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INVESTIGATION OF PERFORMANCE OF NANO SILICA CEMENT ADDITIVE ON SULPHATE ATTACK IN GEOTHERMAL WELLS

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ABSTRACT

Purpose: This research was intended to evaluate Nano silica as an additive to improve the sulphate resistance of cement used in geothermal wells.

Design/ Methodology/ Approach: Sulphate resistance was determined by measuring the longitudinal change in cement cube specimens that were cured in sodium sulphate solution for 21 days. Cube specimens with varied concentrations of Nano silica (0%, 0.3%, 0.6%, 0.9% and 1.2%) were used in the study. Five separate solutions were maintained at 23℃, 40℃, 65℃, 70℃ and 80℃ for 21 days. Final length measurements were taken and compared as a percentage of initial length measurements.

Findings: Beyond 65℃, the sulphate resistance of cement improved for each percentage concentration of Nano silica replacement. Control specimens with 0% Nano silica had the most inferior performance at all temperatures. Higher concentrations of 1.2% and 0.6% Nano silica replacement gave the most resistance between 23℃ and 65℃. A lower concentration of 0.3% proved more suitable between 65℃ and 80℃.

Research limitation: The results of the experiment indicate performance in low-temperature geothermal wells.

Practical implication: The application of this additive can improve the durability and strength of the cement, reducing the potential for degradation due to exposure to sulphates. This can lead to a longer lifespan of the geothermal well, reducing maintenance costs and increasing its overall efficiency.

Social implication: Improved cement designs that create longer-lasting cement sheaths can be developed from this research, thereby fostering geothermal energy development. The option to replace certain volumes of cement with Nano silica contributes to a reduction of the carbon footprint by minimising the demand for, and therefore the production of cement.

Originality/ Value/ Novelty: Previous research that tested cement at high temperatures analysed mechanical resistance. This research examined the sulphate resistance of cement at high temperatures.

***Keywords**: Cement-elongation. ettringite. permeability. porosity. sulphate attack.*

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INTRODUCTION

Cement integrity refers to its ability to successfully isolate formations from the well, lend strength to good casings and protect casings from chemical attack by brine throughout the entirety of the well's lifetime (Brandl et al., 2011; Teodoriu et al., 2019). A cement sheath plays a vital role in geothermal good drilling and geothermal energy production. Cement slurry is applied in the annulus after a casing string has been run through the good bore during drilling (Teodoriu et al., 2019). The cement sheath seals off and protects the wellbore from the formation by preventing seepage of formation fluids into the good bore (Philippacopoulos & Berndt, 2002). It is also used to seal lost circulation zones, or areas where there is a reduction or absence of flow within the well (Teodoriu et al., 2019). In directional drilling, cement is used to plug an existing well from that point. Cement is also used to plug a well that is intended for abandonment. Most importantly, a cement sheath lends strength to well and protects them from possible chemical attack by brine. However, the cement itself is not completely resistant to chemical attack by sulphates and sulphates thermal brine. Sulphate attack, in particular, can cause the cement to soften, swell, crack or completely fail (Al-Amoudi et al., 1999; Smith, 1986).

Current protection against sulphate attack in geothermal wells is based on the use of cement containing fewer proportions (<5%) of tri-calcium aluminate (Al-Amoudi et al., 1999). While useful, it does not offer special protection against attack on the hydrated calcium silicate (CSH) cement matrix or calcium hydroxide produced from the hydration of cement (Bensted et al., 2007). Cement possesses superior mechanical characteristics but it has been unable to meet the standards of durability (Khan et al., 2022). When exposed to geothermal good condition attacks are still deterred by chemical sulphate attacks. This research was done to create cement formulations with superior sulphate resistance suitable for geothermal environments.

LITERATURE REVIEW

Cement used in zonal isolation of geothermal wells has to withstand many aggressive down-hole conditions such as high temperatures, high pressures and corrosive brines. As such, modification of its properties is required to minimize strength retrogression and improve its mechanical properties and sulphate resistance. Research into the use of Nano silica to modify mechanical properties and minimize strength retrogression has been done, mainly for the oil and gas industry but is also emergent in geothermal resource exploitation.

