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Temperature-Dependent Corrosion Behavior of Martensitic Stainless Steel in Simulated Seawater Environments

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Abstract

In this work, the temperature-dependent corrosion rates of AISI 440 martensitic stainless steel are explored in simulated seawater (3.5 wt% NaCl solution) with temperatures typical for offshore platforms. Cylindrical samples are corroded for 17-85 hours at 25 °C, 30 °C, and 60 °C, with the latter showing increased corrosion rates of up to five times the room-temperature rates, reaching a five-fold increase in corrosion rates from 25 °C to 60 °C. Monte Carlo simulation results using n = 1,000 iterations are used to quantify the probabilistic distribution of the corrosion rates, suggesting increased variability in the corrosion rates at higher temperatures, with standard deviations within triplicate experiment groups also being larger. Arrhenius analysis revealed an activation energy of 38.7 kJmol^{-1}, while the Q_{10} analysis suggested an 80% increase in the corrosion rates over 10 °C increments. The results verify the prominence of temperature in the chloride-induced corrosion process of martensitic stainless steel. An integrated experimental and simulation framework has been developed that constitutes the principles of temperature-coupled corrosion rates, thereby aiding in the determination of the temperature effects on the corrosion process, which can then assist in the inspection and predictive evaluation of the structure. These results highlight the significance of temperature in the choice of materials and the assessment of subsea structures.

Keywords: *AISI 440C, Martensitic Stainless Steel, High-Temperature Corrosion, Seawater Simulation, Monte Carlo Modeling, Offshore Integrity.*

1.0 Introduction

Martensitic stainless-steel grades feature rising demand in offshore/marine applications due to these structural components facing heavier mechanical forces under severely abrasive environments, with variations in temperatures (Akpan et al., 2022; Eke & Okoro, 2021). Of these grades, only Type 440 stainless steel alloys, despite high hardness/strength, possess intrinsic metallurgical limitations that significantly impact adversely their potency in corrosion protection demands against those of austenitic/duplex SS counterparts (Li et al., 2019; Zhu et al., 2021). In most cases, these can be related to high carbon composition levels, chromium carbides, and degradation of passive film stability coinciding together to lower the performance time of martensitic grades in chloride media (Wang & Lin, 2019; Bai et al., 2022; Liu et al., 2023).

These, hence, form the foundation for future research work related to Type 440 stainless steel for use in offshore environments, in terms of structural integrity as well as resistance to corrosion (Akpan et al., 2022; Ibrahim & Etim, 2020). "Localized corrosion, in the form of pitting and crevice corrosion, has been found to be the most prevalent mode of metal deterioration in aggressive environments like seawater" (Sahoo et al., 2022; Jiang et al., 2021). In principle, an increase in temperature would enhance the severity of these phenomena in terms of their characteristic physical and chemical properties. From the physical point of view, an increase in temperature would increase ionic mobility and facilitate the diffusion of chloride ions, which would deteriorate the adhesive properties of the oxide layer and reduce the effectiveness of protection offered by the layer along with the passive layer. From the chemical aspect, rapid electrochemical reaction due to higher temperatures would enhance the deterioration potential of the Cr_2O_3 passive layer in terms of anodic dissolution and cathodic reaction of oxygen, leading to a relatively high rate of deterioration of the layer" (Song et al., 2020; Mahmoud & Idris, 2021; Zhang et al., 2023). Differences in temperature above 50 °C would increase the oxygen solubility and the de-passivation potential of metals. These would generally induce the inception of metastable pits and lead to deep localized attack on metals in particular environments (e.g., seawater) (Ali & Rahman, 2018; Yuan et al., 2023). The temperature dependence of overall corrosion for Fe-Cr alloys generally shows an Arrhenius-type dependence related to activation energies in the 30-45 kJ/mol region (Guo et al., 2020; Kim et al., 2021; Ren et al., 2022).

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The overall tendency for martensitic stainless steel to undergo corrosion, despite being covered in different studies, currently lacks models on a quantitative or temperature-dependent basis for the case of Type 440 stainless steel (Li et al., 2019; Bai et al., 2022). Moreover, in most similar studies, the rate of corrosion is considered in a qualitative manner or lacks integration between experimentation and models incorporating concepts of uncertainty (Mahmoud & Idris, 2021; Wang & Luo, 2018). It would thus logically follow that a partial understanding is present on the interplay between temperature variation and microstructural factors for the activation energy related to initiation/propagation for pits (Zhu et al., 2021; Kim et al., 2021).

