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Corrosion Reaction Kinetics of Rusty Iron in HCl, H_2SO_4, and NaOH: Determination of Reaction Order and Dissolution Rate

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ABSTRACT

Corrosion is the degradation of metals resulting from chemical interactions with their surrounding environment, leading to significant impacts on industrial systems and infrastructure. This study investigates the corrosion kinetics of rusted iron in hydrochloric acid (HCl), sulfuric acid (H_2SO_4), and sodium hydroxide (NaOH) solutions by determining dissolution rates and reaction order. The corrosion behavior was evaluated using a mass loss method, in which the initial and final masses of rusted iron were measured after immersion in solutions of varying concentrations and exposure times. The results indicate that H_2SO_4 exhibits the highest dissolution rate, followed by HCl, while NaOH shows the lowest corrosion activity. Kinetic analysis reveals that the dissolution process follows first-order reaction kinetics. Furthermore, increasing acid concentration significantly accelerates the corrosion rate, whereas alkaline conditions result in comparatively slower iron dissolution.

Keywords: corrosion kinetics, iron rust, dissolution rate, reaction order.

1. INTRODUCTION

Corrosion is the degradation of metallic materials resulting from chemical reactions with their surrounding environment and is commonly associated with rust formation. The term corrosion originates from the Latin word corrosus, meaning "eroded." This phenomenon can occur under a wide range of environmental conditions and represents a major challenge in the utilization of metal materials across various industrial applications.[1]

In general, corrosion occurs due to the natural tendency of metals to return to a thermodynamically stable state, such as oxides or other naturally occurring compounds. This process is influenced by several factors, including the intrinsic properties of the material, temperature, and the chemical composition of the surrounding environment.[2] Under oxidizing conditions, the corrosion reaction rate is strongly dependent on these factors, which collectively govern the kinetics of metal degradation.

Fundamentally, the corrosion process represents the reverse of metal production. During metal extraction, a substantial amount of energy is required to separate metals from their ores. In contrast, corrosion releases this stored energy as metals recombine with oxygen or other reactive species, reverting to a more stable compound form. Consequently, corrosion may be regarded as a spontaneous process through which metals return to their natural state.[3]

From an electrochemical perspective, corrosion involves anodic oxidation reactions coupled with cathodic reduction reactions occurring in the presence of an electrolyte. In acidic environments, hydrogen ions (H^+) play a significant role in accelerating anodic metal dissolution, thereby increasing the corrosion rate. Acidic solutions such as hydrochloric acid (HCl) and sulfuric acid (H_2SO_4) contain aggressive anions, including Cl^-, which facilitate the dissolution of iron by destabilizing the metal surface and promoting ion release.[4] Conversely, in alkaline environments such as sodium hydroxide (NaOH) solutions, corrosion rates are generally lower due to the reduced availability of cathodic reactions that enhance metal oxidation. Nevertheless, under certain conditions, corrosion may still occur in alkaline media through simultaneous anodic and cathodic processes.[5]

Corrosion produces significant adverse impacts, both directly and indirectly.[6] In industrial and infrastructural systems, corrosion leads to material deterioration, resulting in substantial economic losses due to maintenance, repair, and equipment replacement.[7] Additionally, corrosion can disrupt industrial operations and transportation systems, reducing overall efficiency.[8] In marine environments, corrosion is further intensified by the presence of chloride ions in seawater, which accelerate metal degradation, particularly in materials exposed directly to seawater or salt-laden air.[9]

Numerous studies have investigated the corrosion behavior of metals in various corrosive media. Previous research indicates that sulfuric acid (H_2SO_4) generally induces higher corrosion rates than hydrochloric acid (HCl), although prolonged exposure may result in the formation of passivation layers that reduce further metal dissolution. The mass loss method is widely employed in such studies to quantify corrosion rates by measuring the reduction in metal mass over time.[10]

Moreover, extensive experimental evidence consistently demonstrates that acidic environments exhibit significantly greater corrosiveness than basic environments, such as NaOH solutions. This enhanced aggressiveness is primarily attributed to the high concentration of hydrogen ions (H^+), which actively participate in electrochemical reactions that weaken metal structures and accelerate dissolution. These findings reinforce the well-established understanding that solution chemistry, particularly pH, plays a critical role in determining corrosion rates by influencing surface electrochemical reactions.[11]

Further studies focusing on sulfuric acid environments have shown that strong acids exert a more pronounced effect on metal degradation than bases or naturally corrosive environments such as seawater. This behavior is largely due to the ability of strong acids to promote rapid oxidation reactions through enhanced electron transfer mechanisms. The elevated concentration of hydrogen ions intensifies the attack on metal surfaces, leading to higher dissolution rates and more severe corrosion damage.[12]

Although corrosion has been extensively studied, limited research has systematically examined the combined effects of three different solutions—HCl, H_2SO_4, and NaOH—on the mass loss of iron nails with variations in concentration and immersion time. Furthermore, studies focusing on the determination of corrosion reaction order based on experimental data remain scarce. Therefore, this research aims to address these gaps by analyzing the corrosion rate of iron nails in different chemical environments and quantitatively determining the reaction order.

