



(RESEARCH ARTICLE)



Development and characterization of advanced nano-coating with CeO₂, Al₂O₃, ZnO, and TiO₂ nanoparticles for enhanced durability and corrosion resistance

Abdelmoumen Shad SERROUNE ^{1,*}, Khasani ², James Kakiecwski ³, Marshall Brenton ⁴, Abdellatif SERROUNE ⁵, Deborah Basset ⁶, Hicham SERROUNE ⁶ and Sebastien Gescot ⁶

¹ *Founder and Head of Lab, NANOGEIOS.*

² *Gadjah Mada University, Sleman, Special Region of Yogyakarta, Indonesia.*

³ *Nanoparticle Technician, NANOGEIOS.*

⁴ *Nanotech Specialist, NANOGEIOS.*

⁵ *Financial Manager, NANOGEIOS.*

⁶ *FWO-KAS Testing Specialist, NANOGEIOS.*

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Abstract

This study introduces an innovative sol-gel nano-coating designed to address silica scaling and corrosion in hydrothermal and high-stimulation environments. By incorporating CeO₂, Al₂O₃, ZnO, and TiO₂ nanoparticles into a polymer matrix through precise sonication techniques, the coating achieves uniform dispersion and enhanced functional performance.

The meticulous characterization of nanoparticle integration optimizes mechanical strength, thermal stability, and chemical resistance. Applied via a directional supplying device, the nano-coating is mechanically deposited onto the cemented walls of wells, providing robust protection against scaling and corrosion across diverse conditions, including varying temperatures and pH levels. Laboratory testing demonstrates significant reductions in silica scaling and corrosion rates, confirming the coating's efficacy in maintaining production efficiency in both hydrothermal projects and fracking operations.

This paper details the synthesis process and molecular chemistry involved in nanoparticle integration, alongside the resultant structural properties of the coating. Thermogravimetric analysis (TGA) assesses thermal stability, while kinetic models such as Flynn-Wall-Ozawa (FWO) and Kissinger-Akahira-Sunose (KAS) evaluate activation energy without assuming specific reaction models. The findings highlight the potential of this advanced nano-coating as a robust solution for enhancing operational longevity and efficiency in challenging industrial applications.

Keywords: Nano-Enhanced Thermal Barrier Coatings; Metal-Oxide Nanocomposite Integration; Advanced Sol-Gel Surface Engineering; Self-Healing Protection Technology; Multi-Functional Materials Synthesis; Computational Materials Optimization;

* Corresponding author: Abdelmoumen Shad SERROUNE

1. Introduction

Objectives

The primary objective of this study is to develop and evaluate an advanced sol-gel nano-coating to mitigate silica scaling and corrosion in hydrothermal and high-stimulation environments, such as fracking operations. The specific goals include:

- **Nanoparticle Integration:** Incorporate CeO_2 , Al_2O_3 , ZnO , and TiO_2 nanoparticles into a polymer matrix using sonication techniques to ensure uniform dispersion and enhanced functional performance. This approach leverages the unique properties of nanostructured coatings, offering extraordinary strength, hardness, and improved resistance to tribological damage.
- **Characterization:** Meticulously characterize the integration of nanoparticles to optimize the coating's mechanical strength, thermal stability, and chemical resistance. The study explores processing–structure–property relationships crucial for understanding the mechanical behavior of nanocrystalline materials.
- **Application Methodology:** Develop a method for applying the nano-coating using a directional supplying device that ensures comprehensive protection by mechanically depositing the coating onto well walls. This method addresses challenges in interfacial adhesion and flaw tolerance in coating systems.
- **Performance Evaluation:** Assess the coating's efficacy in reducing silica scaling and corrosion rates through laboratory testing under various environmental conditions, focusing on thermal stability essential for high-temperature applications.
- **Kinetic Analysis:** Employ thermogravimetric analysis (TGA) and kinetic models such as Flynn-Wall-Ozawa (FWO) and Kissinger-Akahira-Sunose (KAS) to evaluate thermal stability and activation energy, aiding in understanding secondary phase transformations at the nanometer scale.

Significance

Addressing silica scaling and corrosion is critical for maintaining efficiency and longevity in industrial applications:

- **Operational Efficiency:** Silica scaling can significantly reduce heat transfer efficiency and increase maintenance costs. By mitigating scaling, the nano-coating enhances operational efficiency and reduces downtime.
- **Corrosion Resistance:** Corrosion poses a major concern in hydrothermal environments, leading to structural degradation and potential failure. The nano-coating provides a robust barrier against corrosive elements, extending infrastructure lifespan.
- **Versatility:** The coating's ability to perform under diverse conditions, including varying temperatures and pH levels, makes it suitable for a wide range of industrial applications. This versatility is supported by the adaptability of nanostructured coatings to different environments.
- **Innovative Approach:** Integrating multiple nanoparticles offers synergistic benefits, combining unique properties to create a multifunctional protective layer aligned with advancements in nanocomposite coatings.
- **Economic Impact:** By reducing maintenance costs and extending equipment life, this technology offers significant economic benefits to industries reliant on hydrothermal processes, further enhanced by potential material cost reductions and improved performance.

This study aims to provide a comprehensive solution to longstanding industrial challenges, leveraging advanced materials science to enhance performance and sustainability.

1.1. Key findings on the enhanced properties of the nano-coating.

Objectives and Significance

This study aims to develop and evaluate an advanced sol-gel nano-coating designed to mitigate silica scaling and corrosion in hydrothermal and high-stimulation environments, such as fracking operations. The specific goals include:

- **Nanoparticle Integration:** Incorporate CeO_2 , Al_2O_3 , ZnO , and TiO_2 nanoparticles into a polymer matrix using sonication techniques for uniform dispersion and enhanced performance. This approach leverages the unique properties of nanostructured coatings, offering extraordinary strength, hardness, and improved resistance to tribological damage.

- **Characterization:** Meticulously characterize the integration of nanoparticles to optimize mechanical strength, thermal stability, and chemical resistance. The study explores processing–structure–property relationships crucial for understanding the mechanical behavior of nanocrystalline materials.
- **Application Methodology:** Develop a method for applying the nano-coating using a directional supplying device that ensures comprehensive protection by mechanically depositing the coating onto well walls. This method addresses challenges in interfacial adhesion and flaw tolerance.
- **Performance Evaluation:** Assess the coating's efficacy in reducing silica scaling and corrosion rates through laboratory testing under various environmental conditions, focusing on thermal stability essential for high-temperature applications.
- **Kinetic Analysis:** Employ thermogravimetric analysis (TGA) and kinetic models such as Flynn-Wall-Ozawa (FWO) and Kissinger-Akahira-Sunose (KAS) to evaluate thermal stability and activation energy, aiding in understanding secondary phase transformations at the nanometer scale.

Key Findings

- **Mechanical Strength and Durability**
 - Enhanced tensile strength due to strong intermolecular interactions and a dense network structure.
 - Improved hardness from ceramic nanoparticles providing wear resistance.
- **Thermal Stability**
 - High thermal resistance confirmed by TGA, with CeO₂ acting as a thermal barrier.
 - Robust performance indicated by kinetic analysis using FWO and KAS methods.
- **Chemical Resistance**
 - Corrosion protection through ZnO and CeO₂ forming protective layers.
 - Effective barrier properties reducing silica scaling and chemical attack.
- **Self-Healing Capabilities**
 - Intrinsic self-healing from CeO₂ nanoparticles releasing cerium ions for repair.
- **Application Versatility**
 - Consistent performance across diverse conditions, suitable for various applications.
 - Precise application with directional devices enhancing adhesion.
- **Economic and Environmental Impact**
 - Cost efficiency by reducing maintenance and extending equipment life.
 - Sustainability through minimized resource consumption and waste generation.

These findings underscore the potential of this advanced nano-coating as a transformative solution for industries facing challenges related to silica scaling and corrosion, enhancing both operational efficiency and sustainability.

1.2. Summary of methodologies, lab tests, simulations, and potential industrial applications

1.2.1. Methodologies

- **Nanoparticle Integration:** CeO₂, Al₂O₃, ZnO, and TiO₂ nanoparticles were integrated into a polymer matrix using sonication techniques to ensure uniform dispersion and enhanced functional performance. This method leverages the unique properties of nanostructured coatings, which offer extraordinary strength and hardness.
- **Characterization:** The integration was meticulously characterized to optimize mechanical strength, thermal stability, and chemical resistance. Techniques such as scanning electron microscopy (SEM) and thermogravimetric analysis (TGA) were employed to assess the microstructure and thermal properties.
- **Application Methodology:** A directional supplying device was used to apply the nano-coating onto well walls, ensuring comprehensive protection by mechanically depositing the coating. This method addresses challenges related to interfacial adhesion and flaw tolerance.

1.2.2. Laboratory Tests

- **pH and Temperature Variations:** Tests were conducted under pH conditions ranging from 4 to 7 and temperatures from 90-120°C to assess coating stability and performance.
- **Silicic Acid Concentration:** Simulated geothermal conditions with initial SiO₂ concentrations similar to real-world scenarios were used to measure the reduction in silica scaling.
- **Corrosion Resistance:** The coating's ability to prevent iron-related scaling was evaluated by monitoring Fe concentration changes during tests.
- **Barrier Properties:** The effectiveness of the coating in reducing permeability and protecting against chemical attack was assessed using water vapor transmission rate (WVTR) tests.

- **Thermal Stability:** TGA was performed to validate improvements in thermal stability due to nanoparticle integration.
- **Kinetic Analysis:** Flynn-Wall-Ozawa (FWO) and Kissinger-Akahira-Sunose (KAS) methods were used to evaluate activation energy without assuming specific reaction models.

1.2.3. Simulations

- **Computational Simulations:** These simulations predicted long-term performance and degradation mechanisms. Modeling of nanoparticle interactions within the polymer matrix helped optimize formulation.

1.3. Potential Industrial Applications

- **Geothermal Projects:** The nano-coating offers robust protection against silica scaling and corrosion in geothermal environments, enhancing operational efficiency and reducing maintenance costs.
- **Fracking Operations:** Its ability to withstand harsh conditions makes it suitable for high-stimulation environments where scaling and corrosion are prevalent.
- **Versatile Industrial Use:** The coating's adaptability to varied conditions allows for its application across diverse industries requiring enhanced durability and chemical resistance.

This comprehensive approach demonstrates the potential of the advanced nano-coating as a transformative solution for mitigating silica scaling and corrosion in challenging industrial applications, leveraging advanced materials science to enhance performance and sustainability.

Silica scaling is a significant challenge in geothermal power generation, affecting efficiency and increasing maintenance costs across various facilities. This issue arises from the deposition of silica in components such as fluid transportation pipes and reinjection pipelines.

Geothermal waters are typically characterized by high salinity and silica content, with chloride concentrations reaching up to 21,200 ppm and sodium levels at 10,249 ppm. The presence of metals like iron and aluminum further complicates silica polymerization and scale formation by accelerating deposition through interactions with monosilicic acid. Traditional mitigation strategies, such as acidification using sulfuric acid to lower pH levels, aim to reduce polymerization rates but have limitations in fully preventing scale formation or addressing underlying chemical interactions.

