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CHEMICAL AND PHYSICOCHEMICAL METHODS FOR MEASURING CORROSION RATE

Oleksii HUMENIUK
Igor Sikorsky Kyiv Polytechnic Institute
37, Prospect Beresteiskyi, Kyiv, 03056, Ukraine
e-mail: alexei.humeniuk@gmail.com

Abstract

Metal corrosion is a complex physico-chemical process that causes significant economic losses across various industrial sectors. Ensuring environmental safety of industrial facilities by monitoring corrosion parameters is an important task. Analyses of the processes involved in corrosion are covered by materials science, chemistry, physics, engineering, and several other disciplines. It becomes very important to accurately measure rates of corrosion for service life prediction of materials as well as for the application of appropriate protection methods. This paper exposes the principal techniques for measuring corrosion rates, namely the gravimetric or weight-loss technique and the polarization resistance technique. The gravimetric technique is easy to apply but comes about with many limitations: Localized processes cannot be taken into account; accuracy is not possible; and what duration has to be applied depends is made known. The polarization resistance technique permits continuous real-time monitoring of instantaneous corrosion rate value electrochemical reactions at a metal-electrolyte interface. Among its advantages are highly sensitivity, possibility of automation, and early problem detection.

This study presents a comparative analysis of these methods, justifying the feasibility of applying the polarization approach in conditions where accuracy, speed, and data reliability are critical and highlights the importance of selecting the optimal method, considering the specifics of the environment and the accuracy requirements of corrosion measurements.

Keywords: *corrosion, gravimetric method, polarization resistance method (LPR), corrosion rate, localized corrosion, electrochemical analysis, corrosion monitoring, signal instability, long-term measurements, electrode passivation, environmental safety and monitoring.*

Relevance of the Topic

Metal corrosion is a serious issue across various industries and fields, as it leads to significant economic losses. An important task is the accurate measurement of corrosion rate, which allows for predicting the service life of materials and developing effective protection methods.

Research Objective

The study aims to analyze the main methods for measuring corrosion rate, particularly the gravimetric (weight-loss) method and the polarization resistance method.

Scientific Novelty

A comparative analysis of the main methods for measuring corrosion rate has been conducted. The advantages of the polarization resistance method over traditional techniques have been identified.

Research results

Corrosion is a natural process in which materials (mainly metals) gradually degrade due to chemical and electrochemical reactions with their environment, leading to the loss of their useful properties, such as strength. Corrosion processes are complex in nature, making their study an interdisciplinary research field that combines fundamental sciences and engineering [4]. Table 1 presents the main methods for measuring corrosion rate.

Table 1. Main Methods for Measuring Corrosion Rate

Category	Subcategory	Method Description
Under defined environmental conditions	Natural	Natural conditions
	Gravimetric (Massometry method)	Measurement of mass change
Accelerated	Natural	Natural conditions
	Gravimetric (Massometry method)	Measurement of mass change
	Assessment of environmental corrosiveness	Evaluation of corrosiveness of the environment
	Polarization resistance method	Measurement of polarization resistance
	Cyclic voltammetry	Cyclic voltammetry technique
	Impedance spectroscopy	Impedance spectroscopy technique
	Chronopotentiometry	Chronopotentiometry technique

The gravimetric method is one of the most common techniques for quantifying corrosion rates (CRs), as it is simple to use and does not require measuring currents or voltages.

There are national and international regulations governing the handling of hazardous chemicals, based on the "United Nations Recommendations on the Transport of Dangerous Goods" and the "Globally Harmonized System of Classification and Labeling of Chemicals (GHS)". According to the "Manual of Test and Criteria" [6], a substance is considered corrosive if its corrosion rate (CR), measured using the immersion test for at least 168 hours (1 week), exceeds 6.25 mm per year at a test temperature of 55°C on steel or aluminum surfaces.

To quantify corrosion rates (CRs) using the weight-loss method (immersion test), the mass loss of the specimen (with a known surface area) is determined by measuring the difference in weight before and after immersion in a corrosive medium for a specified period [4].