This study seeks to provide a comprehensive understanding of the corrosion behavior of iron nails immersed in HCl, H_2SO_4, and NaOH solutions at varying concentrations and exposure times. Additionally, it aims to determine the reaction order of the corrosion process based on experimental observations, thereby offering quantitative insight into the mechanisms governing material degradation under different environmental conditions.

2. EXPERIMENTAL

2.1. Chemicals, Equipment and Instrumentation

This study employed several analytical-grade chemicals, including hydrochloric acid (HCl, 12 M), sulfuric acid (H_2SO_4, 16 M), and sodium hydroxide (NaOH, 99% purity, Sigma-Aldrich). All solutions were prepared by dissolving the respective chemicals in distilled water (H_2O) prior to use. The experimental apparatus consisted of 50 mL beakers, a 50 mL graduated cylinder, a digital analytical balance with an accuracy of ±0.01 g, a watch glass for sample weighing, a glass stirring rod, and a stopwatch for precise measurement of immersion time

2.2. Research Procedure

Solutions of 12 M hydrochloric acid (HCl), 16 M sulfuric acid (H_2SO_4), and 7 M sodium hydroxide (NaOH) were prepared by dissolving the calculated amounts of each reagent in distilled water to obtain a final volume of 50 mL. Concentrated HCl and H_2SO_4 were diluted based on stoichiometric calculations, while 14 g of solid NaOH was dissolved in distilled water and diluted to a final volume of 50 mL.

Prior to each experiment, rusted iron nails were cleaned of loose debris, dried, and weighed to determine their initial mass. Each sample was then immersed in 50 mL of the prepared solution contained in a beaker, and the reaction time was recorded using a stopwatch. The solution was gently stirred to ensure homogeneity during immersion. After 10 min of exposure, the sample was removed, filtered, rinsed with distilled water, dried, and weighed again to determine the mass loss. The corrosion rate was subsequently calculated based on the measured mass loss.

2.3. Reaction Order

To accurately determine the reaction order governing the corrosion process, the general rate law equation was employed to describe the relationship between reactant concentration and reaction rate, as presented in Table 1

Table 1. Kinetic equations for first-order (n = 1) and second-order (n = 2) reactions.

First Order Reaction (n=1)	**Second Order Reaction (n=2)**
$v = k[A]^1$	$v = k[A]^2$
$\ln[A] = \ln[A_0] - kt$	$\frac{1}{[A]} = \frac{1}{[A_0]} + kt$
$t\frac{1}{2} = \frac{\ln 2}{k}$	$t\frac{1}{2} = \frac{1}{k[A_0]}$

Where:
v = reaction rate (mol/L.s)
k = rate constant (s-1)
[A] = concentration of reactant A at time t (mol/L)
[A0] = initial concentration of reactant A (mol/L)
t = reaction time (s)
t1/2 = waktu paruh reaksi(s)
ln = natural logarithm

3. RESULTS AND DISCUSSION

3.1. Analysis of Rust Mass Changes Over Time

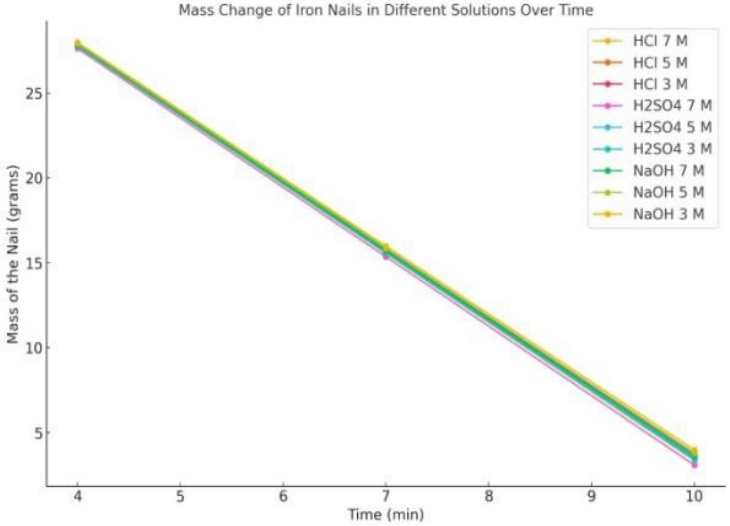

Figure 1. Dissolution behavior of iron rust as a function of solution concentration.

