Enhancements and Mechanisms of Nano Alumina (Al$_2$O$_3$) on Wear Resistance and Microstructure Characteristics of Concrete Pavement

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Abstract. Nano materials are being used in concrete technology to enhance performance grade sustainably of construction field works like rigid highway pavement. Nano materials like Nano A12O3 are used as admixture for the cementitious materials to improve the mechanical and durability properties related to the physio-chemical reactions. The overall objective of this research is to evaluate the effects of Nano Al2O3 addition on the abrasion durability response of concrete pavement. These investigations are conducted to study different Nano Al2O3 contents (0.5, 1, 1.5, 2%) by weight of cement on the concrete strength and abrasion resistance by using the manufactured calibrated rotary cutter device for evaluation process and microstructure analysis by Scanning Electronic Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) tests. The compressive strength was tested at 28 days of curing and the results showed that the compressive strength of concrete increases up to 36% at 28 days by addition of 1% nano-alumina as a replacement of cement; Optimal content (1% by weight of cement) is found that appears better abrasion, durability abrasion performance and at the same time, achieves the main requirement of concrete highway pavement (strength and workability).

Keywords. Nano Al2O3, Durability, Microstructure, Abrasion Resistance, Rotary Cutter Device, Concrete Pavement.

1. Introduction
Concrete durability against wearing on which named abrasion resistance related to the ability of the surface to resist being wear away by rubbing and friction. High quality concrete pavement is recognised as enhancing abrasion durability under traffic loading. Improved abrasion durability may minimize construction and maintenance costs of pavement lifetime [1]. Nano particles which cause to reduce in pore size and concrete strength will be more dense and durable therefore, nanoparticles behaved as filler to improve microstructure leading to dense morphology [2]. NanoAlumina(Al$_2$O$_3$) particles were very effective in improving the mechanical properties of the concrete. Mix containing less than 3% Nano Al$_2$O$_3$ (N.A) particles shows better mechanical properties than the control concrete [3].

Using of (N.A) result in formation of C.A.S (calcium-Alumina-silica) gel in concrete by reaction with calcium hydroxide produce from hydration and the reaction rate depending on surface area (particle) that leading to fast increase of highly active atoms dense and resulting fast hydration [4]. The addition of (N-A) enhanced the mechanical properties and reduced the initial setting time of concrete composite and SEM (scanning electron microscopy) induced the N.A, was uniformly distributed by improving the microstructure of concrete [5]. However, traditional concrete has relatively low strength. By adding small amount of nano particles (not exceed 2% of cement wt.), the concrete performance will modify. Applying Nano particle treatment makes the surface area of nano material larger and cement hydration in the production of chemical bonds easier. Nano particles has a special network structure and with cement slurry, new network can be produced forming a three dimensional network structure that can enhance the physical and mechanical characteristics and achieve the durability ones. Hence, nano alumina can be applied to high performance highway pavement materials.
2. Experimental Work

2.1 Materials

2.1.1. Cement
Iraqi cement type (V) was used which satisfy the requirement of (No. 5/1984) [6].

2.1.2. Aggregate
Natural fine and crushed coarse aggregate were used in these investigations. The grade and properties of them were within the requirements of (No.45/1984) [7].

2.1.3. Water
Tap water was used for mixing and curing throughout the experimental work.

2.1.4. Superplasticiser
A highly efficient third generation of polycarboxylic based high-range water reducer admixture (Hyperplast PC175) was used to enable the water content of the mixes to perform with more effectiveness. The recommended dosage by the manufacturer was (0.5) liters/100 kg of cementitious materials. According to ASTM C494-03, this superplasticizer is classified as type A and G.

2.1.5. Nano Alumina particles
Nano Alumina is pozzolanic materials with acceptable degree of purity and well defined particles (40 nm) with pozzolanic activity index P.A.I=143% was purchased from local market as shown in Plate (1). The crystallinity of nano alumina particles was determined by X-ray diffraction (XRD) as shown in Figure (1). X-ray florescence (XRF) is a simple non-destructive method for testing the quantities and qualitative analysis of nano alumina chemical composition as shown in Table (1).