Effects of Nano silica on physical and mechanical properties

Porosity and permeability

Nano silica decreases the porosity and permeability of concrete/mortar. Research by (Wang et al., 2020) determined that the addition of Nano silica lowered the share of capillary pores in which channels could be generated. It also reduced the dimensions of the pores present and hence contributed to the reduction in permeability. Similar findings were reported by (Makwana et al., 2021; Nie et al., 2022; Thakkar et al., 2020). Mercury Intrusion Porosimetry (MIP) tests by (Ghafoori et al., 2020) showed that for mortars containing 6% Nano silica, the void volume proportion of gel pores and micropores increased in comparison with those of the control, and there was an overall reduction in the capillary macro pores. However, (Makwana et al., 2021) noted that at higher concentrations of Nano silica, the results for permeability were reversed while the porosity kept on decreasing.

Compressive strength

Addition of Nano silica was reported to increase the compressive strength of cement (Makwana et al., 2021; Moslemi et al., 2014; Nie et al., 2022; Thakkar et al., 2020; Wang et al., 2020). Research (Rzepka & Kędzierski, 2020) found that early compressive strength amounting to 3.5 MPa was achieved by slurries after times between approximately 7 h and 14 h. After 28 days of hydration, the compressive strength of the hardened cement stones had very high values up to 50 MPa (Rzepka & Kędzierski, 2020). Similarly, a Nano silica-Basalt Fibre composite (NSBF) presented by (Wang et al., 2020) achieved a compressive strength of 3.5 MPa between approximately 8 h and 14 h. After 28 days of hydration, NSBF samples with 0.5% Nano silica addition had approximately 34–36 MPa compressive strength and those with 1% Nano silica addition had approximately 37–39 Mpa.

However, an excess of Nano-silica in the cement slurry was reported to cause a decrease in the compressive strength of cement instead (Thakkar et al., 2020). When a comparison was made between cement containing 0% and 1% Nano-silica, a 100% increase in compressive strength was observed. The compressive strength of cement containing 1.5% Nano-silica was observed to be 7% lower than that of slurry containing 1% Nano-silica.

Thickening time

There have been numerous suggestions that the addition of Nano-silica to cement slurry led to a decrease in the thickening time (Rzepka & Kędzierski, 2020; Thakkar et al., 2020) of slurry. Available literature generally has no contradictions about the effects of Nano silica on thickening time.

Fluid loss

Nano silica decreases fluid loss in cement. When cement slurry samples with different amounts of Nano-silica were observed, the results showed that as the percentage of Nano-silica in the cement slurry increased, the fluid loss decreased (Thakkar et al., 2020). This was in agreement with later research by (Makwana et al., 2021) who in addition, included higher yield stress as an advantage of Nano silica addition to cement.

Thermal resistance

Nano silica can improve the thermal resistance of mortar (Horszczaruk et al., 2017). A study that made use of Nanomaterials in concrete mixes showed an increase in the residual compressive and flexural strength after exposure to elevated temperatures (Sherif, 2017). In general, the reduction in the compressive and flexural strength due to the exposure to elevated temperatures decreased as the Nanomaterials percentage increased (Sherif, 2017).

Another research aimed at evaluating the effect of Nano silica and various types of aggregates on the performance of cement mortars at elevated temperatures demonstrated that there was an optimal Nano silica content which can be beneficial for improving the thermal resistance of cement mortars (Horszczaruk et al., 2017). In the cement mortar containing quartz and magnetite aggregate, Nano silica (up to 3% bwoc) improved the thermal resistance and prevented crack extension (especially in the range of 200–400 °C). It was also concluded that the resistance of cement mortars to elevated temperatures is highly related to the type of aggregate used (Horszczaruk et al., 2017). Cement mortars containing barite aggregate tended to crack and exhibit spalling as a result of the low thermal resistance of the aggregate (Horszczaruk et al., 2017) This effect was more pronounced in the presence of Nano silica, which increased thermally induced explosive spalling and severe internal cracking (Horszczaruk et al., 2017).