The graph shows a progressive decrease in rust mass over time upon exposure to HCl, H_2SO_4, and NaOH solutions at varying concentrations. At the initial observation time (4 min), all samples exhibit comparable mass values, indicating the early stage of the dissolution process. A marked reduction in mass is observed at 7 min for all solutions, reflecting a continuous dissolution of rust.

Among the tested solutions, sulfuric acid (H_2SO_4) demonstrates the highest dissolution rate, particularly at the highest concentration (7 M), as indicated by the steepest mass reduction. Hydrochloric acid (HCl) also exhibits significant rust dissolution, whereas sodium hydroxide (NaOH) shows the lowest dissolution efficiency, with a relatively higher residual mass remaining at 10 min. By the end of the 10 min exposure period, all solutions substantially reduce the rust mass; however, the extent of dissolution strongly depends on both the solution type and concentration.[13]

3.2. Analysis of the Relationship Between Solution Concentration and the Dissolution Rate of Iron Rust

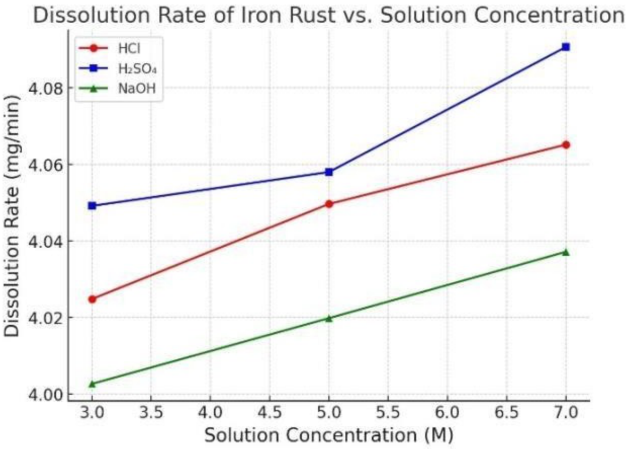

Figure 2. Dissolution rate of iron rust as a function of solution concentration.

Among the three solutions, H_2SO_4 exhibits the highest dissolution rate, followed by HCl and NaOH, indicating a stronger corrosive effect of sulfuric acid within the investigated concentration range. The pronounced increase in the dissolution rate of H_2SO_4 at higher concentrations suggests a concentration-dependent enhancement of the corrosion process, resulting in more rapid rust dissolution.

Hydrochloric acid (HCl) also shows a clear increase in dissolution rate with increasing concentration, although its effect remains slightly lower than that of H_2SO_4. This behavior is consistent with the strong reactivity of HCl toward iron oxides, which facilitates effective rust dissolution without the formation of inhibiting surface layers.

In contrast, NaOH exhibits the lowest dissolution rate across all concentrations. This behavior can be attributed to its different corrosion mechanism compared to strong acids, in which increasing alkalinity does not substantially promote iron oxide dissolution. The relatively weak concentration dependence observed for NaOH indicates that higher NaOH concentrations do not significantly enhance rust removal efficiency.[13]

3.3. Analysis of of pH Changes in Solution Over Time

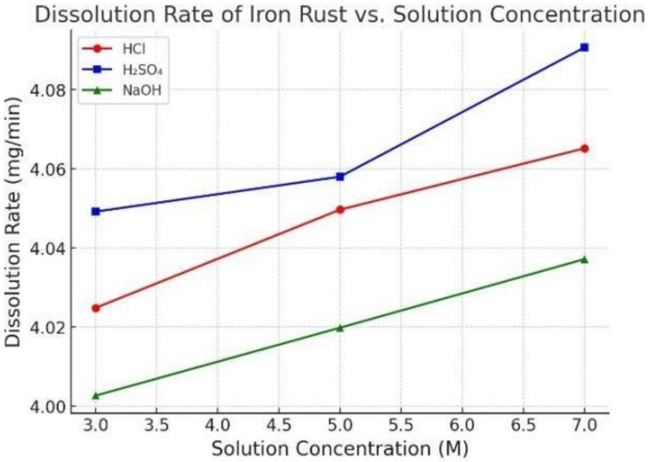

Figure 3. pH variation of acidic and basic solutions as a function of time

The graph illustrates the temporal variation of pH in acidic and basic solutions during the rust dissolution process, providing insight into the progression of the corrosion reactions and their influence on solution chemistry.