![Figure 1. XRD Analysis of Al₂O₃ Nano Particles (Germany-Iraqi Laboratory, College of Science, University of Baghdad).](image-url)
Plate (1): Nano Alumina (Al₂O₃) Admixture

Table 1. XRF Results of Al₂O₃ Nano Particles

| Sample Name Description | Al₂O₃  | Date of Receipt | 8/3/2019 12:35:23 TurboQuant-Powders |
|-------------------------|--------|----------------|-------------------------------------|
|                         | Symbol | Concentration | Abs. Error                          |
| Z | Element | Nom. Int. | % | % | % |
|---|---------|----------|---|---|---|
| 12 | MgO | Magnesium | 30.9113 | 0.884 | 0.023 |
| 13 | Al₂O₃ | Aluminum | 10468.2744 | 72.36 | 0.06 |
| 14 | SiO₂ | Silicon | 14.3687 | 0.0603 | 0.0058 |
| 15 | P₂O₅ | Phosphorus | 277.3495 | 0.4908 | 0.0036 |
| 16 | SO₃ | Sulfur | 23565.127 | 22.81 | 0.02 |
| 17 | Cl | Chlorine | 97.7489 | 0.00933 | 0.00012 |
| 18 | K₂O | Potassium | 4.3755 | 0.0270 | 0.0026 |
| 20 | CaO | Calcium | 48.0543 | 0.1974 | 0.0031 |
| 21 | TiO₂ | Titanium | 11.6795 | 0.0394 | 0.0014 |
| 22 | V₂O₅ | Vanadium | 0.0000 | <0.0029 | <0.0029 |
| 24 | Cr₂O₃ | Chromium | 9.7836 | 0.00413 | 0.00017 |
| 26 | MnO | Manganese | 3.8583 | 0.00210 | 0.00020 |
| 27 | Fe₂O₃ | Iron | 163.9286 | 0.04617 | 0.00029 |
| 28 | CoO | Cobalt | 0.5567 | <0.0009 | <0.0009 |
| 29 | NiO | Nickel | 29.8742 | 0.00346 | 0.00007 |
| 30 | CuO | Copper | 1.2925 | 0.00014 | 0.00006 |
| 31 | ZnO | Zinc | 4.193382 | 0.05244 | 0.00013 |
| 32 | Ga | Gallium | 171.5064 | 0.00833 | 0.00006 |
| 33 | Ge | Germanium | 0.0000 | <0.00005 | <0.00005 |
| 34 | As₂O₃ | Arsenic | 0.0000 | <0.00007 | <0.00007 |
| 35 | Se | Selenium | 0.0000 | <0.00005 | <0.00005 |
| 36 | Br | Bromine | 0.0000 | <0.00005 | <0.00005 |
| 37 | Rb₂O | Rubidium | 7.5955 | 0.00011 | 0.00001 |
| 38 | SrO | Strontium | 50.2799 | 0.00074 | 0.00001 |
| 39 | Y | Yttrium | 21.0680 | 0.00024 | 0.00002 |
| 40 | ZrO₂ | Zirconium | 1.2710 | 0.00020 | 0.00005 |
| 41 | Nb₂O₅ | Niobium | 0.0000 | <0.00014 | <0.00014 |
| 42 | Mo | Molybdenum | 7.2643 | 0.00098 | 0.00004 |
| 47 | Ag | Silver | 4.0819 | 0.00082 | 0.00011 |
| 48 | Cd | Cadmium | 3.9764 | 0.00037 | 0.00005 |
| 56 | SnO₂ | Tin | 5.7733 | 0.00055 | 0.00006 |
| 51 | Bi₂O₅ | Antimony | 5.9249 | 0.00100 | 0.00010 |
| 52 | Te | Tellurium | 7.3581 | 0.00057 | 0.00005 |
| 53 | I | Iodine | 5.9542 | 0.00078 | 0.00013 |
| 55 | Cs | Cesium | 0.0000 | <0.00040 | <0.00040 |
| 56 | Ba | Barium | 8.6282 | 0.00364 | 0.00044 |
| 57 | La | Lanthanum | 0.0000 | <0.00020 | <0.00020 |
| 58 | Ce | Cerium | 0.0000 | <0.00020 | <0.00020 |
| 72 | Hf | Hafnium | 1.6750 | <0.00011 | 0.00000 |
| 73 | Ta₂O₅ | Tantalum | 33.1656 | 0.00738 | 0.00013 |
| 74 | WO₃ | Tungsten | 1.1037 | <0.00013 | <0.00013 |
| 80 | Hg | Mercury | 1.7815 | 0.00007 | 0.00002 |
| 81 | Tl | Thallium | 1.4892 | <0.00005 | 0.000005 |
| 82 | PbO | Lead | 5.7850 | <0.00031 | <0.00003 |
| 83 | Bi | Bismuth | 0.0000 | <0.00010 | <0.00010 |
| 90 | Th | Thorium | 3.8726 | <0.00013 | <0.00002 |
| 92 | U | Uranium | 7.1114 | <0.00010 | <0.00010 |

