



Effect of Partial Substitution of Raw Gypsum with Thermally Treated Phosphogypsum on the Properties of Portland Pozzolanic Cement

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ARTICLE INFO

Received: 26 February 2019

Revised: 11 April 2019

Accepted: 02 May 2019

Available online: 04 May 2019

DOI: 10.33945/SAMI/AJCA.2019.4.4

KEYWORDS

Phosphogypsum

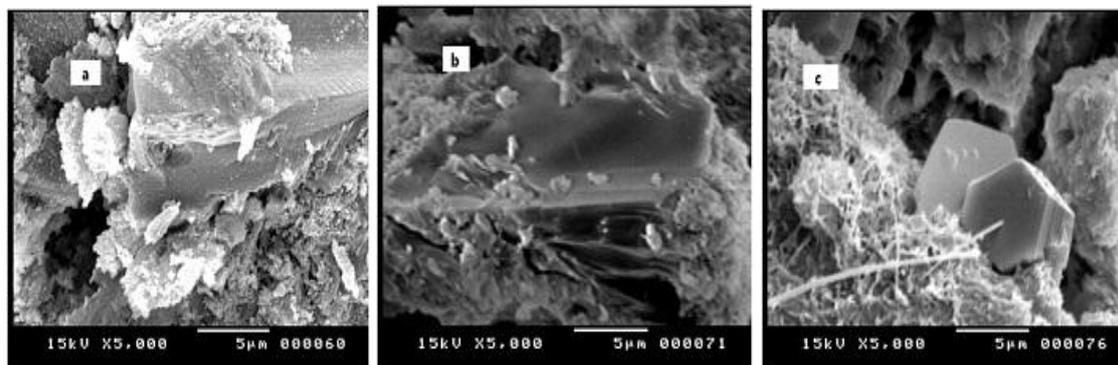
Clinker

Pozzolanic cement

ABSTRACT

Long years of production of phosphate fertilizer at very large amounts of phosphogypsum (PG) occupied large area, causing chemical and radiological environmental substances. The use of PG in building materials represents a good method for lowering the cost of cement production and dispose of phosphogypsum as chemical and radioactive waste. Fresh wet hemihydrate phosphogypsum, cement and pozzolana additive were mechanically activated together and from mixing Portland pozzolanic cement (PPC) with PG, these mixes were prepared at different replacements (by weight) of raw gypsum (RG) with purified PG ranging from 1–5%. The purified PG was obtained by calcining PG at temperatures of 200, 400, 600, 800 and 1000 °C. The compressive strength, bulk density, total porosity, combined water and free lime of different hardened mortars were obtained following 3, 7, 28 and 90 days of curing. In addition, the setting time of cement pastes. The highest percentage increase in strength was found to be for PG calcined at temperatures of 800 and 1000 °C. The incorporation of PG in the cement paste has dramatically increased its initial and final setting times. FTIR spectroscopic analysis and scanning electron microscopy (SEM) were used to investigate the change in structure of mortars after curing and change in morphology and microstructure of some hardened pastes.

GRAPHICAL ABSTRACT



Micrographs of mixes (PPV) contain thermally treatment PG at 600 °C after 3(a), 28 (b) and 90 (c) days curing

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Introduction

The quantity of PG produced is very large: for each 1 ton of phosphate (P_2O_5) produced, there is a coproduction of 5 tons of calcium sulfate (PG). The annual world production of this material is up to 180 million tons and is expected to reach up to 300 million tons by the year 2000 [1]. Only 15% of the PG is utilized by the cement and gypsum industries as a setting moderator for cement and for making gypsum plaster. The impurities in PG have been found to delay the setting time and reduce the rate of early strength development of cement to a greater extent than pure gypsum, although strengths at later ages are not affected. Fortunately, either chemical processing or heat treatment can reduce these impurities. The remaining 85% of PG is not used, causing an environmental problem and creating need for large areas for disposal. Therefore, attempts were made to use PG in applications such as road and rail works fills, stabilization of base course, and building constructions. In addition, the potential for using PG in making roller-compacted concrete [2-9]. Smadi, Haddad and Akour studied utilization of phosphogypsum as cement (OPC and PPC) replacement agents in mortars and found decrease in compressive strength. The incorporation of phosphogypsum in the cement has drastically increased its initial strength. Also, this strength development was attributed to formation of anhydrate at higher temperatures [10]. Treated phosphogypsum can be used as an ingredient of plaster [11-13]. The most important and motivating use of phosphogypsum could be in the construction industry. In the manufacturing process of cement, phosphogypsum could be used as a replacement of natural gypsum which plays the role of a set retarder [14,15] on the other hand. Bagade *et al.*, studied the partial replacement of cement by various percentage of phosphogypsum gave good result with concrete specimens [16]. Researches [17,18]

on the basic engineering properties of phosphogypsum-based concrete mixtures concluded that the unique properties of dehydrate phosphogypsum under compaction-consolidation can significantly contribute to the compressive strength of concrete mixes. However, with higher percentage of phosphogypsum, the strength of concrete mixtures is affected by the moisture at the time of testing. Better compressive strength attained with calcined phosphogypsum [19]. Reddy *et al.*, studied the replacement cement by phosphogypsum and they have found the replacement at 10% act optimum [20]. At present, phosphogypsum is mainly used in building materials industry, including cement retarder, building gypsum powder, gypsum board, exterior gypsum board, fiber plaster board, mine filling agent and road bed material [21]. However, prospective processes for large-scale utilization of phosphogypsum are still under investigation. The utilization of phosphogypsum is realistically a significant problem in phosphoric acid industry [22]. Al-Jabbari *et al.*, [8] adopted a physical method for the purification of PG prior to using it as a building material. The method consists of washing PG with water using sieve no. 100 μ , burning the PG at different temperatures (low and high), and adding some accelerators (such as calcium hydroxide) to the calcined PG in order to improve the setting time and the compressive strength of the produced material. The purified PG was analyzed chemically and tested physically. The results indicated that the best and cheapest method for the purification of PG was through washing with water, then neutralizing with calcium hydroxide. Roy *et al.*, [23] studied the potential of using a by-product slag, produced by sulfur-recovery process from PG, as an aggregate in Portland cement concrete. The phase composition and microstructure of two different samples of produced slag were studied. The study showed that although both

slags have different microstructure, mineralogically both are suitable as aggregate in concrete as long as the amount of sulfate is not too high (4.5%).

Experimental

Materials

In this study, the clinker used in the present experimental study has been obtained from Manaseer Cement Company (Jordan), The Clinker was procured from local market. Phosphogypsum (PG) are produced as by-products of phosphoric acid manufacture process in Jordan Abyad Fertilizers and Chemicals Company (Jordan). Millions tons from PG wastes are stockpiled over open areas. Major negative environmental impacts are highly expected due to dissolution of various hazardous chemicals the stockpiled contains. Its

chemical composition and mineralogical constituents are illustrated in Table 1. Raw Gypsum (RG) is one of the non-metallic minerals, composed mainly of hydrated calcium sulfate. It is usually formed by precipitation of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ due to evaporation of solution with high content of SO_4^{2-} and Ca^{2+} ions. Finally, Pozzolana (Pz) Tuff as pozzolanic material was obtained from Tal-Hassan which is located about 120 km northeast of Jordan. Portland Pozzolanic Cement (PPC) was prepared by mixing 70% from clinker, 25% pozzolana and 5% from raw gypsum. Several pastes were made in this investigation by partial substitution of raw gypsum with thermally treated phosphogypsum at different temperatures 200, 400, 600, 800 and 1000 °C at different proportions Table 2. The initial water/solid ratio used in this study were varied from 0.3-0.5 according to the amount of replaced thermally treated phosphogypsum.

Table 1. The chemical compositions (%) of the raw materials

Contents	PCC	PG before Firing	PG at 200 °C	PG at 400 °C	PG at 600 °C	PG at 800 °C	PG at 1000 °C	RG	Pz
CaO %	64.48	35	35.12	35.8	36.71	37.5	40.53	39.82	10.61
SiO ₂ %	21.32	8.32	8.48	8.56	9.07	9.50	10.52	6.81	41.23
Al ₂ O ₃ %	5.32	0.15	0.16	0.33	0.56	0.29	0.25	1.1	12.15
Fe ₂ O ₃ %	3.78	0.17	0.15	0.2	0.16	0.16	0.15	0.56	15.41
MgO %	2.08	0.42	0.42	0.45	0.47	0.482	0.2	1.59	8.78
K ₂ O %	0.58	0.04	0.04	0.04	0.036	0.043	0.003	0.35	2.07
Na ₂ O %	0.58	0.1	0.74	0.01	4.62
SO ₃ %	0.89	42.06	39	35.32	33.63	36.21	33.1	22.18	0.098
P ₂ O ₅ %	0.33	6.79	6.44	3.94	3.77	2.55	2.35	0.39	0.74
CL %	0.002	0.01	0.28	0.34	0.43	0.02	0.003
LOI %	0.00	10.1	9.63	7.43	3.6	1.01	0.82	31.04	0.96
Cr ₂ O ₃ %	0.011	0.087
TiO ₂ %	0.56	0.054	0.056	0.054	0.052	0.047	0.052	0.12	4.14
Mn ₂ O ₃ %	0.022	0.27
ZnO %	0.000	0.045	0.015	0.045	0.048	0.037	0.018	0.008	0.025
SrO %	0.045	0.46	0.29	0.52	0.55	0.47	0.333	0.35

Table 2. The mix composition of PPC pastes made by partial substitution of RG with thermally treated PG at different temperatures

Mix No	Composition of Mixes
PPC	70% clinker + 5% RG + 25% Pz
PPI	70% clinker + 4% RG + 1% PG + 25% Pz
PPII	70% clinker + 3% RG + 2% PG + 25% Pz
PPIII	70% clinker + 2% RG + 3% PG + 25% Pz
PPIV	70% clinker + 1% RG + 4% PG + 25% Pz
PPV	70% clinker + 5% PG + 25% Pz