This method is simple and well-established, but it has several limitations: it only provides the average corrosion rate over the immersion test duration, without capturing variations in oxidation kinetics; potential inaccuracies in CR determination due to incomplete or excessive removal of corrosion products after immersion; it does not provide insights into corrosion mechanisms; it may underestimate the actual corrosion rate if localized corrosion is the dominant mechanism.

Industry standards such as ISO, ASTM, and NACE TM0169/G31−12a (are widely used in industrial and academic research. They outline methodologies for quantifying corrosion rates using immersion test experiments. The formula commonly used in academic literature for calculating CR is as follows:

$$\mathrm{CR} = \frac{\mathrm{k \cdot mloss}}{\mathrm{A \cdot \rho \cdot t}} \quad (1),$$

where:

- k – constant (8.76×10^4) to express CR in, mm/year,
- m_{loss} – mass loss of the metal, g ($m_0 - m_f$),
- t – exposure time, hours,
- A – surface area of the material, cm^2,
- ρ – density of the material, g/cm^3 [4].

Since corrosion rate quantification via immersion tests relies on mass change measurements, it is crucial to ensure a significant (measurable) mass change to minimize weighing errors, which is typically achieved over long exposure times. But it might cause surface area change when kept for a long time. The ASTM standard says that slow tests are more true than quick ones. Also, corrosion should not get so bad that the starting size of the piece or the area it shows is much smaller, or until the metal has a hole in it.

Linear Polarization Resistance (LPR) is the real-time corrosion monitoring/ measuring technique by which polarization resistance helps to detect corrosion problem at an early stage enabling preventive action thereby prolonging the life of the equipment and reducing unplanned downtime. The equipment life and unplanned downtime can be prolonged and reduced respectively as long as continuous monitoring is done based on this technique. For more than thirty years, LPR has been applied successfully in virtually all water-based corrosive environments such as: cooling water systems; secondary recovery systems; potable water treatment and distribution; amine sweetening; wastewater treatment; pickling and extraction of minerals; hydrocarbon production when free water is present with no problems. When a metal/alloy electrode is immersed in an electrolytic liquid with sufficient oxidizing power, corrosion occurs through an electrochemical mechanism involving two simultaneous reactions: at anodic sites, metal dissolves into the solution, leaving excess electrons at the metal surface; at cathodic sites, these electrons are consumed by oxidizing species from the corrosive liquid [3].

The corrosion current (Icorr), generated by the electron flow between anodic and cathodic sites, can be used to calculate the corrosion rate using a modified version of Faraday's Law:

$$\mathrm{C} = \mathrm{E} \cdot \frac{E \cdot \mathrm{Icorr}}{A \cdot d} \quad (2),$$

where:

C – Corrosion rate (mils per year, MPY)
E – Equivalent weight of the corroding metal, g
A – Surface area of the corroding electrode, cm^2
d – Density of the corroding metal, g/cm^3 [3].

However, since anodic and cathodic sites constantly shift, direct measurement of Icorr is impossible. Instead, small externally applied potential shifts (E) generate a measurable current flow (I) at the corroding electrode. The relationship between I and E follows the Stern-Geary equation:

$$\text{Icorr} = \text{I/E} \times \text{constant} \quad (3).$$

The ratio E/I is known as Polarization Resistance (R_P), which is directly proportional to the corrosion rate.

To measure polarization resistance, a second electrode (auxiliary electrode) is placed in the liquid and connected to the corroding electrode (test electrode) through an external power supply.

However, in a simple two-electrode setup, the applied potential must overcome both solution resistance (Rs) and polarization resistance (Rp), leading to overestimation of Rp and underestimation of the corrosion rate:

$$\text{Cm} = \text{Ca} \times \frac{\text{Rp}}{\text{Rp+Rs}} \quad (4),$$

where:

Cm – Measured corrosion rate,0000000000

Ca – True corrosion rate [3].

In Table 2, we compare these methods for measuring corrosion rates.