Effects of Nano silica on sulphate resistance

The addition of Nano silica can effectively reduce the mass growth rate and the formation of sulphate expansion products after a sulphate attack (Huang et al., 2022) thereby enhancing the resistance of mortars to sulphate attack. Scanning Electron Microscope test results indicated that the addition of hybrid Nano silica and PVA fibres was effective in limiting the generation of sulphate erosion products and keeping materials from expansive failure after sulphate attack (Huang et al., 2022). During the analysis of high-performance concrete (HPC) that was mixed with Nano-Silica and exposed to sulphate attack, (Nie et al., 2022) discovered that the incorporation of Nano silica decreased the mass loss in prepared specimens. Nano silica replacement of 1% decreased the mass loss by 13.5% in comparison to unmodified HPC. Examination of the comparative sulphate resistance performance of Nano silica and silica fumes in mortar specimens showed that the mortars containing Nano silica were physically more impermeable and more resistant to ion transport, therefore more sulphate resistant (Ghafoori et al., 2020). In another study by (Huang et al., 2020), it was found that the sulphate resistance of mortars increased as their Nano silica content increased. The incorporation of Nano silica refined the pores and reduced the pore connectivity, which improved the sulphate resistance of the mortars. A study by (Tobón et al., 2015) evaluated the effect of Nano silica on the sulphate resistance of mortars made with Portland cement (control) and partially replaced with a commercial Nano silica of 1, 3, 5, and 10 % by weight of cement. It was found that mortars with 5 and 10 % of Nano silica decreased expansion by 90% and 95 % respectively after two years of immersion.

However, higher concentrations of Nano silica were reported to delay or decrease the sulphate resistance of concrete and mortars due to agglomeration of the Nanoparticles (Nie et al., 2022), especially after long-term reactions. In a contrast study by (Ghafoori et al., 2020), conclusions from the results were that doubling the concentration of colloidal Nano silica had a positive effect on the sulphate resistance of mortars.

Research by (Huang et al., 2020) showed that coarse Nano silica (which featured an average particle size of 50 nm) was found to have presented a better potential for enhancing the sulphate resistance of the specimens compared with fine Nano silica (average particle size of 10 nm). This was in line with previous research by (Ghafoori et al., 2018) which showed that micro-silica replacement mortars outperformed both Nano silica-only and the micro-Nano silica combination replacement mixtures. It was concluded that the agglomeration of the fine-sized silica particles during mixing negated the expected superior pozzolanic activity of the nanomaterial.

In summary, the following conclusions were drawn from the above review of literature about the subject;

i) Nano silica improved sulphate resistance (Moslemi et al., 2014) by reducing the porosity and permeability of the concrete or mortar specimens (Ghafoori et al., 2020; Huang et al., 2020; Nie et al., 2022).
ii) Large-sized/coarse particles, high concentrations or poor mixing of Nano silica lead to agglomeration of the nanomaterial (Ghafoori et al., 2018; Huang et al., 2020; Nie et al., 2022). This was counterproductive to its typical superior performance characteristics.
iii) At lower concentrations, sulphate resistance was directly proportional to the amount of Nano silica replacement (Huang et al., 2020).
iv) Doubling the concentration of Nano silica replacement had a positive effect on sulphate resistance (Ghafoori et al., 2020).
v) Chemical sulphate attack was the main mechanism of damage on test specimens (Huang et al., 2020).
vi) Incorporation of Nano silica increased compressive strength (Nie et al., 2022) in the early stages of hydration (Moslemi et al., 2014).
vii) Resistance of cement mortars to elevated temperatures was highly related to the type of aggregate used (Horszczaruk et al., 2017).
viii) There was an optimum value of Nano silica replacement for improvement of sulphate resistance (Ghafoori et al., 2020; Moslemi et al., 2014), similar to mechanical strength (Rzepka & Kędzierski, 2020; Thakkar et al., 2020) and thermal resistance improvement.

The following limitations in the literature are cited;

i) Research was done on mortars and concrete. Geothermal cement makes no use of aggregates. It is prepared as slurry. As reported by (Horszczaruk et al., 2017), sulphate resistance depends on the type of aggregate used. This leaves a knowledge gap on sulphate resistance where there are no aggregates used.
ii) Studies on sulphate resistance did not take temperature variation into account. Studies which took temperature variation into account were analysing mechanical and physical properties, not sulphate resistance.

This research, therefore, was aimed at analysing the variation of sulphate resistance with increasing temperatures (from 23℃ to 80℃) as would be the challenge in a geothermal well environment (temperatures above room temperature).

Formation of ettringite

When water was added to cement, a gelatinous calcium silicate hydrate (C-S-H) was formed (Locher, 1966), giving necessary strength and dimensional stability to the set cement (Gaurina-Medimurec et al., 1994). Calcium hydroxide or portlandite (CH) was also liberated as a hydration by-product (Locher, 1966).