Pz: Pozzolana RG: Raw Gypsum PG: Phosphogypsum

Methods and Instruments

The mixes (PPI-PPV) were prepared by mixing thermally treated phosphogypsum at different temperatures 200, 400, 600, 800 and 1000 °C at different portions with clinker and raw gypsum. The thermal treated of PG has been done by heating 2 h (10 °C/min) in muffle furnace for the required temperatures. PG was cooled in room temperature after every calcined temperature then crushed and ground in jaw crusher machine. The chemical composition and mineralogical constituents of Portland Cement Clinker (PCC), Phosphogypsum (PG), and Raw Gypsum (RG), are illustrated in Table 1 by XRF 9900, all these material were separately crushed and ground in the jaw crusher machine. The ingredients of each mix blended in the lab ball mill for 2h to insure complete homogeneity. Specimens were cast into mold of (2.54*2.54 cm), then the specimens in the mold were stored curing in humidity chamber at 20±1 °C for 24 h. then demolded and immersed in tap water until tested. After the predetermined curing time 3, 7, 28 and 90 days, groups of three specimens were used to determine the residual compressive strength. Setting times of cement mixed by mixing different proportions were measured by Vicat apparatus according to EN-196-3 [24]. Bulk density and total porosity were determined after any time of hydration as described

elsewhere [25]. The hydration of cement pastes were stopped by employing alcohol-ether method [26]. The samples were dried at 105 °C for 1 h and then collated in polyethylene bags; sealed and stored in desiccators for analysis. The degree of hydration was followed by determination of free lime [26] and chemically combined water content [27]. On the other hand, the raw materials characterized by XRF (Fluorescence (XRF Thermo Scientific ARL 9900 Total Cement Analyzer) and the change in structure of mortars after curing characterize by FTIR spectroscopic (a Perkin-Elmer System 2000 FTIR spectrometer) and scanning electron microscopy SEM (JEOL JSM-840 SEM) were used for investigate and change in morphology and microstructure of some hardened pastes, finally the compressive strength of hardened pastes determined by the digital compressive strength machine (Toni/ technik).

Results and Discussion

Setting time and water consistency

Normal setting of cement is associated with the hydration of Alite (impure C3S) and formation of the calcium silicate hydrate (CSH) phase. On the contract, the initial and final setting time pasts PPC- PG treated at 200, 400, 600, 800 and 1000 °C increases

with increasing the substitution of RG with PG and decreased by increasing treatment temperature of PG, the reasons of all these results are attributed to thermal treatment of PG which decrease the pronounced effect of water soluble P_2O_5 and present phosphorus, sulfate, fluoride, and organic impurities contained in PG interfere in an unpredictable way to delay the setting time in PG [11]. Form protective coating as by the impurities on the surface of cement grains during the gauging of cement with water and thus suppression of the hydration of cement temporarily [30]. In general, the setting time decreasing with increasing temperature, hence, OPC containing PG treated at 800 °C and 1000 °C have lowest setting time. The water/cement ratio W/C of hardened specimens made from PPC-PG with treatment at 200 °C decreases by increasing the amount of PG gradually from 24.4 % (PPI) to 23.4 % (PPV) respectively, by increasing firing temperature of PG the water/cement ratio W/C decreases this may be anhydrite higher water demand. The specimens from PPC-PG fired at 800 °C and 1000 °C possess the lowest water of consistency value 23%. Hence, by increasing firing temperature the water/cement ratio decreases.

Compressive strength

The compressive strength of cement mortar is considered to be one of the most important aspects of Pozzolanic Portland cement. Five representative mixes were chosen to study the influence of the replacement PG (at different temperatures) on the compressive strength. Figures 1-5 showed the relation between compressive strength and curing time at different percentage of PG, the trend of the strength increases by curing time, therefore, the pastes of hardened made from PPC and PG treated at 1000 °C have strength at 3, 7, 28, 90 days higher than blank sample. It was clear that, compressive strength values increased by increase the firing temperature, this is due to calcinations of lime presence in PG at 1000 °C which causes development in the strength and the strength depends primarily on the formation of hydrated calcium silicate as the main hydration product, which is precipitated into the water filled spaces to form a more compact body. This is mainly attributed to crystallization of the initially formed hydrates, having strong binding forces and/or their transformation into other hydration products having weaker binding forces. Finally, Mix PPV containing 5% thermally treated PG at 1000 °C possesses the highest compressive strength value after 90 days curing.

Table 3. Setting time from mixes (PPC-PPV) containing thermally treated PG at different temperature

Mix	200 °C		400 °C		600 °C		800 °C		100 °C	
	Initial (min)	Final (min)								
PPI	335	425	350	430	330	440	200	285	180	265
PPII	460	600	560	640	610	730	205	290	190	270
PPIII	720	840	630	720	740	810	220	310	200	270
PPIV	780	860	680	740	750	815	215	275	205	280
PPV	730	810	715	830	605	700	210	300	200	265
PPC	185	255								

Bulk density and total porosity

Figures 6-10 illustrated the bulk density of the hardened pastes containing calcined PG at different temperatures as a function of curing time. Clearly, at different temperature the bulk density increases with longer hydration time for all samples, so the results of the bulk density progress at 90 days it's highest. On the contract, the compressive strength increases with decreases the total porosity, so when the compressive strength increases the total porosity decreases [28] and increases the bulk density this is due to hydration products fill parts of the total pore volumes. Porosity can govern the properties of the materials, especially affecting material strength. High porosity will result in low material strength, whereas decreasing porosity can enhance material strength [29]. The results in Figures 11-15 indicate that the total porosity for all samples PPC contain firing PG at different temperature decrease gradually for long time, the results for all samples possess higher porosity at 3 days, on the other hand the lowest total porosity at 90 days [30]. Generally, the results show that for all pastes

at all ages, the porosity decreased as the curing age increased, this is due to the filling up of a part of the available pore volume with the hydration products, as the hydration proceeds.

Chemically combined water content (%)

According to Figures 16-20 the chemically combined water content of hardened specimens made from PPC which contain PG treated at 200, 400, 600, 800 and 1000 °C increases by increasing curing time, the results of hydration kinetics indicated that chemically-combined water contents increases with increasing age of hydration for all types of hardened PPC-PG pastes. Mix PPI (70% PCC: 25% Poz: 4% RG: 1% PG treated at 200 °C) possesses higher combined water content values, while mixes PPIV and PPV (which contain PG treated at 1000 °C) possesses the lowest values. These results are in harmony with that obtained with respect to the compressive strength, bulk density and porosity results which indicated that mixes PPIV and PPV at 1000 °C have the highest values.

Figure 1. Compressive strength of hardened pastes made from mixes (PPC-PPV) containing thermally treated PG at 200 °C after 3, 7, 28 and 90 days curing

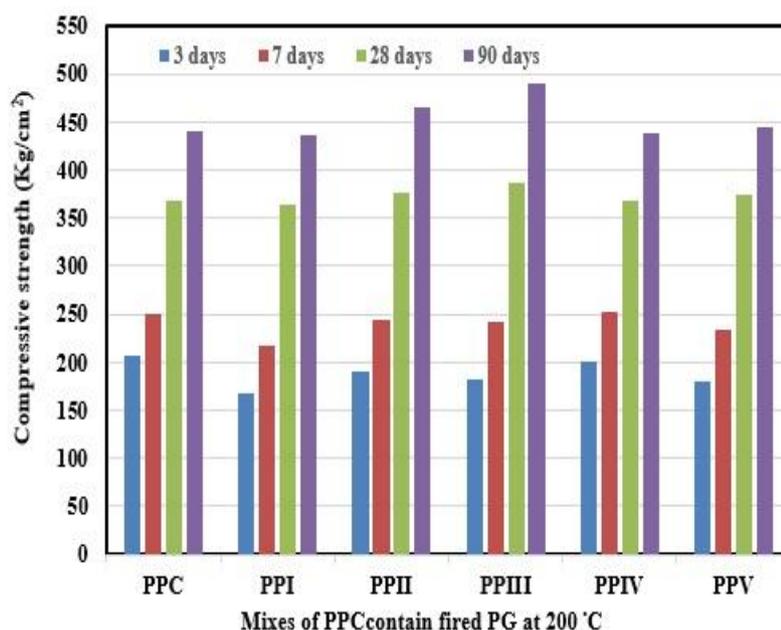


Figure 2. Compressive strength of hardened pastes made from mixes (PPC-PPV) containing thermally treated PG at 400 °C after 3, 7, 28 and 90 days curing

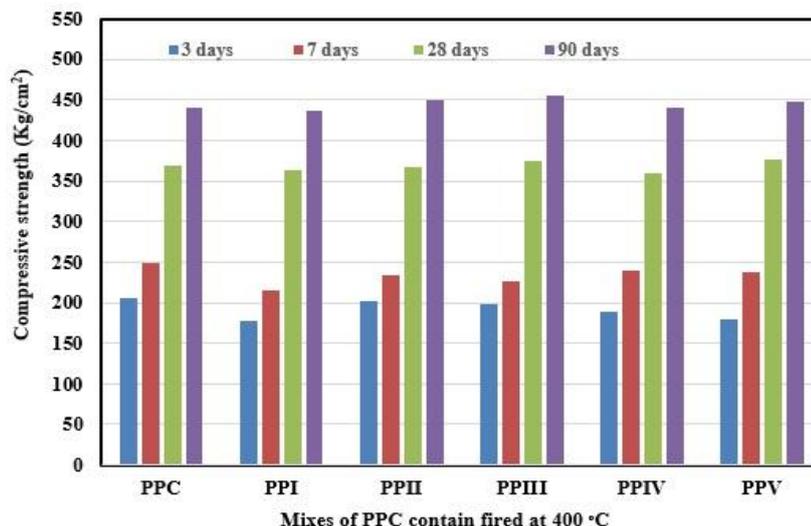


Figure 3. Compressive strength of hardened pastes made from mixes (PPC-PPV) containing thermally treated PG at 600 °C after 3, 7, 28 and 90 days curing