The current study combines coupling-control weight loss experiments with the Monte Carlo stochastic simulation approach to model: i) temperature-dependent corrosion rate variation, ii) determining activation energy values, and iii) the propagation of uncertainties arising from experimental measurements (ASTM, 2017; Ryu et al., 2020; Mendoza et al., 2022; Silva et al., 2023). In this regard, the proposed approach is coupled to the identified knowledge-gap, such that it enhances the level of rigor to comprehend degradation processes in 440 martensitic stainless steels, hence facilitating informed decisions with respect to the installed assets at offshore platforms and temperature compensation considerations (Akpan et al., 2022; Ibrahim & Etim, 2020).

2.0 Materials and Methods

2.1 Materials

The choice of commercial Type 440 martensitic stainless steel was for the reasons of proven use within previous subsea pumps, valves, and high-hardness assemblies where localized corrosion and temperature-related degradation had been of specific concern. The typical composition of this alloy is summarized within Table 1 below.

Table 1: Nominal Composition of Type 440 Martensitic Stainless Steel (wt%)

C	Mn	Si	Cr	Mo	P	S
0.95–1.20	1.0	1.0	16–18	0.75	0.04	0.03

These cylindrical specimens were machined from one bar stock of the size 18mm in diameter × 10mm in height to ensure uniformity in the microstructure in the longitudinal direction." In the three specimens mentioned above, the reason for choosing the cylindrical shape is:

- There is a current- and mass-transfer field present throughout immersion.
- For any random or square shape,it minimizes edge effects and
- The expression of the area of the analytical surface helps to accurately normalize the rate of corrosion.
- In point of fact, previous studies conducted on martensitic stainless steel revealed that the cylindrical sample geometry fails to influence the fundamental corrosion process, accentuating, however, the results' accuracy by minimizing the turbulence-induced local artefacts (Ryu et al., 2020; Jiang et al., 2021; Sahoo et al., 2022).

The value for the exposed surface area (~12.6 cm^2) was calculated on the assumption that the faces were all unmasked using the formula:

The Surface Area AAA of the cylinder with the radius r (radius) and the height h(height) is given by the formula:

$$A = 2 \times \pi \times r \times (h + r) \quad [1]$$

where

A = surface area

r = radius

h = Height

where r = 0.9 cm and h = 1.0 cm.

For further analysis (SEM, EDS, hardness testing), PTFE (Polytetrafluoroethylene) tape was used to mask off all lateral surfaces, except for top surface exposure. This ensured that the area analyzed was clearly defined and not affected by artifacts from multiple surface exposures.

2.2 Methods

The prepared specimens have been ground to 1200 grit and polished with 1 µm diamond suspension, afterward degreased in acetone, and finally rinsed in deionized water (ASTM, 2017; Ryu et al., 2020). Following the comment of the reviewer about missed characterization, Further confirmation that complete removal of corrosion products and residual oxides was achieved following cleaning in accordance with the procedure in ASTM G1 was obtained by SEM/EDS analysis (ASTM, 2017; Bai et al., 2022; Liu et al., 2023). XRD studies have been conducted to confirm the martensitic phase and to eliminate retained austenite (Li

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et al., 2019; Zhu et al., 2021). The following Vickers hardness testing was done: HV10, since the request has been made to document the initial mechanical condition of the alloy (Ali & Rahman, 2018; Wang & Luo, 2018). Hardness, indeed, influences the passivation response, but also the susceptibility to micro-pitting (Jiang et al., 2021; Sahoo et al., 2022; Zhang et al., 2023).

The corrosion tests were carried out in 3.5 wt% NaCl solution, and pH was adjusted to 4 by dilute HCl to simulate mild acid subsea conditions. Since one of the main variables that control corrosion is the concentration of oxygen, control of this was done according to: Prior to immersion, the solutions were saturated up to atmospheric saturation (≈8 ppm at 25°C). Dissolved oxygen (DO) levels were measured every 6 h using an optical DO probe that was previously calibrated. These were stirred at 100 rpm to keep the oxygen uniformly distributed. The pH was continuously monitored and kept within ±0.1 units by means of an automated titration controller. That avoids any drifting of the pH by chloride-acid interactions during the long exposures.