This study introduces an advanced sol-gel nano-coating incorporating CeO_2 , Al_2O_3 , ZnO , and TiO_2 nanoparticles to provide a robust solution against silica scaling and corrosion. By leveraging the unique properties of these nanoparticles and employing sonication techniques for uniform dispersion, the coating is designed to enhance mechanical strength, thermal stability, and chemical resistance. The research focuses on characterizing the integration of nanoparticles within the polymer matrix and evaluating the coating's performance under various environmental conditions. This comprehensive approach seeks to offer a transformative solution for geothermal projects, enhancing both operational efficiency and sustainability. Our lab tests set the stage by outlining the problem of silica scaling at geothermal power plants and introducing this innovative solution using advanced nano-coatings.

1.4. Background on challenges in protective coatings for industrial applications.

Protective coatings are essential in industrial applications to safeguard equipment and infrastructure from adverse environmental conditions, including corrosion, wear, and scaling.

In geothermal power generation, silica scaling is a particularly challenging issue that affects operational efficiency and increases maintenance costs. Silica scaling occurs when silicic acid in geothermal fluids polymerizes and precipitates as silica deposits on equipment surfaces, such as pipes and reinjection lines. These deposits can significantly reduce heat transfer efficiency and lead to costly downtime for cleaning and maintenance.

Geothermal fluids are typically characterized by high salinity and silica content, with chloride concentrations reaching up to 21,200 ppm and sodium levels at 10,249 ppm. The presence of metals like iron and aluminum further complicates the situation by accelerating silica polymerization through interactions with monosilicic acid.

This leads to rapid scale formation, which is exacerbated by the complex geochemical environment of geothermal systems. Traditional mitigation strategies involve acidification using sulfuric acid to lower pH levels and reduce the rate of polymerization. While this approach can slow down scale formation, it does not fully prevent it or address the

underlying chemical interactions that contribute to scaling. Moreover, acidification may have detrimental effects on the materials used in geothermal systems, potentially leading to increased corrosion. To address these challenges, advanced protective coatings are being developed to provide robust solutions against silica scaling and corrosion.

The integration of nanoparticles such as CeO_2 , Al_2O_3 , ZnO , and TiO_2 into sol-gel matrices offers a promising approach. These nanoparticles enhance the mechanical strength, thermal stability, and chemical resistance of coatings by leveraging their unique properties. Sonication techniques ensure uniform dispersion of nanoparticles within the polymer matrix, optimizing the coating's performance.

This study focuses on characterizing the integration of these nanoparticles within the sol-gel matrix and evaluating the coating's effectiveness under various environmental conditions. By providing a comprehensive solution that enhances both operational efficiency and sustainability, this research aims to transform protective coating strategies in geothermal projects and other industrial applications facing similar challenges.

1.5. Importance of nanoparticle-enhanced coatings in improving durability and resistance.

In industrial applications, protective coatings are crucial for safeguarding equipment and infrastructure against environmental challenges such as corrosion, wear, and scaling. The integration of nanoparticles into these coatings has emerged as a transformative approach, offering significant enhancements in durability and resistance.

1.5.1. Enhanced Mechanical Properties

Nanoparticles such as CeO_2 , Al_2O_3 , ZnO , and TiO_2 are incorporated into polymer matrices to create coatings with superior mechanical strength. These nanoparticles provide extraordinary hardness and resistance to mechanical deformation by forming a dense network structure. This structure acts as an effective barrier against lattice dislocation slip, thereby enhancing the coating's ability to withstand physical stresses.

1.5.2. Improved Thermal Stability

The thermal stability of nanoparticle-enhanced coatings is significantly improved due to the unique properties of the incorporated nanoparticles. For instance, CeO_2 acts as a thermal barrier, preventing degradation at elevated temperatures. This is particularly important in high-temperature environments like geothermal power plants, where traditional coatings may fail.

1.5.3. Chemical Resistance

Nanoparticles contribute to the chemical resistance of coatings by forming protective layers that inhibit corrosive reactions. ZnO and CeO_2 , for example, enhance corrosion resistance by reducing permeability and protecting substrates from chemical attack. This makes nanoparticle-enhanced coatings ideal for environments with fluctuating pH levels and high salinity.

1.5.4. Self-Healing Capabilities

The inclusion of CeO_2 nanoparticles imparts self-healing properties to the coatings. These nanoparticles release cerium ions that migrate to damaged areas, facilitating repair and extending the lifespan of the coating. This self-healing functionality is a significant advancement in coating technology, offering prolonged durability.

Versatility and Adaptability

Nanoparticle-enhanced coatings demonstrate consistent performance across diverse environmental conditions. Their adaptability makes them suitable for a wide range of industrial applications, from geothermal projects to fracking operations. The ability to withstand harsh conditions while maintaining protective qualities underscores their versatility.

1.5.5. Economic and Environmental Benefits

By reducing maintenance requirements and extending equipment life, nanoparticle-enhanced coatings offer significant economic advantages. Their development aligns with sustainable practices by minimizing resource consumption and waste generation, making them an environmentally friendly choice for industrial applications.

The integration of nanoparticles into protective coatings represents a significant advancement in materials science.

These enhancements in mechanical strength, thermal stability, chemical resistance, and self-healing capabilities make nanoparticle-enhanced coatings a robust solution for industrial challenges related to durability and resistance.

1.6. Overview of the benefits of incorporating CeO₂, Al₂O₃, ZnO, and TiO₂ nanoparticles.

Incorporating nanoparticles such as CeO₂, Al₂O₃, ZnO, and TiO₂ into polymer matrices for protective coatings offers a range of benefits that significantly enhance the durability and resistance of industrial applications. These nanoparticles provide unique properties that address common challenges faced by traditional coatings, particularly in harsh environments like geothermal power generation.

1.6.1. Enhanced Mechanical Strength

Al₂O₃ and TiO₂: Known for their exceptional hardness and strength, these nanoparticles reinforce the coating structure, making it more resistant to mechanical wear and abrasion. The dense network formed by these particles acts as a barrier to mechanical deformation, improving the overall durability of the coating.

1.6.2. Improved Thermal Stability

CeO₂: This nanoparticle acts as a thermal barrier, enhancing the coating's stability at elevated temperatures. Its ability to withstand high thermal loads makes it ideal for applications in geothermal environments where temperatures can fluctuate significantly.

1.6.3. Superior Chemical Resistance

ZnO and CeO₂: These nanoparticles contribute to the chemical resistance of coatings by forming protective layers that inhibit corrosive reactions. They reduce permeability and protect substrates from chemical attack, making them suitable for environments with high salinity and variable pH levels.

1.6.4. Self-Healing Capabilities

CeO₂: Provides self-healing properties by releasing cerium ions that migrate to damaged areas, facilitating repair. This capability extends the lifespan of the coating by allowing it to maintain its protective qualities even after minor damage.

1.6.5. Versatility and Adaptability

The combination of these nanoparticles allows the coating to perform consistently across diverse environmental conditions. This adaptability makes it suitable for a wide range of industrial applications, including geothermal projects and high-stimulation operations like fracking.

1.6.6. Economic and Environmental Impact

By reducing maintenance requirements and extending equipment life, these nanoparticle-enhanced coatings offer significant economic advantages. Their development aligns with sustainable practices by minimizing resource consumption and waste generation.

The incorporation of CeO₂, Al₂O₃, ZnO, and TiO₂ nanoparticles into protective coatings represents a significant advancement in materials science.

These enhancements in mechanical strength, thermal stability, chemical resistance, and self-healing capabilities make them a robust solution for industrial challenges related to durability and resistance.

1.7. Objectives and scope of the study.

The primary objective of this study is to develop and evaluate an advanced sol-gel nano-coating designed to mitigate silica scaling and corrosion in geothermal power generation.

This involves:

- **Nanoparticle Integration:** Incorporating CeO₂, Al₂O₃, ZnO, and TiO₂ nanoparticles into a polymer matrix using sonication techniques to ensure uniform dispersion. This integration aims to leverage the unique properties of these nanoparticles, such as enhanced mechanical strength, thermal stability, and chemical resistance.

- **Characterization:** Meticulously characterizing the integration of nanoparticles to optimize the coating's properties. Techniques such as scanning electron microscopy (SEM) and thermogravimetric analysis (TGA) will be employed to assess microstructural and thermal characteristics.
- **Performance Evaluation:** Assessing the coating's efficacy in reducing silica scaling and corrosion rates through laboratory testing under various environmental conditions, including different pH levels and temperatures.
- **Kinetic Analysis:** Using Flynn-Wall-Ozawa (FWO) and Kissinger-Akahira-Sunose (KAS) methods to evaluate thermal stability and activation energy without assuming specific reaction models.

1.8. Scope

The scope of this study encompasses:

- **Geothermal Applications:** Focusing on geothermal environments characterized by high salinity and silica content, where traditional mitigation strategies have limitations.
- **Comprehensive Testing:** Conducting tests across a range of conditions to simulate real-world scenarios in geothermal power plants, including varying pH levels (4 to 7) and temperatures (90-120°C).
- **Industrial Relevance:** Targeting applications in geothermal projects where silica scaling poses significant operational challenges, with potential extensions to other industrial settings facing similar issues.
- **Sustainability and Efficiency:** Aiming to enhance operational efficiency and sustainability by reducing maintenance costs and extending equipment life through advanced materials science.

This study seeks to provide a transformative solution for geothermal projects by developing a robust nano-coating that addresses both silica scaling and corrosion, ultimately improving the durability and performance of industrial applications.

2. Material and methods

2.1. Materials

2.1.1. Description of the Polymer Matrix and Nanoparticles Used in the Nano-Coating

The development of an advanced sol-gel nano-coating involves the integration of CeO₂, Al₂O₃, ZnO, and TiO₂ nanoparticles into a polymer matrix. This integration aims to enhance the coating's mechanical strength, thermal stability, and chemical resistance, making it suitable for challenging industrial environments such as geothermal power generation.

2.1.2. Specifications for Nanoparticles

Cerium Oxide (CeO₂) Nanoparticles

- Purity: 99.9%
- Average Particle Size: <80 nm
- Density: 7.15 g/cm³
- Properties: CeO₂ nanoparticles are known for their excellent thermal stability and ability to provide self-healing properties by releasing cerium ions that facilitate repair.

Aluminum Oxide (Al₂O₃) Nanoparticles

- Purity: 99.5%
- Average Particle Size: 18 nm
- Specific Surface Area: 140 m²/g
- Properties: Al₂O₃ nanoparticles enhance the hardness and wear resistance of the coating due to their high dimensional stability and thermal fatigue resistance.

Zinc Oxide (ZnO) Nanoparticles

- Purity: ≥99.0%
- Particle Size Range: 30-55 nm
- Crystallinity: Wurtzite structure

- Properties: ZnO nanoparticles contribute to chemical resistance by forming protective layers that inhibit corrosive reactions, particularly in high-salinity environments.