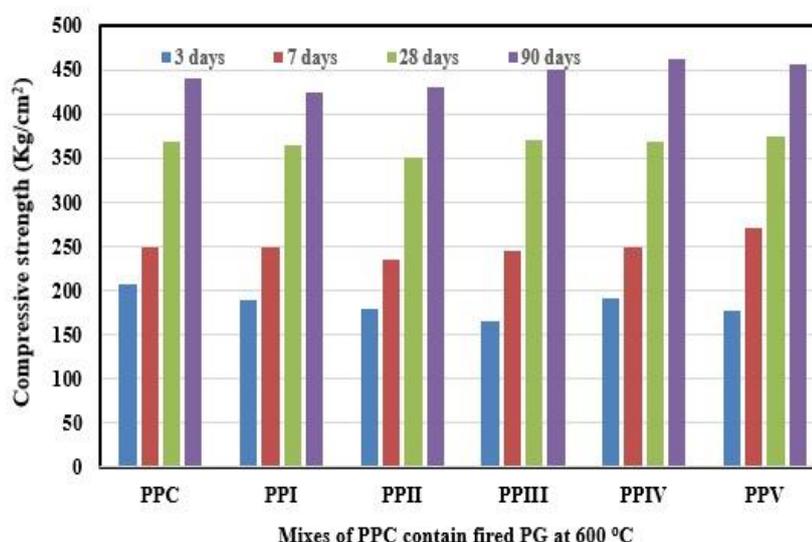


Figure 4. Compressive strength of hardened pastes made from mixes (PPC-PPV) containing thermally treated PG at 800 °C after 3, 7, 28 and 90 days curing

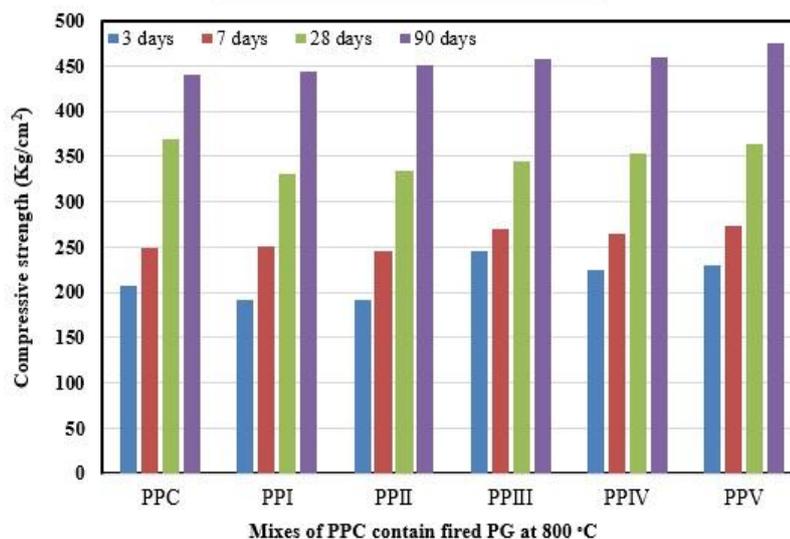


Figure 5. Compressive strength of hardened pastes made from mixes (PPC-PPV) containing thermally treated PG at 1000 °C after 3, 7, 28 and 90 days curing

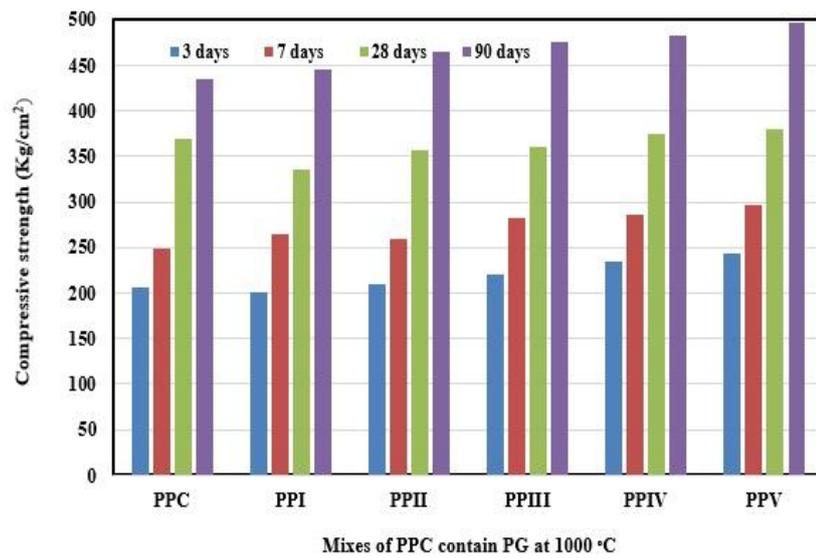


Figure 6. Bulk density (g/cm³) hardened pastes made from mixes (PPC-PPV) containing thermally treated PG at 200 °C after 3, 7, 28 and 90 days curing

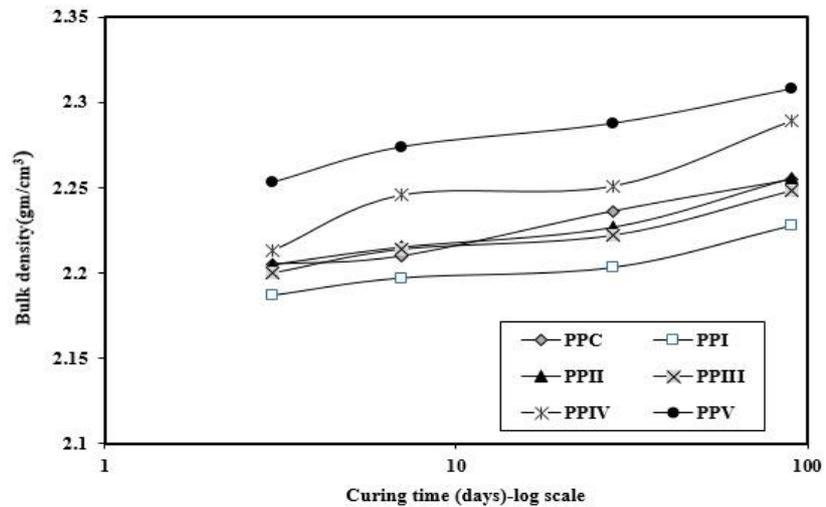


Figure 7. Bulk density (g/cm³) hardened pastes made from mixes (PPC-PPV) containing thermally treated PG at 400 °C after 3, 7, 28 and 90 days curing

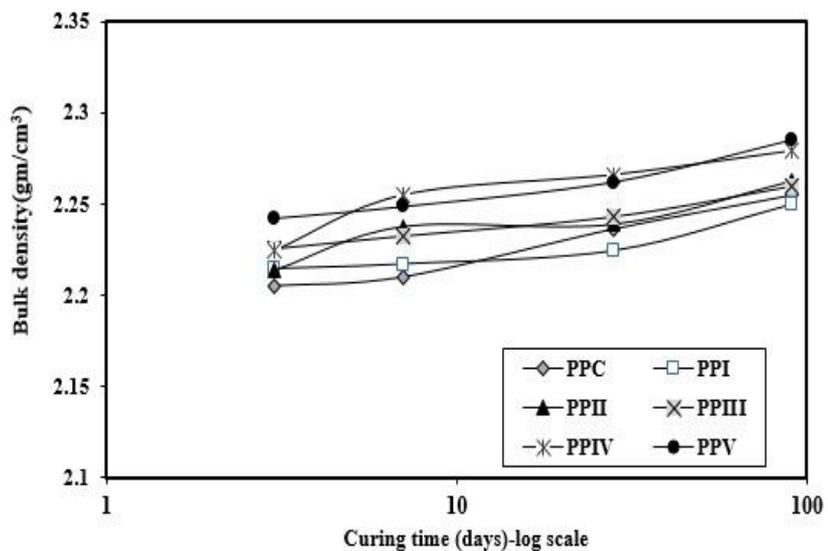


Figure 8. Bulk density (g/cm^3) hardened pastes made from mixes (PPC-PPV) containing thermally treated PG at $600\text{ }^\circ\text{C}$ after 3, 7, 28 and 90 days curing

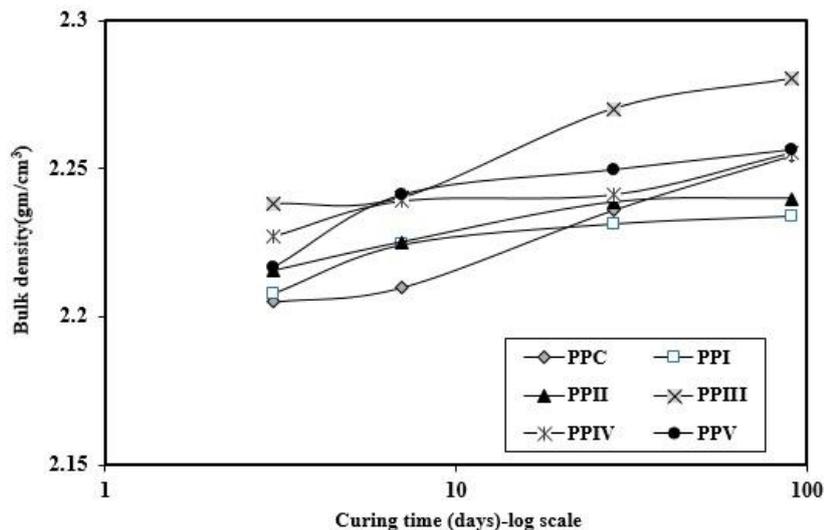


Figure 9. Bulk density (g/cm^3) hardened pastes made from mixes (PPC-PPV) containing thermally treated PG at $800\text{ }^\circ\text{C}$ after 3, 7, 28 and 90 days curing

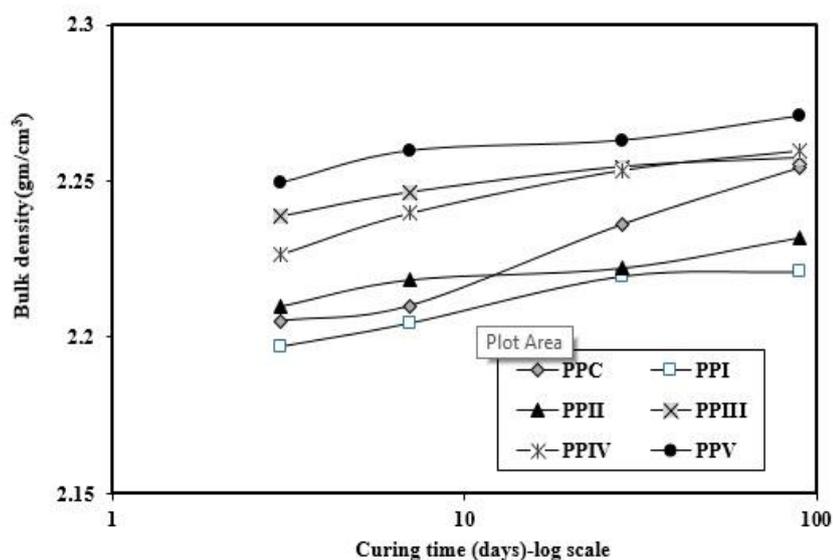


Figure 10. Bulk density (g/cm^3) hardened pastes made from mixes (PPC-PPV) containing thermally treated PG at $1000\text{ }^\circ\text{C}$ after 3, 7, 28 and 90 days curing