Testing was done at ~25°C, 30°C and 60°C. Only the temperature of the solution should be measured, and not that of the bath. The temperature was recorded continuously using a submerged K-type thermocouple 5 mm off each specimen surface. (±0.2°C accuracy). This was done by measuring the temperature for the solution against the set point for the bath temperature in order to confirm thermal stability. The exposures were for 17, 34, 51, 68 and 85 hrs.

These three intervals have been chosen because:

•Pilot tests showing minimal mass loss before ~12–15 h;

• The studies conducted so far on kinetics in the early stage of chloride-induced corrosion of martensitic stainless steel have been supported, and

• Specify the linearity-to-transience requirement window for model uncertainty.

These then provide the extracted durations, not arbitrarily chosen but designed to reflect the behavior of the initiation and propagation.

The HCl solution inhibited cleaned the specimens according to ASTM G1-03, Method C.3.5. Assuming incomplete removal of oxide at 60 °C is the problem. Certain selected specimens were also tested by SEM/EDS to make sure that indeed no residues of the oxides remained behind after cleaning. The mass loss was measured using an analytical balance with a precision of ±0.1 mg. Keeping in view the possible variations of cleaning and in the surface heterogeneity of the test specimens, the estimated total uncertainty of the measurements is about ±3.5%.

Corrosion rate (CR) is calculated using the equation:

$$CR = \Delta W / (A \times t) \quad [2]$$

where:

ΔW = weight loss in milligrams (mg)

A = exposed area in square centimeters (cm^2)

t = exposure time in hours (h)

n = 1,000 was used to quantify the statistical distribution of corrosion rates via Monte Carlo analysis.

Input distributions were defined from experimentally measured uncertainties:

• Mass-loss error : normal (μ = measured value, σ = 3.5%),

• Surface area tolerance: the same ±0.05 cm^2,

• Temperature fluctuation: triangular ± 0.2°C,

• pH drift: Within ± 0.1 units consistently.

The following relationships between the variables, like temperature ↔ DO; pH ↔ mass loss rate have been addressed by the Spearman rank correlation matrices embedded in the resampling routine.

The outcome is a probability distribution of corrosion rates, not single-point estimates

3.0 Results and Discussions

3.1. Temperature-Dependent Weight Loss

Figure 1 below shows the evolution of mass loss for AISI 440 martensitic stainless steel exposed to 3.5 wt% NaCl at 25 °C, 30 °C, and 60 °C for up to 85 h. Under all conditions, weight loss increased monotonically with exposure time, with markedly steeper slopes at elevated temperatures. After 85 h, cumulative mass losses reached approximately 3.1 mg (25 °C), 6.3 mg (30 °C), and 18.5 mg (60 °C).

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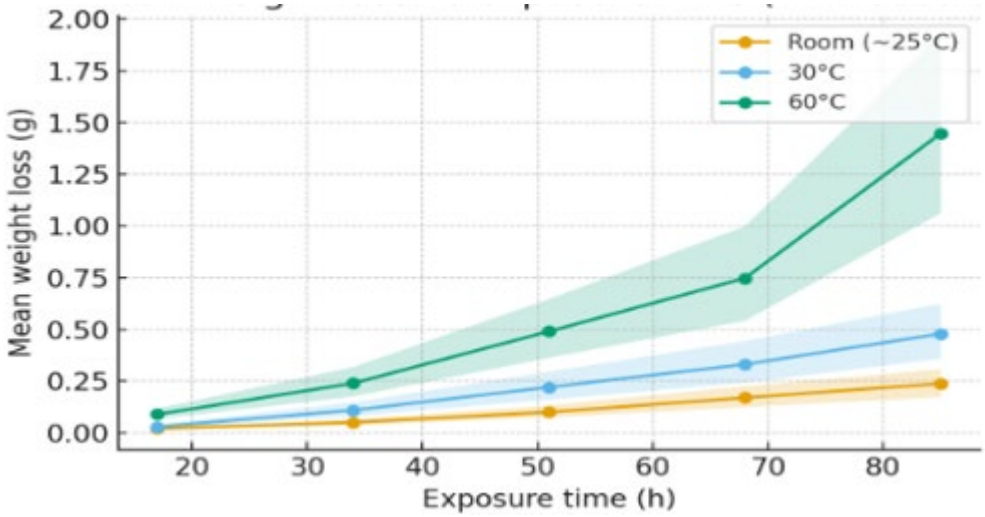

