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A Comparative Study of Al_2O_3, ZnO and Bentonite Effect on Structural Grade Mortar

Suvash Chandra Paul[1], Adewumi John Babafemi[2], Md Jihad Miah[3]
[1]Department of Civil Engineering, International University of Business Agriculture and Technology
Dhaka 1230, Bangladesh
suvashpl@iubat.edu
[2]Department of Civil Engineering, Stellenbosch University
Private Bag X1, Matieland 7602, Stellenbosch, South Africa
ajbabafemi@sun.ac.za
[3]Department of Civil Engineering, University of Asia Pacific
74/A, Green Road, Dhaka-1205, Bangladesh
jihad.miah@uap-bd.edu

Abstract **-** In recent years, nanoparticles have gained much attention in producing cementitious materials to modify both fresh and hardened properties, including their long-term durability characteristics. Due to its higher fineness and surface area, superior pozzolanic properties, nanoparticles have shown more significant improvement in cementitious materials' microstructure. Additionally, some micro filler materials also can improve the properties of hardened cementitious materials by filling up the micropores. Within this context, the focus of this paper is to investigate the optimum dosages of nano-Al_2O_3, nano-ZnO and bentonite in the production of medium strength (about 25-35 MPa) structural grade mortar. For the characterisation of materials properties, a compressive strength test is performed. The experimental results showed that up to a certain dosage of both nano-Al_2O_3 and bentonite, compressive strength is increased. After that, increasing dosages lead to a decrease in strength. However, strength can be significantly reduced when nano-ZnO is used in the mix.

Keywords**:** nano-Al_2O_3; nano-ZnO; bentonite; compressive strength; microstructure

1. Introduction

Different types of nanoparticles have received significant attention in many applications to fabricate materials with new functionalities [1]. For cementitious materials, it may be too early to make this assertion due to the limited uses of nanoparticles. However, up to a specific limit, the replacement of nanoparticles with binders in conventional building materials can significantly alter the rheological, mechanical, and durability properties [2]. Nanoparticles possess a high surface area to volume ratio that could lead to tremendous chemical activity. This can be attributed to the improvement in the hydration process: the formation of a strong calcium silicate hydrate (C-S-H) gel network in the cementitious matrix [2]. It is also anticipated that nanomaterials' behaviour can activate secondary reaction with binders to improve the microstructure and control the microcrack growths, shrinkage, and a protective barrier for entering CO_2, chloride, oxygen inside the cementitious materials [3, 4]. Though nanomaterials have received much attention from researchers, lack of guideline is still one of the major barriers to their widespread application.

Nanomaterials can be used as smart materials, for example, energy storage application, thermal insulation, antimicrobial coating, self-sensing, and self-cleaning. Though researchers [5-8] have already investigated some of these topics, a copious data pool is still necessary to raise nanomaterials' awareness before being used in conformist areas like the construction industry. Additionally, information on nanomaterials' impact on the environment and human health is necessary before application in the public domain [2, 9]. From the economic point of view, nanomaterials' cost is one of the major challenges to its usage. Natural resources for nanomaterials such as a seashell, volcano emission, metal or anion containing rocks could be explored. Depending on the source, nanoparticles' chemical compositions may vary considerably, hence necessitating a careful selection for a defined purpose. Despite these challenges, a vast pool of research data is available on using different types of nanoparticles in cementitious composites [10-12]. Different types and dosages of nanoparticles have been used in the cementitious materials, and their rheological, mechanical and durability performances reported [13, 14].

An increase of more than 33% in compressive strength and reduced initial setting time has been reported for cement concrete with 1% nano-Al_2O_3 when compared with the reference concrete [15]. In another study, different dosages of nano-Al_2O_3 (0.5%, 1.0%, 1.5% and 2.0% by wt. of cement) were used to produce low grade (M20) plain cement concrete, and their effect on fresh and hardened properties was investigated [16]. The results revealed that though the compressive strength of concrete samples improved, the workability of fresh concrete decreased as the dosages of nano-Al_2O_3 increased.