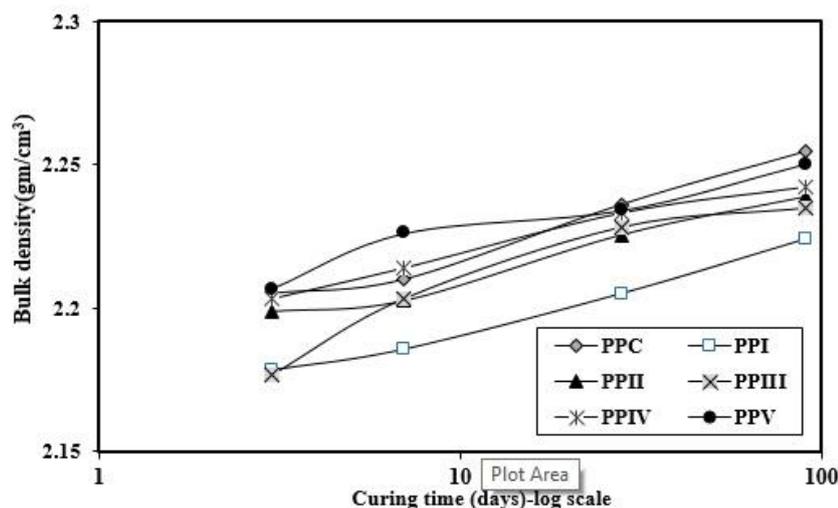


Figure 11. Porosity (%) hardened pastes made from mixes (PPC-PPV) containing thermally treated PG at 200 °C after 3, 7, 28 and 90 days curing

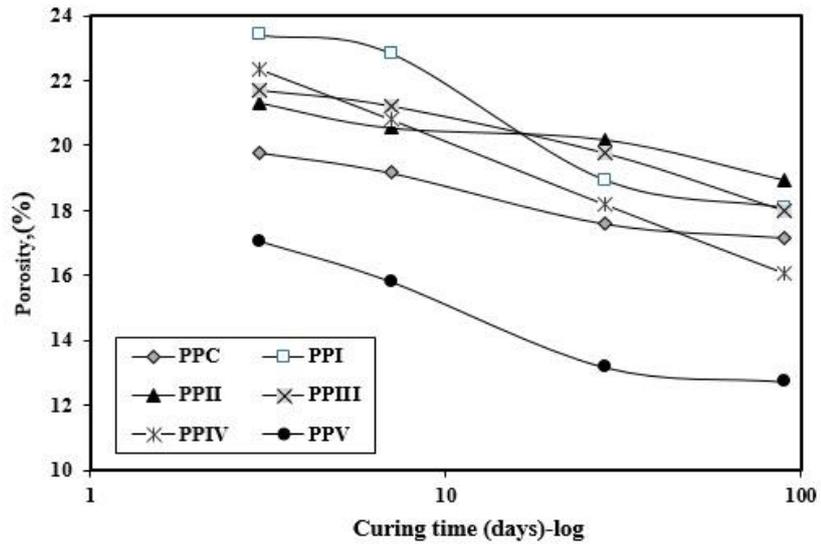


Figure 12. Porosity (%) hardened pastes made from mixes (PPI-PPV) containing thermally treated PG at 400 °C after 3, 7, 28 and 90 days curing

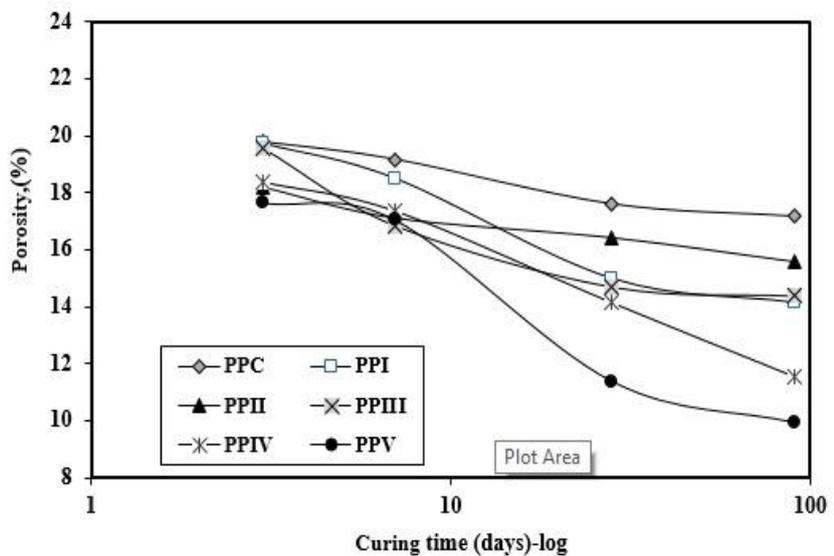


Figure 13. Porosity (%) hardened pastes made from mixes (PPC-PPV) containing thermally treated PG at 600 °C after 3, 7, 28 and 90 days curing

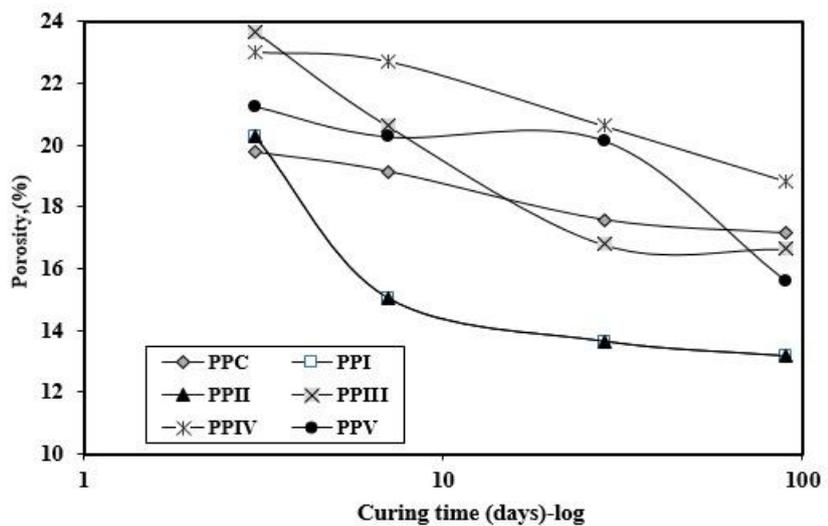


Figure 14. Porosity (%) hardened pastes made from mixes (PPC-PPV) containing thermally treated PG at 800 °C after 3, 7, 28 and 90 days curing

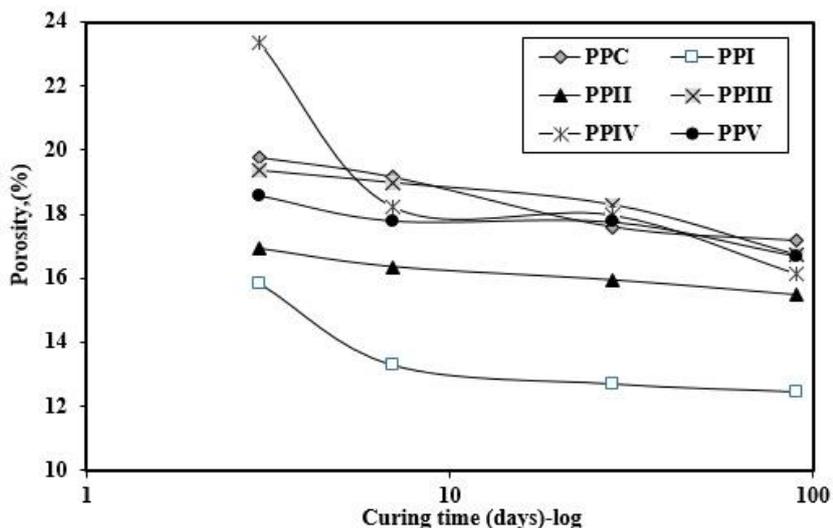


Figure 15. Porosity (%) hardened pastes made from mixes (PPC-PPV) containing thermally treated PG at 1000 °C after 3, 7, 28 and 90 days curing

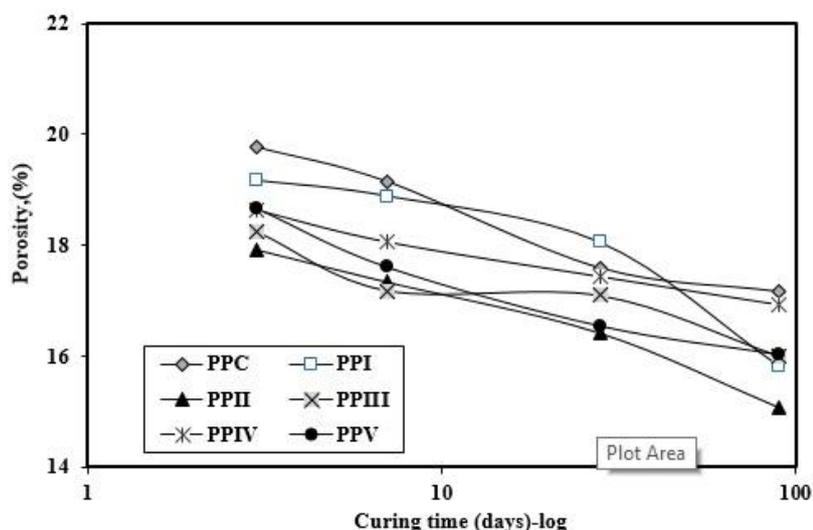


Figure 16. Chemically-combined water contents (Wn %) hardened pastes made from mixes (PPC-PPV) containing thermally treated PG at 200 °C after 3, 7, 28 and 90 days curing

