
**PREPARATION AND CHARACTERIZATION OF THE LOW ENERGY
PORTLAND CEMENT**

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Abstract

Synthesis of Portland cement clinker from kiln feed raw materials containing zinc carbonate was studied. The kiln feed of the Portland cement was substituted by different contents of zinc oxide (0.0, 0.5, 1.0 and 1.5 wt. %). The ingredients of mixes were intimately homogenized, mixed, molded into a compact mass and fired at 1250, 1275, 1300 and 1325°C for two hours soaking time. The burnability of each sample was investigated by the determination of insoluble residue, free lime contents and phase composition of the fired products. The data show that the clinker formation was completed at 1300°C in the presence of 0.5-1.5 wt. % zinc oxide. Also, the prepared low energy cement has good hydraulic properties than those of the ordinary portland cement.

Introduction

Portland cement clinker manufacture requires higher energy consumption, about 1800 kJ/kg of clinker [1]. The thermal energy for the decomposition of calcium carbonate of raw meal takes the main part of the total energy. This involves massive quarrying for raw materials (limestone, clay, etc.), as it takes 1.7 tonnes to produce 1 tonne of clinker, as well as the emission of greenhouse and other gases (NO_x, SO₂, CO₂) into the atmosphere. Around 850 kg of CO₂ are emitted per tone of clinker produced. The cement industry is looking for solutions to these problems, to attain sustainability and comply with the Kyoto Protocol commitments [2]. For that reason, experimental ways are being explored to develop cements with low energy consumption, less damaging to the surrounding environment and with lower tendency to emit polluting gas.

Mineralizers are inorganic compounds which accelerate the process of reactions in solid phase, liquid phase and solid-liquid interface. They lead to major impacts on the determination of burning zone, the composition and formation of clinker minerals [3].

The effect of different mineralizers on lowering the burning temperature of Portland cement clinker was the object of many researches. Various researches

related to the study of oxides effect on the decrease of clinker burning temperature. Alkaline oxides, alkaline-earth oxides and heavy metal oxides, according to their percentages in the mixture as well as their nature, act differently on the clinker formation reactions [4, 5].

Chlorides, carbonates, sulfates and phosphates present as adequate mineralizers affect the clinker formation [6, 7]. The effect of these mineralizers on the clinker properties was also studied by many researchers [8-14], which determined the influence of mineralizers on the chemical, mineralogical, structural, textural, mechanical and physical properties of clinker minerals. The mineralizer effect of previous pure compounds led the researchers to study industrial wastes containing proportions of such mineralizers studied above.

This work aims to study the effect of zinc carbonate as flux and mineralizer for the clinker formation by adding different percentages of zinc carbonate to the kiln feed.

Experimental Work.

The materials used in this study were kiln feed received from National Cement Company, Egypt and pure zinc carbonate. The chemical oxide composition of the raw Kiln feed was determined by using XRF technique. Its chemical composition is summarized as follow: SiO₂, 13.31; Al₂O₃, 3.87; Fe₂O₃, 2.47; CaO, 41.46; MgO, 0.51; SO₃, 0.76; Na₂O, 0.26; K₂O, 0.37 and L.O.L 36.12, wt%.

To prepare the Portland cement clinker (according to the ASTM specification (150-92) and (B.S., 1370:1991), the ingredient of the mixes were homogenized, mixed with 27 wt% water, molded into a compact samples. The samples were fired using a heating rate of 5°C/min. at 1250, 1275, 1300 and 1325°C for two hours soaking time with suddenly cooling in the atmospheric air. The raw kiln feed of cement raw material was partially substituted by zinc carbonate in the following ratios, 100:0.0, 99.5:0.5, 99:1.0, and 98.5:1.5 wt % to prepare different samples denoting as C₀, C₁, C₂ and C₃ respectively. The degree of clinker formation of each mix was tested by the free lime (ASTM C114)^(15, 16) and insoluble residue contents at different firing temperatures. Also, the burnability of some selected fired samples was also investigated by the aid of XRD technique.

The prepared clinker was ground with 5% gypsum; the prepared cements were denoted M_0 , M_1 , M_2 and M_3 respectively. The pastes were molded in 0.5-inch cubic moulds, cured in humidity chamber at $23\pm 1^\circ\text{C}$ for 24 hours, and then immersed in tap water for the time of testing up to 90 days. The mixing of the pasts was carried out with the water of consistency (ASTM C187) ⁽¹⁷⁾ and setting time was determined (ASTM C191) ⁽¹⁸⁾. The kinetics of hydration was followed as a function of curing time by the determination of the free lime ^(15, 16) and combined water contents.