Sum of concentration: 96.69 %

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2.2. Concrete Mix Design
Five mixes of concrete were designed according to ACI committee 211.1-2008 C3O [8]. These mixes were with different percentage of Nano Alumina addition (0.5, 1.5, and 2)% by weight of cementitious materials. All these mixes at curing age 28 days were investigated. To overcome the problem of agglomeration due to high surface area of Nano Alumina, Dry process by using rotary mixer for Nano Alumina application was adopted (which considered the more effective method from common ones for the related purpose). Nano alumina material was added to part of cement binder in a small container and mixed by using rotary mixer for (25 min period) as shown in plate 2. The first part of mixing water was mixed with the superplasticiser (0.5 liter/100 kg of cementitious material) by using electrical mixer. The Final step of preparing nano alumina concrete mixer was done by adding solution and modified cement to the other components (sand, gravel) and the concrete mixes were poured into steel models of specimens, compacted by vibratory table for (3-4) seconds and cured in water bathes at 20-25 °C temp.

Plate 2. Rotary Device For Dry Mixing Method (a- Rotary Device, b- Nano Alumina And Cement Before And After Mixing)

2.3. Experimental Tests
2.3.1. Fresh Concrete Test
The slump requirement of each mix were performed immediately after mixing according to (ASTM C143-89) [9].

2.3.2. Hardened concrete test
- Compressive Strength Test
  Cubic specimens (150×150×150 mm) were fabricated and investigated according to (ASTM C39-83) [10].
- Abrasion Resistance Test
  Cylindrical specimens (152 mm D.x 75 mm H) were cast and investigated by using the rotary cutter device (locally manufactured and calibrated) according to specification (ASTM C 944 M-12) [11]. The device is shown in plate (3).
Plate 3. Rotary Cutter Device (Locally manufactured and calibrating)

- Microstructure analysis test
  Scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS) analysis for control concrete and nano alumina concrete mixes are used for phase identifications micrograph and chemical characterisation of unknown elements in the hydrated cement paste of concrete.

3. Results And Discussion
Table (2) shows all the results of fresh and related hardened concrete properties including slump test, compressive strength test and Abrasion resistance test. For all mixes (control 0% N.A (M1), 0.5% N.A (M2), 1% N.A (M3), 1.5% N.A (M4) and 2% N.A (M5)) by weight of cementitious material.

| Mix Type | Slump (mm) | Compressive Strength (MPa) | Abrasion Resistance |
|----------|------------|---------------------------|---------------------|
|          |            |                           | Weight Loss (gm)    |
|          |            |                           | Wear Depth (mm)     |
| M1       | 60         | 34.5                      | 22.8                |
| M2       | 55         | 38.1                      | 16.6                |
| M3       | 30         | 47.0                      | 5.1                 |
| M4       | 25         | 45.3                      | 13.3                |
| M5       | 20         | 44.5                      | 14.2                |
3.1. Workability Test (Slump Test)

Workability is one of the most important features that must be investigated to ensure the specification of pavement requirements (25-75 mm) due to the agglomeration effect of nano Al₂O₃ addition. In spite of dispersion processes used throughout the concrete mixing. Figure (2) shows the results of workability for the different mixes. It can be seen that the slump value reduces with concrete mixes containing nano alumina but these results are conform to acceptable criteria of highway concrete pavement until nano materials content (1%) by weight of cement mix type (M3) then the values begin to be below the desired criteria as shown in Figure (1). The reason of this behavior is attributed to increase of the specific surface area of nano materials which increases the inter particles friction, and these for the superplasticiser dosage must be increased to avoid this problem and to satisfy the required workability [12].

3.2. Hardened Concrete Tests

Nano Al₂O₃ admixture was very effective in improving the mechanical properties of the modified concrete in comparison with control ones [5].

Uses of nano Al₂O₃ admixture results in formation of CAS gel by reaction with Ca(OH)₂ produced from hydration process and the rate of this reaction depending on surface area (finesse) of the utilised admixture. That leads to high enhancement of compressive strength in nano alumina concrete [13].

- Compressive strength

The results showed that the nano Al₂O₃ particles blended concrete has higher compressive strength compare to the concrete one (without nano Al₂O₃). It was found that the max limit of addition was 2% (M5 mix) with average particle size of 40 nm and the optimal level content of addition was 1% by weight of cement (M3 mix) and at this level the workability of fresh concrete decreased (slump value reaches 30 mm) in spite of using the superplasticiser after then. The slump value not satisfied the required limitation and the over dosage of superplasticiser made negative effect. The development in compressive strength reaches to the max rate (36%) for nano concrete mix with 1% nano Al₂O₃ addition (M3 mix) compared to control mix (M1) as shown in Figure (3).