ZnO is widely used as an additive in numerous materials and products, including plastics, ceramics, paints and glass. ZnO is considered one of the most promising metal oxide semiconductors investigated extensively for photocatalytic degradation of organic compounds. In concrete, ZnO can be used as self-cleaning materials, but little is known about its hydration and effect on setting time and strength [17]. Therefore, this research investigates the effect of zinc oxide nanoparticles on the mechanical properties of cementitious materials.

Bentonite is generally used as filler in cementitious materials. Partial substitution of cement by bentonite in cementitious materials can lower the cost, yet a similar range of strength can be achieved [18]. Bentonite is a natural pozzolan containing both sodium and calcium ions. In a study [19], when bentonite (3% to 21%) was incorporated into the concrete mixture, the resulting samples have shown many beneficial properties, including high ultimate strength and low permeability even at 21% of the replacement level. In another study [20], concrete with bentonite showed low compressive strengths and relatively high permeability at an early curing age. Still, for longer curing age (beyond 28 days) sudden increase in the same properties was shown. It proves that if an appropriate dosage of bentonite is used in cementitious materials, it can provide some benefits such as lower cost and strength improvement.

In this study, the effect of different dosages of nano-Al_2O_3, nano-ZnO and bentonite on the compressive strength of fly ash-based structurally graded mortar is reported. The addition of nano-Al_2O_3 increased the mechanical behaviour of mortar, but they can negatively influence the properties beyond this dosage. On the contrary, the slower hydration reaction in nano-ZnO led to a significant reduction of the mortar strength. Additionally, bentonite is also used to replace cement in mortar production, and the respective modification in compressive strengths is investigated. The outcome of this research may help the user of nanoparticles in designing the cementitious materials. The details of the results are discussed in the subsequent sections below.

2. Mechanism of Nanoparticles in Cementitious Composite

It is already established that concrete properties are related to many factors such as water-binder ratio (w/b), the design constituents, mixing, placement, and curing methods. When all these factors are constant, lower w/b provides higher mechanical strength of concrete. However, lower w/b often causes lower workability of concrete, which may increase porosity inside the matrix. Another problem with lower w/b is that it may also increase the amount of unhydrated binder particles in the matrix. It is well known that enough water is required for binders to participate in the hydration reaction. Therefore, insufficient water leads binders to remain un-hydrated, thereby not contributing to concrete strength. In this regard, many researchers found that nanoparticles can initiate a secondary reaction with binders and improve both the microstructure and mechanical strength of concrete [21, 22]. Typically, for the same amount of binder and nanoparticles, nanoparticles' total surface area is larger than the traditional binder materials such as cement, fly ash, slag, etc. This large surface area of nanoparticles is more chemically reactive than binders. Also, nanoparticles significantly reduce the number and size of pores within C-S-H and reinforce cement-based materials' nanostructures. For example, in nano-SiO_2, all atoms of Si are connected with oxygen atoms, creating a tetrahedron, also known as a triangular pyramid. This triangular shape of nanoparticles can improve interlocking properties in the cement-based matrix [10]. Therefore, the accumulation of nanoparticles can speed up the pozzolanic reaction in a cement-based matrix. The higher surface area of nano-SiO_2 creates a more silica network, which can, successively, prolong pozzolanic reactivity and form a significant quantity of C-S-H [23]. The secondary reaction of nanoparticles produces a thicker C-S-H gel around the unreacted binder grain. It thus creates a denser matrix compared to the traditional concrete without any nanoparticles in it [24]. C-S-H gel is the main hydration product that connects all particles and considered the primary source of strength in cementitious materials.