The total porosity, as well as compressive strength were also measured. The combined water content was estimated after ignition the dried samples at 1000°C for 30 minutes minus the weight of water in $\text{Ca}(\text{OH})_2$. The stopping of hydration of cement pastes was described elsewhere ⁽¹⁹⁾.

Results and Discussion.

The burnability of the prepared mixes

The burnability of the prepared mixes was studied as a function of firing temperature up to 1325°C by the determination of the free lime and insoluble residue contents.

Figure (1) shows that the free lime content sharply decreases with zinc carbonate and the firing temperature. The clinkers (C_1 , C_2 and C_3) gives the best clinkerability and minimum amount of free CaO content at 1300 - 1325°C . During firing the raw mix up to clinkering temperature, the clay minerals loose their adsorbed and lattice water up to 600°C giving rise to a mixture of active amorphous SiO_2 , Al_2O_3 and Fe_2O_3 . Between 600 and 850°C variable amounts of impurities oxides of iron, titanium, alkaloids and alkaline earth are librated together with CaO, SiO_2 and Al_2O_3 . These oxides in addition to the added amount of ZnO act at temperature higher than 800°C and onwards, as fluxing materials, as well as mineralizers for the combination of CaO and SiO_2 at lower clinkering temperature. At the same time, the sample without mineralizer needs higher temperature to complete clinker formation. Therefore, as the zinc oxide content increases the best burnability and maximum amounts of clinker phases of lowest possible temperature enhance.

Figure (2) shows the insoluble residue of the fired samples as a function of firing temperature as well as the ZnO content. The data show that as the ZnO content

increases the insoluble residue decreases at any firing temperature. This is mainly due to that sample without mineralizer gives higher values of free silica as well as Al_2O_3 , which lead to give higher insoluble residue with firing temperature. The fired batches C_1 , C_2 and C_3 give the lower amounts of insoluble residue at $1325^\circ C$. These values of are in an agreement with those of free lime contents.

