm the corrosiveness of geothermal waters, with higher corrosion rates for the Săcuieni aquifer than the Oradea aquifer. The measured values of the electrochemical parameters indicate that mild carbon steel presents some stability in Oradea geothermal waters, but the utilization for Săcuieni waters is not recommendable, unless some protective methods are applied, like corrosion inhibitors.

This research, based on the current knowledge of the corrosion of steels that can be used in thermal installations, highlights the unique character of each geothermal water/utilization system, which depends both on the physico-chemical characteristics of waters and the design and choice of materials. This is why every type of geothermal water should be analyzed and specifically treated for efficient and sustainable utilization.

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Data Availability Statement: Data is contained within the article.

Conflicts of Interest: The authors declare no conflicts of interest.

Nomenclature

Abbreviation	Definition
p	the corrosion rate expressed as penetration index [mm/year]
Δm	the weight loss calculated by subtraction between initial and final weights of metal coupons [mg]
S	the area of the specimen surface exposed to the working solution [m ²]
t	the duration of the experiment [hours]
ρ	the density of the specific carbon steel [g/cm ³]
SSCE	the saturated silver chloride electrode (reference electrode)
TDS	total dissolved solids
CaCO ₃	calcite
SiO ₂	chalcedony
FeOOH	goethite
Fe ₃ O ₄	magnetite
OCP	open circuit potential
PP	potentiodynamic polarization plots
E _{corr}	the corrosion potential [mV]

R_p	the polarization resistance [$\Omega \cdot \text{cm}^2$]
i_{corr}	the density of corrosion current [$\mu\text{A}/\text{cm}^2$]
b_a and b_c	the anodic and cathodic Tafel slopes [mV/dec]
EIS	electrochemical impedance spectroscopy
R_s	the solution resistance [$\Omega \cdot \text{cm}^2$]
R_{ct}	the charge transfer resistance [$\Omega \cdot \text{cm}^2$]
C_{dl}	the double-layer capacitance [$\mu\text{F}/\text{cm}^2$]

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