Generally, the hydration of cement clinker develops ettringite, calcium hydroxide ($Ca(OH)_2$), and C-S-H gel, impacting the mortar's strength. Ettringite and $Ca(OH)_2$ exist in shapes similar to fibre, needle, and rod with the disorder. This hydration product may affect the brittleness of the mortar [25]. The hydration products that grow on the surface of unhydrated cement particles have different morphology and size than the hydration in the oxide of nanoparticles. After incorporating nanoparticles into the cement mix, the formation of ettringite crystals on the surface of both oxide particles and the unhydrated cement particles can be promoted. Ettringite can alter from thin needles into thicker rods and intersect to form a complex network. This phenomenon is known as the nuclei effect, which has shown that nanoparticles have controls over hydrates' development points and development patterns. With the provision of a nucleation site that contributes to hydrates' precipitation, the C-S-H gel may distribute more uniformly in the cement-fly ash matrix and restrain $Ca(OH)_2$ formation.

Consequently, the density and homogeneity of the cement matrix can be enhanced. On the other hand, nanoparticles can also fill and interlock the pores in the cement matrix, hence, lead to a decrease in porosities and bridge failure plane of cement and strengthen the microstructure of the composite. Therefore, nanoparticles can provide nucleation sites, which accelerate the precipitation of hydration products, make C-S-H disperse better, and limit the growth of $Ca(OH)_2$, thus improving the density and homogeneity of the cement matrix [26].

3. Materials and Methods

For the fabrication of mortar samples, sand, cement, fly ash (class F), water, different nanoparticles, and bentonite dosages were used. Ordinary Portland Cement (OPC) is replaced by 30% of fly ash in all mixes as it is known that fly ash is a by-product with a pozzolanic behaviour like cement. Therefore, adding this into the mix may give some environmental benefit. A scan electron microscopy (SEM) image of fly ash is shown in Figure 1, where large amounts of amorphous materials can be found. The chemical composition and physical properties of OPC and fly ash are shown in Table 1. Nano-Al_2O_3, nano-ZnO and bentonite are also replaced with cement weight at different percentages as part of the mortar's constituent and finalised the mix proportion. The nanomaterials and bentonite's physical properties in this study, as provided by the suppliers, are shown in Table 2.

The materials compositions of different mixes are also presented in Table 3. All the nanoparticles were purchased from the US Research Nanomaterials, Inc. A reference mix (without any nanoparticles) was also used as a reference mix. A total of ten mixes are prepared with a constant w/b of 0.485. Before choosing this w/b, various trial mix design tests were carried out with varying w/b ratios from 0.35 until 0.70. The most appropriate and optimum w/b was selected by comparing each sample's workability using the slump test and the compressive strengths obtained from them. Note that the nanoparticles were first sonicated in the water to facilitate dispersion before adding them into the dry powders.

3.1. Slump Test of Mortar

The early age properties of cementitious composites are often linked to rheological properties such as workability, yield stress, viscosity, etc. For determining the workability of mortar mixes, small slump cone tests were carried out for each mix compositions. In this research, the slump flow range of most mix compositions was between 150-200 mm. For nano-Al_2O_3 and bentonite mixes, the slump value was reduced as the dosage percentages were increased. However, for the nano-ZnO mix, there was no change in the slump noticed.

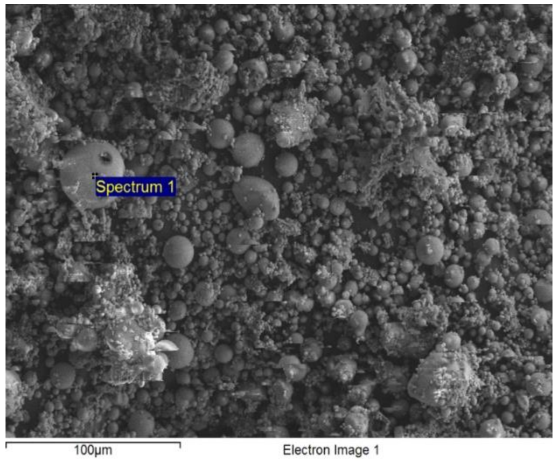

Fig. 1: Scan electron microscopy (SEM) images of fly ash.