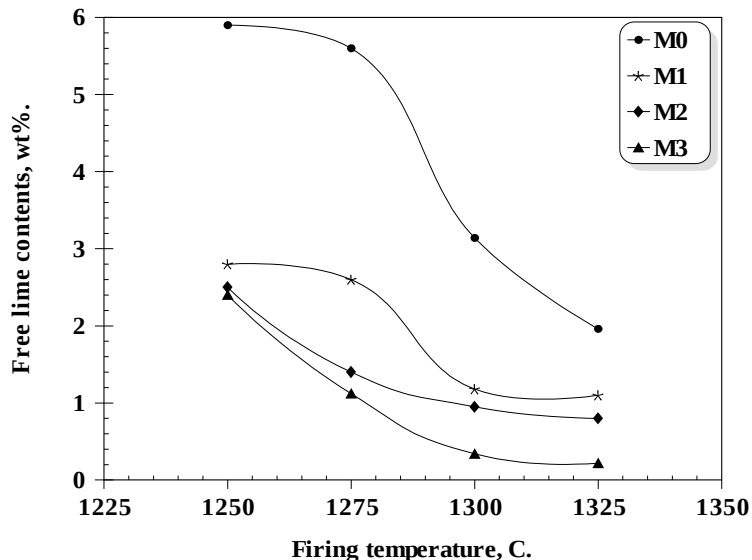


Fig. (1): Free lime contents of raw mixes fired at different temperatures

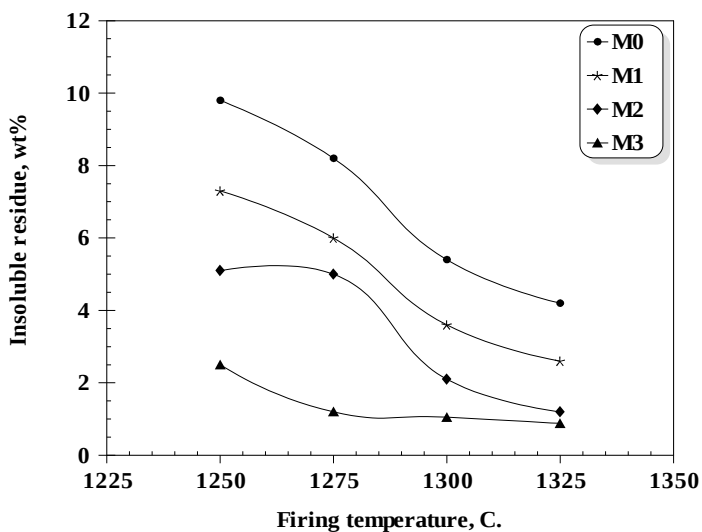


Fig (2): Insoluble residue contents of raw mixes fired at different temperatures

Figure (3) illustrates XRD patterns of the raw mixes C_0 , C_1 , C_2 and C_3 fired at 1250°C, for two hours. The patterns illustrate singlet peak at 18.1, 34.2, 47.12 (2θ -values) indicating the presence of free lime in the four mixes in decreasing order of mix $C_0 < C_1 < C_2 < C_3$. Also, the presence of single peaks at 29.4, 32.30 and 34.40 (2θ -values) illustrates the presence of alite phase in a small amount in mix (C_0) in comparison with other mixes (C_1 - C_3). On the other side the belite decreases with the ZnO content on the expense of alite.

Figure (4) shows that XRD patterns of cement mixes fired at 1300°C, the data show that the amount of alite phase (singlet peaks at 29.40, 32.30 and 34.40 2θ -values) increases in mixes C_1 , C_2 and C_3 with the complete disappearance of free lime peaks in comparison with mix (C_0).

Figure (5) illustrates the XRD patterns of raw mixes fired at 1325°C, the results show that as the ZnO content increases the amount of alite phase (singlet peak at 29.40, 32.30 and 34.40 2θ -values) sharply enhances with the complete disappearance of free lime in all mixes. On the side, the samples C_1 , C_2 and C_3 containing ZnO as mineralizer give a higher degree of burnability than the control sample. This may indicate the important role of ZnO mineralizer in lowering the maturing temperatures of the fired cement raw mix. In all cement clinkers the C_3A is formed.

The addition of ZnO in the cement raw mix promotes the combination of the free lime especially in the temperature range between 1000-12000C. This fact leads to the conclusion that ZnO does not affect only the formation of the melt but is capable of promoting the solid reactions as well. The presence of ZnO affects not only the formation of silicates but also the combination of CaO with Al_2O_3 [7, 10, 20-22].

Characteristics of the prepared cements

The water consistency as well as initial and final setting times of cement pastes are graphically represented in Figure (6). The results show that the water of consistency increases as well as initial and final setting times shorten with ZnO contents. This may be attributed to the effect of ZnO as an active component in the cement phase formation, i.e. the rate of formation of alite phase increases and the amount of hydration products also enhances. In addition, as the alite content in the cement increases the water of consistency enhances.

The combined water content of cement of cement pastes of clinker fired at 1325°C cured for 3, 7, 28 and 90 days are graphically plotted in Figure (7). It can be seen that the combined water content increases with curing time for all hardened cement pastes, due to the progress of the hydration and to increasing the amounts of hydration products. This indicates that the ZnO plays an important role in the burning process as well as the clinker phases formation, especially the alite phase. On the other hand, M0 has lower values of combined water than the other cement pastes at all ages of hydration and the amount of combined water content increases with the ZnO content.

