Pergamon

CEMENT AND CONCRETE RESEARCH

Cement and Concrete Research 29 (1999) 1419–1425

Potential use of phosphogypsum in concrete

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Received 28 May 1998; accepted 11 May 1999

Abstract

An experimental study was conducted to investigate the potential use of phosphogypsum (PG) in concrete. This was accomplished by preparing mortar mixes at a water/cement ratio of 0.6 using two types of cement, ordinary Portland cement (OPC) and pozzolanic Portland cement (PPC), and two types of fine aggregate, natural river sand and limestone. These mixes were prepared at different replacements (by weight) of PG and purified PG ranging from 10–100%. The purified PG was obtained by calcining PG (washed in water and not washed) at temperatures of 170, 600, 750, 850, and 950°C. The compressive, tensile, and flexural strengths of different hardened mortars were obtained following 3, 7, and 28 days of curing in air and in a moist room. In addition, the setting time and the soundness of cement pastes, prepared using OPC and PPC at a water/cement ratio of 0.6 and at different replacements of PG, were evaluated. At a particular PG percentage of replacement, the results indicated an increasing trend in strength gain over curing time. The strengths of mortars, cured for a specific time, showed a decrease in the strength with further replacement with PG. The purification process, by heating PG up to 900°C, has resulted in improving the strengths of the mortar mixes. The highest percentage increase in strength was found to be for PG calcined at temperatures of 850 and 900°C. The incorporation of PG in the cement paste has dramatically increased its initial and final setting times and has increased the percentage elongation of paste prisms used to evaluate the soundness. The improvement in strength upon calcination is primarily due to the formation of anhydrate at higher temperatures, which subsequently hydrates to gypsum; the latter has some cementing value.

Keywords: Gypsum; Sulfate; Expansion; Mechanical properties; X-ray diffraction

1. Introduction

Phosphogypsum (PG) is a by-product resulting from the phosphoric acid process for manufacturing fertilizers. It consists mainly of $CaSO_4 \cdot 2H_2O$ and contains some impurities such as P_2O_5, F^-, and organic substances. 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. Yet, caution should be exercised when using blends of Portland cement with gypsum due to the high possibility of volume instability (expansion) caused by the formation of ettringate once the concrete or mortar has hardened.

The remaining 85% of PG is not used, causing an environmental problem and creating a 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, supersulfated cement, and high alumina cement, as well as in ordinary concrete, has been investigated [2–9].

PG has been used in roller-compacted concrete (RCC) to construct parking facilities [2]. The results indicated that PG, without being detrimental to strength, contributed to good mix compaction and surface finish as a result of its fine grading. Using PG in RCC has proven to be beneficial due to: (a) the improvement in bonding at construction joints as a result of PG set retardation action, and (b) the reduction in the occurrence of cracking when saw cut joints are not provided, due to drying shrinkage compensation by the PG.

Using PG in supersulphated cement (SSC) has resulted in shortening its setting time without affecting its ultimate strength. Nevertheless, curing SSC in seawater has resulted in reducing its ultimate strength compared to that of specimens cured in drinking water [3,4].

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PII: S0008-8846(99)00107-6

The effects of PG and purified PG (washed with milk of lime or water) on the hydration of Portland cement and trass cement were investigated by measuring the setting time and the strength of pastes, as well as performing chemical analysis and scanning electron microscopic (SEM) on the hydration products [5]. It was concluded that PG can be used as a retarder directly in trass cement, whereas it should be purified before being used in Portland cement.

In another study, Ölmez and Yilmaz [6] washed PG in water or milk of lime, then exposed it to thermal treatments at 140–150°C for 30 min and at 130–150°C for 60 min to improve its chemical and physical properties. The results showed that all of the water-soluble impurities can be removed by the simple washing treatment with water or milk of lime, but the P_2O_5, substituted in the crystal lattice of PG, and other impurities cannot be removed by the washing process and needed a thermal treatment. The amount of impurities in PG was evaluated using the infrared spectroscopy technique.