Table 1: Chemical composition and physical properties of OPC and fly ash

Chemical Analysis	OPC	Fly ash
SiO_2	21.41	48.27
Al_2O_3	5.53	38.23
Fe_2O_3	2.66	4.58
CaO	64.16	2.84
MgO	1.33	2.92
SO_3	2.60	0.75
TiO_2	-	1.42
K_2O	-	0.21
Na_2O	-	1.16
LOI	-	5.38
Specific gravity (g/cm^3)	3.14	2.00
Specific surface area (cm^2/g)	3490	4350

Table 2: Physical properties of nanoparticles and bentonite

Nanoparticle	Average diameter (nm)	Surface-volume ratio (m^2/g)	True density (g/cm^3)	Purity (%)
Alumina oxide, Al_2O_3	50	35	3.95	99.0
Zinc oxide, ZnO	35-45	65	5.606	99.0
Bentonite	1000-5000	869	2.6	-

Table 3: Materials compositions of nanoparticles and bentonite mixes

Mix Id.	Compositions (kg/m^3)
Reference	Cement: 280, fly-ash: 120, sand: 1000, water: 194
nano- Al_2O_3	1%, 2% and 3% cement from the reference mix is replaced by nano- Al_2O_3. Other compositions remained the same.
nano- ZnO and Bentonite	2%, 4% and 6% cement from the reference mix is replaced by nano- ZnO and bentonite. Other compositions remained the same.

3.2. Sample Preparation for Mechanical Properties and Microstructure Analysis

The mechanical properties of hardened mortar samples were examined using the compressive strength test. 50×50×50 50×50×50 mm cubic specimens according to the ASTM C109 [27] were used in this study. Three samples are tested for each each mix at each testing age of 3, 7 and 28 days to monitor strength evolution. After casting in the moulds, all the samples, samples, except for nano-ZnO, were left at the ambient temperature for 24 hrs. After that period, samples were removed from the moulds and water cured (temperature 21 ± 2ºC and humidity 55 ± 5%) until testing. In the case of ZnO samples, demoulding was done after 96 hrs; the reasons for this is discussed in the result section.

Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray analyser (EDX) tests were conducted to study the mortars' microstructure and hydration products. The specimens were first coated with a platinum layer by applying a sputtering current of 30 mA and sputter time of 40 seconds via Quorum Q150R S machine. The SEM test was conducted using a Field-emission scanning electron microscope (FE-SEM, Hitachi SU8010). EDX test was conducted using X-max Horiba to contribute to elemental analysis of the specimens.

4. Results and Discussion

4.1. Mechanical Properties of the Hardened Mortar Sample

From the compressive test results obtained in Figure 2, it is apparent that the incorporation of nano-Al_2O_3 in fly ash-based cement mortar enhances the compressive strength when compared with the reference mortar. At 28 days, mortar samples with 1%, 2% and 3% nano-Al_2O_3 showed 90%, 49% and 70% higher strength than the control sample, respectively. This is because ultra-fine particles (size: max 30 nm, i.e., higher surface area) of nanoparticles contribute to increased hydration reaction and pozzolanic reactivity, which leads to the formation of more C-S-H gel in the paste. Hence, the nucleation effect of nanoparticles and space-filling (i.e., less void and lower porosity) increased paste samples' strength.

The cementing property, which is mainly produced from the C-S-H gel, binds the particles together by filling the spaces between the particles in the matrix. The pores in the matrix system are also filled up through pozzolanic reaction by consuming $Ca(OH)_2$, which changed to an additional C-S-H and densified the matrix's microstructure. In nano-Al_2O_3, maximum compressive strength is achieved at 1% dosages wherein bentonite (see Figure 3), except for longer curing age (28 days) strength decreases for all the dosages when compared with reference mortar.

For bentonite samples, maximum strength was observed for 4% dosages of bentonite (50% higher than the control sample). Strength was gradually decreased for higher dosages (6%) of bentonite mortar samples. The reduction of strength at higher dosages of nano-Al_2O_3 and bentonite can be attributed to the mixes' lower slump value. At a lower slump, the sample could suffer self-desiccation and internal cracking, which lead to lower strength. However, since the particle size of nano-Al_2O_3 is finer compared to bentonite particles, nano-Al_2O_3 particles can fill smaller pores present in the mixture of cement mortar resulting in more gaps being closed. Hence, the higher compressive strengths in nano-Al_2O_3 samples compared to that of the bentonite samples.

