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Synergic Effects of Corrosive Ions on Concrete and Nano Additives Situated in Nuclear Power Plants in Arid Climatic Conditions

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Abstract - In arid climates, where temperatures, salt concentrations, and humidity levels are elevated, one significant issue is the increased risk of external sulfate attack (ESA) on the concrete. While the effects of ESA on concrete durability have been widely studied, this work introduces a new experimental approach to improve the understanding of the effects of temperature, thermal and humidity gradients, and sulfate-chloride, and sodium-magnesium interactions. To achieve our objective, both ordinary, SG, and nano-enhanced mortar beams and cubes are used. Samples are exposed to 10% w/v solutions for accelerated testing at room temperature or 50°C. Preliminary findings indicate that chloride mitigates sulfate attack in early stages, but later accelerates sulfate attack, while magnesium delays expansion in the initial stages. Nano-infused samples show better resistance to corrosion when compared to other samples. Further investigation is recommended to elucidate the multiple ion interaction mechanisms and evaluate the performance of nano-infused samples under diverse exposure conditions.

***Keywords*:** Sulfate attack, concrete durability, gradient conditions, nano materials, arid climate.

1. Introduction

The durability of concrete structures in Nuclear Power Plants (NPPs) is a critical concern, particularly in marine environments where they face simultaneous assaults from sulphate and chloride ions [1]. The NPP has various points of sulfate and chloride exposure at the reactor containment building, support structures, and intake structure. Sulphate attack induces strength loss and volumetric expansion, leading to cracking, while chloride intrusion exacerbates the corrosive potential [2]. The partial exposure of sulfate can lead to physical sulfate attack when the sulfate salts are absorbed by one end of the concrete causing crystallization. The expansion caused by these compounds can be exacerbated by temperature gradients usually occurring in large concrete structures [3]. However, there is no prior research on the effect of temperature gradient on sulfate ion penetration or external sulfate attack.

Graphene oxide (GO) is an oxygen-rich nanomaterial which can promote the formation of hydration products, thus improving the mechanical properties of concrete [4]. Similarly, carbon nanotubes (CNTs) enhance the mechanical properties of concrete by closely interacting with C-S-H [5]. As such, this research paper focuses on investigating the intricacies of concrete degradation caused by the synergistic impact of sulphate and chloride attacks and sulfate resistance from nano enhanced concrete in the challenging environment of NPPs.

2. Experimental Procedure

The experimental approach involves using mortar samples of NPP mix design, and nano-additive blended mixes, and subjecting them to different corrosive environments for 1, 2, and 4 months.

2.1 Mortar exposure in corrosive environment

Mortar sample beams and cubes were prepared in 40*40*160 mm and 50*50*50 mm molds respectively with the mix design mentioned in Table 1. The samples were cast and cured for 28 days. The samples are exposed to sodium sulfate (Na_2SO_4) (S2F), combination of Na_2SO_4 and sodium chloride (NaCl) ions (CS2F). The Anion combination of Na_2SO_4 and magnesium sulfate ($MgSO_4$) was also another exposure condition (MS2F). In arid regions, concrete structures often experience partial exposure to sulfate leading to uneven sulfate ingress and localized degradation over time. This scenario is examined by immersing 40mm of mortar samples in solutions (S2P). The temperature differences across concrete structures leading to uneven expansion and degradation due to differential thermal and chemical stresses is examined by immersing 40mm of mortar samples in solutions maintained at 50°C (S5P). Thermocouples were placed inside the samples at 40, 60, 100, and 140 mm to monitor the constant temperature gradients (Fig1(a)). Samples are completely exposed to 50°C (S5F) to resemble high temperature exposure in these regions. Graphene infused samples at 5% and 10% are G5 and G10, and multiwalled carbon nano tubes (MWCNTs) at 5% are CN5 samples. A sonicator was used to distribute the nanoparticles evenly.