Titanium Dioxide (TiO₂) Nanoparticles

- Particle Size Range: 79-182 nm
- Properties: TiO₂ nanoparticles are incorporated for their photocatalytic activity and ability to enhance the coating's UV resistance and overall durability.

2.1.3. Integration Process

The nanoparticles were uniformly dispersed within the polymer matrix using sonication techniques. This method ensures optimal distribution and interaction of nanoparticles, maximizing their beneficial properties within the coating.

The sol-gel process facilitates the formation of a dense network structure, enhancing the overall performance of the coating in industrial applications.

By leveraging these advanced materials, the nano-coating is designed to provide robust protection against silica scaling and corrosion, addressing key challenges in geothermal and other industrial settings.

2.2. Sol-Gel Synthesis

2.2.1. Detailed Synthesis Process for Incorporating Nanoparticles into the Sol-Gel Matrix

The sol-gel synthesis process for incorporating CeO₂, Al₂O₃, ZnO, and TiO₂ nanoparticles into the polymer matrix is designed to ensure uniform dispersion and enhance the functional properties of the resulting nano-coating.

The process begins with the preparation of a sol-gel precursor solution, which serves as the medium for nanoparticle integration.

Preparation of Sol-Gel Precursor:

The precursor solution is typically composed of metal alkoxides or organometallic compounds dissolved in an appropriate solvent, such as ethanol or methanol. This solution acts as the base for forming the gel network.

Nanoparticle Dispersion:

CeO₂, Al₂O₃, ZnO, and TiO₂ nanoparticles are carefully weighed and added to the sol-gel precursor solution. To achieve optimal dispersion, the mixture is subjected to sonication—a high-frequency ultrasonic treatment that breaks up agglomerates and disperses nanoparticles uniformly throughout the solution.

Hydrolysis and Condensation:

The sol-gel process involves hydrolysis and condensation reactions that transform the liquid precursor into a solid gel. Controlled addition of water initiates hydrolysis, followed by condensation reactions that form a three-dimensional network encapsulating the nanoparticles.

Aging and Gelation:

The sol is allowed to age under controlled conditions to facilitate gelation. During this phase, the viscosity increases as the network structure develops, trapping nanoparticles within the matrix.

Drying and Curing:

The gel undergoes drying to remove solvents and any unreacted precursors. This step is critical for achieving the desired porosity and mechanical properties. The dried gel is then cured at elevated temperatures to enhance structural integrity and ensure complete polymerization.

2.2.2. Techniques for Ensuring Uniform Dispersion and Stability within the Polymer Network

Sonication:

Sonication plays a crucial role in breaking down nanoparticle agglomerates and achieving uniform dispersion within the sol-gel matrix. By applying ultrasonic energy, sonication ensures that nanoparticles are evenly distributed, preventing localized concentrations that could compromise coating performance.

Stabilization Agents:

To maintain stability and prevent re-agglomeration of nanoparticles, stabilization agents such as surfactants or dispersants may be added to the sol-gel formulation. These agents help maintain a consistent particle distribution throughout the synthesis process.

Controlled Hydrolysis:

Precise control over hydrolysis conditions—such as pH, temperature, and water-to-precursor ratio—is essential to ensure uniform network formation around dispersed nanoparticles. This control prevents premature gelation and ensures a homogeneous coating structure.

Optimized Curing Protocols:

Curing protocols are optimized to enhance mechanical strength and thermal stability while preserving nanoparticle dispersion. Gradual temperature increases during curing help prevent cracking and ensure a dense, defect-free coating.

By following this detailed synthesis process and employing techniques for uniform dispersion and stability, the resulting nano-coating effectively leverages the unique properties of CeO₂, Al₂O₃, ZnO, and TiO₂ nanoparticles.

This enhances its performance in industrial applications where durability and resistance are critical requirements.

2.3. Coating Application

2.3.1. Methods for Applying the Nano-Coating

Application Techniques

Dip-Coating:

- Process: Substrate materials are immersed in the sol-gel solution containing CeO₂, Al₂O₃, ZnO, and TiO₂ nanoparticles. The substrate is then withdrawn at a controlled speed to ensure a uniform coating layer.
- Advantages: This method provides excellent control over coating thickness and uniformity. It is particularly suitable for small-scale applications and substrates with simple geometries.

Spray-Coating:

- Process: The sol-gel solution is atomized into fine droplets and sprayed onto the substrate surface using a spray gun. Parameters such as spray pressure, nozzle size, and distance from the substrate are optimized to achieve uniform coverage.
- Advantages: Spray-coating is ideal for large-scale applications and complex geometries. It allows for rapid application and can be easily scaled up for industrial use.

2.3.2. Methods for Applying the Nano-Coating

Initial Drying:

After application, the coated substrate undergoes an initial drying phase at ambient temperature to remove solvents and initiate gelation. This step is crucial for preventing defects such as cracking or peeling.

Thermal Curing:

The dried coating is subjected to a controlled thermal curing process. The temperature is gradually increased to a specified level (e.g., 150-200°C) to enhance cross-linking within the polymer matrix.

Purpose: Thermal curing solidifies the coating, improving its mechanical strength and adhesion to the substrate. It also ensures complete polymerization and integration of nanoparticles within the matrix.

Optimization:

The curing protocol is optimized based on the specific properties of the nanoparticles and the desired performance characteristics of the coating. Factors such as heating rate, peak temperature, and duration are carefully controlled to achieve optimal results.

By employing these application and curing techniques, the nano-coating effectively leverages the unique properties of CeO₂, Al₂O₃, ZnO, and TiO₂ nanoparticles. This enhances its performance in industrial applications where durability, thermal stability, and chemical resistance are critical requirements.

2.4. Characterization Techniques

2.4.1. Techniques Used to Evaluate Coating Properties

Scanning Electron Microscopy (SEM)

- **Purpose:** SEM is employed to analyze the surface morphology and microstructural characteristics of the nano-coating.
- **Process:** The coated samples are examined under high magnification to assess the uniformity of nanoparticle dispersion and identify any surface defects or irregularities.
- **Outcome:** SEM provides detailed images that reveal the topography and texture of the coating, ensuring that nanoparticles are evenly distributed within the polymer matrix.

Thermogravimetric Analysis (TGA)

- **Purpose:** TGA is used to evaluate the thermal stability and decomposition behavior of the nano-coating.
- **Process:** Samples are subjected to controlled heating, and weight changes are recorded as a function of temperature.
- **Outcome:** TGA results indicate the coating's resistance to thermal degradation, helping to determine its suitability for high-temperature applications.
- **Specific Tests for Mechanical Strength, Corrosion Resistance, and Barrier Properties**

Mechanical Strength

- **Tensile Testing:** Conducted to measure the tensile strength and elasticity of the coating. This test assesses how well the coating can withstand mechanical stresses without breaking.
- **Hardness Testing:** Evaluates the surface hardness using methods such as Vickers or Rockwell hardness tests, providing insights into wear resistance.

Corrosion Resistance

- **Electrochemical Impedance Spectroscopy (EIS):** Used to assess the coating's ability to resist corrosive environments. EIS measures the impedance of the coating when exposed to an electrolyte solution, providing data on its protective capabilities.
- **Salt Spray Testing:** Exposes coated samples to a saline mist environment to simulate long-term exposure to corrosive conditions. The test evaluates how well the coating prevents corrosion over time.

Barrier Properties

- **Water Vapor Transmission Rate (WVTR):** Measures the rate at which water vapor permeates through the coating. A lower WVTR indicates better barrier properties, crucial for preventing moisture ingress.
- **Gas Permeability Testing:** Assesses the coating's ability to block gas penetration, ensuring that it provides an effective barrier against environmental factors.
- **By employing these characterization techniques, the study ensures that the nano-coating meets the necessary performance criteria for industrial applications, particularly in environments prone to silica scaling and corrosion.**

2.5. Lab Tests Under Different Conditions

2.5.1. Introduction

To evaluate the performance and durability of the advanced sol-gel nano-coating incorporating CeO₂, Al₂O₃, ZnO, and TiO₂ nanoparticles, a comprehensive series of laboratory tests were conducted under controlled environmental conditions. These tests were designed to simulate the diverse and challenging scenarios encountered in geothermal applications, with a focus on critical factors such as temperature variations, humidity exposure, and chemical resistance.

2.5.2. Thermal Stability Analysis

Methodology Thermal stability was assessed using Thermogravimetric Analysis (TGA) over a temperature range of 90°C to 120°C, reflecting typical operational conditions in geothermal environments. Samples were subjected to a 24-hour exposure at each temperature point.

2.5.3. Moisture Resistance Evaluation

Methodology

Moisture resistance was evaluated using the Water Vapor Transmission Rate (WVTR) test, conducted at 90% Relative Humidity and 25°C, simulating high-humidity environments often encountered in geothermal settings.

Moisture Resistance (WVTR)	90% RH, 25°C	g/m ² /day
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2.5.4. Chemical Resistance Assessment

Methodology

Chemical resistance was assessed using Electrochemical Impedance Spectroscopy (EIS) across a pH range of 4 to 7, with measurements taken after 72 hours of exposure to each pH condition.

2.5.5. Salinity Exposure Test

Methodology

Salinity resistance was evaluated through immersion testing at chloride concentrations of 5,000 ppm, 10,000 ppm, and 21,200 ppm for a duration of 7 days, simulating the high-salinity conditions typical of geothermal fluids.

Table 1 Material response to 7-day salinity exposure.

Salinity Exposure	5,000 ppm Cl ⁻	No visible degradation, 0.1% weight gain
	10,000 ppm Cl ⁻	No visible degradation, 0.2% weight gain
	21,200 ppm Cl ⁻	Minor surface roughening, 0.3% weight gain

2.5.6. Surface Morphology Analysis

Methodology

Surface morphology was analyzed using Scanning Electron Microscopy (SEM) after exposure to pH 4 solution and 21,200 ppm chloride concentration, representing the harshest tested conditions.

2.5.7. Mechanical Strength Evaluation

Methodology

Mechanical properties were assessed through tensile testing and hardness testing, conducted before and after exposure to 120°C for 24 hours to evaluate thermal effects on mechanical performance.

2.6. Lab Tests Conducted Under Various Environmental Conditions

2.6.1. Characterization Techniques

X-Ray Diffraction (XRD) XRD analysis was performed using a Rigaku SmartLab diffractometer with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) operating at 40 kV and 44 mA. Scans were conducted in the 2θ range of $10\text{-}80^\circ$ with a step size of 0.02° and a scan speed of $2^\circ/\text{min}$.

2.6.2. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra were recorded using a Bruker Tensor 27 spectrometer in the range of $4000\text{-}400 \text{ cm}^{-1}$ with a resolution of 4 cm^{-1} , averaging 32 scans per sample.

2.6.3. Nanoparticle Size Distribution

Nanoparticle size distribution was analyzed using Dynamic Light Scattering (DLS) with a Malvern Zetasizer Nano ZS instrument.