Figure 1: Weight Loss vs. Time for Martensitic Stainless Steel at Different Temperatures

The corrosion response was therefore strongly temperature dependent, with the mean corrosion rate at 60 °C approximately five times greater than that at room temperature, indicating pronounced thermal acceleration of chloride-induced degradation in the martensitic microstructure.

3.2. Corrosion Kinetics

The weight-loss curves exhibit near-linear to quasi-linear behavior over the investigated exposure window, with no evidence of early saturation. The systematic increase in slope with temperature reflects progressive enhancement of corrosion kinetics rather than isolated transient effects.

Although the present data clearly demonstrate thermally activated corrosion, no mechanistic interpretation of passive-film breakdown, pit chemistry, or transport phenomena is attempted, as no electrochemical or surface-analytical measurements were performed. The results are therefore confined to quantitative kinetic trends.

3.3. Monte Carlo Uncertainty Quantification

Monte Carlo resampling (n = 1,000) was applied to propagate experimentally defined uncertainties—mass-loss precision, surface-area tolerance, temperature fluctuation, and pH stability—through corrosion-rate calculations and kinetic fitting.

The simulations were not used to impose kinetic laws, but to assess the statistical robustness of the experimentally observed temperature dependence. The resulting corrosion-rate distributions yielded 95% confidence interval widths corresponding to approximately 10–14% of the mean values across the temperature range. The previously cited ±12% therefore represents the normalized width of the confidence interval, not a coefficient of variation.

These results demonstrate that the temperature–corrosion trend and fitted kinetic parameters remain stable within realistic experimental variability.

3.4. Arrhenius Behavior

Arrhenius analysis of the experimentally derived mean corrosion rates produced an apparent activation energy of **38.7 kJ/mol**.

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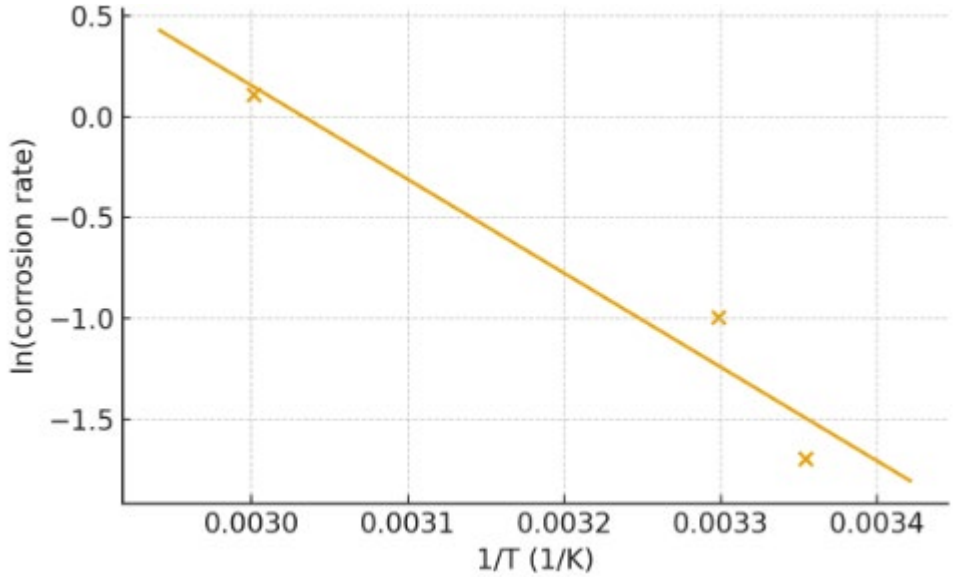

Figure 2: Arrhenius Plot (Ea= 38.7 kJ/mol)

As shown in Figure 2 above, ln (CR) varies linearly with reciprocal temperature, confirming thermally activated behavior over the investigated range.