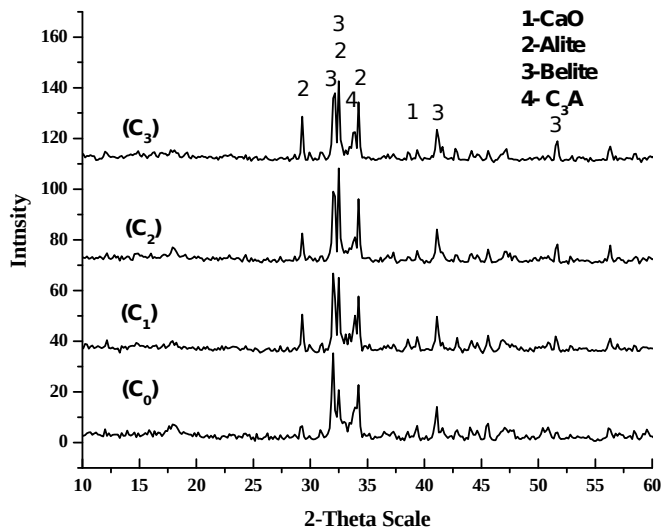


Fig (3) :XRD patterns of low energy cement clinker fired at 1250 °C

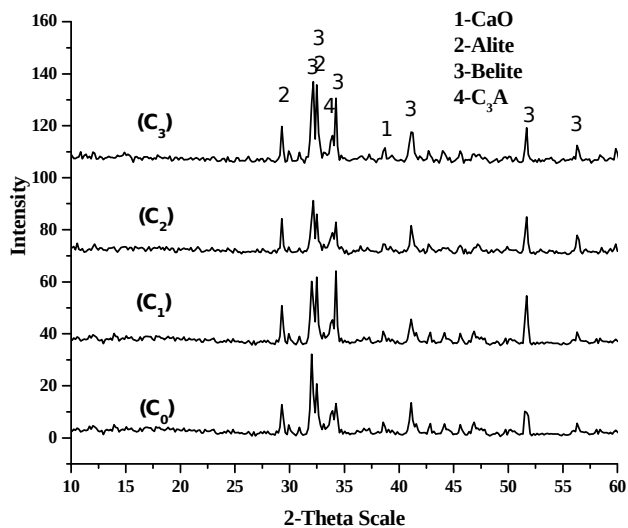


Fig (4) :XRD patterns of low energy cement clinker fired at1300 °C

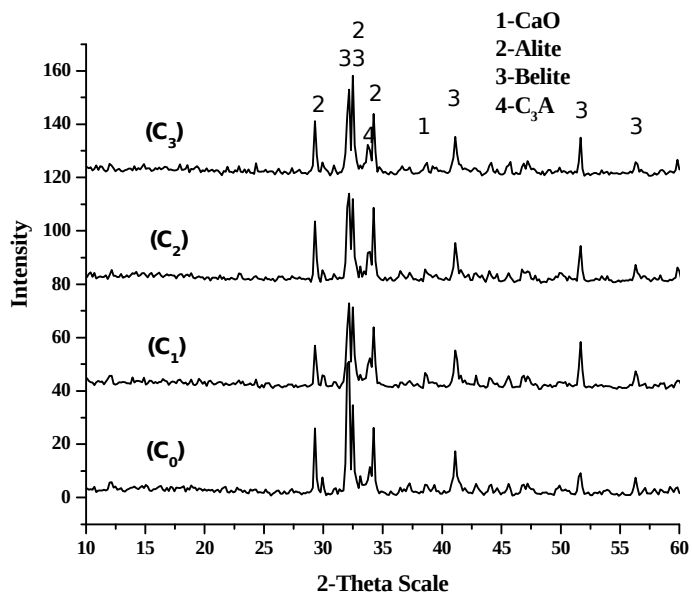


Fig (5): XRD patterns of low energy cement clinker fired at 1350 °C

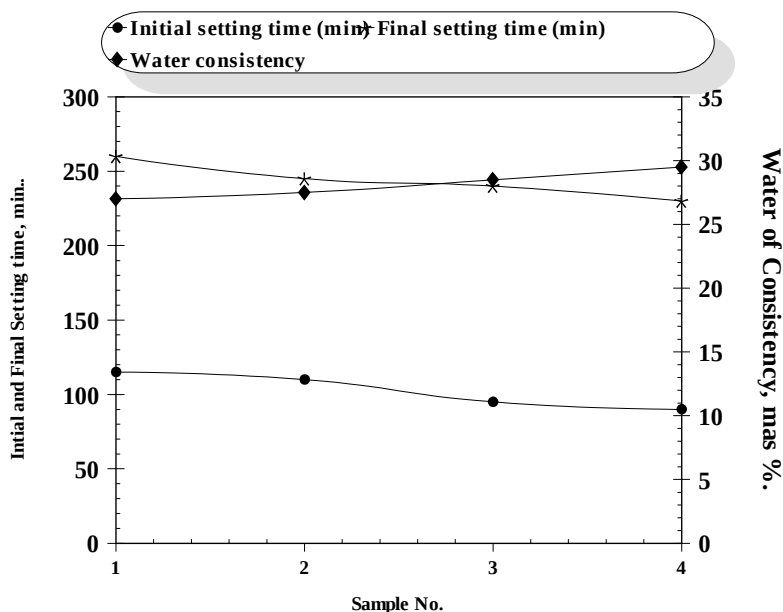


Fig. (6): The water consistency as well as initial and final setting times of cement pastes cement pastes of clinkers M0-M3