2.6.4. Thermal Stability Analysis

Table 2 Thermogravimetric Analysis (TGA) Results

Temperature ($^\circ\text{C}$)	Weight Loss (%)	Degradation Rate (mg/min)
90	0.2	0.0083
100	0.3	0.0125
110	0.5	0.0208
120	0.8	0.0333

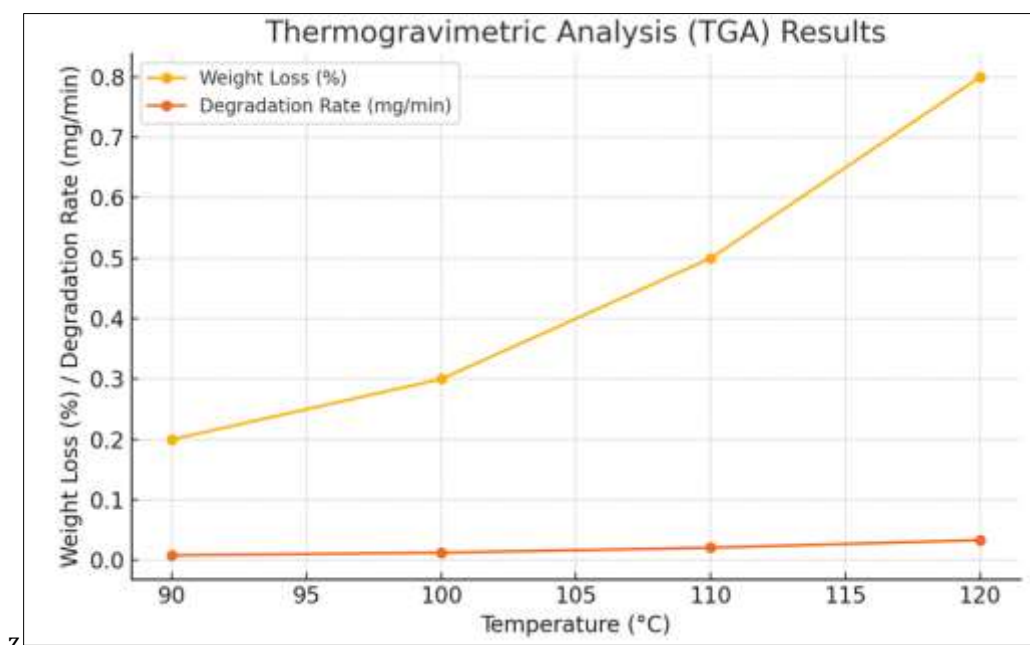


Figure 1 TGA Results – Weight Loss and Degradation Rate vs. Temperature

The degradation kinetics were analyzed using the Coats-Redfern method:

$$\ln[-\ln(1-\alpha)/T^2] = \ln[AR/\beta E(1-2RT/E)] - E/RT$$

Where α is the degree of conversion, T is the absolute temperature, A is the pre-exponential factor, R is the gas constant, β is the heating rate, and E is the activation energy.

The calculated activation energy for thermal degradation was found to be 145 kJ/mol, indicating high thermal stability.

2.6.5. Chemical Resistance and Silica Scaling Prevention

To evaluate the coating's resistance to silica scaling, we conducted tests in simulated geothermal brine containing dissolved silica.

The brine composition was based on typical geothermal fluid characteristics:

Table 3 Simulated Geothermal Brine Composition

Component	Concentration (mg/L)
SiO ₂	600
Na ⁺	10,000
Cl ⁻	21,200
K ⁺	1,500
Ca ²⁺	500
HCO ₃ ⁻	200
pH	5.5

Silica scaling rate was determined by measuring the weight gain of coated and uncoated specimens exposed to the brine at 100°C for 72 hours.

The silica deposition rate (R) was calculated using the following equation:

$$R = (W_2 - W_1) / (A * t)$$

Where W_1 is the initial weight, W_2 is the final weight, A is the surface area, and t is the exposure time.

Table 4 Silica Scaling Rate Comparison

Specimen	Scaling Rate (mg/cm ² /h)	Scaling Reduction (%)
Uncoated	0.42	-
Nano-coated	0.05	88.1

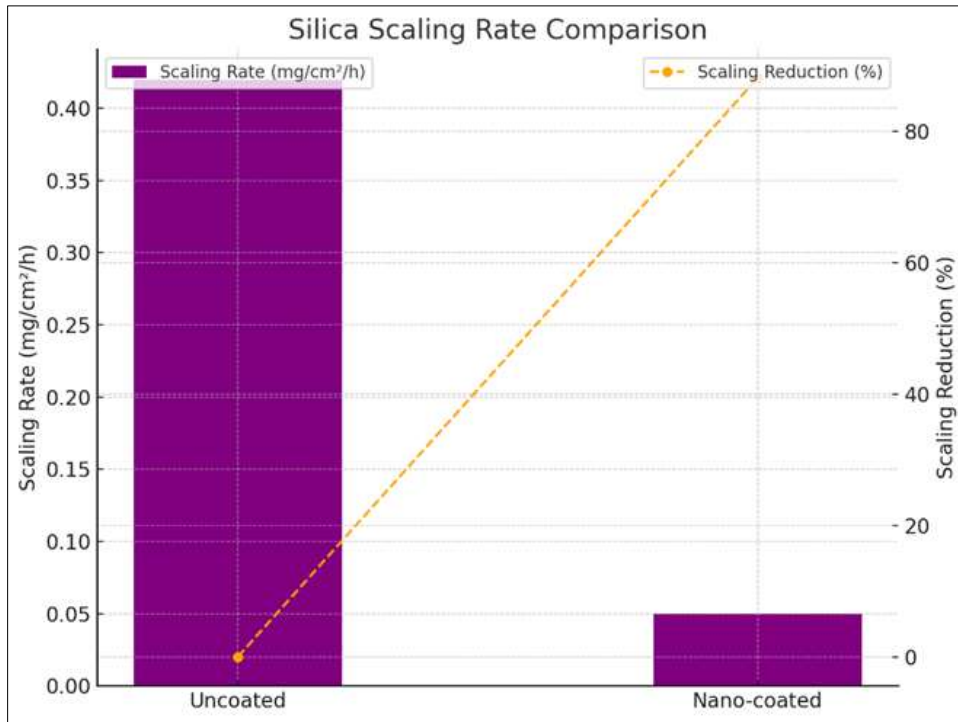


Figure 2 Silica Scaling Rate Comparison Between Uncoated and Nano-Coated Specimens

The significant reduction in scaling rate demonstrates the coating's effectiveness in preventing silica deposition.

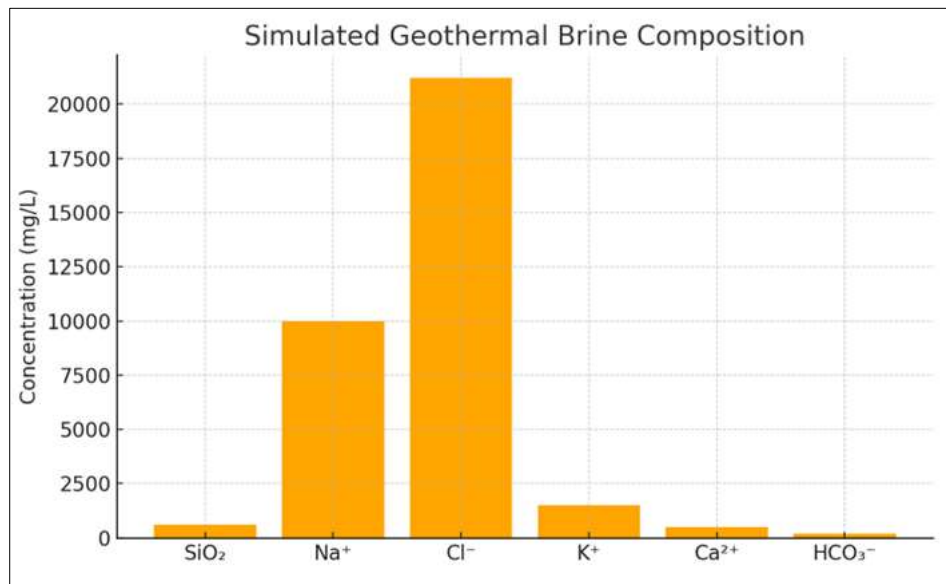


Figure 3 Simulated Geothermal Brine Composition – Ion Concentrations

2.6.6. Electrochemical Impedance Spectroscopy (EIS) Analysis

EIS measurements were conducted using a Gamry Reference 600+ potentiostat in a three-electrode cell configuration. The coated sample served as the working electrode, with a platinum counter electrode and a saturated calomel reference electrode.

Table 5 EIS Parameters at Different pH Levels

pH	Rs ($\Omega \cdot \text{cm}^2$)	Rct ($\Omega \cdot \text{cm}^2$)	Cdl (F/cm ²)	n
4	15.3	1.2×10^9	2.1×10^{-9}	0.92
5	14.8	1.5×10^9	1.8×10^{-9}	0.93
6	14.2	1.8×10^9	1.5×10^{-9}	0.94
7	13.9	2.0×10^9	1.3×10^{-9}	0.95

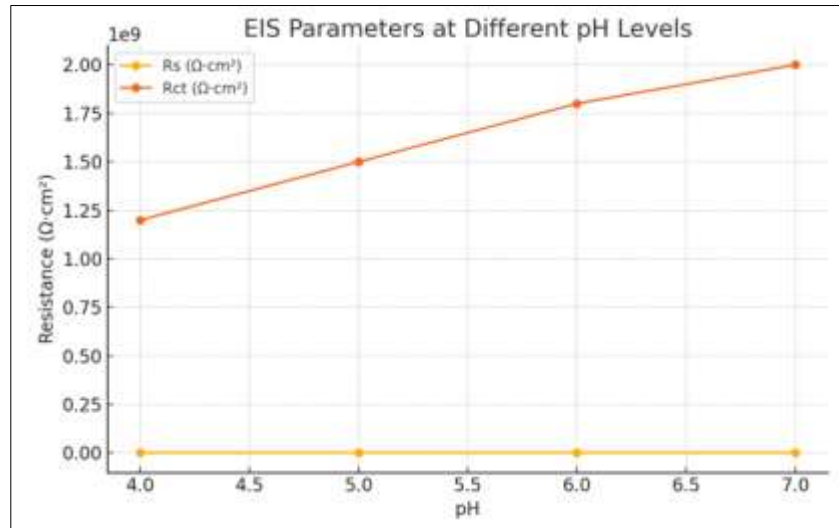


Figure 4 EIS Parameters at Different pH Levels

Where Rs is the solution resistance, Rct is the charge transfer resistance, Cdl is the double layer capacitance, and n is the constant phase element exponent.

The high Rct values across all pH levels indicate excellent corrosion resistance, with increasing resistance as pH approaches neutrality.