The compressive strength with a coefficient of variation (CoV) of different nano-ZnO samples dosages is also reported in Table 4. For all dosages, a significant reduction in the compressive strength of the nano-ZnO samples is found. The addition of nano-ZnO adversely affected the hydration behaviour of fly ash-based cement mixes. As discussed in Section 3.2, the setting time of nano-ZnO samples was much longer than others, and thus, the samples were demoulded after 96 hrs of casting. Even after this period, most of the samples were soft and thus kept in the laboratory's ambient temperature for one more day before they were placed in the water tank. While testing for compression, it was visually observed that most of the samples were crushed due to the composite's settlement, which means there was not enough bonding between the particles in the mix. It depicts that nano-ZnO is detrimental to the hydration of the cement particles.

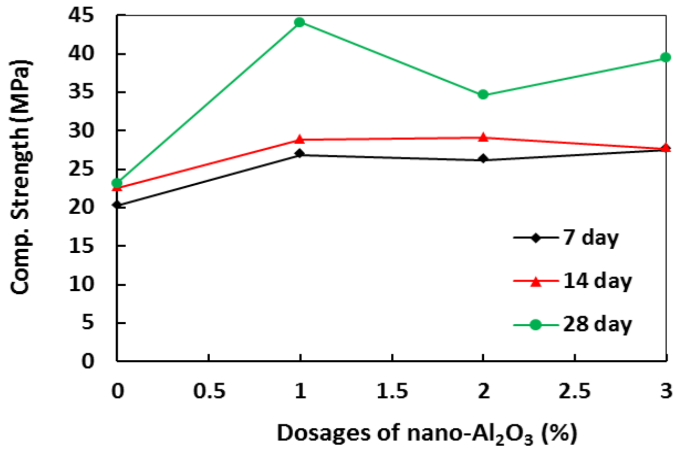

Fig. 2: Compressive strength development at different dosages of nano-Al_2O_3.

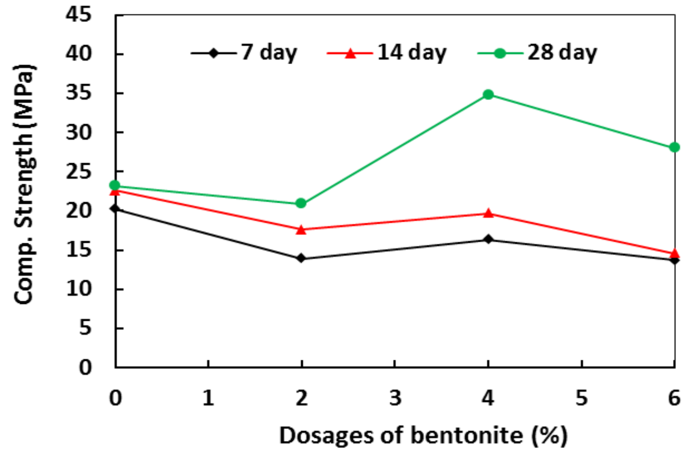

Fig. 3: Compressive strength development at different dosages of bentonite.

Table 4: Compressive strength (f'_c) and coefficient of variation (CoV) in different dosages of nano-ZnO mortar samples tested at different days

Mix type	7 day		14 day		28 day	
	f'_c (MPa)	CoV (%)	f'_c (MPa)	CoV (%)	f'_c (MPa)	CoV (%)
ZnO 0%	20.26	12.7	22.57	3.5	23.2	8.9
ZnO 2%	0.32	0.72	0.41	3.48	14.85	20.08
ZnO 4%	0.33	6.58	0.44	1.32	0.58	21.53
ZnO 6%	0.4	3.64	0.52	6.93	0.79	11.01

