Open access • Journal Article • DOI:10.1061/(ASCE)MT.1943-5533.0003196

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Published on: 01 Jun 2020 - Journal of Materials in Civil Engineering (American Society of Civil Engineers)

Topics: Energy consumption, Zinc and Cement

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Abstract

The present study investigates the possibility of introducing zinc oxide nanoparticles into the cement raw mix so as to reduce the energy consumption and CO_2 emissions during processing. Zinc oxide nanoparticles are prepared via hydrothermal growth method using zinc acetate dihydrate and sodium hydroxide, as precursors. The percentages of zinc oxide nanopowder added to the cement raw material was varied between 1 - 3%. The resulted clinker and cement samples were characterized using X-ray fluorescence (XRF), X-ray diffraction (XRD), Scanning electron microscopy (SEM), Energy dispersive X-ray spectrometer (EDS) and compressive strength test. It is concluded that the addition of 1% synthesized zinc oxide nanopowder, into Portland cement production, improves the burnability of the cement raw mixture. A reduction of clinker temperature up to 1300°C, instead of 1450 -1500°C usually required, was achieved, thereby enabling a reduction in both energy consumption and greenhouse gas emissions.. The 28 days strength is within the target design compressive strength of 42.5 N/mm^2.

Keywords

Zinc Oxide nanoparticles, mineralizer, clinkerization process, compressive strength.

1. Introduction

Cement is produced in large, capital intensive production plants generally located near limestone quarries or other raw carbonate mineral sources as these sources are the principal raw materials used in the cement production process. Despite the popularity and profitability of cement manufacturing, the cement industry faces many challenges due to environmental concerns and sustainability issues. It is fundamentally an energy intensive operation and not at all environmentally friendly by nature.

Furthermore, it consumes large amounts of non-renewable raw materials that 1.7 tones raw materials is needed to produce 1 ton clinker (Tavakoli and Heidari 2013) and generates substantial amounts of carbon dioxide. Approximately 850 kg of CO_2 is emitted per ton of clinker produced (Shivaram 2014) and environmental particulate matter in the process. It is estimated that 5-8% of all carbon dioxide greenhouse gases generated by human activities originates from cement production (Potgieter 2012, Scrivener 2014, Olivier et al. 2015). Carbon dioxide is predominant among the greenhouse gases (GHG) emitted as a by-product of clinker production, an intermediate product in cement manufacture, in which calcium carbonate ($CaCO_3$) is calcinated and converted to lime (CaO). CO_2 is also emitted during cement production by fossil fuel combustion (Hu and Kavan 2014, Habert 2010). Approximately 60% of the CO_2 emissions originate from the calcination process, with the remaining CO_2 emissions being linked to fuel combustion (Karstensen 2008, Rootzen 2015).

Cement industry is one of a chemical industries of a highly energy intensive production process together with steel, paper and petrochemical industries. The percentage of energy cost in Portland cement production cost is 20 to 30% (The Energy Conservation Center 1994). If the energy cost is reduced, the manufacturing cost is lowered. A large proportion of the energy consumed by the cement industry is in the process and more especially to fire kilns to produce clinker. The kiln process consumes more than 90 percent of the cement manufacturing energy. The remaining 10 percent is consumed in almost equal amounts by activities related to fuel and raw materials preparation, grinding of clinker and the blending of materials to prepare the finished cement product (5.4% Finishing, Grinding-1.9% Raw materials Grinding) (Natural Resources Canada 2009). The need for breakthrough energy solutions for cement manufacturing is very important. Efforts are urgently needed to produce energy technological options through manufacturing process that can allow both climate stabilization, economic development in the industry and sustainability on the other hand.

Nanotechnology is an emerging technology that has significantly potential to achieve these needs and contribute to sustainable cement and concrete industry. The application of nanotechnology became a key topic in the field of cement and concrete in the last decade, and consequently the nanoparticle technology started to play an important role as well due to their reduced dimension and increased surface area, these materials possess new physical and chemical properties distinctively different from their bulk counterparts. For example, crystals in the nanometer scale have a lower melting point compared to the bulk crystals, due to the large fraction of the surface atoms or ions which plays a significant role in the thermal stability.

Most of the application of nano particles in cement industry is related to their addition into the cement based materials like concrete, mortar, fiber reinforcement and others building materials used as an admixture. Several nano-particles have been used as an admixture or as filler material (Rahhal 2012), which can decrease the voids and permeability of mortar in cement based materials and tested in order to improve their performance and durability leading to an eco-efficiency use for this binder (Nivethitha1 2016). The use of those nanoparticles are considered one of the pathways of decreasing the cement content in concrete by the partial substitution of cement and so reduce the environmental footprint of cement based materials (PuthurJayapalanc 2013). Recently many oxide nanoparticles like nano-SiO_2, nano-TiO_2 (PuthurJayapalanc 2013), nano-Fe_2O_3, nano-Al_2O_3 (Nivethitha 2016a,b), nano-$CaCO_3$ (Ge et al. 2014), nano-ZnO_2 (Nazari and Riahi 2011a,b), nano-cement particles of C_3S (Alite) and C_2S (Belite) (Jo et al. 2014), nano-clays (Patel 2012) and Carbon Nanotubes have been tested (Mendes et al. 2015).

2. Mineralizers in clinker production

In cement manufacturing, appropriate proportions of raw materials containing calcium, silica, alumina, and iron are fused together at approximately 1500°C to form a product known as clinker (EPA 2007). The theoretical heat requirement for clinker making, the main substance of cement, is calculated to be about 1.75 ± 0.1 MJ per kg (Taylor 1997). The actual heat requirement is higher, and depends on the type of process applied (wet or dry process).Many solutions have been proposed to address the cement production drawbacks. Among them, the use of mineralizers has proven to be a very good option in this regard, but it is not yet fully understood (Tobón et al. 2016). So the use of mineralizers in the cement industry is widely known. The incorporation of compounds other than those usual in low proportions improves the clinkering conditions as well as decreases the maximum clinkering temperature or improves the phase formation in the clinker without affecting the final properties of the product (LuizaGrilloRenóa et al. 2012).

Mineralizers can be defined as substances which promote the formation of clinker compounds without participating in the formation reactions, and can generally lower the temperature at which the clinker melt begins to form (Worrell and Kermeli 2013). Clinker liquid phase or clinker melt is the fraction of the kiln feed that melts between the upper transition and the burning zone. The liquid has a critical role in clinker nodulization and clinker mineral development and properties. In the absence of liquid, the conversion of C_2S and free lime to C_3S would be almost impossible in the kiln. The properties of the melt are indeed important for the formation and crystal growth of C_3S. The formation of the liquid phase produces an important shrinkage and micro-structural changes. The formation of liquid marking the beginning of the sintering occurs between 1260 and 1310°C. At temperatures near 1450°C, the liquid phase is about 20±30 % by weight, depending on the material composition (less when the silica content is higher). At the beginning of the clinkering process, non-combined CaO reacts with belite (C_2S) through liquid phase to form the alite (C_3S) phase by intermediate compounds, which is the main objective. Concerning the reactions produced through the liquid, the diffusion mechanisms between CaO and C_2S in the melt and the extension of the liquid phase are of great importance. The reactions may be accelerated as the amount of liquid phase increases and its viscosity decreases. Components such as Al_2O_3 and Fe_2O_3 are in liquid phase at about 1400°C, while C_2S and C_3S phases are solid at this stage. The addition of different enhancers or mineralizers has an important influence on the sintering behavior of clinker.

This paper aims to develop and suggest ways lower in cost and more effective to reduce energy consumption in the process, and enhance the Portland cement properties through adoption of minerlizer and by exploiting the properties of nanomaterials. New higher performance materials such as zinc oxide nanoparticles which can result in significantly improved properties and also expected to have an effect in the kinetic chemical reaction inside the cement kilns.

Zinc oxide nanoparticles is one of transition metal oxide that has attracted much attention, providing the advantages of controlled shape, size, crystallinity and functionality, as well as being ecologically benign, corrosion resistance, easily scalable and relatively cost effective (Jana et al. 2017). Among a variety of nanoparticles, zinc oxide nanoparticles (ZnO) have advantages because of the extraordinary physical and chemical properties (Haq et al. 2017). The applications of zinc oxide powder are numerous. Most applications exploit the reactivity of the oxide as a precursor to other zinc compounds. For material science applications, zinc oxide has high refractive index, high thermal conductivity, binding, antibacterial and UV-protection properties. Consequently, it is added into materials and products including plastics, ceramics, glass, cement, rubber, lubricants, paints, ointments, adhesive, sealants, pigments, foods, batteries, ferrites, fire retardants.