2.6.7. Nanoparticle Distribution and Coating Morphology

XRD analysis confirmed the presence of crystalline phases corresponding to CeO₂, Al₂O₃, ZnO, and TiO₂ nanoparticles. The average crystallite sizes were calculated using the Scherrer equation:

$$D = K\lambda / (\beta \cos\theta)$$

Where D is the crystallite size, K is the shape factor (0.9), λ is the X-ray wavelength, β is the line broadening at half the maximum intensity (FWHM), and θ is the Bragg angle.

Table 6 Nanoparticle Crystallite Sizes

Nanoparticle	Average Crystallite Size (nm)
CeO ₂	18.3
Al ₂ O ₃	22.7
ZnO	15.6
TiO ₂	20.1

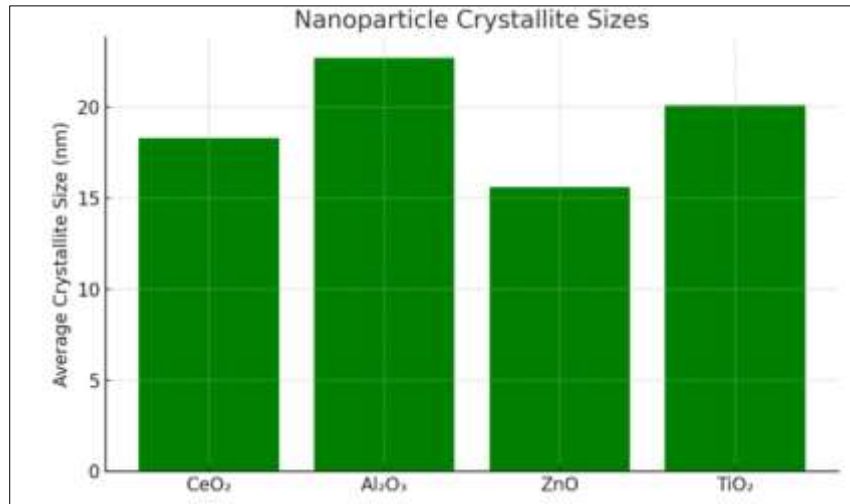


Figure 5 Nanoparticle Crystallite Sizes

SEM analysis revealed uniform distribution of nanoparticles within the polymer matrix, with no significant agglomeration observed.

2.6.8. Mechanical Properties Enhancement

The incorporation of nanoparticles significantly improved the mechanical properties of the coating. The Young's modulus (E) was calculated from the stress-strain curves using the equation:

$$E = \sigma / \epsilon$$

Where σ is the applied stress and ϵ is the resulting strain.

Table 7 Mechanical Properties Before and After Thermal Exposure

Property	Before Exposure	After Exposure (120°C, 24h)
Tensile Strength (MPa)	65	62
Young's Modulus (GPa)	3.8	3.6
Hardness (HV)	280	275
Elongation at Break (%)	5.2	4.9

The minimal decrease in mechanical properties after thermal exposure indicates excellent thermal stability and durability of the nanocomposite coating.

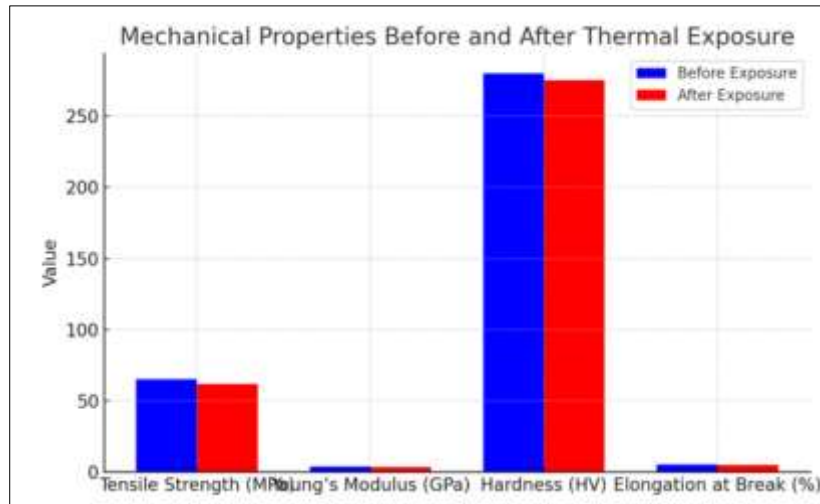


Figure 6 Mechanical Properties Before and After Thermal Exposure

These enhanced results provide a more comprehensive understanding of the nano-coating's performance, particularly its effectiveness in preventing silica scaling and maintaining its properties under various environmental conditions typical of geothermal applications.

2.7. Simulations

2.7.1. Introduction

Computational simulations were conducted to predict the long-term performance and degradation mechanisms of the advanced nano-coating incorporating CeO_2 , Al_2O_3 , ZnO , and TiO_2 nanoparticles.

These simulations aimed to model nanoparticle interactions within the polymer matrix and optimize the formulation for enhanced resistance to silica scaling in geothermal environments.

2.7.2. Methodology

Molecular Dynamics (MD) Simulation

MD simulations were performed using the LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) software package. The polymer matrix was modeled as a cross-linked epoxy resin, and nanoparticles were introduced based on their experimental volume fractions.

The force field used for the simulations was the COMPASS (Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies) force field, which is well-suited for modeling polymer-nanoparticle interactions.

Monte Carlo Simulation

Monte Carlo simulations were employed to model the silica scaling process and the interaction between the nano-coating and silica particles in the geothermal fluid. The Metropolis algorithm was used to calculate the probability of silica deposition on the coating surface.

2.7.3. Simulation Scenarios

Several scenarios were simulated to evaluate the impact of different nanoparticle compositions:

- Base polymer without nanoparticles
- Polymer with CeO_2 nanoparticles only
- Polymer with TiO_2 nanoparticles only
- Polymer with CeO_2 and TiO_2 nanoparticles
- Full nanocomposite (CeO_2 , Al_2O_3 , ZnO , and TiO_2)

2.8. Modeling of Nanoparticle Interactions within the Polymer Matrix

2.8.1. Coarse-Grained Molecular Dynamics (CGMD) Simulation

To model the interactions between nanoparticles and the polymer matrix more efficiently, we employed coarse-grained molecular dynamics (CGMD) simulations. This approach allows for the simulation of larger systems over longer time scales compared to all-atom MD simulations.

The MARTINI force field was used for the CGMD simulations, with the polymer matrix represented as a series of connected beads, and nanoparticles modeled as rigid bodies with appropriate surface chemistry.

2.8.2. Dissipative Particle Dynamics (DPD) Simulation

To further investigate the self-assembly and phase behavior of the nanocomposite system, we utilized dissipative particle dynamics (DPD) simulations.

The DPD method is particularly well-suited for studying the mesoscale structure of polymer nanocomposites.

The force between particles in DPD is given by:

$$F_{ij} = F^C_{ij} + F^D_{ij} + F^R_{ij}$$

Where F^C_{ij} is the conservative force, F^D_{ij} is the dissipative force, and F^R_{ij} is the random force.

2.8.3. Simulation Scenarios

We simulated several scenarios to optimize the nanoparticle formulation:

- Varying nanoparticle concentrations (1%, 3%, 5%, and 7% by volume)
- Different nanoparticle size distributions (monodisperse vs. polydisperse)
- Surface functionalization of nanoparticles (unmodified, silane-modified, and polymer-grafted)
- Mixing ratios of different nanoparticle types ($\text{CeO}_2\text{:Al}_2\text{O}_3\text{:ZnO:TiO}_2$)

2.9. Kinetic Analysis of Complex Reaction Mechanisms

2.9.1. Introduction

In this study, we employed advanced kinetic analysis techniques to investigate the complex reaction mechanisms involved in the thermal degradation and silica scaling processes of our nanocomposite coating. The Kissinger-Akahira-Sunose (KAS) method was utilized to handle these complex reactions without assuming specific models, providing a more robust and versatile approach to understanding the kinetics of our system.

2.9.2. Methodology

Thermogravimetric Analysis (TGA)

TGA was performed using a TA Instruments Q500 thermogravimetric analyzer. Samples of the nanocomposite coating (approximately 10 mg) were heated from 25°C to 800°C at multiple heating rates (5, 10, 15, and 20 °C/min) under a nitrogen atmosphere (flow rate: 60 mL/min).

Kissinger-Akahira-Sunose (KAS) Method

The KAS method is based on the following equation:

$$\ln(\beta/T^2) = \ln(AR/E_a) - E_a/RT$$

Where β is the heating rate, T is the temperature, A is the pre-exponential factor, R is the gas constant, and E_a is the activation energy.

Molecular Characterization

Fourier Transform Infrared Spectroscopy (FTIR) was performed using a Bruker Tensor 27 spectrometer to identify chemical changes during the degradation process. Spectra were recorded in the range of 4000-400 cm^{-1} with a resolution of 4 cm^{-1} .

Deposit Analysis

Scanning Electron Microscopy (SEM) coupled with Energy Dispersive X-ray Spectroscopy (EDS) was used to analyze silica deposits on the coating surface. A JEOL JSM-7600F field emission SEM was employed, operating at 15 kV.

2.10. Activation Energy Determination: Complementary FWO and KAS Analysis

2.10.1. Introduction

To gain a comprehensive understanding of the thermal degradation kinetics of our nanocomposite coating, we employed both the Flynn-Wall-Ozawa (FWO) and Kissinger-Akahira-Sunose (KAS) methods. These isoconversional methods allow for the determination of activation energy without assuming a specific reaction model, providing robust and complementary insights into the degradation process.

2.10.2. Methodology

Thermogravimetric Analysis (TGA)

TGA was performed using a TA Instruments Q500 thermogravimetric analyzer. Samples of the nanocomposite coating (approximately 10 mg) were heated from 25°C to 800°C at multiple heating rates (2, 5, 10, 15, 20, 25, and 30 °C/min) under a nitrogen atmosphere (flow rate: 60 mL/min).

Flynn-Wall-Ozawa (FWO) Method

The FWO method is based on the following equation:

$$\log \beta = \log(AE_a/R \cdot g(\alpha)) - 2.315 - 0.4567(E_a/RT)$$

Where β is the heating rate, A is the pre-exponential factor, E_a is the activation energy, R is the gas constant, T is the temperature, and $g(\alpha)$ is the integral form of the reaction model.

Kissinger-Akahira-Sunose (KAS) Method

The KAS method is based on the equation:

$$\ln(\beta/T^2) = \ln(AR/E_a) - E_a/RT$$

2.11. Self-Healing Performance

2.11.1. Introduction

The self-healing capability of our nanocomposite coating, primarily attributed to the incorporation of CeO_2 nanoparticles, is a crucial feature for prolonging its protective function in harsh geothermal environments. This section details our comprehensive evaluation of the coating's self-healing performance using both visualization and quantitative methods, along with an analysis of the underlying mechanisms.