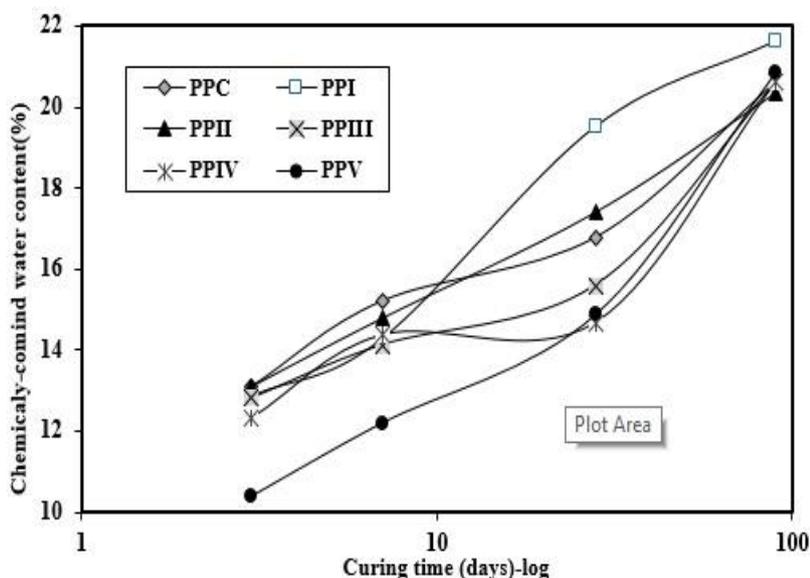


Figure 17. Chemically-combined water contents (Wn %) hardened pastes made from mixes (PPC-PPV) containing thermally treated PG at 400 °C after 3, 7, 28 and 90 days curing

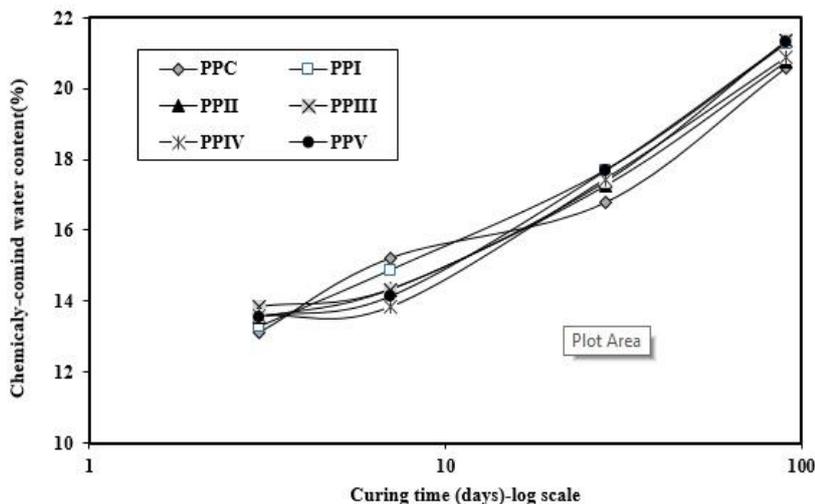


Figure 18. Chemically-combined water contents (Wn %) hardened pastes made from mixes (PPC-PPV) containing thermally treated PG at 600 °C after 3, 7, 28 and 90 days curing

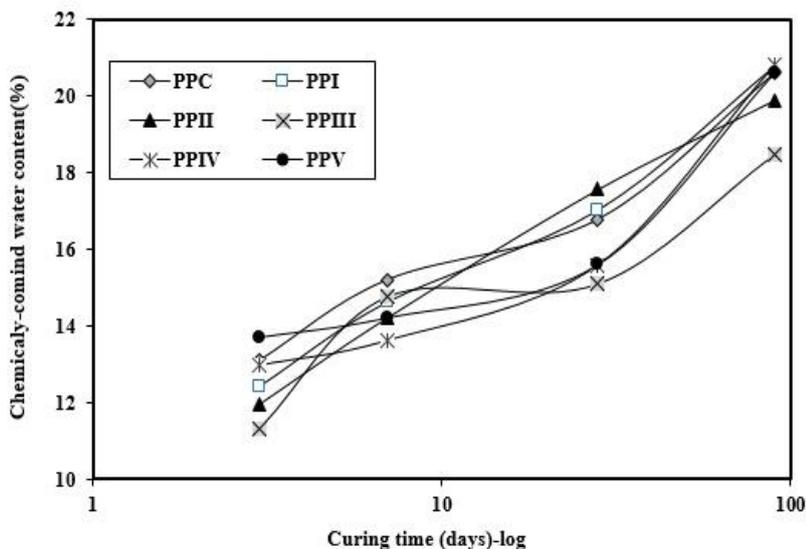


Figure 19. Chemically-combined water contents (Wn %) hardened pastes made from mixes (PPC-PPV) containing thermally treated PG at 800 °C after 3, 7, 28 and 90 days curing

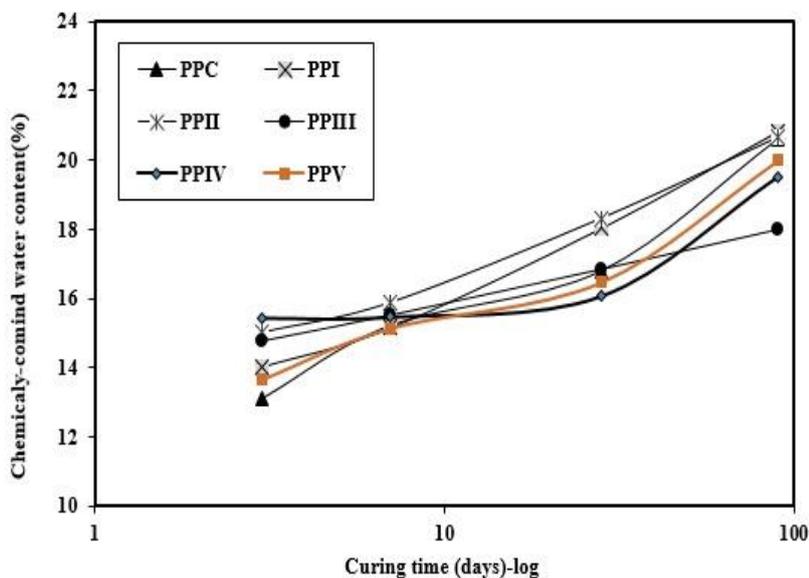
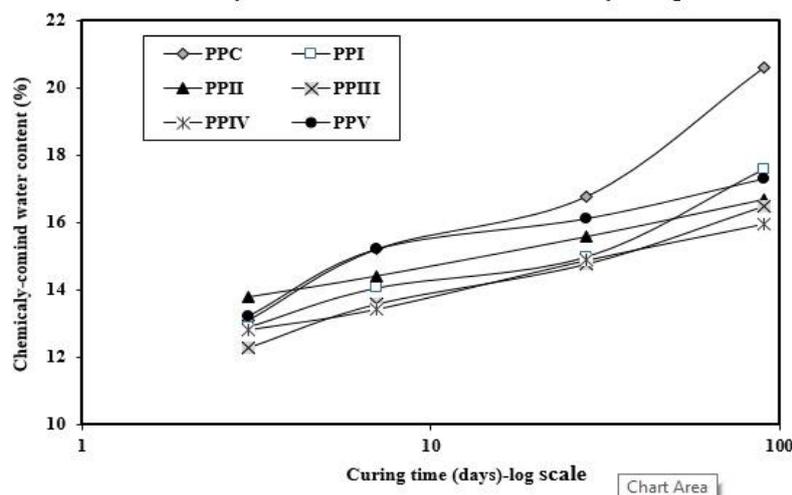


Figure 20. Chemically-combined water contents (W_n %) hardened pastes made from mixes (PPC-PPV) containing thermally treated PG at 1000 °C after 3, 7, 28 and 90 days curing



Free lime (CaO %)

The results of free lime contents indicated that the free lime was consumed gradually with increasing age of hydration for all types of the hardened PPC-PG pastes. The free lime increased with increasing PG contents in PPC-PG pastes. Free lime content increases by increasing thermal treatment of PG also increasing by PG content, so mix PPV (70% PCC: 25% Poz: 5% PG treated at 1000 °C) possesses the higher free lime values at all pastes and all time of curing and mix PPIII (70% PCC:25% Poz: 2% RG: 3% PG treated at 800 °C) possess the lowest free lime values this is due to PG containing % of P_2O_5 (6.79%: 2.35%) respectively, this lead to completely decomposition clinker phases especially C3S phase into α 'H-C2S and free lime content phases [30].

FTIR analysis

Figure 26 showed the IR analysis of hardened pastes made from PPC-RG after 3, 28 and 90 days curing to identify the phases coexisting during hydration process. It is clear that, there is a sharp band at 3646 cm^{-1} and 1460 cm^{-1} due to formation of C_2S accompanied by liberation of lime [31], weak bands at 1650 cm^{-1} and 875 this is due to partial carbonate of unreacted lime, broad band at 970 cm^{-1} (vibration of SiO_4 groups)

[32] and the weak intensity band at 470 cm^{-1} is attributed to Si-O bending mode [33]. Figure 27 illustrated the IR spectra of hardened pastes of mix PPV contain PG thermally treated at 200 °C after 3, 28 and 90 days curing. As hydration progresses, the following bands are observed the intensity of the band at 3650 cm^{-1} increases indicating liberation of more $Ca(OH)_2$ the broad band at 3420 cm^{-1} are intensified with hydration, indicating that the increase of hydrated products associated with water and the strong asymmetric stretching Si-O band (ν_3) is shifted to high frequencies centered at 970 cm^{-1} with hydration indicates that the formation of C-S-H [34]. The decrease and increase in intensities of the out-of-plane and in-plane Si-O bending vibrations are occur in significant changes with hydration and it indicates SiO_4 units in cement at 510 cm^{-1} . The IR analysis of hardened pastes of mix PV contain PG treated at 600 °C after 3, 28 and 90 days curing are shown in Figure 28 shows a sharp band at 3645 cm^{-1} associated to O-H stretching vibrations of portlandite ($Ca(OH)_2$) and the peaks at 3420 and 1640 cm^{-1} are correspond to stretching and bending modes of water of crystallization particularly. The carbonates peak at 1470 cm^{-1} and 876 cm^{-1} are observed due to the reactions of atmospheric CO_2 with calcium hydroxide. The broad band at 976 cm^{-1} is due to Si-O asymmetric stretching

vibration of C3S and/or C2S and very weak band at 465 cm^{-1} is attributed to Si-O bending mode [35]. As far as we are aware, spectroscopic of hardened pastes of mix PPV contain PG thermally treated at $1000\text{ }^{\circ}\text{C}$ after

3, 28 and 90 days curing. Different bands appear at intensities $3644, 3460, 1655, 1455, 967, 874$ and 466 cm^{-1} which were illustrated before.