A 'traditional' form of sulphate attack (Batilov, 2016), also known as 'the classic form' of sulphate attack (Traegardh & Bellmann, 2007), occurred when C_3A reacts with gypsum in cement to form primary ettringite according to the equation 1 below:

$$3CaO.Al_2O_3+3(CaSO_4.2H_2O) \rightarrow Ca_6[Al\ (OH)_6]2.\ (SO_4)_3.26H_2O\ldots\ldots\ldots\ (1)$$

This process is completed within the first 24 hours of hydration (Morales et al., 2003). As the amount of gypsum decreased, part of the ettringite was transformed into calcium monosulfo aluminate hydrate following the equation below:

$$Ca_6[Al(OH)_6]_2(SO4)_3.26H_2O+2(CaO.Al_2O_3)+4H_2O\rightarrow 3(3CaO.Al_2O_3.CaSO_4.12H_2O)\ldots..\ (2)$$

Sodium sulphate attack was initiated by the reaction of sodium sulphate with calcium hydroxide/portlandite – a hydration product of cement (Smith, 1986). The reaction occurred according to equation 3 below:

$$Ca(OH)_2 + Na_2SO_4 + 2H_2O\rightarrow CaSO_4.(H_2O)_2 + 2NaOH\ldots\ldots\ldots..\ (3)$$

Calcium monosulfo aluminate hydrate reacted with calcium sulphate (gypsum) from the above reaction to produce the crystalline secondary ettringite with 32 water molecules (Morales et al., 2003; Winter, 2009) as shown in equation 4 below:

$$3(CaO.Al_2O_3.CaSO_4.12H_2O) + 2(CaSO_4.2H_2O) + 16H_2O\rightarrow 3CaO.Al_2O_3.3CaSO_4.32H_2O\ldots..\ (4)$$

Ettringite, a crystalline mineral is expansive in nature and its formation was accompanied by growth in weight (Batilov, 2016; Morales et al., 2003). As the ettringite continued to fill up the pores of cement, internal pressure built up (Scrivener et al., 1999). This generated expansive stresses (Morales et al., 2003; Skalny et al., 2003) that initiated the cracking of cement and loss of strength (Scrivener et al., 1999) in a phenomenon called sulphate attack (Morales et al., 2003).

Pozzolanic reaction of Nano silica

Nano silica is a high-purity, highly reactive siliceous pozzolan nanoparticle admixture (Batilov, 2016). A sulphate attack is initiated by the reaction of sodium sulphate with the portlandite

(Calcium Hydroxide) produced by the hydration of cement (Smith, 1986). Mitigation of calcium hydroxide through extensive conversion into secondary C-S-H via a pozzolan (Brandl et al., 2011) is an effective approach to increasing the sulphate resistance of the cementitious matrix. The reaction between portlandite Nano silica that produces secondary silica gel happens according to equation 5 below: (Lin et al., 2011). $x\,Ca(OH)_2 + y\,SiO_2 + z\,H_2O \rightarrow x\,CaOSiO_2.(x+z)H_2O \ldots.$ (5)

During the hydration of cement, water is added to make a homogenous paste from the powder and Nano silica. The Nano silica comes into contact with saturated Ca $(OH)_2$ which acts as an activator (Lin et al., 2011). The silicon covalent bonds in Nano silica are severed by attack from OH^- ions released from the dissolution of calcium hydroxide according to equation 6 below:

$$\equiv Si - O - Si \equiv + OH^- \rightarrow \equiv Si - O^- + \equiv Si - OH \ldots. \quad (6)$$

Metastable Si-OH may provide favourable sites for OH^- to break the Si-O-Si network. Further breakdown of this network changes the appearance of Nano silica particles (Lin et al., 2011). Subsequently, Ca^{2+} offsets the charge imbalance by bonding to Si-OH and Si-O^- giving rise to the basic units of CSH gel. The reaction is according to the equation below: $\equiv Si - O^- + HO - Si \equiv + Ca^{2+} + \ OH^- \rightarrow \equiv Si - O - Ca - O - S \equiv + H_2O \ldots.$ (7)

The setting and strength of the cement are mainly attributed towards the polymerization and solidification of the CSH gel. The reaction is complete when Nano silica particles are completely attacked by calcium hydroxide and surrounded by CSH gel as the reaction product (Lin et al., 2011).

MATERIALS AND METHODS

Materials

The test specimens were made of cement, water and different concentrations of colloidal Nano silica.

Cement

CEM IV B-P CEM C 32.5R cement was used in experiments. Table 1 shows the mechanical, physical and chemical properties of the above cement as cited (Okumu, 2018).