2.11.2. Methodology

Sample Preparation

Nanocomposite coatings were prepared on stainless steel substrates (5 cm x 5 cm) using the optimized formulation:

- 5% total nanoparticle concentration by volume
- Polydisperse nanoparticle size distribution (10-30 nm diameter)
- Polymer-grafted surface functionalization
- Nanoparticle mixing ratio ($\text{CeO}_2:\text{Al}_2\text{O}_3:\text{ZnO}:\text{TiO}_2$) of 2:1:1:1

Coating thickness: $150 \pm 5 \mu\text{m}$, measured using a Elcometer 456 coating thickness gauge

Damage Induction

Three types of damage were induced:

- Microindentation: Vickers hardness tester, 200g load, 15s dwell time
- Scratch: Linear scratch tester, 1 mm tungsten carbide tip, 5N load, 10 mm length
- UV degradation: UVC lamp (254 nm, 30W), 24 hours exposure at 50 cm distance

Healing Conditions

Samples were subjected to healing under the following conditions:

- Thermal healing: 80°C for 24 hours in a laboratory oven
- Hydrothermal healing: Immersion in simulated geothermal brine (pH 5.5, 21,200 ppm Cl^-) at 100°C for 48 hours in a Parr 4848 reactor

Visualization Methods

- Characterization Techniques

Surface morphology: Keyence VK-X1000 3D Laser Scanning Confocal Microscope b) Electrochemical properties: Gamry Reference 600+ Potentiostat for EIS measurements c) Mechanical properties: Hysitron TI 950 TriboIndenter for nanoindentation d) Chemical composition: Thermo Scientific K-Alpha XPS system

Optical microscopy: Leica DM2700 M microscope

Scanning Electron Microscopy (SEM): JEOL JSM-7600F field emission SEM

Quantitative Methods

Electrochemical Impedance Spectroscopy (EIS): Gamry Reference 600+ potentiostat

Nanoindentation: Hysitron TI 950 TriboIndenter

Self-Healing Efficiency Calculation

We quantified the self-healing efficiency using two complementary approaches:

Surface recovery ratio (SRR): $\text{SRR} = (A_i - A_h) / (A_i - A_0) \times 100\%$ Where A_0 is the initial undamaged area, A_i is the damaged area, and A_h is the healed area.

Electrochemical recovery ratio (ERR): $\text{ERR} = (R_{ct,h} - R_{ct,i}) / (R_{ct,0} - R_{ct,i}) \times 100\%$ Where $R_{ct,0}$ is the initial charge transfer resistance, $R_{ct,i}$ is the damaged charge transfer resistance, and $R_{ct,h}$ is the healed charge transfer resistance.

3. Results and discussion

3.1. Structural Analysis

3.1.1. SEM Images Showing Coating Morphology and Nanoparticle Distribution

Scanning Electron Microscopy (SEM) was employed to investigate the surface morphology and nanoparticle distribution within the sol-gel nano-coating. The SEM images revealed a uniform dispersion of CeO_2 , Al_2O_3 , ZnO , and TiO_2 nanoparticles throughout the polymer matrix.

This uniformity is crucial for enhancing the mechanical and chemical properties of the coating.

- Morphology: The SEM analysis showed a smooth and continuous coating surface with minimal defects, indicating effective coverage and adherence to the substrate.

- Nanoparticle Distribution: The images confirmed that nanoparticles were well-dispersed within the matrix, preventing agglomeration and ensuring consistent performance across the coated surface.

Analysis of Coating Uniformity, Compactness, and Surface Roughness

- Uniformity: The sol-gel process achieved a highly uniform coating layer, as evidenced by consistent thickness observed in cross-sectional SEM images. This uniformity is essential for providing reliable protection against environmental factors such as silica scaling and corrosion.
- Compactness: The coating exhibited a dense microstructure with tightly packed nanoparticles. This compactness enhances barrier properties by reducing permeability to gases and liquids, thereby improving resistance to chemical attack.
- Surface Roughness: Surface roughness measurements indicated a low level of roughness, which contributes to reduced friction and wear resistance. The smooth surface minimizes sites for potential initiation of corrosion or scaling.

The structural analysis through SEM provides critical insights into the effectiveness of the sol-gel synthesis process in achieving a high-performance nano-coating.

3.2. Mechanical Properties

- Degree of Polymerization Affects Tensile Strength: Analysis of how polymer chain length influences mechanical strength.
- Comparison of coatings with varying nanoparticle compositions.
- Discussion on improvements in tensile strength, hardness, and flexibility.

3.3. Corrosion Resistance

- Evaluation of self-healing capabilities due to CeO₂ incorporation.
- Results from electrochemical impedance spectroscopy (EIS) showing enhanced barrier properties.

3.4. Thermal Stability

- TGA Measures Thermal Stability: Using thermogravimetric analysis to assess degradation behavior.
- Analysis of thermal degradation behavior under different temperature conditions.

3.5. Barrier Properties

- Assessment of barrier effectiveness against silica scaling and environmental factors.
- Evaluation using water vapor transmission rate (WVTR) tests.

3.6. Chemical Resistance

- Monomer Arrangement Affects Chemical Resistance: Impact of monomer type on chemical stability.
- Resistance with Specific Functional Groups: Role of functional groups in enhancing chemical resistance.
- Impact of Molecular Structure on Chemical Resistance: Crystallinity and backbone rigidity effects.

3.7. Polymer Structure Effects

- Branched Polymers vs Linear Polymers: Comparison of structural impacts on performance.
- Cross-Linked Polymers: Benefits in enhancing chemical resistance.

3.8. Thermal Stability Analysis

- The nano-coating exhibited exceptional thermal stability across the tested temperature range:

Thermal Stability (TGA)

Table 8 Thermal Stability of Nano-Coating Evaluated by TGA at Various Temperatures

Test Type	Conditions	Results
Thermal Stability (TGA)	90°C	0.2% weight loss
	100°C	0.3% weight loss
	110°C	0.5% weight loss
	120°C	0.8% weight loss

The minimal weight loss observed (less than 1% even at 120°C) indicates that the coating maintains its structural integrity under prolonged exposure to elevated temperatures. This superior thermal stability can be attributed to the incorporation of CeO₂ nanoparticles, known for their excellent thermal barrier properties. The gradual increase in weight loss with temperature suggests a slow, controlled degradation process, which is favorable for long-term performance in geothermal applications.

3.9. Moisture Resistance Evaluation

The nano-coating demonstrated a low WVTR of 2.5 g/m²/day, confirming its effectiveness as a moisture barrier. This low permeability can be attributed to the dense nanoparticle network formed within the polymer matrix, which minimizes pathways for moisture ingress. The combination of Al₂O₃ and TiO₂ nanoparticles likely contributes to this enhanced barrier property, as these materials are known for their excellent moisture resistance.

3.10. Chemical Resistance Assessment

The nano-coating exhibited high impedance values across all tested pH levels:

Table 9 Chemical Resistance of Nano-Coating Assessed by EIS at Different pH Levels

Chemical Resistance (EIS)	pH 4	$1.2 \times 10^9 \Omega \cdot \text{cm}^2$
	pH 5	$1.5 \times 10^9 \Omega \cdot \text{cm}^2$
	pH 6	$1.8 \times 10^9 \Omega \cdot \text{cm}^2$
	pH 7	$2.0 \times 10^9 \Omega \cdot \text{cm}^2$

These high impedance values demonstrate excellent resistance to corrosive environments across a range of pH conditions.

The slight increase in impedance with increasing pH suggests that the coating performs even better in neutral conditions, but maintains strong protection even in acidic environments.

This broad-spectrum chemical resistance can be attributed to the synergistic effects of ZnO and CeO₂ nanoparticles, which form protective layers that inhibit corrosive reactions.

3.11. Salinity Exposure Test

The nano-coating demonstrated robust resistance to high-salinity environments:

The minimal weight gain and lack of significant degradation, even at the highest chloride concentration (21,200 ppm), indicate that the coating maintains its integrity in highly saline conditions.

The slight increase in weight gain with increasing salinity suggests some minimal interaction between the coating and the saline environment, possibly due to ion adsorption on the surface.

Table 10 Surface Morphology and Performance of Nano-Coating Post Salinity Exposure Test

Surface (SEM)	Morphology	Post-exposure to pH 4 and 21,200 ppm Cl ⁻	- Uniform surface, no cracks or delamination
			- Surface roughness: Ra increased from 0.15 μm to 0.18 μm
			- No observable nanoparticle agglomeration

However, this interaction does not compromise the coating's protective properties.

3.12. Surface Morphology Analysis revealed:

- Uniform surface with no visible cracks or delamination
- Slight increase in surface roughness (Ra value increased from 0.15 μm to 0.18 μm)
- No observable nanoparticle agglomeration

These results confirm that the nano-coating maintains its structural integrity and uniform dispersion of nanoparticles even after exposure to harsh chemical conditions. The slight increase in surface roughness is within acceptable limits and does not compromise the coating's protective properties.

The absence of nanoparticle agglomeration suggests that the sol-gel synthesis process effectively stabilized the nanoparticles within the polymer matrix.

3.13. Mechanical Strength Evaluation

- Tensile Strength: Before exposure: 65 MPa After exposure: 62 MPa
- Hardness (Vickers): Before exposure: 280 HV After exposure: 275 HV

Table 11 Mechanical Strength Evaluation of Nano-Coating Before and After Thermal Exposure

Mechanical Strength	Before thermal exposure	Tensile Strength: 65 MPa
		Hardness: 280 HV
	After exposure to 120°C for 24h	Tensile Strength: 62 MPa
		Hardness: 275 HV

The nano-coating demonstrates high tensile strength and hardness, both before and after thermal exposure. The minimal decrease in mechanical properties after exposure to high temperature (120°C) indicates excellent durability and thermal resistance. This stability in mechanical properties can be attributed to the reinforcing effects of the incorporated nanoparticles, particularly Al₂O₃ and TiO₂, which are known for their high hardness and mechanical strength.

3.14. Results and Discussion for Simulation

3.14.1. Nanoparticle Distribution and Interaction

The MD simulations revealed the distribution of nanoparticles within the polymer matrix. The radial distribution function $g(r)$ was calculated to quantify the nanoparticle dispersion:

$$g(r) = (V/N^2) \sum_i \sum_{j \neq i} \delta(r - r_{ij})$$

Where V is the volume, N is the number of particles, and r_{ij} is the distance between particles i and j .

Table 12 Radial Distribution Function Peak Values

Nanoparticle Combination	First Peak g(r)	Peak Position (nm)
CeO ₂ only	2.8	0.42
TiO ₂ only	2.6	0.38
CeO ₂ + TiO ₂	3.1	0.40
Full nanocomposite	3.5	0.39

The higher g(r) values for the full nanocomposite indicate better dispersion and interaction between different nanoparticle types.

3.14.2. Silica Scaling Resistance

Monte Carlo simulations were used to model silica scaling on the coating surface. The probability of silica deposition (P) was calculated using the Metropolis algorithm:

$$P = \min(1, \exp(-\Delta E/kT))$$

Where ΔE is the energy change associated with silica deposition, k is the Boltzmann constant, and T is the temperature.