2.1. Zinc oxide as mineralizers in cement industry

Zinc can be brought to cement kilns through lime (22–24 ppm of zinc), clay (59–115 ppm of zinc) and fuels (16–200 ppm of zinc). Incineration of oil, which can contain up to 3000 ppm of zinc, and tires, which can contain 10,000 ppm of zinc can introduce the zinc into the cement kiln (Barros et al. 2004). ZnO reduces the temperature of the liquid phase formation by about 50–100°C, which helps the clinkering reaction kinetic (Taylor 1997, Barros et al. 2004).

Trezzaa and NéstorScianb (2009) studied the effect of adding different levels of scrap tire ashes, which mainly contain ZnO and other materials by partially replacing traditional fuel in cement kilns. They found that the substances introduced by the added tire ashes during clinkering introduced substances that produce modifications in the microstructure as shift and inversion of relative intensities of main peaks of silicates.

Zhongyuan et al. (2007) studied the effect of grain size of $CaCO_3$ and SiO_2 on the formation of C_3S under various conditions. When the grain size of $CaCO_3$ and SiO_2 is below 1 μm, the rate of the formation of C_3S is greatly raised. A rapid sintering rate and the presence of ZnO have an important effect on the formation of C_3S and can lower the temperature of the formation of C_3S by about 50 ℃.

Kolovos et al. (2005) studied the effect of 1.0 wt.% of chemical grade CuO and ZnO when added in cement raw mix. They found that the added oxides promote the sintering reactions and improve the burnability of the mixture without altering the mineral composition of the clinker and they decreases the melt temperature by at least 50°C however they affect the size and shape of alite and belite grains. Also they favor the cement strength development and do not affect the physical properties of the cements.

3. Materials and Methods

3.1 Materials

3.1.1 Zinc Oxide nanoparticles

Zinc oxide nanoparticles were synthesized via low temperature hydrothermal growth using zinc acetate dihydrate and sodium hydroxide as precursors (Osman et al. 2015). The average crystallite sizes were estimated to be about 54 nm according to the Debye-Scherrer formula (Zheng 2009). The predominate particle morphologies were nanotubes, spherical and Nanorods as shown in Figure1.

Figure .1: Characterization of ZnO nanopowder (a) XRD pattern (b) SEM image

3.1.2Raw meal (raw mix) for clinker Production

An industrial "ready to use" raw meal from a cement plant was used for the clinker formation. Detailed raw meal properties, i.e. the chemical composition, the resulting Lime saturation factor (LSF), Silica module (MS), Alumina module (MA) were determined through chemical analyses by XRF (Table 1).

Table.1: Chemical composition of raw meal by XRF

3.2 Methods

3.2.1 Production of clinker in laboratory muffle furnace

Different amounts of zinc oxide nanoparticles (1, 2, and 3 % w/w) were added to 25 g of raw meal. The mixture was well mixed and placed into a clean platinum crucible. Inside the crucible the mixture was divided into parts through longitudinal and horizontal lines using a glass rod (Figure 2) and placed in a muffle furnace.

Figure .2: Raw meal preparation for lab clinker production

The mixture was heated at temperature of 500°C for 2 minutes and subsequently raised to 900°C. As the furnace temperature reached 900°C, it was raised again to the targeted clinkerization temperature of 1200°C, 1250°C and 1300°C. The mixture was left at those temperatures for 2 hours as a soaking time. After the soaking period, the material was removed from the furnace and cooled rapidly under a high cold speed air using an electrical fan for one and a half minutes. The resulted clinker samples are shown in Figure 3.

Figure.3: Produced laboratory clinker samples

The different clinker samples were milled at equal times and equal quantities. The effect of the added oxides on burnability of the industrial raw mix was evaluated on the basis of the unreacted lime after sintering (free lime test) and chemical composition (XRF analyses). The clinker samples (Table 2) were grounded and mixed with 5% gypsum to produce the final cement product. The fineness of the final cement product or modified cement was determined by the determination of specific surface (total surface area of all the particles in one gram of cement) using air-permeability apparatus. It was found that the fineness of modified cement was 305m^2/kg. The clinker and the final cement product - modified cement -were analyzed and characterized through number of tests to ensure that the clinker and the modified cement is of the desired quality and that it conforms to the requirements of international standards

Table 2: Chemical composition of Zinc oxide nanoparticles and temperature of produced clinker samples

3.2.2 Characterization techniques

The resulted clinker and cement samples were subjected to different analytical procedures for their characterization. The chemical analysis was carried out using wavelength dispersive X-ray fluorescence (XRF) spectrometry (Axios, PANalytical, Netherlands). X-ray diffraction analysis of the ZnO nanopowder, clinker and cement samples was carried out by use of a Phillips (X'Pert Pro software) powder diffractometer operating with Cu-Ka radiation in order to identify the compounds formed during clinkerization. Scanning electron microscopy (SEM) data was collected using Zeiss EVO/lS10 SEM with W electron source. Analysis was initially performed on cement samples, using an acceleration voltage of 18KV and 3KV. Energy dispersive X-ray spectrometer (EDX) analysis was performed using Inca x-stream and mics software from Oxford Instruments Company to determine the chemical composition of the cement samples.

4. Results and Discussions

4.1 Chemical compositions of laboratory clinker production by XRF

Chemical analysis plays an important part in the categorization of cements and other construction materials. The clinker samples were subjected to different analytical procedures for their characterization using XRF and free lime test to study the effect of adding ZnO nanoparticles into the raw mix on reducing production temperature of clinker. The chemical composition of clinker mineralized by different level of ZnO nanoparticles (1, 2 and 3% w/w) and firing at 1200°C, 1250°C and 1300°C are illustrated in Figure 4.

Figure 4: Chemical composition of Portland clinker mineralized by ZnO nanoparticles at various temperatures

The main oxides of Portland cement are CaO, SiO_2, Al_2O_3, and Fe_2O_3 were determined which are responsible for the composition of the main mineral phases, such as Alite, Belite, Aluminate and Ferrite phase. Minor components such as MgO, SO_3, and alkalis also were also determined which have an influence on the hydration process of the cement. The chemical composition and free lime investigations represent the initial criterions of methods if judging the quality of resulted cement clinker. Based on these criterions it is found that sample G (1%ZnO nanopowder) from Figure 5 meets the requirements of ASTM and BS standard specification for clinker production.

Figure 5: Chemical composition of Portland clinker mineralized by ZnO nanoparticles (sample G) compared with standard specification

4.2. Composition of Clinker

4.2.1 Lime Saturation Factor (LSF)

The LSF is very important in the technology of Portland cement. It represents the ratio of CaO to the other three main oxides.

Figure 6: Mineral wt % vs. Lime saturation factor (LSF)

It is observed from Figure 6 that C_3S increased with increasing the LSF. The LSF is increased with the increase of addition ratio of zinc oxide nanoparticles and sintering temperature till it reached 1300°C with addition ratio of 1% then it began to decrease. For technical purposes good values of LSF ranged between 92-96 so sample G (modified clinker) have a good values of LSF which are 92.01. C_2S is decreased with increasing the LSF whereas. C_3A and C_4AF do not show a clear relation to LSF.

Silica Ratio (SR)

A high silica ratio means that more calcium silicates are present in the clinker and less aluminate and ferrite. SR is typically between 2.0 and 3.0.but the preferable range is 2.3-2.7. It was realized that the SR is decreased with the increase of addition ratio of zinc oxide nanoparticle and sintering temperature. All samples confirm with the standard specifications.

Alumina Ratio (AR)

The alumina ratio determines the potential relative proportions of aluminate and ferrite phases in the clinker. An increase in clinker AR (also sometimes written as A/F) means there will be proportionally more aluminate and less ferrite in the clinker. In ordinary Portland cement clinker, the AR is usually between 1 and 4, the preferable range is 1.3-1.6. The values of AR of all samples are within those limits.

4.2.2 Minerals content in Portland cement clinker: the Bogue calculation

The chemistry of clinker formation could be explained in accordance with the formation of main clinker minerals as a result of clinkering step**.** Bogue phase calculation is an extremely useful and widely-used calculation in the cement industry. It is based on chemical analysis and the assumption that the system has reached equilibrium at high temperatures. Despite the large variety of phases in clinker only four of them are, in common practice such as tricalcium silicate or C_3S, dicalcium silicate, C_2S, tetracalcium aluminate ferrite, C_4AF and tricalcium aluminate, C_3A. They are determined using Bogue equations. Figure 7 shows the main four mineral contents of clinker samples at different sintering temperatures compared with standard specifications. It was observed that the mineral content of sample G, at 1300°C at the lowest percentage addition of ZnO nanoparticles, as shown in Figure 7 meets the standard specification requirements.