From the results shown in Table 4, it is evident that the addition of the proper type of nanoparticle, such as nano-Al_2O_3, can accelerate the hydration and pozzolanic activity of the fly-ash based cement mortar. Hence, integrating nanoparticles into the blended fly-ash based cement mortar can mitigate the slow hydration rate of fly-ash. However, when the optimum dosage is exceeded, the compressive strength of the mortar decreases. This can be explained by the flocculation effect, where fine particles are agglomerated to form a floc. Such tendency to agglomeration is due to their strong inter-particle force attraction, which may prevent the efficient utilisation of the nanoparticle's high surface to volume ratio. At the same time, it may lead to the formation of weak zones in the mortar specimens. Thus, the mechanical strength of the mortar specimens decreases. Also, poor selection of nanoparticles like nano-ZnO can adversely affect the strength of cement-based materials. More research in this direction with an extended curing age is recommended for a definite conclusion.

4.2. Microstructure Analysis of Different Mortar Samples

The microstructural analysis was performed only for the control and bentonite mortar samples through SEM images. From the SEM images, reacted fly ash molecules, ettringite, $Ca(OH)_2$ molecules, and C-H-S molecules were observed in Figure 4. All these samples were collected after 28 days of curing age. From Figure 4a, needle-like ettringite and hexagonal flake of large $Ca(OH)_2$ crystals, as well as micropores, can be seen in the composite. The morphology of the C-S-H gel that appeared in colloidal form seemed to be fibrous and less dense. However, the SEM images for 4% of bentonite, as shown in Figure 4b, indicate that the specimen's microstructure with 4% bentonite appeared to be more compact and denser than the control specimens. For higher dosages of bentonite, the mortar's microstructure can be negatively affected according to agglomeration level. When an excess amount of microparticles are incorporated, there will be under-development of $Ca(OH)_2$ crystals due to lack of space in the matrix. This may lead to higher shrinkage and creep in the matrix, thus, increasing the porosity [11, 28]. Also, microparticles can densify the binding paste matrix and enhance the interfacial transition zone (ITZ), the region between the binding paste and aggregates. The reaction between the microparticles and $Ca(OH)_2$ crystals may produce more C-S-H gel and fill up the pores and enhance the ITZ [24].

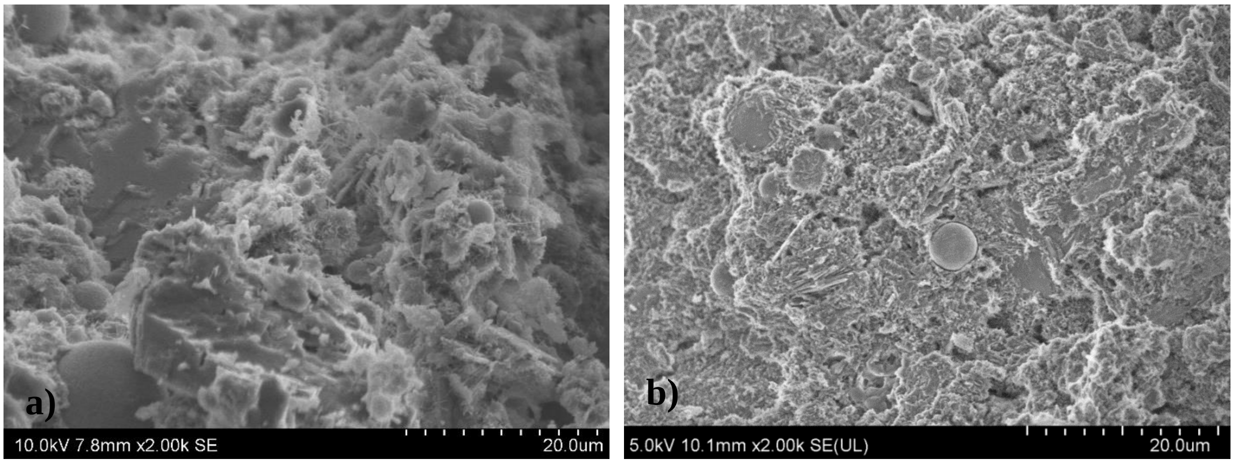

Fig. 4: SEM images of a) control and b) 4% bentonite samples.