Table 1: Properties of CEM IV B-P CEM C 32.5R

Mechanical and physical properties	**Units**		**Chemical properties**	%
Blaine fineness	cm^2/g	4063	Al_2O_3	6.76
Residue micron	%	21.98	CaO	43.85
Compressive strength	MPa		Fe_2O_3	6.16
2 days		20.1	K_2O	2.12
7 days		35.3	MgO	1.32
28 days		45.5	Mn_2O	0.07
Consistency		31.5	Na_2O	2.51
Initial setting time	min	197	P_2O_5	0.06
Final setting time	min	270	SO_3	1.78
Density	kg/m^3	3091	SiO_2	33
			Chloride	0.01
			Loss of Ignition	1.64
			Insoluble Residue	28.43

Nano silica

An aqueous dispersion of silica particles branded Ludox TM-50 colloidal silica from Sigma-Aldrich was used to prepare a slurry. Its physical properties are shown in table 2.

Table 2: Physical properties of Nano silica

Quality level	200
Description	colloidal
Form	Viscous liquid
Concentration	50 wt. % suspension in H_2O
Surface area	~140 m^2/g
pH	9.0
Density	1.4 g/mL at 25 °C
SMILES string	O=[Si]=O
Molecular weight	60.08
Particle size	22 nm

Sodium sulphate

Anhydrous Sodium sulphate with a molecular weight of 142.04 g, which was obtained from Unilab Kenya Limited, was used.

Equipment

Moulds

Rigid steel fabrications of 3 cubical compartments forming a section, were used. Each mould was made of two sections with a lateral separation that was held together by bolts and nuts. These were dislodged before de-moulding to enable the removal of hardened specimens. The image below shows moulds into which slurry was added during the experiment.

Figure 1: Image of moulds that were used to prepare the specimen

Curing tanks

Five plastic drums fitted with temperature-controlled heating elements were used. Temperatures were set at 23°C, 40°C, 65°C, 70°C and 80°C for 21 days.

Figure 2: Plastic drum used as a curing tank.

The methodology of this research was done according to **API 10A** specifications concerning **ASTM C109** for the preparation of cubes, **ASTM C1012-95** for testing the sulphate-attack resistance of cement, **ASTM D1193-99** for specifications of reagent water and **ASTM C183** for specifications of the sieve that was used.

Cube specimens of 50 x 50 mm prepared with a water-to-cement ratio of 0.35 were used in the experiment. Curing was done under full immersion into 5 separate 0.3M sodium sulphate solutions at atmospheric pressure and maintained at 23℃, 40℃, 65℃, 70℃ and 80℃ for 21 days. The percentage elongation of specimens was investigated by comparing initial and final length measurements after 24 hours (initial curing) and 21 days of curing, respectively. Plots of percentage elongation against temperature for different concentrations of Nano silica were used to analyse the performance of cement against the increase in temperature.

Preparation of cubes (ASTM C109 via API 10A)

Cube specimens were prepared according to guidelines from ASTM C109. With water to cement ratio of 0.35, adjustments to cement volumes were made to incorporate replacements of Nano silica including 0%, 0.3%, 0.6%, 0.9% and 1.2% replacements by weight of cement.

Calculations for these adjustments are reported in preparation table 4. Table 3 shows calculations for the volume of each cube.

Table 3: Volume of an individual cube specimen

$V = L \times W \times H$ Water : cement = 0.35

$V = (50\times10^{-3}) \times (50\times10^{-3}) \times (50\times10^{-3})\ m^3$

$V = 1.25 \times 10^{-4}\ m^3$

Table 4: Preparation table for cement slurry

% Nano silica replacement	**Weight of cement (kg)**	**Water volume (l)**	**The volume of nS (l)**
0% (per cube)	Vol. = 0.65x1.25 x 10^{-4} m^3 Vol. = 8.125 x 10^{-5} m^3 Weight = D x V Weight = 1440 x 8.125 x 10^{-5} m^3 Weight = 0.117 kg	Vol. = 0.35 x1.25 x 10^{-4} m^3 Vol.=4.375 x $10^{-5}$$m^3$ Vol. = 0.04375 litres	0 litres
For 69 cubes	Weight = 8.073 kg	Volume = 3.019 litres	0 litres
0.3% (per cube)	W= 0.117- 3.51x10^{-4}kg W=0.116 kg	V=2.879 l –16.547 ml V = 2.862 l	W=(0.003 x 0.117) = 3.51 x 10^{-4}kg V= W/D =2.507x10^{-7} m^3 V= 2.507 x 10^{-4} l V= 0.25 ml V = 0.501 ml (50% saturation)
For 66 cubes	W= 7.699 kg	V= 2.862 litres	V= 33.094 ml
0.6% (per cube)	W= (0.117 - 7.02 x $10^{-4)}$ kg W= 0.116 kg	V = 2.87 l - 33.099 ml V = 2.837	W=(0.006 x 0.117) = 7.02 x 10^{-4}kg V=5.014x10^{-7} m^3 V= 5.014 x 10^{-4} l V = 1.003 ml (50% saturation)
For 66 cubes	W= 7.676 kg	V=2.837 litres	V=66.198 ml