Figure 21. Free lime contents (CaO %) hardened pastes made from mixes (PPI-PPV) containing thermally treated PG at $200\text{ }^{\circ}\text{C}$ after 3, 7, 28 and 90 days curing

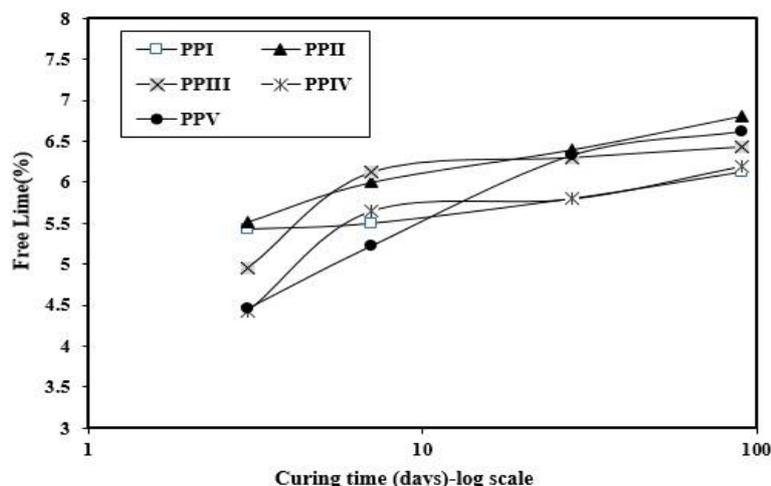


Figure 22. Free lime contents (CaO %) hardened pastes made from mixes (PPI-PPV) containing thermally treated PG at $400\text{ }^{\circ}\text{C}$ after 3, 7, 28 and 90 days curing

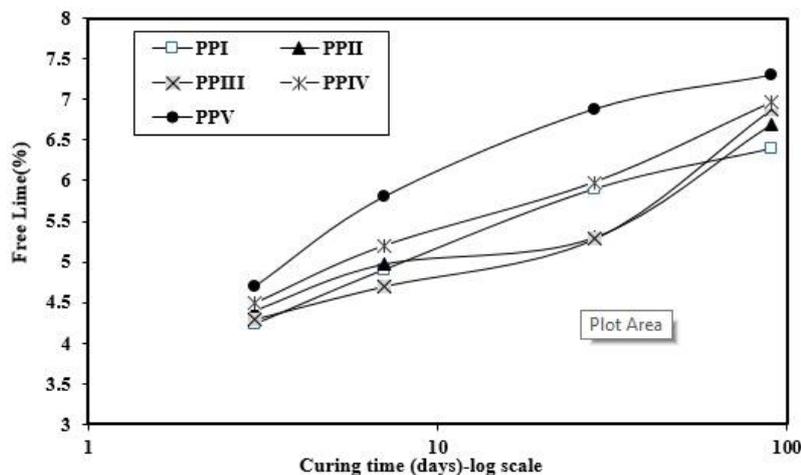


Figure 23. Free lime contents (CaO %) hardened pastes made from mixes (PPI-PPV) containing thermally treated PG at $600\text{ }^{\circ}\text{C}$ after 3, 7, 28 and 90 days curing

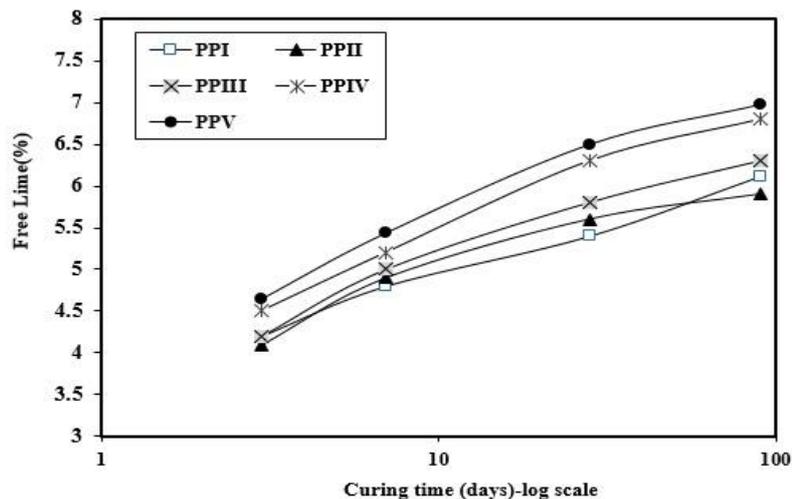


Figure 24. Free lime contents (CaO %) hardened pastes made from mixes (PPI-PPV) containing thermally treated PG at 800 °C after 3, 7, 28 and 90 days curing

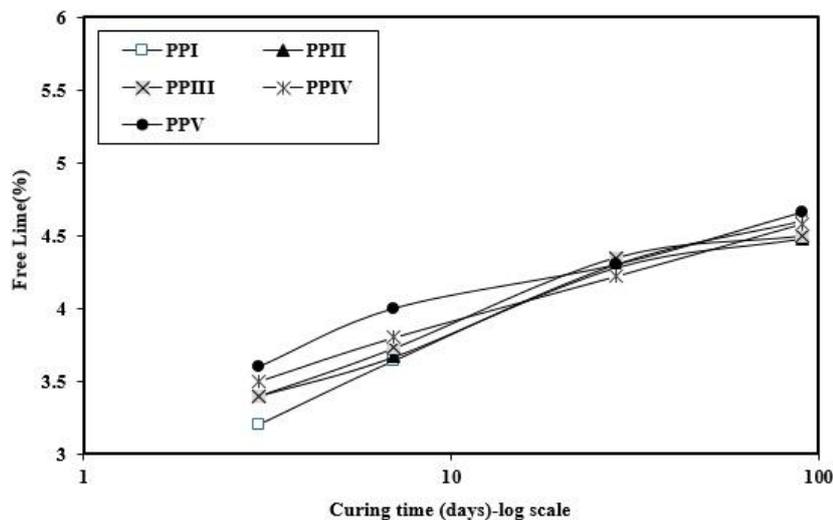


Figure 25. Free lime contents (CaO %) hardened pastes made from mixes (PPI-PPV) containing thermally treated PG at 1000 °C after 3, 7, 28 and 90 days curing

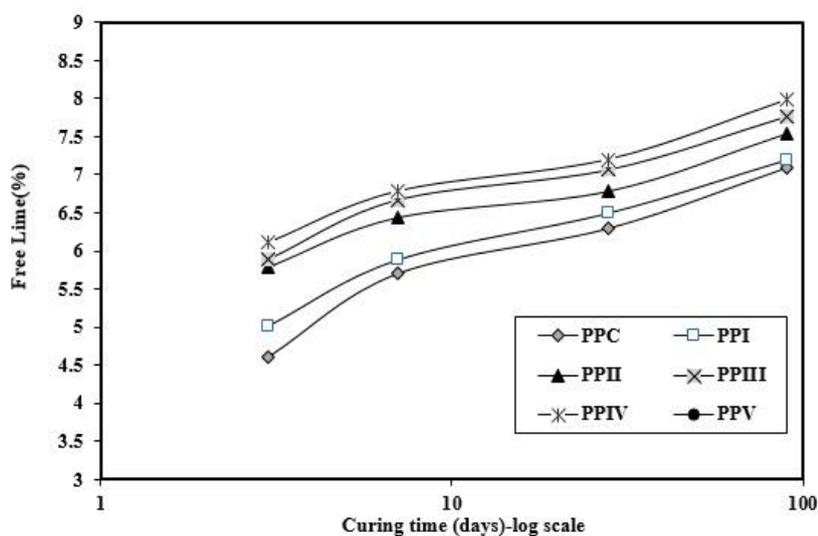


Figure 26. IR spectra of hardened pastes of PPC with RG after 3, 28 and 90 days curing

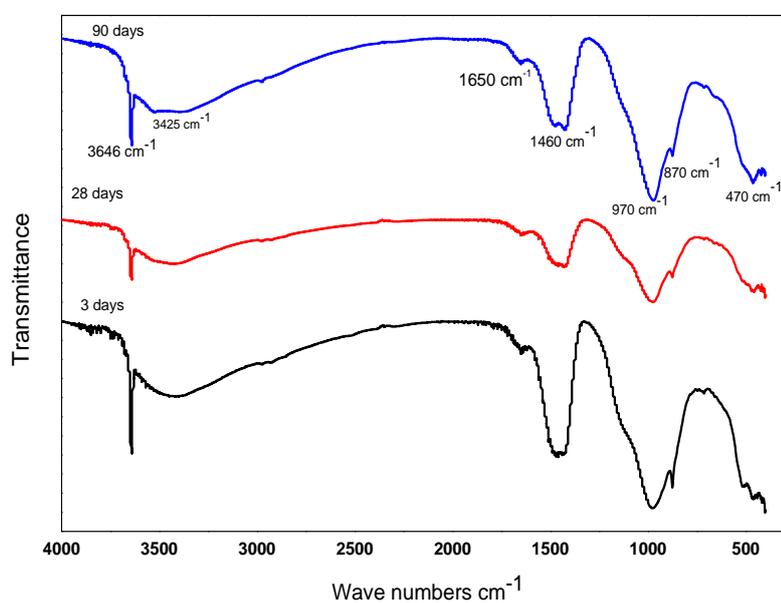


Figure 27. IR spectra of hardened pastes of mix PPC contain PG treated at 200 °C after 3, 28 and 90 days curing

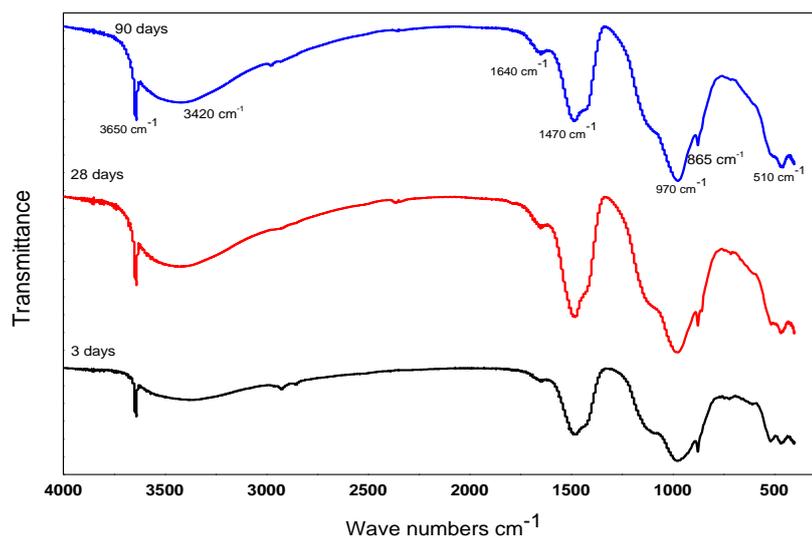


Figure 28. IR spectra of hardened pastes of mix PPC contain PG treated at 600 °C after 3, 28 and 90 days curing