The role of anhydrite in activating low-lime high-alumina granulated blast furnace slag has been investigated with the objective of producing supersulphated slag cement [7]. The optimum amount of anhydrite required for the purpose was found to be in the range of 15–20%. The study indicated that: (a) ettringite and calcium-silicate hydrates are the major hydration products and that the maximum quantity of ettringite is formed in the early ages of hydration; and (b) the strength gain in the later ages of hydration is attributed to the formation of calcium-silicate-hydrates.

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, 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, sieving on no. 100 sieve, then neutralizing with calcium hydroxide.

Roy et al. [9] 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 ($<4.5\%$).

The present work summarizes the findings of a comprehensive study [10] conducted to investigate the potential of using PG, produced as a by-product of the Jordanian phosphate industry, in concrete. This includes studying the compressive, tensile, and flexure strengths of mortars prepared at a water/cement (w/c) ratio of 0.6 at different replacements of PG and purified PG. The effect of using PG on the initial and final setting times and the soundness of pastes, made at a w/c ratio of 0.6 at different replacements of PG, was evaluated. The PG was purified by two methods: washing and unwashing with water then calcining at temperatures of 170, 600, 750, 850, and 950°C. Two types of cements were used, ordinary Portland cement (OPC) Type I and pozzolanic Portland cement (PPC) with two types of aggregate, crushed limestone, and natural river sand. Two curing methods were applied: dry (in laboratory air) and moist (in a moist room at 23°C).

2. Experimental

2.1. Materials

In studying the potential for using PG in concrete on the latter's strengths and fresh properties (consistency, setting time, and expansion) two types of cements, OPC and PCC with two types of aggregate, crushed limestone (L) aggregate, and natural river sand (NS) were used to prepare mortar mixes. These were prepared at a w/c ratio of 0.6 and at total cement to aggregate ratios of 1:2.75, 1:3, and 1:2.75 for compression, tension, and flexure specimens, respectively. Drinking water was used to prepare different pastes and mortars. Jordanian PG (from Jordan Phosphate Mines Co. Ltd, Aqaba, Jordan) was used at different replacements (by weight) of cement, from 10 to 100% at increments of 10%. The gradation of both types of fine aggregate meets the ASTM standards specification C33-90. The bulk specific gravities (dry) and absorptions of the NS and L were found to be 2.62 and 2.56, and 1 and 2.24%, respectively. The chemical compositions of the two cements are listed in Table 1.

2.2. Experiments on pastes

Paste mixes were prepared at a 0.6 w/c with different replacements of PG and were tested for setting time and soundness. Initial and final times of setting were measured by the Vicat apparatus (Controls, Milano, Italy) according to test method C191. The soundness of hardened cement paste is evaluated according to ASTM test method C151 by measuring percent elongation of the paste after autoclaving.

Table 1
Chemical composition and fineness of OPC and PPC

	CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	MgO	Na_2O	K_2O	LOI	SS
OPC (%)	62.0	19.7	5.4	2.9	3	3.5	0.13	0.8	1.6	354
PPC (%)	56.0	21.4	6.2	3.8	2.9	4.60	0.38	0.77	2.7	400

LOI, loss on ignition; SS, specific surface (m^2/kg).

Table 2
Results of setting times and soundness of pastes containing PG

	% expansion		Initial setting (min)		Final setting (min)	
% replacement	OP	PP	OP	PP	OP	PP
0	0.04	0.04	100	120	250	270
10	0.048	0.051	160	190	330	380
20	0.059	0.062	190	220	420	510
30	0.070	0.073	220	260	500	620
40	0.080	0.085	260	295	580	740
50	0.083	0.091	285	330	750	850
60	0.090	0.056	310	395	960	1010
70	0.100	0.106	350	440	1140	1230
80	N/A	N/A	430	520	1360	>1440
90	N/A	N/A	490	600	>1440	>1440
100	N/A	N/A	560	710	>1440	>1440

N/A, not applicable.

The latter was used to test the soundness of pure paste; however, since the same test was applied for all mixtures, the obtained results reflect the effect of other harmful matter such as sulfate compounds. It should be indicated that the standard test method for cement blends incorporating sulfate is C1038. The setting times for different paste mixes and the percentages of autoclave expansion for different paste mixes are listed in Table 2.