Table 1: Mix design of the mortar samples

Material	O Sample	SG Sample	G5/G10/CN5 Sample
Type 1 cement	376	113	376
GGBS	-	244	-
SF	-	19	-
Dune sand	230	230	230
Crushed sand	706	706	706
Graphene/MWCNTs	-	-	0.05 – 5%, 0.1 – 10%
Water	146	146	146
HWRA	4.578	4.578	4.578 – G, 6.867 - CN
Key: O- Ordinary, SG- Silica Fume and GGBS, G- Graphene, and CN- Carbon Nanotubes. w/c – 0.40,			

2.2. Methodology of corrosion analysis

Mortar samples exposed to sulfate and combined sulfate and chloride solutions were analyzed using various techniques. Visual inspection is conducted to identify surface deterioration, crack formation, and crystallization. Changes in volume and mass are measured to assess the extent of physical damage and material loss. Electrical resistivity is used to measure the corrosion resistance of the material. Ultrasonic pulse velocity (UPV) is analyzed to determine structural integrity and microcracks. Mechanical properties are determined through compression and flexure tests to evaluate the strength caused by prolonged exposure to aggressive environments. Finally, sulfate content analysis is carried out to quantify the penetration and concentration of sulfate ions within the partially exposed samples by slicing them into equal pieces of 20mm width (Fig1(b & c)).

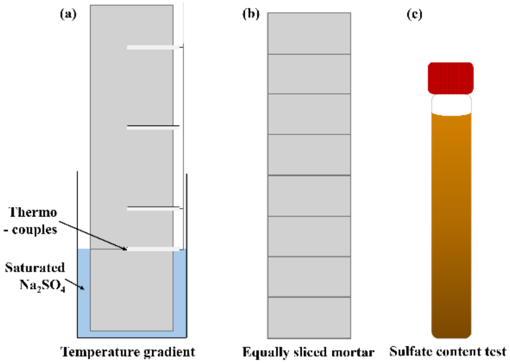

Figure 1: Thermal gradient measurement technique illustration (a) experimental setup for thermal gradient; (b) equally sliced beam samples; (c) sulfate content testing.

3. Results and discussion

This section explores the experimental results obtained. Various analysis techniques are employed to understand the extent of corrosion or corrosion resistance of materials. This includes length and mass change, compression analysis, UPV and resistivity analysis.

3.1 Effect of multiple ions on mortar samples

The compressive strength of ordinary samples exposed to multiple ions for 1 month were compared in Figure 2(a). The results indicate that samples exposed to CS2F exhibit the lowest compressive strength. This can be attributed to chloride increasing the ionic strength and sulfate mobility leading to increased degradation. However, samples exposed to Na_2SO_4 and $MgSO_4$ showed highest compressive strength. This may be due to the presence of $MgSO_4$ which delays expansion in the early stages. Higher exposure temperature (S5F) is shown to have lower compressive strength when compared to room temperature (S2F) as high temperature increases reaction kinetics and permeability of ions as shown in Figure 2(b) resistivity change. The samples exposed to CS2F are compared to S2F over 1, 2, and 4 months are shown in Figure 2(b). The length and mass results after 1 month indicate that there is an initial expansion and weight gain in both samples due to ettringite production and pore filling. After 2 months CS2F sample shows increase in mass compared to decrease in S2F. This is due to the formation of non-expansive Friedel's salt generally depicted as mitigating effect of chloride [6]. The decrease in length in all cases is due to microcracks. After 4 months, both length and mass increase due to deeper penetration of sulfate and crack formation which is not much documented. These results show how chloride increases sulfate attack of concrete.

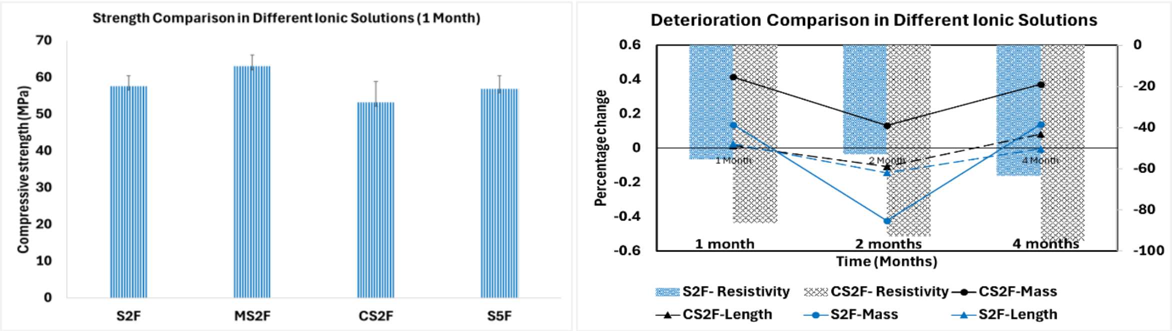

Figure 2: (a) Comparison of ordinary samples exposed to sulfate ions (S2F and S5F) with multiple ions (MS2F and CS2F) exposure using compressive strength; (b) Comparison of SG samples exposed to S2F with CS2F using resistivity, mass, and length.