Figure .7: Mineral content of clinker samples (A - I) mineralized with ZnO nanoparticles compared with standard specifications

4.2.3 Investigation of free lime content in clinker

The free lime content (f-CaO) in the clinkers is an indicator of the burnability of the original raw mixes. It gives a clear measure of the chemical reactions progress inside the rotary kiln. It is also an important parameter to evaluate the quality of cement clinker. Figure 8 shows that the free lime content (w%) of sintering clinker at 1200, 1250 and 1300°C decreases as ZnO nanoparticles content in the raw mix and sintering temperature increase. According to Taylor et al. (1997), Aluminates and Ferrites begin to melt and free lime combined with the free silica and Belite (C_2S) to form Alite (C_3S) above 1300°C during clinkerization process. But in case of introducing 1% w/w of ZnO nanoparticles into the raw mix this stage occurred earlier in temperature less than 1300°C which could be clearly predicted by the free lime and C_3S content specifically of sample G which does not differ much from the reference clinker produced at 1450°C in terms of its chemical specification, i.e. mineral content and free calcium oxide.

Figure .8: Effect of ZnO nanoparticles (1-3 %) on the free lime content of cement clinker at various temperatures (°C)

4.3 XRD analysis of reference and modified clinker

4.3.1 XRD patterns of samples

The microstructure of a material is one of the main links between the process and its final properties. Cement or clinker consists of a number of different phases so as to achieve specific properties such as reactivity, strength and setting time. An accurate XRD analysis was conducted to investigate the effect of introducing zinc oxide nanoparticles, as minerlizer and accelerator, on the cement**.** Figure 9 shows the XRD patterns of the reference Portland cement produced at 1450°C, modified Portland cement produced at 1300°C and the two patterns together, respectively.

Figure .9: XRD pattern of (a) Reference cement (b) Modified cement (c) both cements

Both clinker samples contain alite, belite, aluminate and ferrite as major mineral phases. The modified Portland cement produced at 1300°C pattern proved that dominant phases are well crystallized, giving peaks at the expected 2θ values as compared with the reference Portland cement. It is also observed from the two patterns that the Belite peaks are almost overlapped by those of alite. It can be noticed that the intensity of calcium sulfate dihydrate peaks in modified cement is higher than that of the corresponding peak in the reference and this due to the difference in the proportion of adding calcium sulfate (gypsum) to the clinker, which represent 5% of the cement in the case of modified cement.

4.3.2 Phase identification analyses

A standard database (ICDD database) for X-ray powder diffraction pattern enables phase identification for all of crystalline phases present in both samples. The main four phases commonly present in ordinary Portland cement and clinker are identified by X-ray Diffraction for both samples the reference and modified (Figure 10).

Figure .10: Phase identification in XRD pattern

The Quantitative analysis of these phases in this study was obtained based only on Bogue calculation instead of X-ray Diffraction methods due to a heavily overlapped peaks and different phase polymorphs. Table.3 shows the main mineral content in reference and modified cement clinker

Table.3 Main phases present in ordinary Portland cement and clinker

The crystallographic data for crystalline phases present in reference and modified cement clinkers show that C_3S exists in its common polymorph forms (Monoclinic) in both samples. C_2S exists in the more reactive form, beta C_2S, in addition to, $\alpha^{\backslash}$ C_2S (bredigite) form which is existed in the modified cement. Moreover, some trace phases are present such as lime**.**

Minor phase is detected in the modified cement clinker named as calcium zinc aluminum silicate. This phase is Alite of tetragonal modifications of impure Tricalcium silicate which is generally termed C_3S Substitution of magnesium and aluminum for silicon causes triclinic pseudotrigonal forms to change to monoclinic pseudotrigonal forms; other substitutions may involve iron and sodium (Hashim et al. 2008). Alite may include up to approximately 4 percent impurity (Hashim et al. 2008). Thus the zinc ions of zinc oxide nanoparticles is incorporated into alite phase. The density of this phase is 3.19 g/cm^3 and it is within density range of alite (3.13 to 3.22 g/cm^3).

4.4 Scanning Electron Microscopy (SEM) Analysis

SEM and Energy dispersive X-ray spectroscopy (EDX) provides a lot of information about the surface of the samples which is particularly of interest as it is the surface of the cement that is generally the first place at which any reactions will occur.

4.4.1 Ordinary Portland Cement clinker (reference and modified)

SEM studies were conducted in order to examine the structure and the distribution of the foreign elements in its main phases of the clinkers (reference without addition of zinc oxide nano powder to the raw meal) and the resulted clinker from clinkerization process modification (Figure 11). The obtained SEM – micrographs show Alite with well-developed external shape and hexagonal outline and it is larger than the other existing phase in both samples Figure (11-c) and (11-d). Alite minerals represent a major content required in the Portland cement because it contributes to instant hydration and is responsible to early stage of concrete hardening. Figure (11-d) shows that Alite mineral phase was completely formed at clinkering temperature of 1300°C, despite the temperature that is required for the production of cement is 1450°C in order to achieve suitable condition for formation of $Ca_3.SiO_5$ or known as Alite. The size of the majority phase Alite crystals in modified clinker varies, being much smaller (5-20 μm). The more rounded and irregular outline, crystals are Belite. Very few Belite clusters are observed in modified clinker than in the reference clinker. Pore structure is a very important microstructure feature in porous solid because it affects physical, mechanical and durability properties of the material. From the SEM image of clinker it is observed that modified cement has large pore relative to reference cement.

Figure 11: SEM micrographs of Reference Portland clinker and Modified Portland clinker

4.4.2 Ordinary Portland Cement (reference and modified)

Figure12 (a-d) represent the scanning electron micrographs of the reference Portland cement (produced at 1450°C) and modified Portland cement (produced at 1300°C), respectively. From Figure 11, it is clearly visual that the surfaces of reference cement were rough and the shapes of particle were found to be angular with non-uniformed shapes and wide range of particles size distribution, whilst the surfaces of modified cement were slightly soft to some extent. The shapes of particle were found with more-uniformed shapes and narrow particles size distribution, which provides a large surface area and thus higher activity due to more atoms at the surface.

Figure 12:SEM micrographs of the **(a)** Reference Portland cement(produced at 1450°C) mag 365X and **(b)**Modified Portland cement(produced at 1300°C) mag365X**(c)**Reference Portland cement (produced at 1450°C) mag1.17X**(d)**Modified Portland cement(produced at 1300°C) mag1.17X

4.5 Energy dispersive X-ray spectroscopy (EDX) Analysis

EDX was also performed to clarify the chemical constituents present in the modified Portland cement. Figure 13(a) and (b) show the elemental composition of reference and modified Portland cement respectively in a typical representative EDS spectrum. All the peaks are identified as calcium, oxygen, silicon, aluminum, iron, magnesium from which the cement phases are usually composed.

Figure 13: EDX spectra of (a) Reference (b) Modified ordinary Portland cement

Both spectra of the Reference and Modified OPC contain similar elements, but in slightly different proportions as it is seen in Table 4. There are also significant calcium peaks at about 3.7 keV, and other elements such as gold, as a result of gold coating process. Very small peaks of zinc are observed at 1keV and 8.4keV in the modified cement. The presence of zinc element in modified cement particles is attributed to the modified raw mix with 1% w/w zinc oxide nanoparticles burned at 1300°C.

Table4: Elemental composition for reference and modified Portland Cement

Figure 14 shows a semi-quantitative analysis of the elements present at each of the two selected points. EDS confirms the existence of the basic elements that constitute the main phases, which are mainly responsible for the properties of cement it also provides further evidence about the mineral phase, calcium zinc aluminum silicate which is identified by the X - ray diffraction.

Figure 14: Quantitative results of samples elements

4.6 Loss on ignition test results

A high loss on ignition LOI indicates pre-hydration and carbonation, which may be caused by improper and prolonged storage or adulteration of OPC during transport or transfer. The modified cement samples are found to be competent with regard to maximum LOI limit of less than 5.0 % as specified by EN-196-2.

4.7 Cement Insoluble residue test results

Insoluble residue represents that fraction of cement which is insoluble in hydrochloric acids. Almost all of the clayey compounds present in the raw mixture of Portland cement are insoluble in acids. After burning to clinker, all the minerals present become soluble in acids. For this reason, the amount of insoluble residue in given cement can serve as an indication of the completeness of the clinkering reactions which have occurred in the kiln, it is found that the insoluble residue of modified cement produced at 1300°C is 0.23 % and of reference cement produced at 1450°C is 0.34 %.