The chemical element compositions, especially the Ca/Si ratio for the samples, were calculated using the EDX analysis data shown in Figure 5 for the bentonite sample. The Ca/Si ratio values obtained for the control sample, and 4% bentonite samples were 0.80 and 0.76. The Ca to Si ratio can vary, but the ratio is approximately 0.60 for mortar with fly ash and nanoparticles [29]. Generally, for a lower Ca/Si ratio, the compressive strength of that particular sample increases. Furthermore, the molar volumes of the C-S-H phases decrease with decreasing Ca/Si ratio, along with the high surface area present in nanoparticles results in enhanced compressive strengths [30].

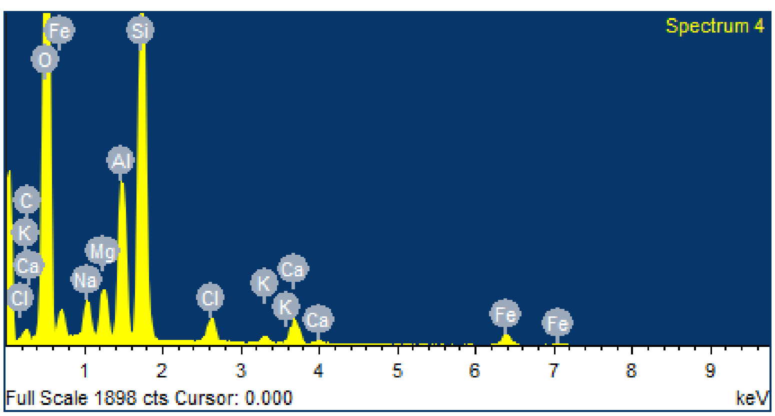

Fig. 5: Chemical element compositions of the specimens examined by EDX for bentonite sample after 28 days of curing.

5. Conclusion

A comparative study on the different dosages of nano-Al_2O_3, nano-ZnO and bentonite, including their effect on slump flow, compressive strength, and microstructure, is investigated. Based on the experimental observations, the following conclusions may be drawn:

- The slump flow of fly-ash-based cement mortar with nano-Al_2O_3 and bentonite shows that increasing these particles' dosages reduces the slump flow. For the addition of 6% of bentonite, the mixes contributed about 25% higher slump value than the control mix. Conversely, for different dosages of nano-ZnO, there was no noticeable difference in the slump value. However, the addition of nano-ZnO significantly increased the setting time of the mixes.
- Compressive strengths of the mortar samples made with nano-Al_2O_3 increased proportionally up to an optimum dosage of 1%. Beyond this dosage, a reduction in strength is noticed. For all dosages, the compressive strength of nano-ZnO samples reduced significantly. This is because nano-ZnO works against the binder's hydration reaction, and thus the binder particles remain unhydrated.
- In the case of bentonite samples, strength development was lower for shorter curing age. However, it increased as the curing period increased (28 days), and the optimum dosages of bentonite was 4%.
- The reduced strength beyond the optimum dosages of nano and microparticles may be explained by the flocculation effect that leads to weak zones in the mortar samples. Thus, the potential of nano and microparticles may not be utilised completely.
- A denser microstructure was also observed for the 4% bentonite sample. The Ca/Si ratio of this sample was also lower than the control sample.

In summary, there are four mechanisms involved in enhancing the strengths and the microstructure of the mortar, which are (i) filling up the micron pores, (ii) provide additional nucleation site, (iii) producing more C-S-H gel, (iv) controlled crystallisation process of ($Ca(OH)_2$). Nanoparticles have proved to have the capability to accelerate the hydration process with different proportions of binders. Hence, cementitious composites with the incorporation of nanoparticles can enhance the mechanical properties and the microstructure of the mortar. However, each nanoparticle exhibits different physical and chemical properties, leading to different reactivity with the mortar's binders. Hence, the optimum dosages of nanoparticles that are incorporated need to be determined to prevent any wastage of the materials and maximise the cost efficiency of the nanoparticles.

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