Microstructural Characterisation and Durability Enhancement of Concrete with Nano Silica

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Abstract. Deterioration of concrete due to chemicals is aggravated by entry of harmful liquids and gases through its pores. The porosity and pore structure of the concrete play a vital role in transporting harmful substance, due to capillarity and permeability. Concrete’s density, strength and its pore structure can be improved by using Nano Silica (NS). In this study NS was used as an addition and it was proved to improve the properties of concrete. The Scanning Electron Microscope (SEM) image of sample with NS shows that the concrete has denser, more compact and better gel formation with fewer pores than concrete without NS. NS particles fill the nano sized pores in the concrete and improve the pore structure of the concrete. The weight loss of concrete due to sulphuric acid and hydrochloric acid was 27.53% less and 32.34% less respectively, when NS was added.

1. Introduction
Concrete is prone to deterioration due to poor quality of material, improper design, etc., which are under the control of the executing authority. Degradation of a structure can also happen due to acid attack, freezing and thawing, sulphate attack, corrosion of bars in reinforced concrete, etc. These are the factors that cannot be controlled by the authority and these are the problems that have to be studied and mitigated. Intrusion of harmful elements through the external surface and their advancement through the pore system lead to various durability problems [1]. The porosity and pore structure of the concrete play a vital role in transporting harmful substance, due to capillarity and permeability. Capillarity is governed by the surface tension and permeability by the differential pressure [2], [12-13]. Chemical deterioration due to acid and sulphate attacks is also aggravated by entry of harmful fluids and gases from the surrounding atmosphere.

Zhang & Zong (2014) have studied the effect of water absorption on the durability of concrete. Concrete samples of various water absorption capacities were prepared [3], [14-16]. At 28th day of curing, permeability, sulphate attack, chloride ion diffusion and compressive strength were studied. It was observed that only surface water absorption correlated with the performance of concrete with...
respect to permeability, chloride ion diffusion and sulphate attack. Also, resistance to sulphate attack and increase in impermeability were linearly related to surface sorptivity.

Nano composites made from particles of nano-size ceramics or metals smaller than 100 nanometers can substantially become much stronger than predicted by existing material science models. Nano silica (NS) is one such material that can improve the concrete. Study by Belkowitz et al. (2015) has shown that when NS is added with the mix, it reacts with free calcium hydroxide, increasing the quantity of C–S–H (calcium silicate hydrate), resulting in a higher densification of the matrix which increases the strength and durability [4], [17-22]. Also it has been reported by Yeşilmen et al. (2015) and Mohammed et al. (2016) that the smaller particle size of NS provides a larger surface area, which speeds up the rate of cement hydration and pozzolanic reactions [5],[6]. Various works have been carried out to prove and study the benefits of using NS in concrete and NS is found to improve the compressive strength, increase the tensile strength and enhance abrasive resistance. Also, the concrete becomes denser with improved durability properties. Investigations on permeability features of NS concrete showed drop in water absorption, capillary absorption and water permeability. So it is clear that by using NS in concrete, durability can be improved. In this work, improvement of compressive strength of concrete with NS was confirmed and the resistance of NS concrete against acid attack and sulphate attack was studied. Scanning Electron Microscope (SEM) was used to study the microstructure of the concrete specimens.

2. Materials and Methods

2.1. Materials
NS with specific surface area of 201 m²/g and chemical composition 99.9% SiO₂ was used. The Ordinary Portland Cement (OPC) was used with, river sand as fine aggregate and broken stones as coarse aggregate to make the concrete. Super plasticiser used was of chemical base melamine formaldehyde.

2.2. Mixing of ingredients
The NS was added in proportions of 0.5, 1, 1.5 and 2 wt.% of cement in the concrete mix and the samples were designated C1, C2, C3, and C4 and the base mix with 0% NS was designated C0. All the specimens were water cured. If the super plasticiser interacts with NS first, reactivity gets reduced; to avoid this, water and other ingredients were mixed thoroughly first to ensure proper dispersion of NS. Super plasticiser was added later and mixed to have uniform dispersion.

2.3. SEM Analysis
Small samples were chipped off from the test specimens after 180 days from casting and they were analyzed through a SEM. The size and shape of the specimens were chosen so that they can be accommodated into the SEM and double coated carbon tape was used to fix the sample to the sample holding disks. Gold coating was given by evaporating gold on to the irregular surface of the sample to get better electron scattering in the chamber.

2.4. Acid Resistance Test
Acid resistance test was conducted on cubes of size 150 mm as per ASTM C267-01(2012) [7]. The cubes were water cured in tanks under completely immersed condition and after 28 days of curing, the cubes were wiped off to remove dripping water. Then, they were allowed to dry for 1 day and then they were immersed in acid. The test was conducted using both Hydrochloric acid (HCl) and Sulphuric acid (H₂SO₄) separately. The HCl was 5% of 0.01 normality solution with maintained pH of 3.1 and H₂SO₄ was 5% of 0.01 normality solution with pH of 2.1. The pH was checked periodically, using pH meter and maintained by the addition of acid or distilled water by trial and error method. The test was conducted for 28 days, and at the end of the 28 days the weight loss and compressive strength were measured.