4.8 Compressive strength development test results

Compressive strength tests were performed according to the standard test method where 450g of cement is required for three test specimens. Six cubes were prepared with two cubes each for days 2, 7 and 28. The specimen's dimensions were 40 mm x 40 mm in cross section and 160 mm length. The average compressive strength of the reference and modified cement samples after 2, 7 and 28 days are shown in Figure 15.

Figure 15: (a) Strength development of the tested cements (b) Cubes submerged in clean fresh water

The early ages strength at 2 days for modified cement exceed the specified limits of 10 N/mm^2,but there is no strengths progress after 2 days and this may be due to the amount of gypsum added, which represents about 5% for the modified cement and 3% for the reference cement. The addition ratio of gypsum to the clinker is considered one of the main factors affecting the early stage compressive strength whereas a much faster strength development is attained after 7 days. The 28 days strength is strongly affected by the distribution of the cement particles size (Svinning 2011, Radwan 2012). From the figure it is realized that the modified ordinary Portland cement is within the target design compressive strength of 42.5 N/mm^2.

4.9 Energy saving in cement production results

Thermal energy costs in the cement industry represent a considerable proportion of the total production cost (approximately 30% of the total production cost). On the other hand, for the burning of the clinker kiln plant, thermal energy represents 92-96% of the required energy and the electrical energy accounts for only 4-8%. Therefore, various efforts have been made towards lowering thermal energy consumption in producing cement. It is found that the introduction of 1% of zinc oxide nanoparticle into cement raw mix reduce the clinkerization temperature by about 150°C (the Ordinary Portland cement produced at 1300°C instead of 1450°C) and this leads to saving thermal energy about 221 kJ/kg clinker. This means the thermal energy required to produce 1kg of clinker is reduced to 1467 kJ/kg instead of 1688 kJ/kg. In addition to other environmental benefits such as reducing CO_2 emissions.

5. Conclusions

From the detailed investigation and the results obtained, the following points could be summarized:

- The synthesized zinc oxide nanopowder with estimated particles size of 54 nm and different morphologies was successfully used as minerlizers and flux agent in cement production.
- The addition of 1% synthesized zinc oxide nanopowder into Portland cement production, allowed the reduction of the clinkering temperature up to 1300°C, instead of 1450 - 1500°C

usually required for the clinkerization process of Portland cement thereby enabling a reduction of energy consumption and greenhouse gas emissions.

- Based on chemical composition and free lime content which provide information on the progress of chemical reaction and the quality of burning. It is found that the resulted clinker meets the requirements for the standard specifications for clinker production
- According to the literature review Aluminates and Ferrites begin to melt and free lime combined with the free silica and Belite (C_2S) to form Alite (C_3S) above 1300°C during clinkerization process. However, when ZnO nanoparticles are introduced into the raw mix this stage occurred earlier in temperature less than 1300°C. This could be clearly predicted by the free lime and C_3S content of the resulted clinker. It does not differ much from the reference clinker in terms of its chemical specification, mineral content and free calcium oxide.
- XRD patterns show that the modified Portland cement dominant phases are well crystallized, giving peaks at the expected 2θ values as compared with the reference Portland cement.
- Minor phase is detected in the modified cement clinker named as calcium zinc aluminum silicate. This phase is Alite of Tetragonal modifications of impure Tricalcium silicate (C_3S). This means that the zinc ions of zinc oxide nanoparticles are incorporated into the Alite phase. The density of this phase is 3.19 g/cm^3 and it is within density range of Alite (3.13 to 3.22 g/cm^3).
- SEM studies showed that Alite mineral phase was completely formed at clinkering temperature of 1300°C. The size of its crystals in modified clinker varies, being much smaller. The more rounded and irregular outline, crystals are Belite. Very few belite clusters are observed in modified clinker in comparison to the reference clinker
- Pore structure is a very important microstructure feature in porous solid because it affects physical, mechanical and durability properties of the material. From the SEM image of clinker it is observed that modified cement has large pore relative to reference cement.
- EDS confirms the existence of the basic elements that constitute the main phase, which are mainly responsible for the properties of cement. It also provides further evidence about the mineral phase, calcium zinc aluminum silicate which is identified by the X- ray diffraction.

- The 2 and 28 day compressive strengths of the resulted cement meet the requirements of EN197 standard for Portland cements, however beyond 3-7 days, no enhancement in strength is observed.
- The utilization of nanomaterials such as ZnO nanopowder as minerlizer into Portland cement production makes it possible to lower the clinkerization temperature by 150°C and save fuel.
- The mineralizing action of ZnO may be due to various reasons that it lowers the liquid phase appearance temperature and increases its content. It also modifies the physical properties of the liquids, lowers the activation energy, and accelerates the clinker- forming reactions.

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Table.1: Chemical composition of raw meal by XRF

Oxides	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	LSF	SM	AM	LOI
Chemical Composition in wt.%	13.59	3.54	2.84	42.33	1.21	0.28	0.18	95.55	2.26	1.43	35.21

Table 2: Chemical composition of Zinc oxide nanoparticles and temperature of produced clinker samples

Sample	Temperature	% of Zinc oxide nanoparticles
A	1200°C	1
B		2
C		3
D	1250°C	1
E		2
F		3
G	1300°C	1
H		2
I		3

Table.3 Main phases present in ordinary Portland cement and clinker

Main phases	Reference cement clinker	Modified cement clinker
C_3S	53.83	54.19
C_2S	21.92	21.21
C_3A	8.2	7.5
C_4AF	10.64	10.17

Table4: Elemental composition for reference and modified Portland Cement

Sample	Reference Portland cement		Modified Portland cement	
Element	Weight%	Atomic %	Weight%	Atomic %
O	60.81	0.61	63	79.20
Mg	0.79	1.22	0.98	0.74

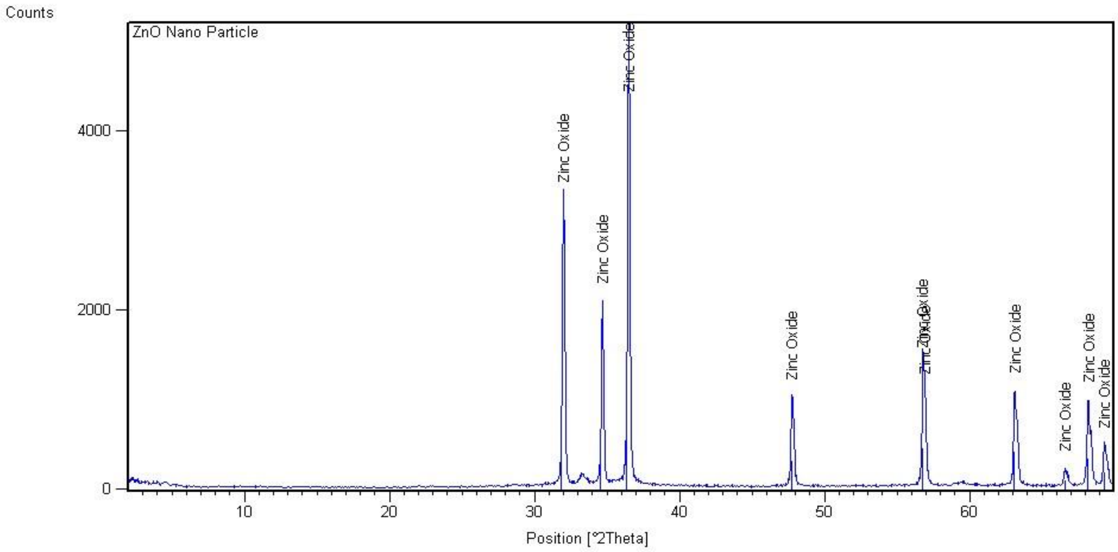
Al	1.69	4.44	2.83	1.99
Si	6.27	1.24	5.89	4.06
S	2.11	13.92	2.46	1.42
Ca	27.44	0.34	23.03	11.44
Fe	0.89	0.42	0.92	0.34
Zn	-	-	0.88	0.28
Total	100.00		100.00	