The free lime contents of hardened cement pastes of clinkers (M_0 - M_3) fired at 1325°C and hydrated for 3, 7, 28 and 90 are graphically plotted as a function of curing time up to 90 days in Figure (8). The free lime content increases with curing time for all cement pastes due to the continuous hydration of silicate phases that liberate free $\text{Ca}(\text{OH})_2$. Also, as the ZnO contents increase the free lime liberated during the hydration of cement paste enhances. This is mainly due to that the alite phase liberates more $\text{Ca}(\text{OH})_2$ and has a higher rate of hydration at early ages comparing to belite phase.

The total porosity of the hardened cement pastes cured for 3, 7, 28 and 90 days are graphically plotted in Figure (9). It is clear that the total porosity for all cement pastes decreases with curing time due to the filling up some of the available pore volume with the hydration products. In addition, as the amount of ZnO increases the total porosity decreases. This is due to the increase of the rate of hydration of cement pastes, which is accompanied by the increase of alite formation. On the other hand, the cement paste without addition (M_0) exhibits higher values of porosity than those containing mineralizers, due to the decrease of hydration products.

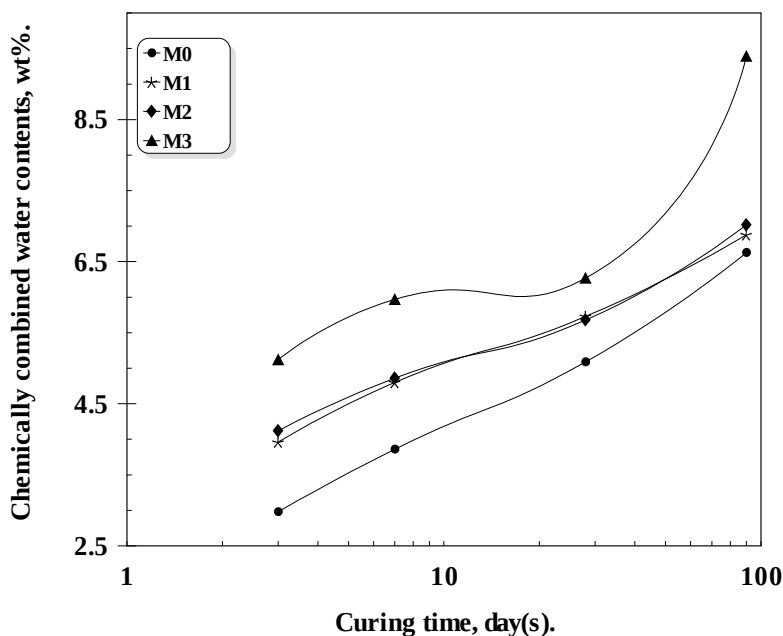


Fig. (7): Chemically combined water contents of hardened cement of pastes clinkers (M_0 - M_3) fired at 1325°C as a function of curing time

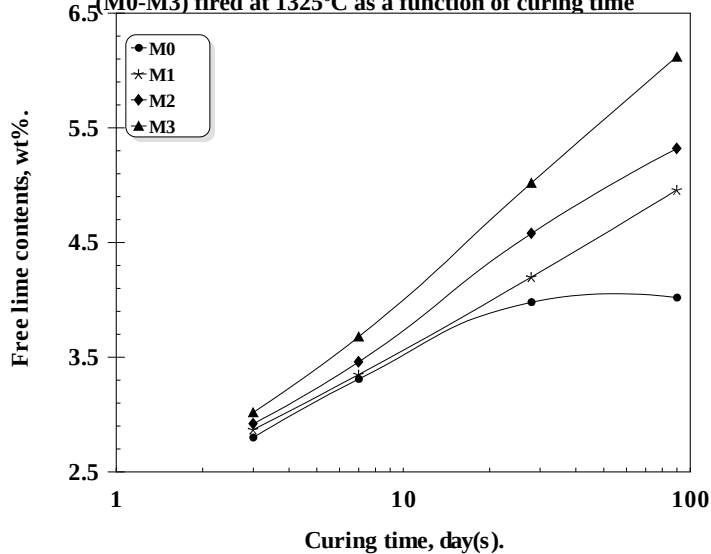


Fig.(8): Free lime contents of hardened cement pastes of clinkers (M0-M3) fired at 1325°C as a function of curing time