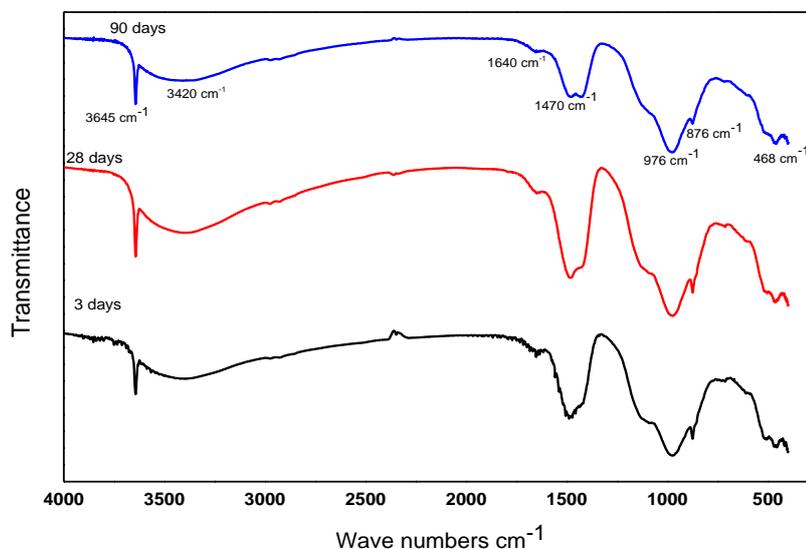
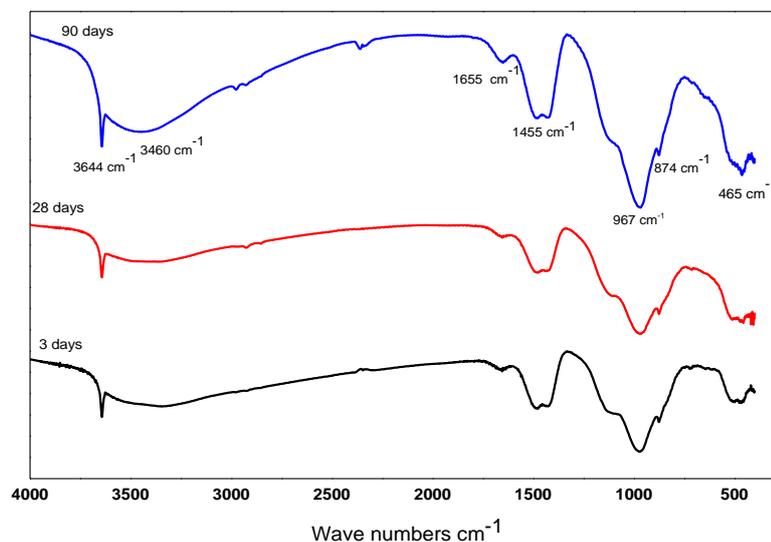


Figure 29. IR spectra of hardened pastes of mix PPC contain PG treated at 1000 °C after 3, 28 and 90 days curing



Morphology and Microstructure

The effect of thermally treated PG at different temperatures on the morphology and microstructure of prepared PPC pastes was analyzed under scanning electron microscope. Hardened specimens of mix PPV contain treated PG at 200, 600 and 1000 °C after 3, 28 and 90 days curing, their SEM micrograph are shown in Figures 30-33. Figure 30a illustrated the micrograph of pastes contain raw gypsum and formation of various hydration products after 3 days a large amount of hexagonal $\text{Ca}(\text{OH})_2$ crystals and C-S-H are generated after the reaction of C3S with water. By continuous hydration process at Figure 30b the micrograph indicated formation of more compact structure composed mainly of calcium silicate hydrates compared to the micrograph formation of amorphous hydrates and a massive structure of ill-crystallized CSH. The microstructure obtained after 90 days curing of PPC- RG, showed in Figure 30c a dense structure and more rod like of nearly amorphous CSH and ettringite ($\text{C}_3\text{A}\cdot 3\text{CS}\cdot 32\text{H}_2\text{O}$) as representing the main hydration products. On the contract, hardened specimens of mix PPV contain treated PG at 200,600 and 1000 °C after 3, 28

and 90 days curing, their SEM micrograph are shown in Figures 31-33. The SEM micrographs displayed the formation of various hydration products after 3 days a large amount of $\text{Ca}(\text{OH})_2$ crystals are generated after the reaction of C3S with water, the generation of $\text{Ca}(\text{OH})_2$ and C-S-H was observed. These are generated from the chemical bonding involving Ca^{2+} around the C3S particle. The hydration microcrystalline crystals of monosulfate ($\text{C}_3\text{A}\cdot\text{CS}\cdot 12\text{H}_2\text{O}$) and some calcium silicate hydrates (CSH), fibrous crystals of ettringite ($\text{C}_3\text{A}\cdot 3\text{CS}\cdot 32\text{H}_2\text{O}$) and Calcium hydroxide $\text{Ca}(\text{OH})_2$. By continuous hydration of the pastes PPC-PG after 28 days the ettringite crystals are much and leads to changes in the morphology of the surface from hexagonal shape to more ettringite crystals. At 90 days, the hydration is decreasing in the porosity and formation of amorphous and ill-crystalline phase indication increases the hydraulic properties of the pastes which there is increasing in the amorphous and ill-crystalline phase with formation of closed texture phase indication increases the hydraulic properties of the pastes. These results are in a good agreement with the obtained physico-chemical measurements of OPC-PG pastes [35].

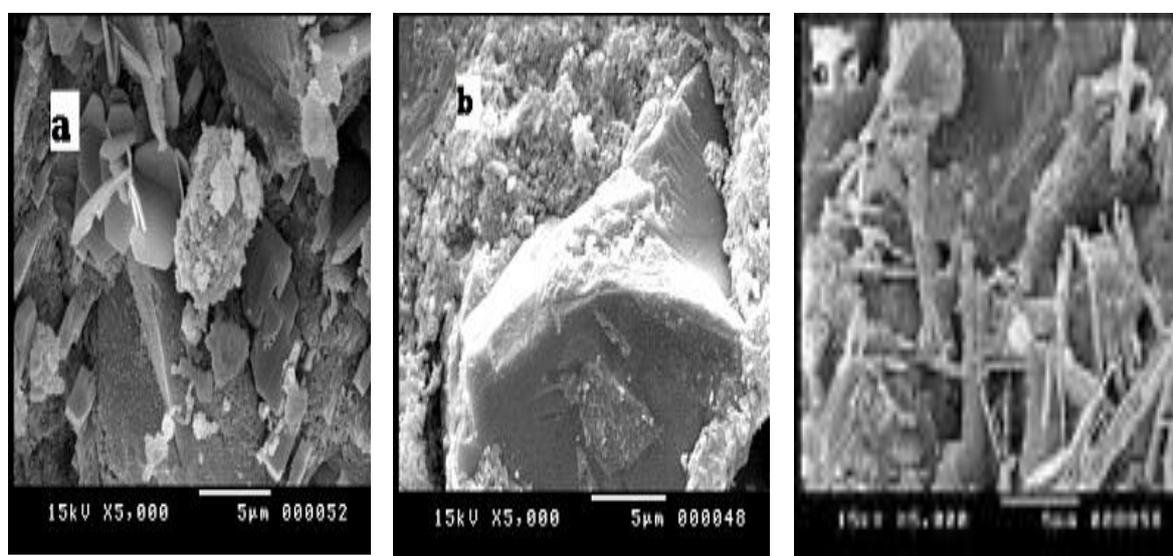


Figure 30. Micrographs of mixes (PPC) contain RG after 3 (a), 28 (b) and 90 (c) days curing

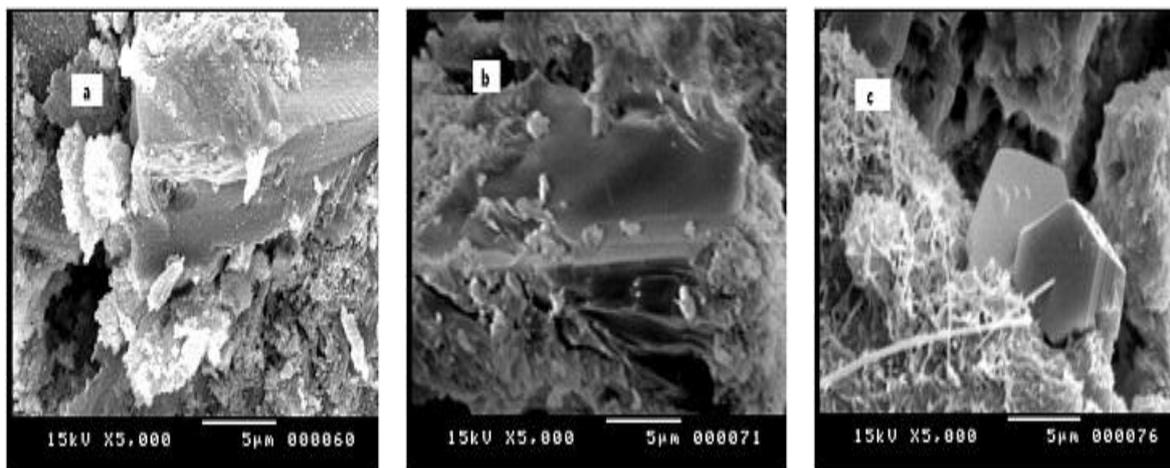


Figure 31. Micrographs of mixes (PPV) contain thermally treatment PG at 200 °C after 3 (a), 28 (b) and 90 (c) days curing