Figure 1: Characterization of ZnO nanopowder (a) XRD pattern (b) SEM image

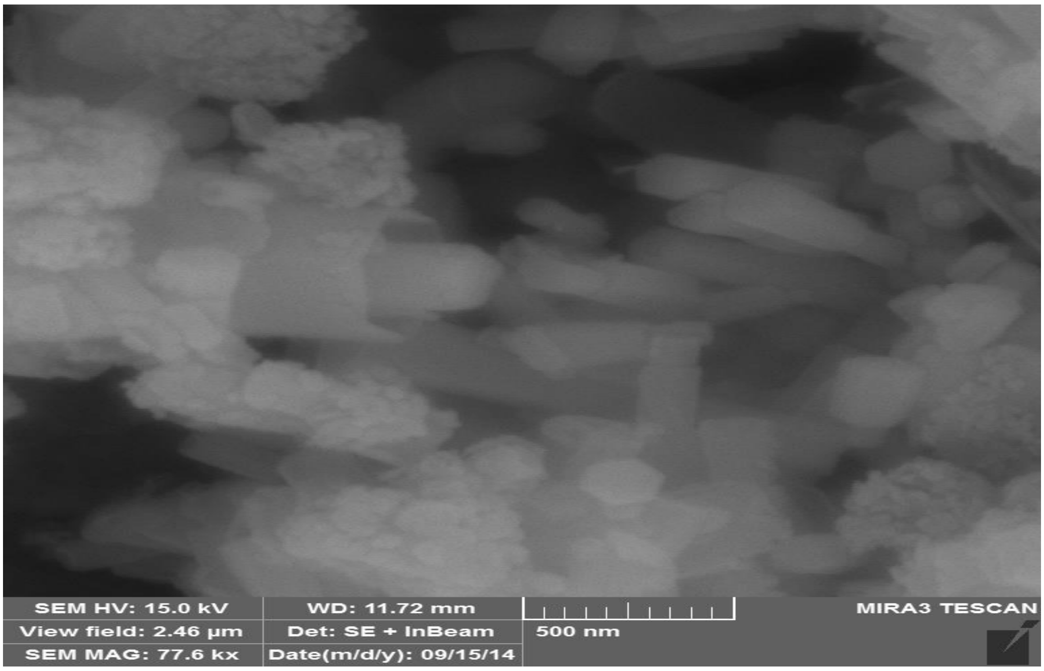
Figure 2: Raw meal preparation for lab clinker production

Figure 3: Produced laboratory clinker samples

Figure 4: Chemical composition of Portland clinker mineralized by ZnO nanoparticles at various temperatures



(a)



(b)

Figure .1: Characterization of ZnO nanopowder (a) XRD pattern (b) SEM image

Figure 2: Raw meal preparation for lab clinker production

Figure 3: Produced laboratory clinker samples

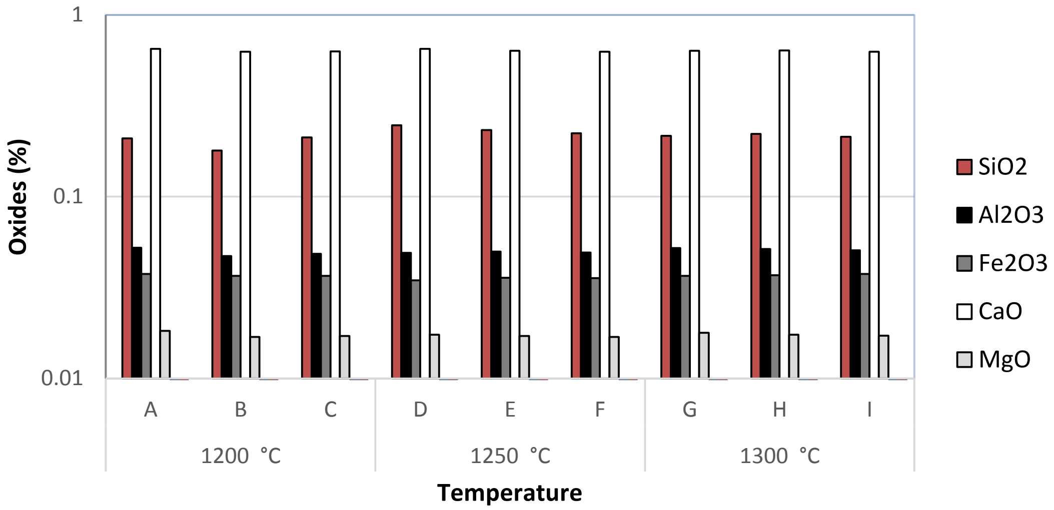


Figure 4: Chemical composition of Portland clinker mineralized by ZnO nanoparticles at various temperatures

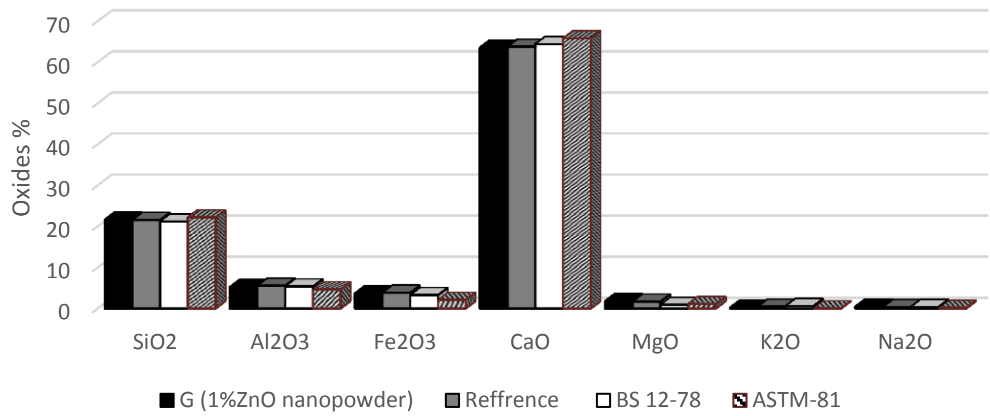


Figure 5: Chemical composition of Portland clinker mineralized by ZnO nanoparticles (sample G) compared with standard specification

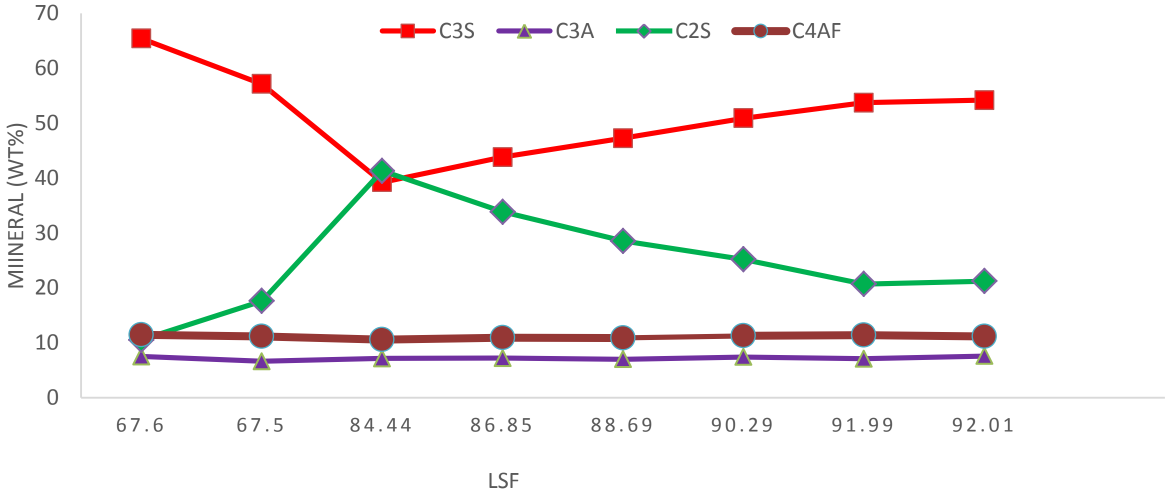


Figure 6: Mineral wt % vs. Lime saturation factor (LSF)