0.9% (per cube)	W= (0.117 – 0.001053) W= 0.115947 kg	V = 2.862-0.04826 V = 2.8137 l	W=(0.009 x 0.117) = 0.001053 kg V=7.3125 x10^{-7} m^3 V= 7.3125 x 10^{-4} l V = 0.73125 ml V = 1.4625 ml (50% saturation)
For 66 cubes	W= 7.6525 kg	V=2.8137 litres	V=96.525 ml
1.2% (per cube)	W= (0.117 – 0.001404) kg W= 0.115596 kg/cube	V = 2.853-0.13233 l V = 2.7207	W=(0.012 x 0.117) = 0.001404 kg V=1.003x10^{-6} m^3 V= 0.001 l/cube V = 2.005 ml (50% saturation)
For 66 cubes	W= 7.6293 kg	V= 2.7207 litres	V= 132.33 ml

Preparation of sulphate solutions

The preparation of sodium sulphate solutions was done according to guidelines from ASTM C1012-95, that is, the volume proportion of sulphate solution to cube specimens was maintained at 4 volumes of solution to 1 volume of cube specimen. Into every 6.75 litres of distilled water in a plastic storage container, 350 g of anhydrous sodium sulphate was dissolved. The solution was then diluted to obtain 7.5 litres of solution in which 15 cubes were immersed for curing. Calculations for the mass of sodium sulphate and volume of distilled water used are reported in table 5.

Table 5: Calculations for preparation of the sulphate solution.

50.0g/l in the solution: specimen volume ratio of 4:1 Solution volume/cube = 4 x1.25 x 10^{-4} m^3 = 5 x $10^{-4}m^3$ For 15 cubes; Solution volume = 15 x 5 x $10^{-4}m^3$ Solution volume = 0.0075 m^3	1 m^3 = 1000 litres 0.0075 m^3 = 0.0075 m^3 x 1000 = 7.5 litres ∴ 7.5 litres of solution per container were used. For 5 containers; Volume = 5 x 7.5 litres Volume = 37.5 litres of solution

Procedure

Curing in sodium sulphate solution

Five plastic containers were used for curing the specimens. Each container with 7.5 litres of sodium sulphate solution was placed with 3 cubes of each concentration of Nano silica replacement to make 15 specimens per container, i.e. 3 cubes containing 0%, 3 cubes containing 0.3%, 3 cubes containing 0.6%, 3 cubes containing 0.9% and 3 cubes containing 1.2%. Each container was then covered with a lid and sealed with duct tape to prevent evaporation from the inside or dilution from the outside. Plastic drums fitted with temperature-controlled heating elements were used as curing tanks, inside of which concrete cylinders were used as risers. The drums were filled with water up to a height slightly above the risers and the prepared containers were placed on top of the risers. The thermostats on the heating elements were adjusted to reach the five different temperatures of 23℃, 40℃, 65℃, 70℃ and 80℃. The five setups were maintained as such and measurements were taken after 21 days.

Note: Only about 80% of the heights of the plastic containers were immersed in water during the experiment.

Measurements

Change in the length of each cube was obtained using the formula below.

$$\Delta L = \frac{Lx - Li}{Li} x\ 100 \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \ (8)$$

Where Li represents the initial value of length and x represents the number of days after which the reading was taken.

RESULTS AND DISCUSSION

The bar graph in figure 3 shows the percentage elongation of specimens with an increase in curing temperature from 23℃ to 80℃. Each bar shows how sulphate resistance changed for each percentage concentration of Nano silica replacement.