The Monte Carlo-derived confidence envelope illustrates the influence of propagated experimental uncertainties on model stability. The simulation quantifies confidence bounds but does not constitute independent validation of mechanistic corrosion laws.

3.5. Comparison of Corrosion Rates at 85 h

The Figure 3 below compares corrosion rates after 85 h of exposure. Mean values increased from approximately **0.18 mg·cm⁻²·h⁻¹ at 25 °C** to **0.36 mg·cm⁻²·h⁻¹ at 30 °C**, and **1.05 mg·cm⁻²·h⁻¹ at 60 °C**.

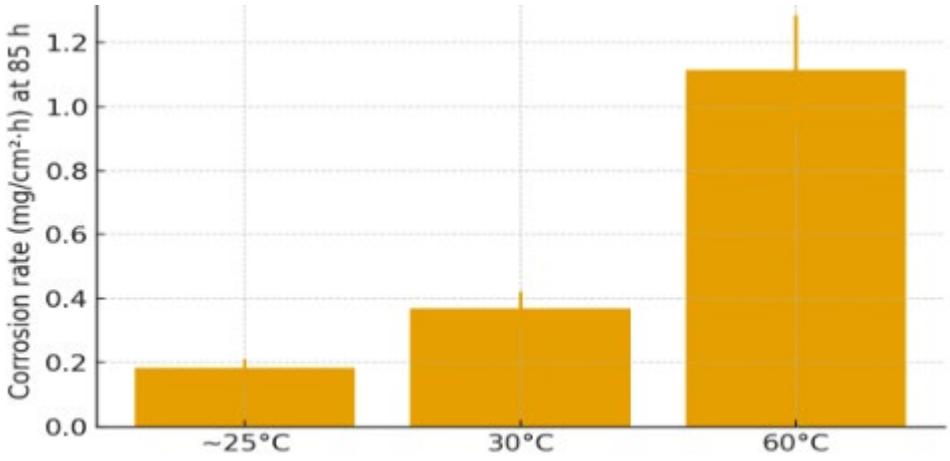

Figure 3: Corrosion rate at 85h with error bars

Standard deviations from triplicate specimens increased with temperature, indicating broader stochastic dispersion of corrosion severity at elevated temperatures. This behavior is consistent with enhanced localization and non-uniform attack commonly observed in martensitic stainless steels under aggressive chloride environments.

3.6. Integrated Experimental–Simulation Framework

The Figure 4 below summarizes the integrated methodology combining controlled immersion testing, kinetic parameter extraction, and Monte Carlo uncertainty propagation. This framework enables probabilistic characterization of corrosion-rate variability under thermal fluctuations relevant to offshore service conditions, providing a quantitative basis for temperature-dependent integrity assessment.