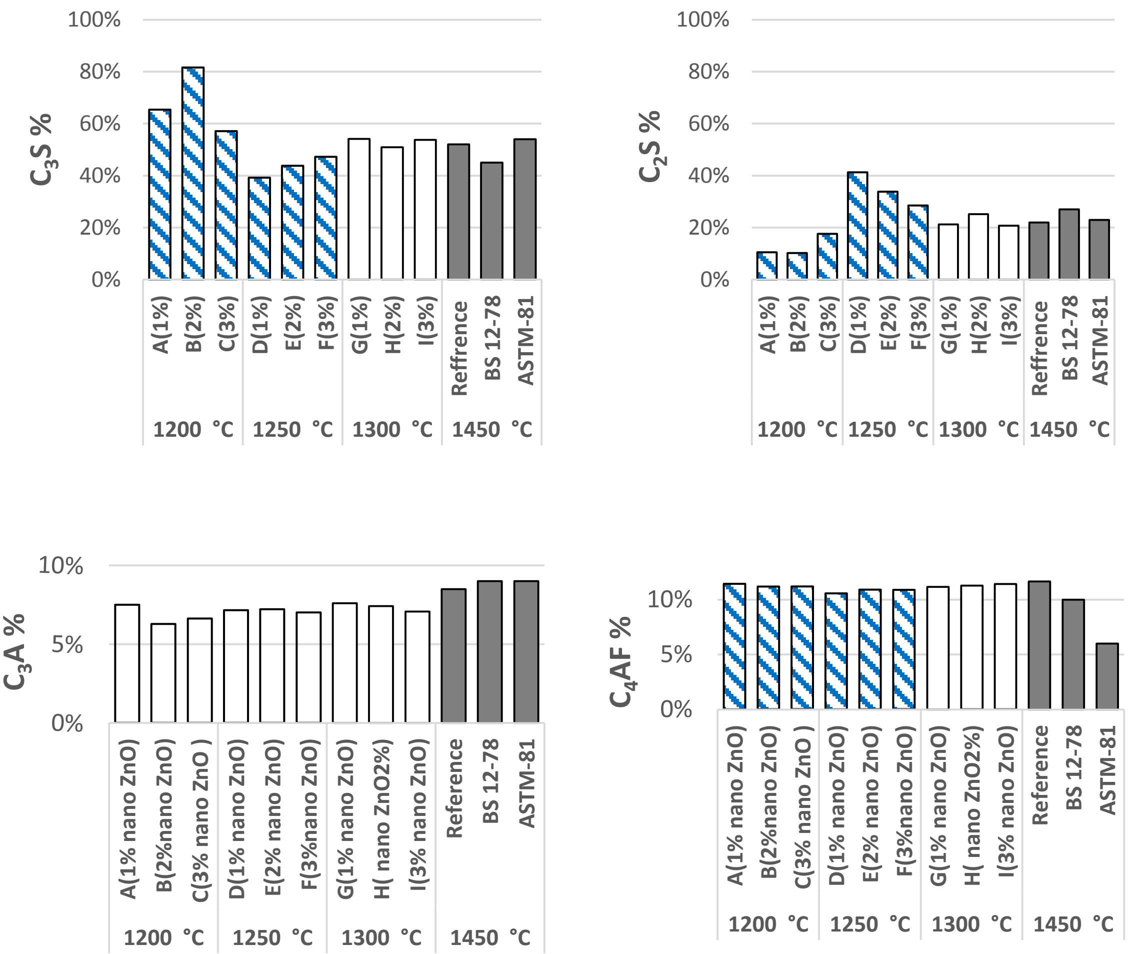
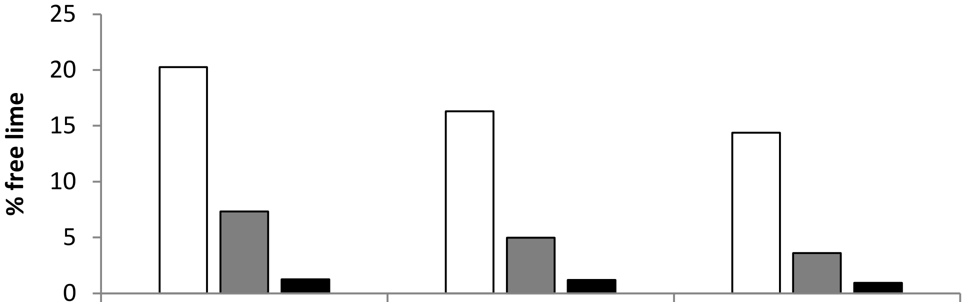
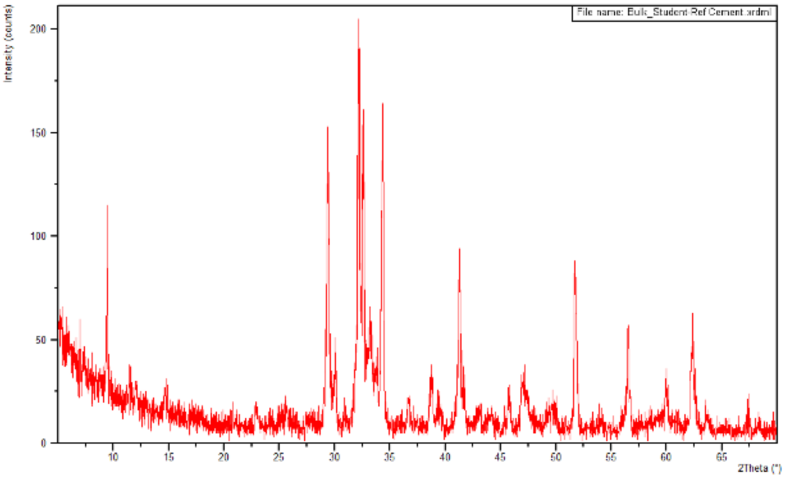


Figure 7: Mineral content of clinker samples (A - I) mineralized with ZnO nanoparticles compared with standard specifications

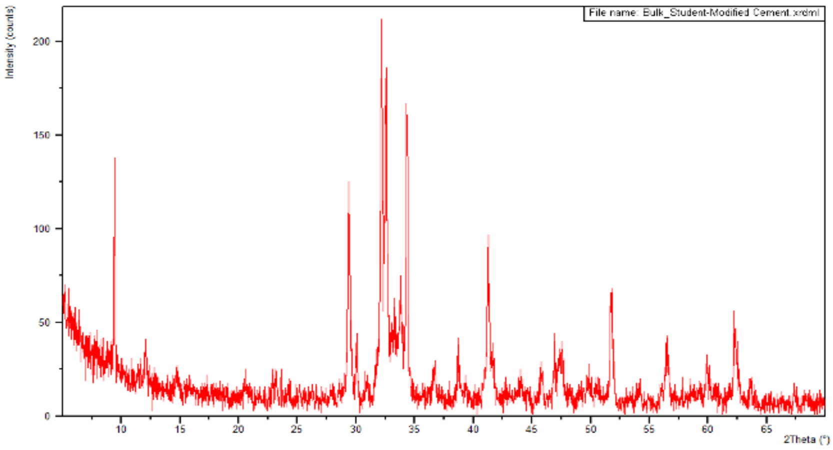


	1%	2%	3%
1200	20.25	16.3	14.39
1250	7.33	4.98	3.61
1300	1.26	1.2	0.93

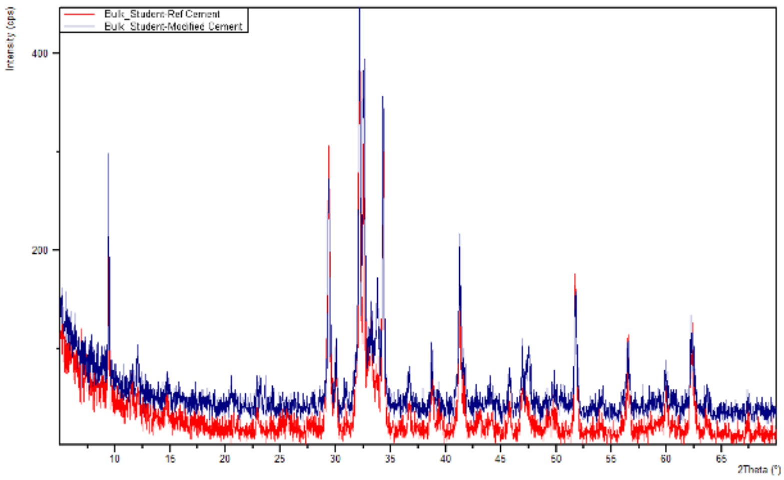
Figure 8: Effect of ZnO nanoparticles (1-3 %) on the free lime content of cement clinker at various temperatures (°C)



(a)