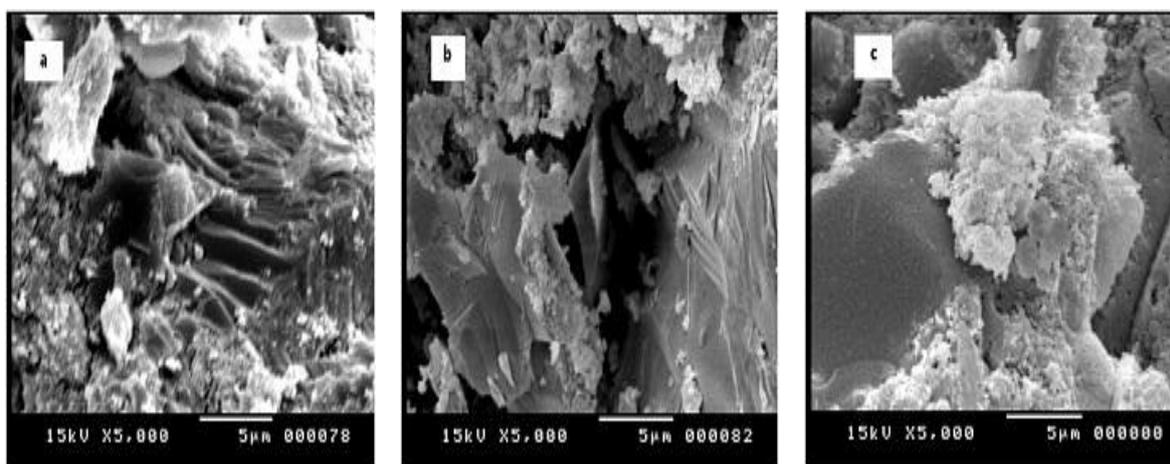


Figure 32. Micrographs of mixes (PPV) contain thermally treatment PG at 600 °C after 3 (a), 28 (b) and 90 (c) days curing

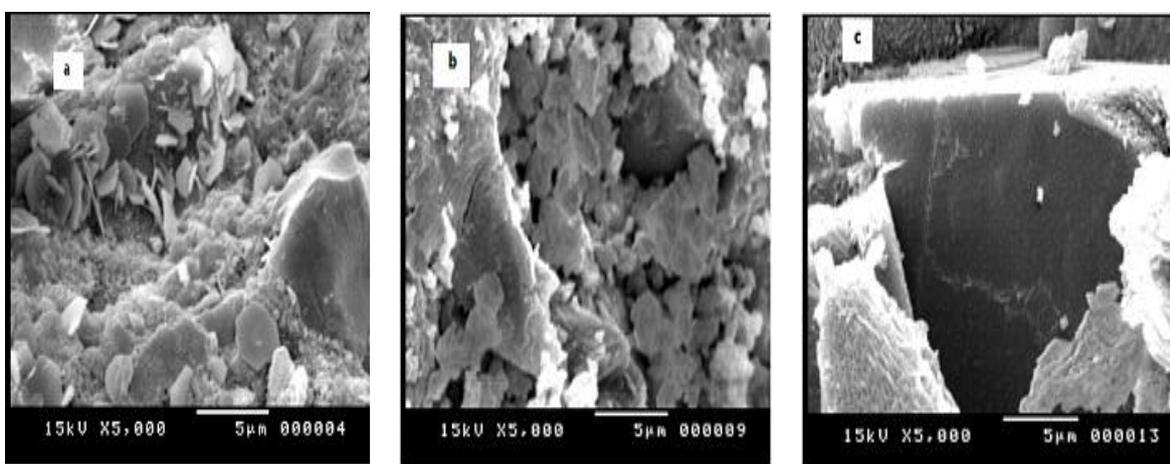


Figure 33. Micrographs of mixes (PPV) contain thermally treatment PG at 1000 °C after 3 (a), 28 (b) and 90 (c) days curing

Conclusion

As a measure to save resources and energy and reuse industrial byproducts in the cement industry, this study evaluated the basic properties of PPC using industrial byproducts. The results are as follows:

- 1-Phosphogypsum can be economically used up to five percent as an ingredient in Ordinary Portland cement, This will eliminate a serious environmental source of pollution; besides, it will decrease the cost of cement production. It is also recommended that further investigations be executed to explore the possibility of extracting gypsum from PG that can be used directly in cement industry.
- 2-The addition of treated PG at different temperature leading to improvement of physio-chemical properties.
- 3- The present study revealed a good efficiency of PG as a set retarder in Pozzolan Portland Cement, utilization calcined PG at 800 and 1000 °C causes the setting time improvement.
- 4-The purified phosphogypsum can be used for the production of gypsum in cement manufactory due to solve the serious negative environmental impacts caused by the dispersion of the harmful chemicals contained in PG into surrounding environment.

Acknowledgment

Thanks are due to the Manaseer Cement Factory for the execution of these experiments.

References

- [1]. K. Friedhelm, K. Juergen, B. Marcel, Seminar on the utilization of phosphogypsum to produce cement and sulphuric acid, in: Proceedings, National Bureau and Veb Industrie-Consult Berlin, Istanbul – Turkey, **1987**, p. 17.
- [2]. A. Nanni, W.F. Chang, *Concrete Int.*, **1989**, *11*, 48-53.
- [3]. E. Erdem, H. Ölmez, *Cem. Concr. Res.*, **1993**, *23*, 115-121.
- [4]. J. Bijen, E. Niël, *Cem. Concr. Res.*, **1981**, *11*, 307-322.
- [5]. H. Ölmez, E. Erdem, *Cem. Concr. Res.*, **1989**, *19*, 377-384.
- [6]. H. Ölmez, V.T. Yilmaz, *Cem. Concr. Res.*, **1988**, *18*, 449-454
- [7]. D.K. Dutta, P.C. Borthakur, *Cem. Concr. Res.*, **1990**, *20*, 711-722.
- [8]. S. Al-Jabbari, F. Faisal, S. Ali, S. Nasir, *J. Build. Res. Sci. Res. Council Baghdad*, **1988**, *7*, 49-69.
- [9]. H.F.W. Taylor, *Cement Chemistry*. Thomas Telford Edition, London, **1997**, pp. 480.
- [10]. M.M. Smadi, R.H. Haddad, A.M. Akour, Potential use of phosphogypsum in concrete”, *Cem. Concr. Res.*, **1999**, *29*, 1419 - 1425.
- [11]. S. Manjit, *Cem. Concr. Res.*, **2002**, *32*, 1033-1038.
- [12]. S. Manjit. *Cem. Concr. Res.*, **2003**, *33*, 1363-1369.
- [13]. S. Manjit. Role of phosphogypsum impurities on strength and microstructure of selenite plaster." *Construct. Build. Mater.*, **2005**, *19*, 480-486.
- [14]. J.H. Potgieter, S.S. Potgieter, R.I. McCrindle, C.A. Strydom, *Cem. Concr. Res.*, **2003**, *33*, 1223-1227.
- [15]. L. Kacimi, A. Simon-Masseron, Z. Derriche, *J. hazard. Mater.*, **2006**, *137*, 129-137.
- [16]. M.A. Bagade, S.R. Satone, *Int. J. Eng. Res. Appl.*, **2012**, *2*, 785-787.
- [17]. N. Ghafoori, W.F. Chang. *J. Mater. Civil Eng.*, **1993**, *5*, 249-264.
- [18]. K.T. Lin, W.F. Chang, Strength properties of compacted phosphogypsum-based mixtures, Volume II. In proceedings of the second International symposium on phosphogypsum, University of Miami, Florida Institute of Phosphate Research, Bartow, Florida, **1988**, pp. 239-254.
- [19]. M.A. Taher, *Resources, Conservat. Recycl.*,

2007, 52, 28-38.

[20]. T. Reddya, D. Siva Sankar, R. Kumarb, H. Sudarsana Raoc. *Asian J. Civil Eng.*, **2010**, 11, 411-420.

[21]. Z. M. Lan, X. J. Lin & F. Wang & H. Zhang & C. R. Chen, *Biol. Fertil. Soils*, **2012**, 48, 579-588.

[22]. P.Y., Han, X.L., Jiao, Wang, L.G., Dong, E.W., J.S Wang, *Chin. J. Eco Agric.* **2010**, 18, 482-485.

[23]. A. Roy, G.P. Byerly, R.K. Seals. *J. Mater. Civil Eng., ASCE* 6, **1994**, 4, 439-445

[24]. British European Standard BS EN-196-3: Methods of testing cement. Determination of setting times and soundness, **2005**.

[25]. M. Abd El Aziz, S. Abd El Aleem, M. Heikal, H. El Dizdamony, *Cem. Concr. Res.*, **2005**, 35, 1592-1600.

[26]. M.A.E. Aziz, S.A.E. Aleem, M. Heikal, H.E. Didamony, *Cem. Concr. Res.*, **2005**, 35, 1592-1600.

[27]. M.P. Javellana, I. Jawed. *Cem. Concr. Res.*, **1982**, 12, 399-403.

[28]. Z. Mingkai, S. Weiguo, W. Shaopeng, Z. Qinglin, *Adv. Build. Technol.*, **2002**, 1, 929-934.

[29]. I.A. Altun, Y. Sert. *Cem. Concr. Res.*, **2004**, 34, 677-80.

[30]. M.N. De Noirfontaine, S. Tusseau-Nenez, M. Signes-Frehel, G. Gasecki, C. Girod-Labianca. *J. Am. Ceramic Soc.*, **2009**, 92, 2337-2344.

[31]. F.A. Rodrigues P.J.M. Monteiro, *J. Mater. Sci. Lett.*, **1999**, 18, 1551-1552

[32]. W. Eitel, *Silicate Science, Volume I: Silicate Structures*, Academic Press, New York, NY, **1964**, USA.

[33]. Y.M., Mollah, A., Palta, T.R., Hess, R.K., Vempati, D.L. Cocke, *Cem. Concr. Res.*, **1995**, 25, 671-682.

[34]. D. Govindarajan, R. Gopalakrishnan. *Front. Sci.*, **2011**, 1, 21-27

[35]. P. Meredith, A.M. Donald, N.Meller, C. Hall, *J. Mater. Sci.*, **2004**, 39, 997-100.

How to cite this manuscript:

Mahmoud. A. Taher, Adel. M. Amine, Bassam Kh. Damarany*. Effect of Partial Substitution of Raw Gypsum with Thermally Treated Phosphogypsum on the Properties of Portland Pozzolanic Cement, *Adv. J. Chem. A*, **2019**, 2(4), 296-315.