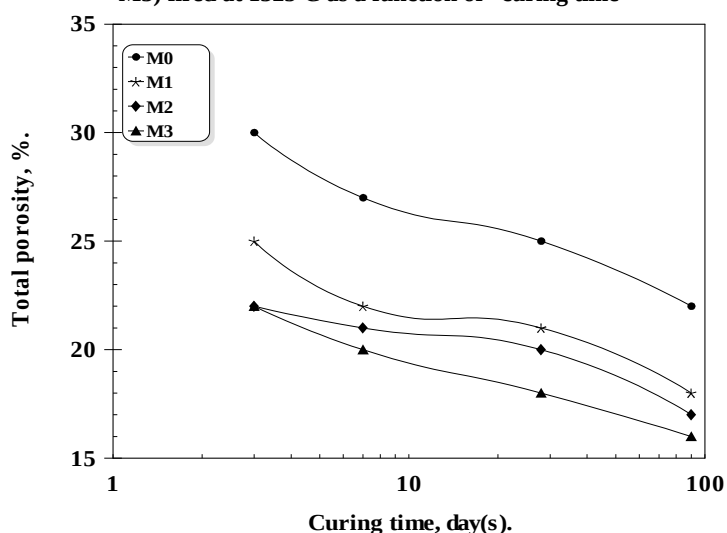


Fig.(9): Total porosity of hardened cement pastes of clinkers (M0-M3) fired at 1325°C as a function of curing time

The compressive strength of the hardened cement pastes cured at 3, 7, 28 and 90 days are graphically plotted in Figure (10). The compressive strength increases with curing time for all cement pastes. This is attributed to the increase of the amount of hydrated products especially tobermorite gel (the main source of compressive strength), so, this leads to a corresponding increase in the compressive strength of the hardened cement pastes. In addition, it can be seen that as the amount of ZnO increases the compressive strength of cement pastes enhances. The cement without addition (M₀) gives a lower rate of hardening up to 90 days. On the other side, the sample (M₃) with 1.5% ZnO gives a maximum rate of hardening at all curing times. These results are in a good agreement with the kinetics of hydration and total porosity as well as the data of XRD of clinker formation, which indicate that the

ZnO plays an important role in the formation of silicate phases (especially the alite phase).

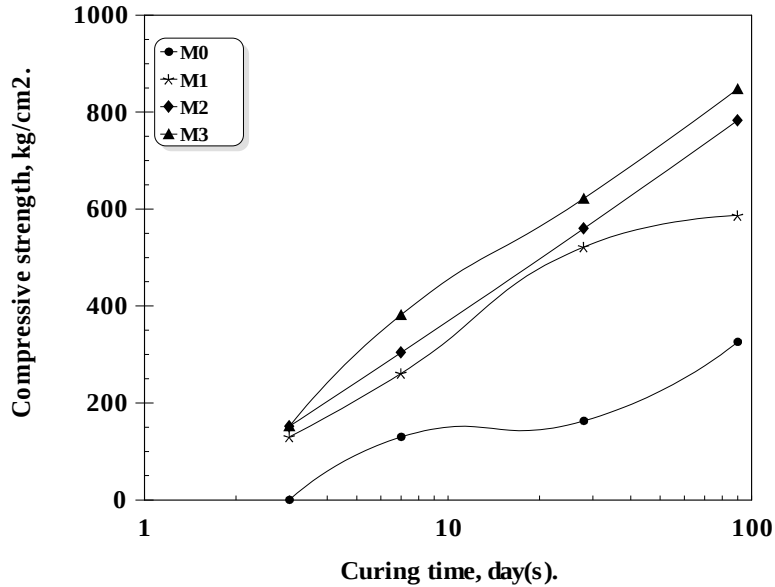


Fig. (10): Compressive strength of hardened cement pastes of clinkers (M0-M3) fired at 1325 °C as a function of curing time.

Conclusion

From the above findings, it can be concluded that:-

- 1- It is possible to use ZnO as mineralizer in the preparation of the Portland cement clinker.
- 2- The free lime and insoluble residue contents sharply decreases with ZnO contents.
- 3- The samples C₁, C₂ and C₃ with ZnO additions give the best burnability with the lower value of free lime and insoluble residue contents at 1300°C, as well as a good hydraulic properties than those without mineralizer.

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