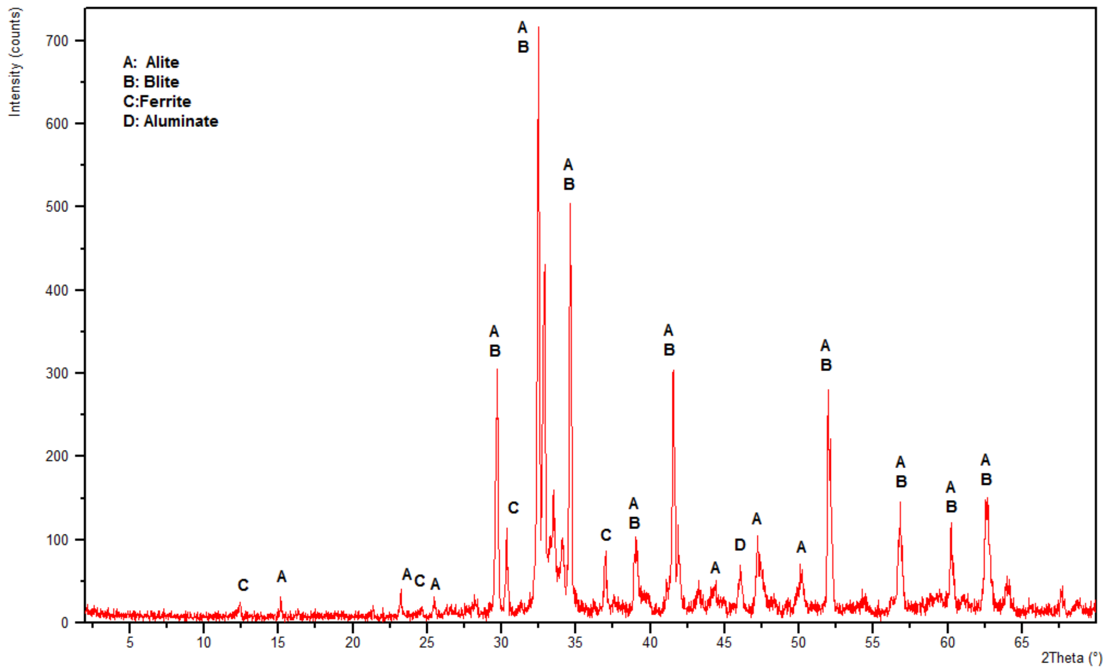


(b)

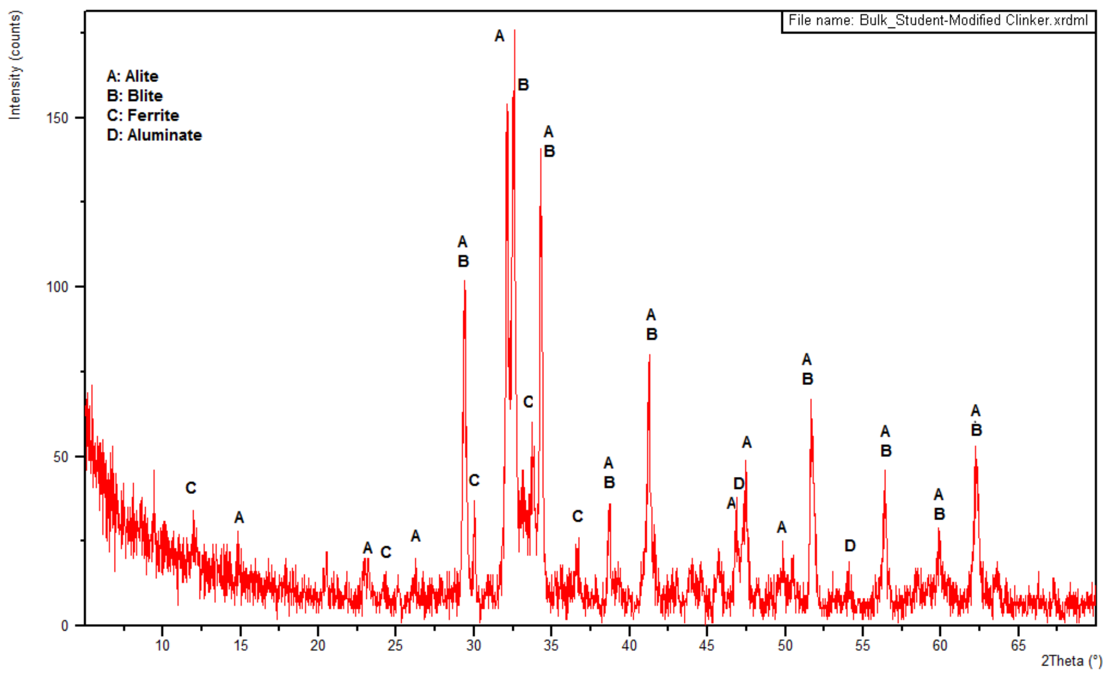


(c)

Figure .9: XRD pattern of (a) Reference cement (b) Modified cement (c) both cements

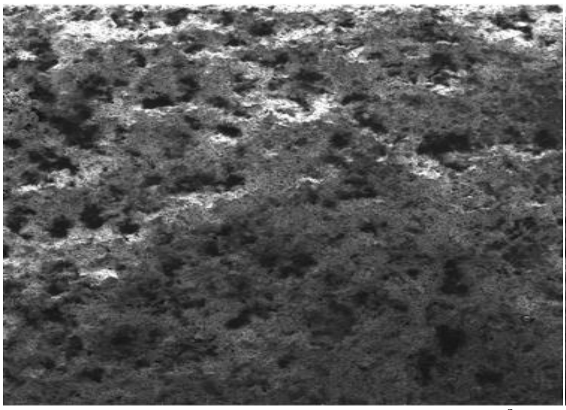


(a) Reference



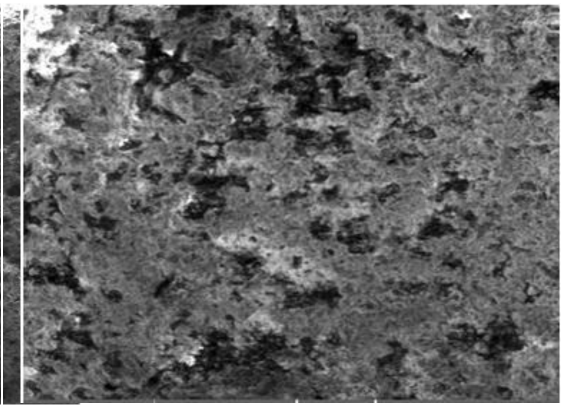
(b) Modified

Figure .10: Phase identification in XRD pattern (a) Reference (b) Modified Ordinary Portland Cement



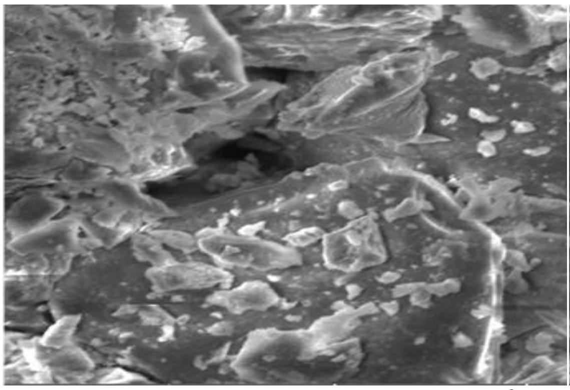
Reference Portland clinker (produced at 1450^{o}C)

a. Magnification 365X



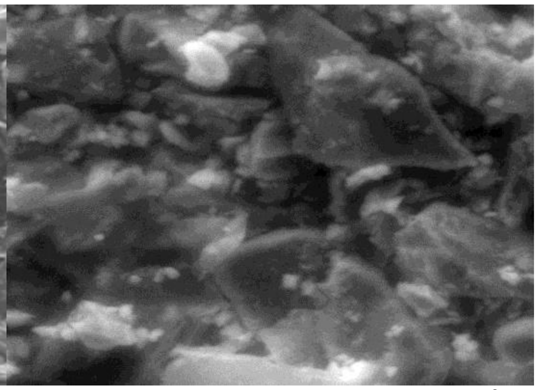
Modified Portland clinker (produced at 1300^{o}C)

b. Magnification 365X



Reference Portland clinker (produced at 1450^{o}C)