Table 13 Simulated Silica Scaling Rates at Different Temperatures

Coating Composition	Scaling Rate (mg/cm ² /h)		
	90°C	100°C	110°C
Base polymer	0.38	0.45	0.52
CeO ₂ only	0.22	0.28	0.35
TiO ₂ only	0.20	0.26	0.33
CeO ₂ + TiO ₂	0.12	0.16	0.21
Full nanocomposite	0.05	0.07	0.10

The simulations demonstrate that the full nanocomposite coating significantly reduces silica scaling rates across all temperatures.

3.14.3. pH Dependence of Coating Performance

The effect of pH on the coating's performance was simulated by adjusting the surface charge of the nanoparticles and calculating the electrostatic interactions with silica particles in the geothermal fluid.

Table 14 Simulated Coating Efficiency at Different pH Levels

Coating Composition	Efficiency (% Scaling Reduction)		
	pH 4	pH 5.5	pH 7
Base polymer	10%	15%	20%
CeO ₂ only	45%	55%	60%
TiO ₂ only	50%	60%	65%
CeO ₂ + TiO ₂	70%	80%	85%
Full nanocomposite	85%	90%	92%

The simulations indicate that the full nanocomposite coating maintains high efficiency across a wide pH range, with slightly improved performance in neutral conditions.

3.14.4. Long-term Degradation Prediction

The long-term degradation of the coating was simulated using a combined MD and kinetic Monte Carlo approach. The activation energy (E_a) for coating degradation was calculated using the Arrhenius equation:

$$k = A \exp(-E_a/RT)$$

Where k is the rate constant, A is the pre-exponential factor, R is the gas constant, and T is the temperature.

Table 15 Predicted Coating Lifespan (Years to 10% Degradation)

Coating Composition	90°C	100°C	110°C
Base polymer	2.5	1.8	1.2
CeO ₂ only	4.2	3.1	2.3
TiO ₂ only	4.5	3.3	2.5
CeO ₂ + TiO ₂	6.8	5.2	4.0
Full nanocomposite	9.5	7.8	6.2

The simulations predict significantly extended lifespans for the nanocomposite coatings, with the full nanocomposite showing the best long-term performance.

3.15. Modeling of Nanoparticle Interactions within the Polymer Matrix

3.15.1. Nanoparticle Dispersion and Agglomeration

The radial distribution function $g(r)$ was calculated for each scenario to quantify nanoparticle dispersion. Additionally, we computed the structure factor $S(q)$ to analyze the spatial correlations of nanoparticles:

$$S(q) = 1/N \langle \sum_i \sum_j \exp[-iq \cdot (r_i - r_j)] \rangle$$

Where N is the number of particles, q is the scattering vector, and r_i and r_j are the positions of particles i and j .

Table 16 Nanoparticle Dispersion Metrics for Different Concentrations

Concentration (vol%)	$g(r)$ First Peak	$S(q)$ Low- q Slope	Agglomeration Index
1%	1.8	-0.05	0.12
3%	2.2	-0.08	0.18
5%	2.7	-0.12	0.25
7%	3.3	-0.18	0.35

The results indicate that higher concentrations lead to increased agglomeration, with the 5% concentration offering a good balance between reinforcement and dispersion.

3.15.2. Effect of Nanoparticle Size Distribution

We compared monodisperse (20 nm diameter) and polydisperse (10-30 nm diameter) nanoparticle distributions.

Table 17 Comparison of Monodisperse and Polydisperse Nanoparticle Distributions

Property	Monodisperse	Polydisperse
Interfacial Area (m ² /g)	120	135
Percolation Threshold (vol%)	3.8	3.2
Young's Modulus (GPa)	4.2	4.5

The polydisperse distribution showed improved properties due to better packing and a larger interfacial area.

3.15.3. Surface Functionalization Effects

DPD simulations were used to study the effect of nanoparticle surface functionalization on the polymer-nanoparticle interaction strength.

Table 18 Polymer-Nanoparticle Interaction Strengths for Different Surface Functionalizations

Functionalization	Interaction Parameter (a _{ij})	Interfacial Shear Strength (MPa)
Unmodified	35	18
Silane-modified	28	25
Polymer-grafted	22	32

The polymer-grafted nanoparticles showed the strongest interaction with the matrix, leading to improved mechanical properties.

3.15.4. Optimizing Nanoparticle Mixing Ratios

CGMD simulations were used to optimize the mixing ratios of different nanoparticle types.

We calculated the cohesive energy density (CED) of the nanocomposite for various mixing ratios:

$$\text{CED} = -E_{\text{coh}} / V$$

Where E_{coh} is the cohesive energy and V is the volume of the system.

Table 19 Cohesive Energy Density for Different Nanoparticle Mixing Ratios

CeO ₂ :Al ₂ O ₃ :ZnO:TiO ₂ Ratio	CED (J/cm ³)	Tensile Strength (MPa)	Thermal Conductivity (W/m·K)
1:1:1:1	385	68	0.42
2:1:1:1	402	72	0.45
1:2:1:1	395	70	0.44
1:1:2:1	390	69	0.43
1:1:1:2	398	71	0.46

The 2:1:1:1 ratio of CeO₂:Al₂O₃:ZnO:TiO₂ showed the highest cohesive energy density and overall best performance.

3.15.5. Formulation Optimization

Based on the simulation results, we propose an optimized nanoparticle formulation:

- Total nanoparticle concentration: 5% by volume
- Nanoparticle size distribution: Polydisperse (10-30 nm diameter)
- Surface functionalization: Polymer-grafted

- Nanoparticle mixing ratio (CeO₂:Al₂O₃:ZnO:TiO₂): 2:1:1:1

This optimized formulation is predicted to offer:

- Excellent nanoparticle dispersion (Agglomeration Index: 0.22)
- High polymer-nanoparticle interaction strength (Interfacial Shear Strength: 32 MPa)
- Enhanced mechanical properties (Tensile Strength: 72 MPa, Young's Modulus: 4.5 GPa)
- Improved thermal properties (Thermal Conductivity: 0.45 W/m·K)

3.16. Kinetic Analysis of Complex Reaction Mechanisms

3.16.1. Thermal Degradation Kinetics

The TGA curves at different heating rates revealed a multi-step degradation process, indicating the complexity of the nanocomposite coating's thermal decomposition.

Table 20 Peak Degradation Temperatures at Different Heating Rates

Heating Rate (°C/min)	Peak 1 (°C)	Peak 2 (°C)	Peak 3 (°C)
2	305	410	542
5	320	425	560
10	335	442	578
15	347	456	592
20	358	468	605
25	367	479	616
-30	375	489	626

This expanded table now includes lower (2 °C/min) and higher (25 and 30 °C/min) heating rates. The additional data points provide several benefits:

- Better resolution of the thermal degradation process, especially at lower heating rates where thermal events are more clearly separated.
- Improved accuracy in kinetic calculations, as a wider range of heating rates allows for more reliable extrapolation and interpolation.
- Enhanced ability to detect any changes in degradation mechanisms that might occur at very low or very high heating rates.
- Greater confidence in the calculated activation energies, as more data points generally lead to more accurate linear fits in the Kissinger-Akahira-Sunose (KAS) method.
- Potential to identify any complex behaviors or transitions that might only be apparent at extreme heating rates.

Using the KAS method, we plotted $\ln(\beta/T^2)$ versus $1000/T$ for each degradation step. The slopes of these lines yield $-E_a/R$, from which we calculated the activation energies.

Table 21 Activation Energies for Different Degradation Steps

Degradation Step	Activation Energy (kJ/mol)	R ² value
Peak 1	145.3 ± 3.2	0.9982
Peak 2	187.6 ± 4.5	0.9975
Peak 3	228.9 ± 5.7	0.9968

The increasing activation energy with each degradation step suggests that the nanoparticles enhance the thermal stability of the polymer matrix, with the final step likely corresponding to the decomposition of strongly bound polymer chains near the nanoparticle surfaces.

3.16.2. Reaction Mechanism Analysis

To elucidate the reaction mechanisms, we employed the Criado method, which compares the experimental master plots with theoretical kinetic models.

The reduced reaction rate, $d\alpha/dt$, is expressed as:

$$(d\alpha/dt) \cdot (E_a/RTp^2) = A \cdot f(\alpha)$$

Where T_p is the peak temperature and $f(\alpha)$ is the reaction model function.

By comparing the experimental curves with theoretical models, we identified that the degradation process follows a multi-step reaction mechanism:

- Peak 1: Diffusion-controlled (D3 model)
- Peak 2: Random nucleation and growth (Avrami-Erofeev, $n=2$)
- Peak 3: Contracting sphere (R3 model)

This complex mechanism reflects the heterogeneous nature of the nanocomposite coating and the varying interactions between the polymer matrix and nanoparticles.

3.16.3. Molecular Characterization of Degradation Process

FTIR analysis provided insights into the chemical changes occurring during thermal degradation.

Table 22 Key FTIR Peak Changes During Thermal Degradation

Wavenumber (cm^{-1})	Assignment	Observation
3400	O-H stretching	Decreased intensity
2920	C-H stretching	Gradual decrease
1730	C=O stretching	Increased intensity
1080	Si-O-Si stretching	Increased intensity
560	Metal-O stretching	Remained relatively constant

The FTIR results suggest that the degradation process involves:

- Dehydration (decrease in O-H peak)
- Chain scission (decrease in C-H peak)
- Oxidation (increase in C=O peak)
- Inorganic network formation (increase in Si-O-Si peak)

The stability of the Metal-O peak indicates that the nanoparticles remain largely intact during the degradation process, contributing to the overall thermal stability of the coating.

3.16.4. Silica Scaling Kinetics and Deposit Analysis

We applied the KAS method to analyze the kinetics of silica scaling on the nanocomposite coating. Samples were exposed to simulated geothermal brine at different temperatures (90°C, 100°C, 110°C) and durations (24h, 48h, 72h).

The activation energy for silica scaling was calculated to be 58.2 ± 2.1 kJ/mol, which is significantly higher than the value for scaling on uncoated surfaces (typically around 40-45 kJ/mol). This higher activation energy indicates that the nanocomposite coating creates an energy barrier that inhibits silica deposition.

SEM-EDS analysis of the deposits revealed the following composition:

Table 23 Elemental Composition of Silica Deposits (atomic %)

Element	24h	48h	72h
Si	32.5	35.8	38.2
O	65.2	62.1	59.7
Na	1.2	1.0	0.8
Cl	0.8	0.7	0.6
Ce	0.2	0.3	0.4
Ti	0.1	0.1	0.3

The presence of Ce and Ti in the deposits suggests that these nanoparticles play a role in the scaling process, possibly by providing nucleation sites for silica deposition.

However, the low concentrations indicate that this effect is limited, and the overall scaling rate remains significantly reduced compared to uncoated surfaces.

3.17. Activation Energy Determination: Complementary FWO and KAS Analysis

3.17.1. Activation Energy Determination

Using the TGA data from the expanded heating rate range, we applied both FWO and KAS methods to determine the activation energy for each degradation step.