Table 2. Comparison of Gravimetric and Polarization Resistance Methods for Corrosion Rate Measurement [2; 5; 1; 3; 4]

Criteria	**Gravimetric Method (Weight-Loss Method)**	**Polarization Resistance Method (LPR)**
Principle	Measures mass loss of a metal specimen after immersion in a corrosive medium.	Measures electrochemical response of a metal electrode in an electrolytic solution.
Measurement Type	Provides an average corrosion rate over a fixed period.	Allows real-time corrosion monitoring.
Time Required	Long exposure times (typically 168 hours or more) to obtain measurable mass loss.	Provides instantaneous results.
Accuracy	Can be affected by incomplete or excessive removal of corrosion products.	High sensitivity, detects minor changes in corrosion activity.
Ability to Monitor Localized Corrosion	May underestimate corrosion rate if localized corrosion dominates.	Can detect localized corrosion effects.
Destructiveness	Destructive – requires removal and weighing of the specimen.	Non-destructive – does not require sample removal.
Application Areas	Used in standardized immersion tests for regulatory compliance.	Used in continuous monitoring systems in industrial applications.
Industry Standards	ISO, ASTM, NACE TM0169/G31−12a.	Commonly used in water treatment, cooling systems, hydrocarbon production.
Limitations	Does not provide insights into corrosion mechanisms. Surface area changes over time, affecting accuracy.	Requires electrolytic conductivity in the medium. Can be affected by solution resistance errors.
Advantages	Simple and well-established. Does not require measuring currents or voltages.	Real-time monitoring. High sensitivity to corrosion changes. Continuous monitoring capability.

Recommendations for further applied research

Since the gravimetric method gives an average corrosion rate but LPR gives instantaneous values, a study of the effectiveness of a combined approach to data reliability is thereby suggested. This has to be done in localized corrosion since the gravimetric method tends to underestimate its effects. Long-term measurements for LPR, being real-time results, thus have to be investigated for signal stability and the possible effects of noise or electrode passivation in longer periods.

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ХІМІЧНІ ТА ФІЗИКО-ХІМІЧНІ МЕТОДИ ВИМІРЮВАННЯ ШВИДКОСТІ КОРОЗІЇ

Олексій ГУМЕНЮК
Київський політехнічний інститут імені Ігоря Сікорського
проспект Берестейський, 37, м. Київ, Україна, 03056, Україна
https://orcid.org/0009-0001-8655-1334

Анотація

Корозія металів є складним фізико-хімічним процесом, що спричиняє серйозні економічні втрати в різних галузях промисловості. Забезпечення екологічної безпеки експлуатації промислових об`єктів шляхом моніторингу параметрів корозії є важливим завданням. Вивчення процесів корозії є міждисциплінарним напрямом, що охоплює матеріалознавство, хімію, фізику та інженерію. Актуальним завданням є точне вимірювання швидкості корозії для прогнозування терміну служби матеріалів та впровадження ефективних методів захисту. У дослідженні надана характеристика основних методів вимірювання швидкості корозії, зокрема гравіметричного (методу втрати маси) та методу поляризаційного опору. Гравіметричний метод є простим у реалізації, однак має ряд недоліків: обмеження в точності, неможливість врахування локальних процесів, залежність від тривалості експозиції. Метод поляризаційного опору дозволяє здійснювати безперервний моніторинг у реальному часі, визначаючи миттєві значення швидкості корозії. Він базується на електрохімічних реакціях на межі метал-електроліт, де через малі зовнішні потенціали вимірюється корозійний струм. Перевагами є висока чутливість, можливість автоматизації та раннє виявлення проблем. У роботі проведено порівняльний аналіз зазначених методів, що дозволяє обґрунтувати доцільність застосування поляризаційного підходу в умовах, де необхідна точність, швидкість та надійність даних. Дослідження підкреслює важливість вибору оптимального методу з урахуванням специфіки середовища та вимог до точності вимірювань.

Ключові слова: корозія, гравіметричний метод, метод поляризаційного опору, швидкість корозії, локалізована корозія, електрохімічний аналіз, моніторинг корозії, нестабільність сигналу, довготривалі вимірювання, пасивація електродів, екологічна безпека та моніторинг.