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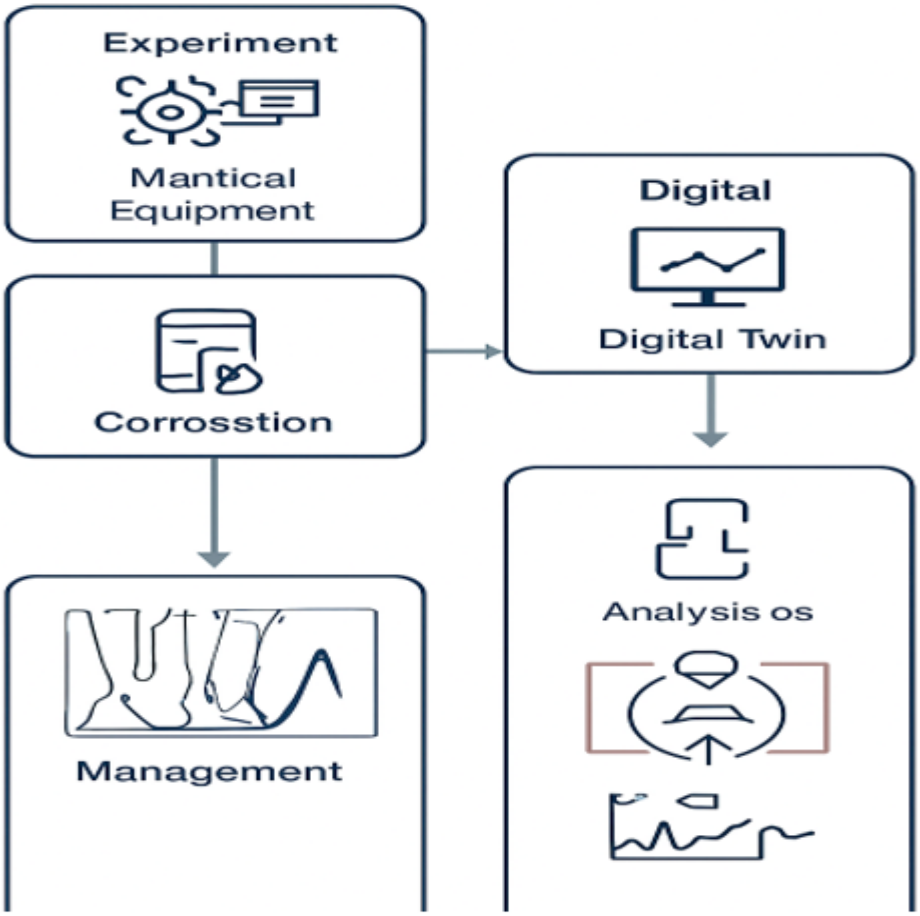

Figure 4: Experimental and Simulation Workflow Corrosion Assessment of AISI

4.0 Discussion

This study shows that temperature largely controls how AISI 440 martensitic stainless steel corrodes in simulated seawater; the corrosion rate rises steadily with heat, following a clear Arrhenius pattern from 25 to 60 °C, much like metal darkening faster as the water warms. At 60 °C, the corrosion rate jumps to about five times higher than at room temperature, clearly showing that heat is the main force driving metal breakdown in salty offshore conditions. The Arrhenius plot showed a tight linear fit ($R^2 = 0.982$), confirming that the measured weight-loss data follow sound, physically consistent kinetics—like points lining up neatly along a single, straight pencil mark. The experimentally determined activation energy of 38.7 kJ·mol^{-1} sits squarely within the 30–45 kJ·mol^{-1} range often reported for Fe–Cr martensitic alloys in chloride solutions, confirming that our gravimetric method produced realistic kinetic values that make physical sense. Along with the Arrhenius analysis, we also measured temperature sensitivity using the standard Q_{10} approach—like noting how reaction rates jump when the sample warms just a few degrees. From the Arrhenius fit, corrosion rates measured at 25 °C and 35 ° C gave a Q_{10} of about 1.8, meaning the metal's attack sped up roughly 80% with every 10 °C climb. This level of thermal acceleration matches what's typically seen with chloride-driven corrosion in martensitic stainless steels, underscoring how strongly temperature controls the pace of corrosion.

4.1 Evidence-Aligned Interpretation of Temperature Effects

The experimental results unambiguously demonstrate that corrosion rate, kinetic constants, and statistical dispersion all increase with temperature. The data clearly show that as the temperature rises, the corrosion rate, kinetic constants, and variability all climb—like metal reacting faster under a steady, rising heat. Still, since no electrochemical or surface analyses—like SEM, XRD, XPS, or EIS—were run, any explanation of the mechanism must rely solely on the visible kinetic changes, such as how fast the surface film grew or faded. As a result, we make no claims about the density of defects in the passive film, how chlorides slip through, changes in the oxide layer, or the chemistry inside a growing pit. The data show that temperature strongly shapes three things: (i) how fast mass is lost, (ii) the calculated kinetic parameters, and (iii) how much corrosion severity varies among specimens that, on paper, should be identical. At 60 °C, the wider spread in values suggests that localized, uneven corrosion—like tiny rough patches creeping across

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the surface—plays a growing role as the temperature rises. This behavior matches what's known about martensitic stainless steels—their tendency to react sharply in chloride-rich environments, where uneven microstructures and a fragile passive film can spark unpredictable corrosion, like tiny pits spreading under a faint salt crust.