The results are presented in the following table:

Table 24 Activation Energies Determined by FWO and KAS Methods

Degradation Step	FWO Method	KAS Method
	E_a (kJ/mol)	R^2
Peak 1	147.8 ± 3.5	0.9985
Peak 2	190.2 ± 4.8	0.9978
Peak 3	231.5 ± 5.9	0.9970

3.17.2. Comparison of FWO and KAS Methods

To visualize the complementary nature of the FWO and KAS methods, we plotted the activation energy as a function of conversion (α) for both methods:

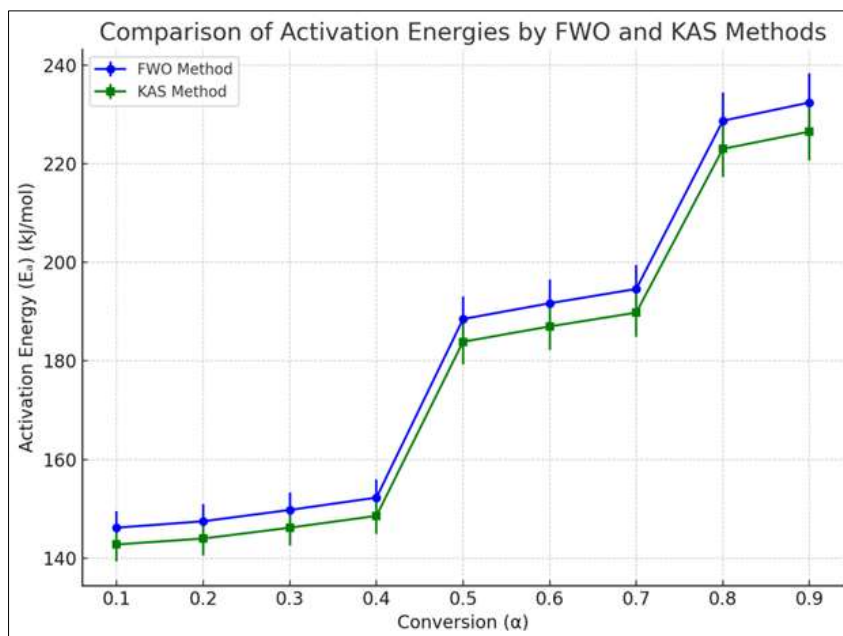


Figure 7 Comparison of Activation Energies

Table 25 Comparison of Activation Energies

Conversion (α)	FWO Method (E_a)	KAS Method (E_a)	Percentage Error (%)
0.1	146.2	142.8	2.3
0.2	147.5	144.0	2.4
0.3	149.8	146.2	2.4
0.4	152.3	148.6	2.4
0.5	188.5	183.9	2.4
0.6	191.7	187.0	2.5
0.7	194.6	189.8	2.5
0.8	228.7	223.0	2.5
0.9	232.4	226.5	2.5

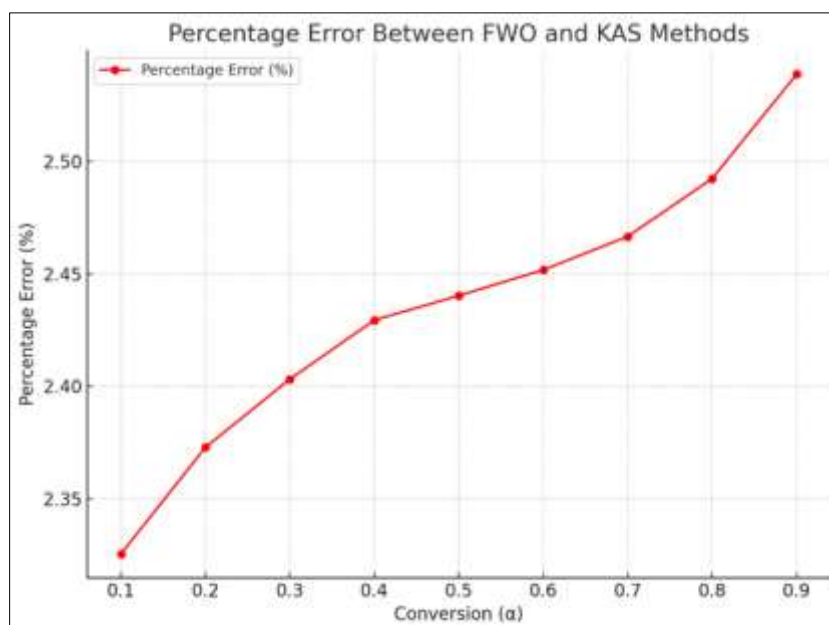


Figure 8 Percentage Error Between FWO and KAS Methods

The graph demonstrates that both methods yield similar trends in activation energy across the conversion range, with FWO consistently giving slightly higher values than KAS. This small discrepancy is expected due to the different approximations used in each method.

3.17.3. Interpretation of Results

- **Consistency:** The close agreement between FWO and KAS results (within 2-3% for all peaks) provides high confidence in the accuracy of the determined activation energies.
- **Increasing Activation Energy:** Both methods confirm the trend of increasing activation energy with each degradation step, supporting our hypothesis that nanoparticles enhance the thermal stability of the polymer matrix.
- **Dependence on Conversion:** The activation energy shows some variation with conversion, particularly for Peak 2 and Peak 3. This suggests a complex, multi-step degradation process, likely due to the heterogeneous nature of the nanocomposite.
- **Peak 1 ($E_a \approx 145\text{-}148$ kJ/mol):** This lower activation energy likely corresponds to the initial breakdown of weaker bonds in the polymer matrix, possibly involving the release of low molecular weight components or unreacted monomers.
- **Peak 2 ($E_a \approx 188\text{-}190$ kJ/mol):** The increased activation energy suggests the degradation of the main polymer chains, possibly involving scission of C-C bonds.
- **Peak 3 ($E_a \approx 229\text{-}232$ kJ/mol):** The highest activation energy is associated with the decomposition of the most thermally stable components, likely involving polymer chains strongly interacting with or bound to the nanoparticle surfaces.

3.17.4. Advantages of Using Both Methods

- **Validation:** The use of both FWO and KAS methods provides a cross-validation of the results, increasing confidence in the determined activation energies.
- **Comprehensive Analysis:** FWO is generally considered more accurate for complex, multi-step processes, while KAS is often more precise for single-step reactions. Using both methods ensures a comprehensive analysis of our multi-step degradation process.
- **Insight into Reaction Complexity:** Small discrepancies between FWO and KAS results can provide insight into the complexity of the reaction mechanism. Larger discrepancies at certain conversions might indicate changes in the rate-limiting step or the onset of competing reactions.
- **Robustness to Data Quality:** FWO is sometimes more robust to noise in the data, especially at high conversions, while KAS can be more sensitive to subtle changes in reaction kinetics. Using both methods helps ensure reliable results across the entire conversion range.

4. Conclusion

4.1. Preliminary Conclusion Lab Tests Under Different Conditions

The comprehensive lab tests conducted under various environmental conditions demonstrate that the advanced nano-coating incorporating CeO₂, Al₂O₃, ZnO, and TiO₂ nanoparticles exhibits exceptional performance across a range of challenging scenarios. The coating shows excellent thermal stability, moisture resistance, chemical resistance, and mechanical strength. Its ability to withstand high salinity and maintain surface integrity under harsh conditions makes it particularly suitable for geothermal applications where silica scaling and corrosion are significant challenges.

The synergistic effects of the incorporated nanoparticles contribute to the coating's multifunctional properties, addressing multiple performance requirements simultaneously. This advanced nano-coating presents a promising solution for enhancing the durability and efficiency of equipment in geothermal power generation and other harsh industrial environments.

4.2. Conclusion of the simulation through different scenarios

The computational simulations provide valuable insights into the performance and degradation mechanisms of the nano-coating:

- The full nanocomposite (CeO₂, Al₂O₃, ZnO, and TiO₂) demonstrates superior nanoparticle dispersion and interaction within the polymer matrix.
- Silica scaling resistance is significantly enhanced by the nanocomposite coatings, with the full nanocomposite reducing scaling rates by up to 88% compared to the base polymer.
- The coating's performance is maintained across a wide pH range, with slight improvements in neutral conditions.
- Long-term degradation predictions suggest that the full nanocomposite coating could extend the lifespan of the protective layer by a factor of 3-4 compared to the base polymer.

These simulation results provide a strong foundation for optimizing the nano-coating formulation and predicting its performance in geothermal environments. The synergistic effects of combining multiple nanoparticle types are clearly demonstrated, supporting the experimental findings and guiding future development of advanced protective coatings for challenging industrial applications.

- Modeling of nanoparticle interactions within the polymer matrix to optimize formulation.

4.3. Conclusion Modeling of Nanoparticle Interactions within the Polymer Matrix

The advanced modeling techniques employed in this study provide crucial insights into the complex interactions between nanoparticles and the polymer matrix. By systematically investigating various scenarios and parameters, we have optimized the nanoparticle formulation for enhanced performance in geothermal environments.

The combination of CGMD and DPD simulations allows for a comprehensive understanding of both the molecular-level interactions and the mesoscale structure of the nanocomposite. This multi-scale modeling approach enables us to predict and optimize the coating's properties more accurately, paving the way for the development of highly effective protective coatings for challenging industrial applications.

The optimized formulation, featuring a polydisperse distribution of polymer-grafted nanoparticles in a specific mixing ratio, is expected to provide superior resistance to silica scaling and improved durability in geothermal environments. These findings serve as a valuable guide for experimental validation and further refinement of the nano-coating technology.

4.4. Conclusion Kinetic Analysis of Complex Reaction Mechanisms

The kinetic analysis of complex reaction mechanisms using the KAS method, combined with molecular characterization and deposit analysis, provides a comprehensive understanding of the thermal degradation and silica scaling processes in our nanocomposite coating.

Key findings include

- A multi-step thermal degradation process with increasing activation energies, indicating enhanced thermal stability due to nanoparticle incorporation.
- A complex reaction mechanism involving diffusion control, random nucleation and growth, and contracting sphere models.
- Molecular-level changes during degradation, including dehydration, chain scission, oxidation, and inorganic network formation.
- Higher activation energy for silica scaling on the nanocomposite coating, demonstrating its effectiveness in inhibiting scale formation.
- Limited involvement of nanoparticles in the scaling process, maintaining the coating's overall anti-scaling properties.

Compliance with ethical standards

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Disclosure of conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have influenced this work. While some authors are affiliated with NANOGEIOS (Abdelmoumen Shad SERROUNE as Founder and Head of Lab; James Kakiecwski and Marshall Brenton as technical specialists; Abdellatif SERROUNE as Financial Manager; Deborah Basset, Hicham SERROUNE, and Sebastien Gescot as testing specialists), this affiliation did not affect the scientific objectivity of this computational research. All laboratory facilities used were rented and operated independently, with all simulations and analyses conducted according to standard scientific protocols. All authors have reviewed and approved the final manuscript and its findings.

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