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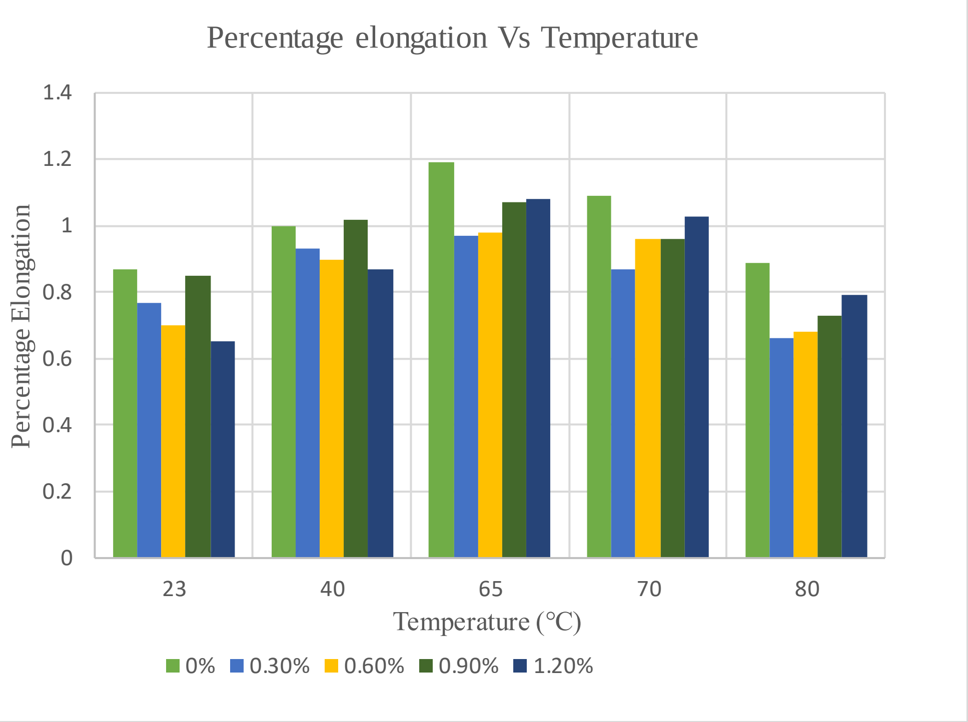

Figure 3: A bar graph showing how the percentage elongation of specimens changed with an increase in temperature from 23℃ to 80℃

From the graph above, it was observed that the percentage elongation of specimens decreased with an increase in the concentration of percentage Nano silica replacements at temperatures below 65℃. Between 65℃ and 80℃, the increase in the concentration of Nano silica led to an increase in elongation instead.

For each percentage concentration of Nano silica replacement, there was an increase in the percentage elongation of specimens with an increase in temperature up to 65℃. Beyond 65℃, the percentage elongation for all specimens started to decline gradually and by 80℃, the highest percentage elongation was observed in specimens with 0% Nano silica replacement.

At 23℃, the percentage elongation of 1.2% had the lowest value compared to 0.3% and 0.6%. However, when temperature increased beyond 65℃, the percentage elongations of 0.3% and 0.6% had lower values than the elongation of 1.2%. At 80℃, the percentage elongation with the lowest value was 0.3% followed by 0.6% and 0.9%.

Initially, the percentage elongation of all specimens gradually increased from 23℃ to 65℃ because an increase in temperature increased the rates of chemical reactions. At the same increasing temperatures, the reaction between calcium hydroxide and sodium sulphate was faster than the pozzolanic reaction of Nano silica because of the nature of the reactants- ionic reactions were faster than pozzolanic reactions. Therefore, the increase in elongation was due to an increase in the amount of ettringite formed from the faster reaction of sodium sulphate. The mechanism of elongation follows the formation of ettringite and depends on the amount of salt formed (Scrivener et al., 1999).

Due to the difference in concentration of Nano silica added to different specimens, elongation was observed to be more in specimens without any Nano silica added. Between 23°C and 65°C, the percentage elongation of 1.2% had the lowest value followed by 0.6% and 0.3% respectively. For the same temperature, the rate of reaction is determined by the concentration of reactants. Therefore, the higher 1.2% concentration of Nano silica consumed more calcium hydroxide and made it less available for reaction with sodium sulphate. As such, less ettringite was formed in specimens with 1.2% Nano silica than in the specimens with 0.3%, 0.6% and 0.9% Nano silica. Similarly (Ghafoori et al., 2020) found that doubling the concentration of colloidal Nano silica had a positive effect on the sulphate resistance of mortars. This explains the performance trend of Nano silica concentrations being 1.2%, 0.6%, 0.3% and 0.9% in the respective descending order.