4.2 Contextualization with Existing Literature

Direct comparison is most relevant to prior studies on martensitic stainless steels of comparable chromium and carbon content exposed to NaCl environments. Still, every interpretation in this study stays rooted in statistically backed kinetic trends, not in guessed-at microstructural mechanisms—like reading the pulse of a reaction, not its hidden bones. The most meaningful comparison draws on earlier studies of martensitic stainless steels with similar chromium and carbon levels, tested under NaCl exposure—where fine salt crystals once clung to the steel's dull surface. The activation energies reported for AISI 410, 420, and 440 steels usually fall between 30 and 45 kJ·mol^{-1}, matching closely with the value we found here—steady numbers, like readings on a well-calibrated gauge.

4.3 Interpretation of Monte Carlo–Based Uncertainty Propagation

Monte Carlo resampling was employed not to validate physical mechanisms, but to propagate experimentally defined uncertainties through corrosion-rate calculations and Arrhenius fitting. Likewise, other studies have noted that as temperature rises, corrosion rates scatter more widely—often a sign of stronger localization and patchy surface wear, like dull streaks spreading unevenly across heated metal. These results line up neatly with known kinetic patterns, yet they push further through modeling that folds uncertainty right into the mix—like tracing a reaction curve through a faint shimmer of data. We used Monte Carlo resampling not to confirm any physical mechanisms, but to carry the experimentally defined uncertainties through the corrosion-rate calculations and the Arrhenius fit—like tracing a ripple through a thin sheet of metal. Probabilistic corrosion-rate distributions accounted for shifts in mass loss, surface area, temperature control, and pH stability—like the slight rise in surface heat that makes metal hiss before it cools.

4.4 Practical Implications for Offshore Integrity Management

The kinetic parameters established in this study—particularly the apparent activation energy and Q_{10} coefficient—provide physically grounded inputs for preliminary lifetime prediction of martensitic stainless steel components operating under moderate thermal conditions. The resulting confidence envelopes spread about ±10–15% at the 95% level, showing both the natural swings of chloride-driven corrosion and a bit of experimental noise—like faint static in careful measurements. The simulations clearly show that both the exponential temperature dependence and the calculated activation energy stay statistically steady, even with the small, real-world fluctuations you'd expect in measurement data. By applying a probabilistic approach, we boost the reliability of the kinetic interpretation and sidestep a common flaw in corrosion research that depends only on fixed point estimates—like judging rust's spread from a single snapshot under the microscope..

4.5 Limitations and Directions for Future Work

Several limitations must be acknowledged. The kinetic parameters found in this study—especially the apparent activation energy and the Q_{10} coefficient—offer solid, physics-based data for estimating how long martensitic stainless steel parts will last when working in moderate heat, such as along a slightly sun-warmed offshore pipeline. The clear thermal sensitivity shows that even a small rise in temperature—just a few degrees can sharply intensify corrosion. These findings point to a clear need for temperature-compensated maintenance and inspection plans, sharper risk rankings for parts facing steep thermal gradients, and smarter choices in materials and corrosion allowances for offshore and subsea systems where salt spray clings to every surface. As shown in Figure 4, the integrated experimental–simulation framework provides a flexible way to embed uncertainty-aware corrosion kinetics into Risk-Based Inspection (RBI) programs and next-generation digital-twin platforms that safeguard offshore assets like a sensor-lined pipeline humming quietly beneath the waves.

5.0 Conclusion

Corrosion rates of AISI 440 Martensitic Stainless Steel were found to be greatly dependent on temperature, and at average corrosion rates of 60 °C, values were found to be five times greater than at room temperature. The apparent activation energy calculated was found to be 38.7 kJ/mol, which is close to other Fe-Cr Martensitic Alloys. The conventional Q_{10} test revealed a corrosion rate increase of about 80% per 10 °C rise. Monte Carlo resampling was done to account for experimental error.

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The results highlight the important role of temperature in corrosion kinetics and variability, where higher temperatures increase not only the mean values of the corrosion rates but also the dispersion thereof. The integrated experimental and modeling approach offers a temperature-dependent corrosiveness assessment strategy, including risk-based inspections and material choices for martensitic stainless steel equipment in the subsea environment.

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