2.5. Sulphate Resistance Test
Sulphate resistance test was conducted on cubes of size 150 mm. The cubes were water-cured in tanks under completely immersed condition and after 28 days of curing, the cubes were wiped off to remove dripping water. Then, they were allowed to dry on surface and after that they were immersed in 10% sodium sulphate (Na$_2$SO$_4$) solution. The test was conducted for 32 days, and at the end of the 32 days (i.e. after 60 days of casting), the weight loss and compressive strength were measured.

3. Results and Discussion

3.1. Sulphate Resistance Test
The UPV test and compressive strength tests were conducted on cubes of size 150 mm × 150 mm × 150 mm. As the age of the concrete increases, the hydration of cement increases and there is reduction of capillary pores. Due to this the pulse velocity increases since resistance against conduction of pulse declines. The samples with NS has higher compressive strength (figure. 1) on the 7th day. Similarly pulse velocity was high for sample with NS at 7 days. The compressive strengths of C3 and C4 samples had very little difference of 0.5%, but the pulse velocity of C3 and C4 had a difference of 7.99% due to the presence of excess NS particles that supports the easy transmission of pulse through the concrete. The presence of NS makes the concrete density increase and improves strength of the matrix.

On the 28th day the compressive strength of sample with 2% NS (C4) was 4.41% less than the sample with 1.5% NS (C3). The compressive strength of C4 sample had decreased than the C3 sample but the excess NS occupied the space in the matrix without contributing to the strength and assisted in the transfer of waves by filling the nano sized pores.

![Figure 1. UPV versus compressive strength](image)

3.2. Microstructure
Figures 2 to 13 show the microstructure of chipped off cement mortar samples with and without NS after 180 days at various magnifications. Figure 2 shows the C0 sample at 2.02 kx magnification, where the aggregate and the cement matrix can be seen clearly with cracks. The C-S-H formation was spread at separate locations as bright massive gel on both cement matrix and aggregate. On further magnification to 3.32 kx, C-S-H formation over CaOH (Calcium Hydroxide) can be noticed clearly in figure 3 and this confirms the presence of excess CaOH that could be used to improve the strength of the matrix. At 6.19 kx magnification, C-S-H formation at various stages over CaOH can be seen as shown in figure 4. The sample C0 had deposits of CaOH even after a long duration from casting.

The SEM image of C1 cement matrix at magnification of 1.24 kx shows the formation of C-S-H over CaOH in figure 5. The C-S-H formation here is better than the C0 sample, but still large area of CaOH is present. On further magnification to 2.59 kx, the better formation of C-S-H was seen clearly.
and C-S-H formation at various stages are also seen in figure 6. At 4.42 kx magnification, dense C-S-H formation is seen clearly with visible CaOH crystal slabs below in figures 7 and figure 8.

**Figure 2.** SEM Image at 2.02 kx magnification of C0 sample

**Figure 3.** SEM Image of 3.32 kx magnified C0 sample.

**Figure 4.** SEM Image of 6.19 kx magnified C0 sample

**Figure 5.** SEM Image of 1.24 kx magnified C1 sample
The SEM image of C2 sample at 1.21kx magnification shows dense formation of C-S-H over CaOH in figure 9. The presence of C-S-H is higher than the C0 and C1 samples. On further magnification to 2.62 kx and 4.67kx, similar dense C-S-H was seen as shown in figure 10.

The SEM image of C3 samples in figure 11 and figure 12 shows very dense formation of C-S-H and very small area of CaOH. The C3 sample shows better C-S-H formation than C0, C1 and C2. This correlates with the compressive strength results where the C3 samples have the highest compressive strength compared to all the other samples.

The SEM image of C4 samples in figure 13 shows dense formation of C-S-H and also clusters of unreacted NS present in the cement matrix. This must be due to the improper dispersion or presence of excess NS. In samples with NS, the gel formation was better than that of C0; nevertheless unreacted calcium hydroxide was also present in samples with NS. The presence of unreacted NS particles was seen in sample C4, which actually occupy the place of cementitious material and reduce
the strength of concrete [8]. The SEM image of sample C3 which gave the highest compressive strength, appears to be denser and more compact.