- Abrasion resistance

From the results of abrasion resistance test, it can be seen that the behaviour of concrete containing nano Al₂O₃ admixture is significantly improved comparing with control ones. This is fact agree with the achieved conclusion in [14] that mentioned: Nano materials are being used in concrete technology to improve the performance and sustainability of the construction materials. Nano materials as mentioned in the previous studies were used as admixtures for the cementitious material to improve the durability and mechanical properties related to the physico-chemical reactions. The abrasion resistance dose not only depend on the compressive strength of concrete, but the microstructure plays important role on the results [15].

The results show a noticeable decreasing trend in the wear depth and amount of weight Loss with the optimal dosage 1% by weight of cement (M3 mix). Plate (4) compares a samples with (0%) nano alumina (M1) to one with (1%) nano alumina (M3), the earlier showing surface irregularities easily removed by the cutters. The scale of the weight loss makes results very sensitive, which explain the above inconsistency. As shown in Figures (4) & (5), the decrement in wear depth (mm) and loss of weight (gm) reach to max rate at optimal percentage 1% nano alumina addition (M3 mix) by (78%) and (77%) wear depth and loss of weight, respectively when compared with control mix (M1). That means significant development in abrasion resistance with better durability performance in which it is compatible with other research [16].
Plate 4. Comparison of: (a) Control sample, (b) 1% Nano Alumina Sample

Figure 2. Effect of Mix Type According to Content of Nano Alumina Addition on Slump Value

Figure 3. Effect of Mix Type According to Content of Nano Alumina Addition on Compressive Strength at 28 Days Age
Figure 4. Effect of Mix Type According to Content of Nano Alumina Addition on Wear Depth for Abrasion Durability at 28 Days Age

Figure 5. Effect of Mix Type According to Content of Nano Alumina Addition on Loss of Weight for Abrasion Durability at 28 Days Age

There is an attempt to relate the compressive strength of the specimens to their abrasion resistance (either wear depth or loss weight) and the best fit equation and R² value of each curve has been illustrated in the corresponding figure (6 & 7). It seems that there is a relatively good relationship between results in most cases. That agree with the facts mentioned in [17] that said; The increase in the content of nano particles was found to remarkably enhanced the resistance to abrasion of samples cured in various curing medias. Compressive strength and abrasion resistance of samples fall in a similar regime.
Figure 6. The Relationship Between Abrasion Resistance (Wear Depth) and Compressive Strength of Control and Nano Al₂O₃ Concrete Mixes at Age of 28 Days

\[
y = 335.46e^{-0.078x} \\
R^2 = 0.89
\]

Figure 7. The Relationship Between Abrasion Resistance (Weight Loss) and Compressive Strength of Control and Nano Al₂O₃ Concrete Mixes at Age of 28 Days

\[
y = 22.879e^{-0.08x} \\
R^2 = 0.86
\]

- **Microstructure analysis**
  The SEM perceptions likewise uncared that the nano alumina particles were going about as filler as well as activator to evaluate hydration demonstration and to enhance the microstructure of the concrete [18] [19]. The SEM pictures and EDS images of concrete mixes demonstrated that these appear contrast between control mix and optimal new mix (1% nano alumina addition) as shown in Figure (8) for control mix (M1) and Figure (9) for optimal mix (M3).

y = 335.46e^{-0.078x} \\
R^2 = 0.89

y = 22.879e^{-0.08x} \\
R^2 = 0.86
4. Conclusion

According to fresh (slump values) and hardened properties (compressive strength and abrasion resistance values) with the microstructure analysis of nano alumina concrete mixes, the following conclusions are obtained:

1. Nano alumina has a great surface energy and it is induced to agglomerate rather than the nano alumina generally absorb water because of high specific surface that cause less workability and don’t achieve the required specification for pavement construction beyond 1% nano addition.

2. Compressive strength of concrete mixes increases by adding 0.5% and continue increment by adding 1% (the optimal dosage) reach to rate of development to (36%) when compared with control mix.

3. The abrasion resistance which responded by wear depth and loss of weight is depended with increasing the nano alumina addition reaching to (77%) at optimal mix (1% nano alumina addition) when compared to control mix then the addition began to have negative reflect.

4. However, relatively good experimental relationships have been presented to correlate compressive strength and abrasion resistance.
5. SEM and EDS analysis indicated that the nano alumina enriched outer C-S-H formed in the modified paste within concrete mix. Exhibited improved compressive strength due to the reduced microspores.

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