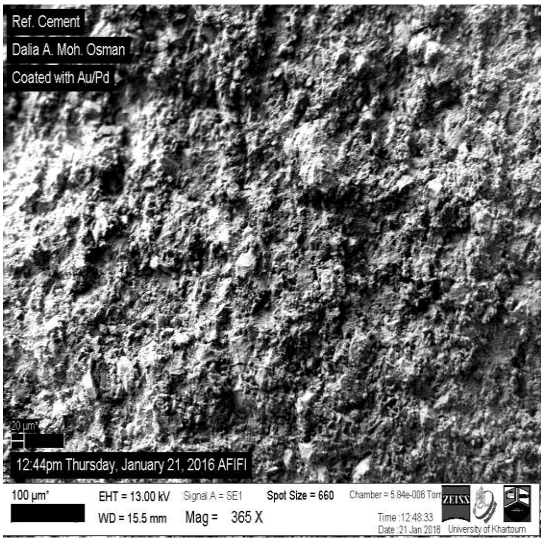
c. Magnification 1.17X



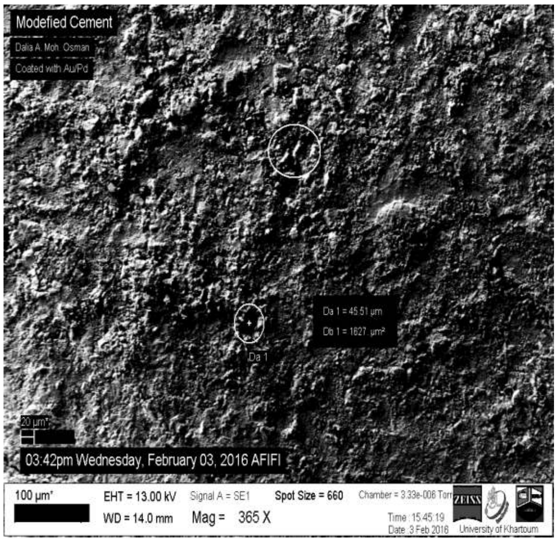
Modified Portland clinker (produced at 1300^{o}C)

d. Magnification 1.17X

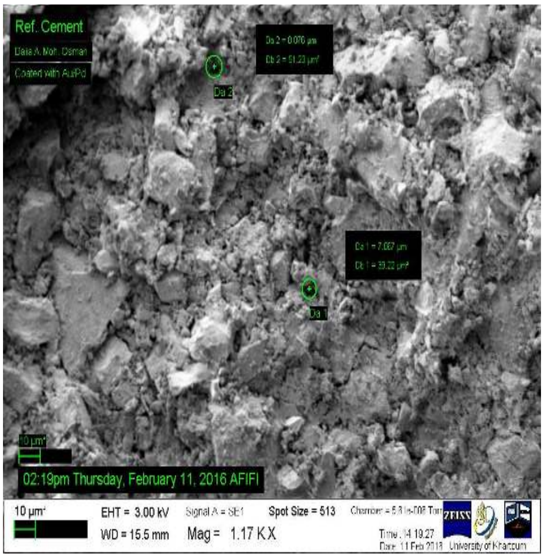
Figure 11: SEM micrographs of Reference Portland clinker and Modified Portland clinker (a) Reference Portland clinker (produced at 1450°C) mag365X and (b) Modified Portland clinker (produced at 1300°C) mag365X (c) Reference Portland clinker (produced at 1450°C) mag1.17X(d) Modified Portland clinker (produced at 1300°C) mag1.17X



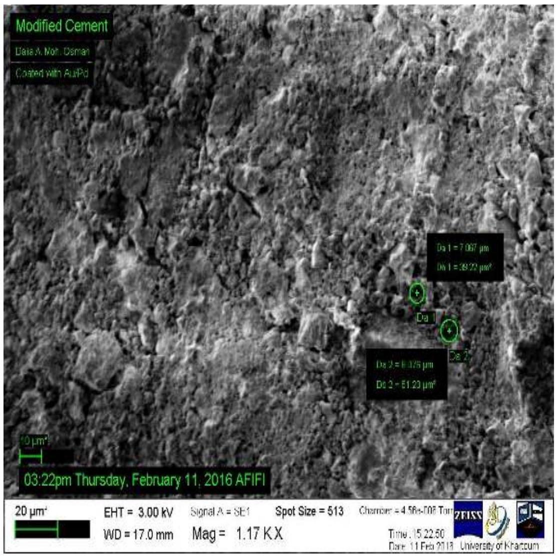
(a)



(b)

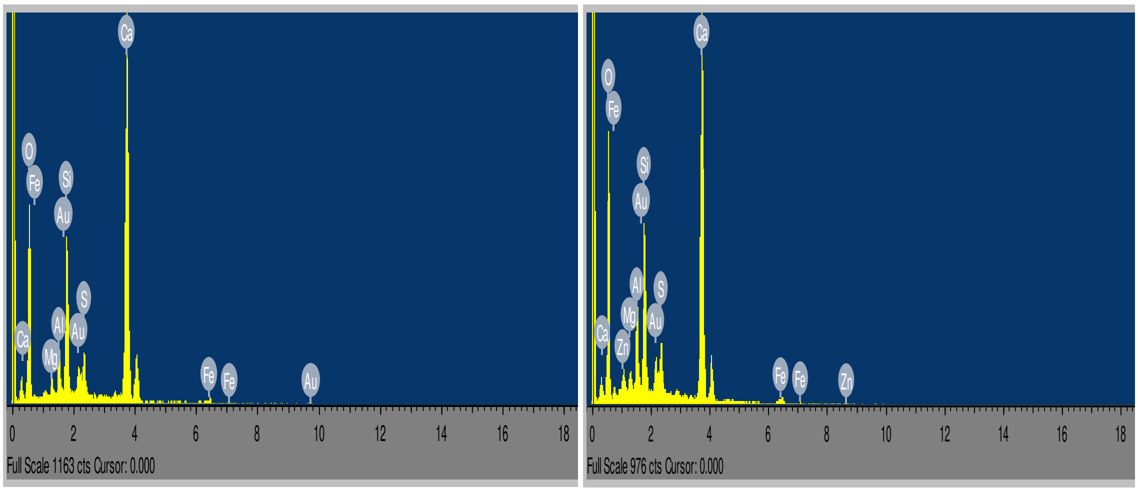


(c)



(d)

Figure 12: SEM micrographs of the (a) Reference Portland cement (produced at 1450^{o}C) mag365X and (b) Modified Portland cement (produced at 1300^{o}C) mag365X (c) Reference Portland cement (produced at 1450^{o}C) mag1.17X (d) Modified Portland cement (produced at 1300^{o}C) mag1.17X



a **b**

Figure 13: EDX spectra of (a) Reference (b) Modified ordinary Portland cement

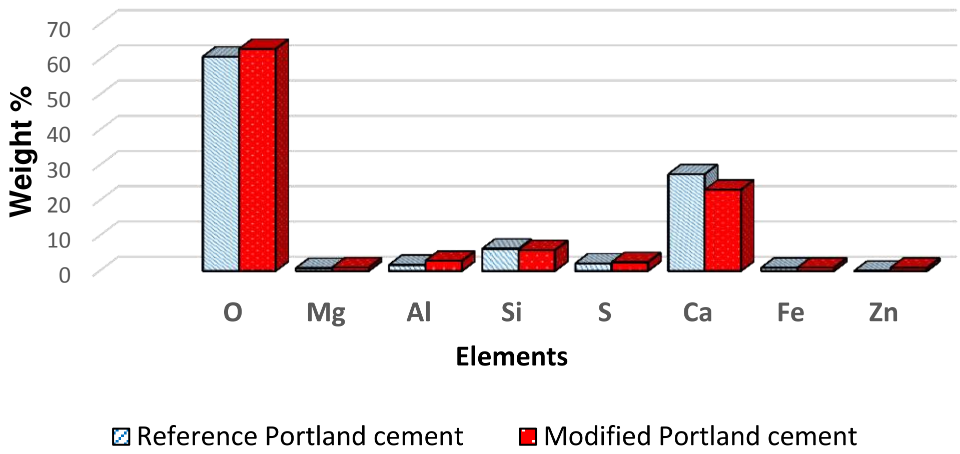
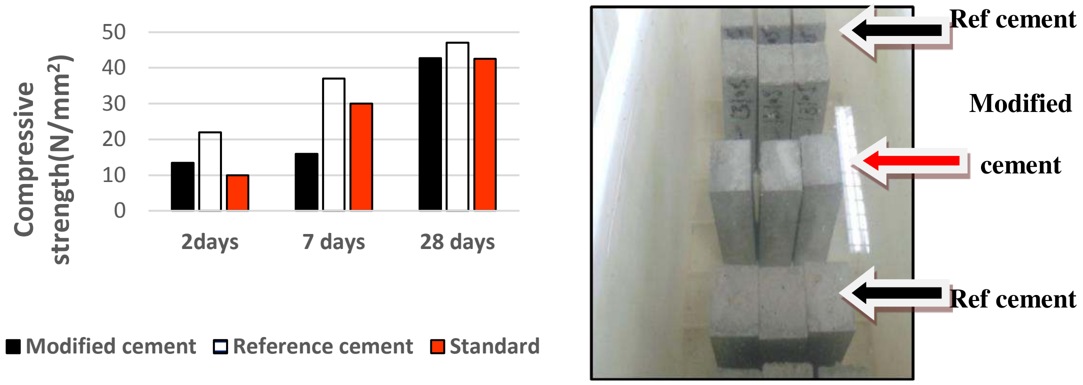


Figure 14: Quantitative results of samples elements



(a) (b)

Figure 15: (a) Strength development of the tested cements (b) Cubes submerged in clean fresh water