![Figure 11. SEM Image of 1.21 kx magnified C3 sample](image1)

![Figure 12. SEM Image of 2.33 and 4.59 kx magnified C3 sample](image2)
3.3. Acid Resistance Test

All the concrete cubes immersed in acid for 28 days showed reduction in the compressive strength and weight loss compared to the cubes that underwent 28 days of water curing. The weight loss of concrete in H\textsubscript{2}SO\textsubscript{4} was greater compared to the weight loss due to HCl as seen in table 1. Figure 14 and figure 15 show the weight loss in H\textsubscript{2}SO\textsubscript{4} and HCl respectively. The weight loss due to H\textsubscript{2}SO\textsubscript{4} was 0.36% (C1), 7.81% (C2), 27.53% (C3) and 25.48% (C4) which was less when compared to the noted C0 sample. The weight loss due to HCl was 15.30% (C1), 22.50% (C2), 32.34% (C3) and 29.63% (C4) which was less when compared to the C0 sample. Here, it can be seen that the concrete with higher NS content had lower weight loss compared to the concrete without NS. The weight loss decreased with an increase in NS content.

| Sl.No | Sample | Weight loss in % |
|-------|--------|------------------|
|       |        | H\textsubscript{2}SO\textsubscript{4} | HCl |
| 1     | C0     | 7.30             | 1.49 |
| 2     | C1     | 7.31             | 1.27 |
| 3     | C2     | 6.78             | 1.16 |
| 4     | C3     | 5.40             | 1.03 |
| 5     | C4     | 5.51             | 1.06 |

Figure 13. SEM image of C4 sample at 180 days

Figure 14. Percentage of weight loss in H\textsubscript{2}SO\textsubscript{4}
The reduction in weight was due to the deterioration of the concrete in acid environment, and this leads to loss of strength. The strength was compared to the 28-day strength of concrete after water curing. Similar to weight loss, the strength loss was greater in H₂SO₄. Figure 16 shows the concrete cube after H₂SO₄ exposure; the aggregates are clearly visible. It can be seen from table 2 that concrete with NS had lower strength loss compared to the concrete without NS and strength loss decreased with an increase in NS content. A better pore structure gives a better resistance to acid attack, and NS helps by reducing the pores [9] [10]. So it can be concluded that NS can improve the concrete’s resistance to acid attack.

### Table 2. Strength loss due to acid attack

| Sl.No | Sample | H₂SO₄ | HCl |
|-------|--------|-------|-----|
| 1     | C0     | 73.18 | 24.40 |
| 2     | C1     | 72.65 | 23.43 |
| 3     | C2     | 71.40 | 22.15 |
| 4     | C3     | 71.02 | 21.59 |
| 5     | C4     | 70.76 | 21.93 |

3.4. Sulphate Resistance Test

All the concrete cubes were immersed in Na₂SO₄ for 32 days. During this time, the Na₂SO₄ enters through the pores in the concrete to react with portlandite and unreacted tricalcium aluminate to form gypsum and ettringite, which cause expansive pressure inside the pores leading to cracking of concrete [11]. The concrete’s weight increases during sulphate resistance test due to the above said fact. But the strength gain is reduced due to the internal deterioration. The strength of concrete, after 60 days of
water curing, is compared with the strength of the concrete cube cured in water for 28 days and 32 days in Na₂SO₄. The weight gain was higher in concrete without NS and the weight gain was less with increase in NS content as seen in table 3. The weight gain due to Na₂SO₄ was 12.03% (C1), 15.59% (C2), 18.15% (C3) and 21.22% (C4) less when compared to C0 sample.

The compressive strength of C1, C2, C3 and C4 samples immersed in Na₂SO₄ were 9.41%, 16.24%, 25.74% and 24.65% higher than C0 sample. The reduced pores in concrete due to NS gives a better resistance to permeation of Na₂SO₄. From figure 17, it can be seen that the strength loss reduces with the increase in NS content. In the presence of NS, the strength of the concrete improves to resist the pressure developed at the pores in addition and the number of pores gets reduced.

Table 3. Effect of Na₂SO₄

| Sl.No. | Sample | Weight Gain in % | Strength Loss in % |
|--------|--------|------------------|--------------------|
| 1      | C0     | 0.66             | 7.98               |
| 2      | C1     | 0.58             | 4.57               |
| 3      | C2     | 0.56             | 1.50               |
| 4      | C3     | 0.54             | 1.44               |
| 5      | C4     | 0.52             | 0.83               |

![Figure 17. Strength loss of cubes after Na₂SO₄ exposure](image)

4. Conclusions
The SEM image of a sample with NS shows that the concrete has denser, more compact and better gel formation with fewer pores than concrete without NS. The addition of NS makes the concrete denser and less porous than the ordinary concrete which attributes to its improved strength properties. The presence of nano sized particles fills the nano sized pores in the concrete and improves the pore structure of the concrete.

UPV test showed an increase in UPV speed with increase in NS content. The increase in UPV speed indicates a reduction in voids and increase in density of concrete due to the introduction of NS.

In acid test it was seen that the concrete with higher NS content had lower weight loss compared to the concrete without NS and also strength of the concrete with NS was higher than the concrete without NS.

Concrete with NS had better resistance against the sulphate attack than the concrete without NS. Nano silica when added to concrete increases its compressive strength and improved all its durability properties.
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