However, between 65°C and 80°C, the percentage elongation of specimens had a decreasing trend with an increase in temperature. Specimens with 0.3% Nano silica had the lowest value followed by 0.6% and 1.2% respectively. The solubility of ettringite increased with temperature until it became completely soluble at around 65°C (Morales et al., 2003). Hence the decreasing trend of specimen elongation with a further increase in temperature above 65°C. Temperature increments accelerated the pozzolanic reaction and depletion of Nano silica (Brier & Jayanti, 2015) at temperatures below 65°C. This made a resultant reduction in the rate of the counteractive pozzolanic reaction above 65°C (Brier & Jayanti, 2015). Subsequently, the formation of more ettringite (than secondary CSH gel) in specimens with 1.2% and 0.6% Nano silica resulted in more elongation than in specimens with 0.3% Nano silica above 65°C.

Due to variations in concentration, the rate of reaction of Nano silica with Calcium hydroxide was slower in specimens with 0.3% concentration than in specimens with 0.6% and 1.2% concentration below 65°C. This slow rate of reaction and therefore depletion between 23°C and 65°C made Nano silica available to mitigate the formation of ettringite between 65°C and 80°C. This is why at 80°C, 0.3% Nano silica had the lowest percentage elongation of specimens. Similar findings were made from research on High-Performance concrete by (Nie et al., 2022) which concluded that agglomeration of nanoparticles at high concentrations caused the decline in the effectiveness of Nano silica in improving sulphate resistance.

Results from this research are in agreement with previous studies on concrete specimens conducted by (Tobón et al., 2015) which found that adding 3% Nano silica resulted in up to a 63% reduction in expansion when compared to a control specimen (Khan et al., 2022). It also showed that a lower replacement amount of Nano silica was useful for increasing concrete resistance to sulphate. Another study by (J. Huang et al., 2022) using both Polyvinyl alcohol and Nano silica in mortars found that mass loss after immersion in 10% sodium sulfate solution for 72 days was about 16% lower than that of the control one. A similar study by (Nie et al.,

2022) found that High-Performance Concrete specimens modified with 1% Nano silica exhibited the most effective inhibition of sulphate corrosion, where the mass loss, porosity increment, as well as compressive and splitting strength reduction were minimal after sulphate solution soaking.

As such, it can be deduced that a combined effect of temperature above 65℃ and appropriate concentration of Nano silica greatly improve the sulphate resistance of cement.

CONCLUSION

The replacement of cement with nano-silica has been shown to significantly improve the sulphate resistance of hardened cement slurry when exposed to sulphate solutions at elevated temperatures. The use of nano-silica as a cement additive represents a promising technological solution for enhancing the performance of geothermal wells in challenging environments, and has important implications for both the energy industry and society at large.
The results from the study indicated

i) Nano silica improved the sulphate resistance of specimens by reducing the porosity and permeability of hardened cement slurry.
ii) At lower concentrations, sulphate resistance is directly proportional to the amount of Nano silica replacement.
iii) Doubling the concentration of Nano silica replacement had a positive effect on sulphate resistance.
iv) There was an optimum value of Nano silica replacement for the improvement of sulphate resistance. In this study, 0.3% exhibited the least elongation at 80℃.

Practical Implications

The use of nano-silica cement additive has practical implications in enhancing the performance of geothermal wells against sulphate attack. The application of this additive can improve the durability and strength of the cement, reducing the potential for degradation due to exposure to sulphates. This can lead to a longer lifespan of the geothermal well, reducing maintenance costs and increasing its overall efficiency. Additionally, the use of nano-silica cement additive can also reduce the environmental impact associated with geothermal well construction and maintenance, by reducing the need for frequent repairs and replacements.

Social Implications

The use of nano-silica cement additive in geothermal wells can also have social implications. It increases the safety and reliability of the geothermal well, reducing the risk of accidents and ensuring a stable supply of energy to the community. This can have a positive impact on the social and economic well-being of the community, as reliable and sustainable energy sources are critical for development and growth. Additionally, the use of environmentally friendly additives such as nano-silica can promote sustainable development and reduce the environmental impact of geothermal energy production, contributing to a more sustainable future.

Recommendation

Further research is to be done utilising model solutions in temperature and pressure conditions mimicking the exact geothermal environment.

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