In the acidic medium, the pH remains constant at 1 between 4 and 7 min, indicating the persistence of strong acidic conditions during the initial stage of the reaction. At 10 min, the pH increases to 3, suggesting a partial neutralization of the solution. This change can be attributed to the consumption of hydrogen ions (H^+) during the dissolution of iron oxides, leading to a decrease in proton concentration and a corresponding increase in pH.

In contrast, the basic solution exhibits a stable pH of 7 at 4 and 7 min, followed by a slight increase to pH 8 at 10 min. This shift indicates a gradual increase in alkalinity, which may result from interactions between NaOH and iron oxide species, as well as the formation of hydroxide-containing iron complexes. Overall, the observed pH changes reflect the dynamic interplay between solution chemistry and the corrosion process over time.[14]

3.4. Determination of Reaction Order Over Time

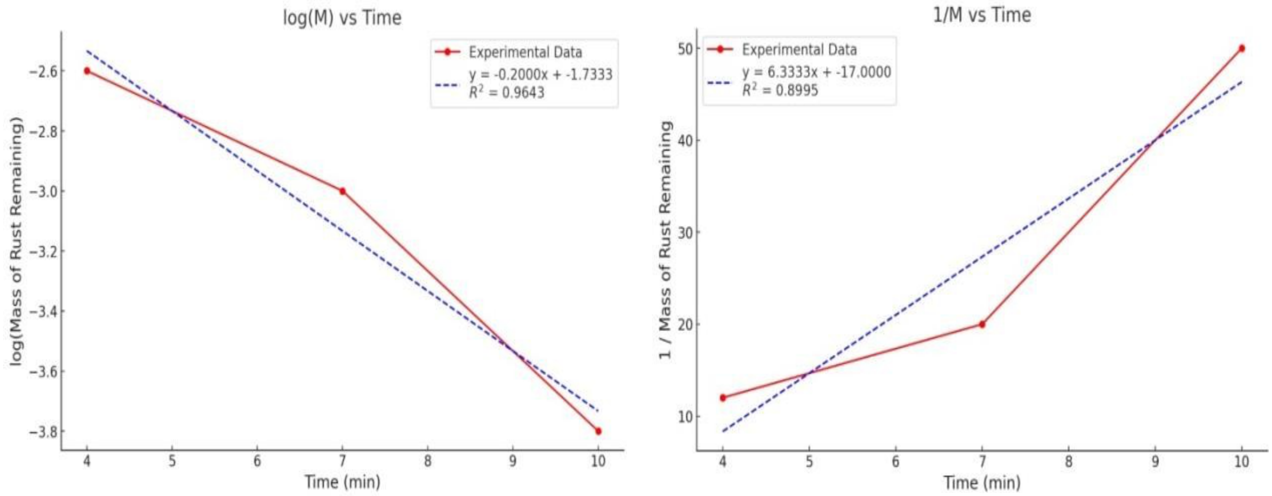

Figure 4. Kinetic plots for reaction order determination: (a) ln(M) versus time and (b) 1/M versus time.

To determine the reaction order of iron rust dissolution with respect to time, kinetic analyses were performed using ln(M) versus time (first-order model) and 1/M versus time (second-order model) plots. The ln(M) versus time plot exhibits a strong linear relationship with a coefficient of determination of R2=0.967R^2 = 0.967R2=0.967, indicating a good fit to the first-order kinetic model. The negative slope of the regression line is consistent with first-order behavior, confirming that the dissolution rate decreases as the remaining mass of iron rust decreases over time.

In contrast, the 1/M versus time plot shows weaker linearity, with a lower coefficient of determination (R2=0.893R^2 = 0.893R2=0.893), suggesting that the second-order kinetic model is less suitable for describing the dissolution process. Based on the comparative regression analysis, the dissolution of iron rust is best described by first-order kinetics, where the reaction rate is directly proportional to the amount of rust remaining in the system.[15]

4. CONCLUSION

This study demonstrates that the corrosion rate of rusted iron in HCl, H_2SO_4, and NaOH solutions is governed by both solution type and concentration, with H_2SO_4 exhibiting the highest dissolution rate, followed by HCl, while NaOH shows the lowest corrosion activity, indicating that acidic environments are significantly more aggressive than alkaline conditions. Kinetic analysis further confirms that the dissolution of rusted iron in all tested solutions follows first-order kinetics, in which the reaction rate decreases proportionally with the reduction in the remaining iron mass over time.

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