3.2 Effect of gradient conditions and nano-infused samples on corrosion resistance

The UPV of samples exposed to gradient conditions are shown in Figure 3(a). The results indicate that complete exposure at room temperature shows initial expansion due to early microcracking. Elevated temperature results in increased microcracking when compared to S2F. However, humidity gradient exposure after 4 months shows a slight increase in UPV. This can be attributed to contraction and temporary UPV recovery which happens after initial expansion. Samples exposed to thermal gradient shows a severe drop in UPV. This is due to re-expansion and widespread cracking which happens after contractions. This shows that gradient conditions accelerate the degradation of mortar samples.

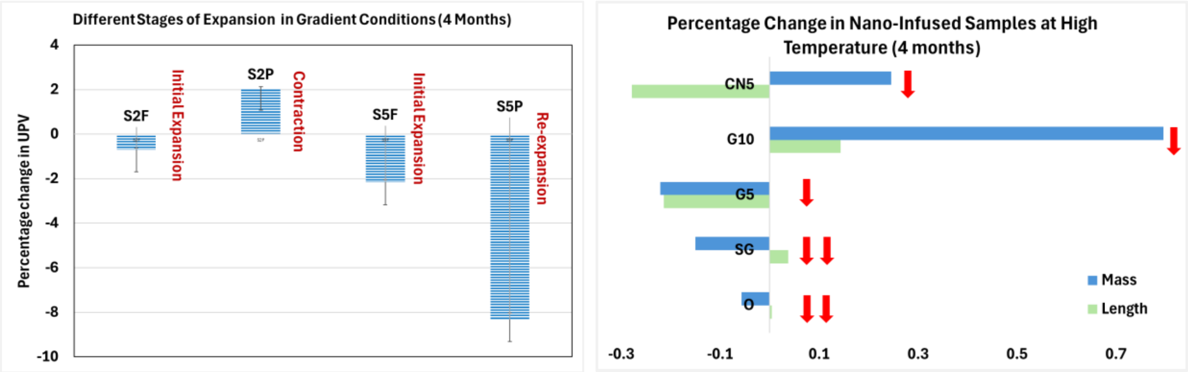

Figure 3: (a) UPV change comparison of samples exposed to different environmental conditions on sulfate corrosion after 4 months; (b) Length and mass change comparison of nano-infused samples with O and SG samples after 4 months of exposure in S5F.

The mass and length change of nano-infused samples with SG and O samples are compared in Figure 3(b). The results shows that nano-infused samples shows early stage sulfate attack (indicated by one downward arrow) when exposed to S5F for 4 months. The SG and O samples exhibit severe degradation (indicated by double downward arrow) in the sample condition. This conclusion is drawn as the decrease in mass and increase in length is attributed to dominant expansion product formation with leaching of calcium containing compounds. This is interpreted as late-stage in degradation.

4. Conclusion and future directions

This study demonstrates complex degradation mechanisms of different mortar samples exposed to multiple ion solutions. Various analytical methods shows that the chloride ions accelerate sulfate degradation, and magnesium ions delay the expansion. The synergic chloride-sulfate study over 4 months shows that chloride initially causes increase in mass due to competitive reactions leading to the formation of Friedel's salt. Even though this stabilizes the expansion, advanced sulfate attack dominated by delayed ettringite formation and pore-filling phases results in further degradation. Further examinations are required for mapping phase distribution and crack evolution using microscopic analysis (SEM, EDS, XRD). Graphene and MWCNTs shows promise in delaying sulfate attack and can be used to test their corrosion resistance under multiple ion and gradient conditions. There is a need for deeper understanding of evaporation interface zone (EIZ) in gradient conditions which can be done using XRD and sulfate concentration analysis. Long-term experiments will clarify delayed ettringite formation and leaching effects, while predictive modelling can bridge lab findings to real-world durability. Combining these approaches will enable optimized mix designs and service-life predictions for infrastructure in aggressive environments. The integration of nanomaterials, multi-scale characterization, and modelling presents a robust pathway to mitigate sulfate attack and extend concrete longevity.

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