2.3. Strengths tests on mortars

The compressive strength of mortars was determined using cubic specimens (50.8 × 50.8 × 50.8 mm) molded according to ASTM test method C109, whereas the tensile strength was determined using briquette specimens molded according to ASTM test method C190. Flexure strength was determined using mortar prismatic specimens (40 × 40 × 110 mm) molded according to ASTM specification C348-90. The flow test was performed on all mortar mixes according to the ASTM test method C230. The flow values for different mixes, prepared using OPC and PPC at different replacements of PG, ranged from 105 to 115; the normal consistency specified in ASTM test method C270 corresponds to a flow of 110 ± 5%. Specimens were left in the curing room from 48 to 52 h at 23°C, demolded, then placed in a moist room (M), or laboratory air (A) until tested. Three or more test specimens were made for each specified testing at ages of 3, 7, and 28 days. The strength tests were performed on mortars prepared using PG and purified PG (after calcination).

2.4. Heat treatment of PG

PG washed with water and not washed was calcined at temperatures of 170, 600, 750, 850, and 950°C for 3 h. The calcination process was carried out using an electrical oven. The composition of PG oxides after calcination was determined by chemical analysis and are presented in Table 3. The compound composition of PG were also determined after calcination using the X-ray diffraction technique and results are given in Table 4.

3. Data analysis and discussion

The fresh mix properties (setting time and soundness) and hardened mix properties of PG mortar (compressive, tensile, and flexural strengths) were investigated. The effect of heat treatment (calcination) of PG, washed and not washed in water, on its performance in concrete was also studied. In studying the behavior of PG concrete, the following parameters were considered: percentage replacement of PG, cement and aggregate type, curing condition, and curing period.

3.1. Effect of PG on setting time and soundness of Portland cement pastes

The replacement of cement by PG has affected the setting time and soundness of the paste mix. This is clear

Table 3
Chemical analysis (%) for PG oxides before and after calcination at different temperatures

		Calcination temperature (°C)									
		Washed with water					Not washed with water				
Component oxide	Before	170	600	750	850	950	170	600	750	850	950
SiO_2	1.24	1.07	3.32	3.59	4.14	3.65	2.24	2.91	3.5	4.14	3.49
CaO	34.09	35.92	41.6	40.10	39.42	40.84	37.92	39.57	40.40	40.43	40.6
SO_3	47.19	51.88	53.0	54.67	53.89	53.82	50.88	54.58	54.38	53.47	54.0
MgO	0.005	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.51
Fe_2O_3	0.64	0.53	0.63	0.44	0.40	0.59	0.41	0.83	0.42	0.53	0.58
Al_2O_3	0.06	0.07	0.06	0.10	0.09	0.10	0.06	0.09	0.11	0.10	0.09
Na_2O	0.34	0.03	0.02	0.0	0.05	0.07	0.08	0.11	0.08	0.09	0.01
K_2O	0.007	0.01	0.01	0.10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
P_2O_5	0.90	0.41	0.31	0.37	0.25	0.32	0.54	0.55	0.43	0.56	0.53
F*	–	0.89	0.93	0.63	0.47	0.27	2.12	0.85	0.39	0.23	0.16
H_2O	–	0.59	0.10	0.01	0.11	0.07	0.15	0.12	0.06	0.03	0.05
LOI	14.19	8.87	0.58	0.49	0.47	0.29	7.59	1.64	0.77	0.36	0.30

* Soluble and insoluble.

Table 4
X-ray diffraction for PG calcined at different temperatures

	Major compounds		Minor compounds		Trace	
Temperature (°C)	Washed	Not washed	Washed	Not washed	Washed	Not washed
170	Bassanite	Gypsum and bassanite	–	Anhydrite	Gypsum	Quartz
600	Anhydrite	Anhydrite	–	–	–	Quartz
750	Anhydrite	Anhydrite	–	–	–	Quartz
850	Anhydrite	Anhydrite	–	–	Quartz	Quartz
950	Anhydrite	Anhydrite	–	–	Quartz	Quartz

through tests performed on cement pastes made at a w/c ratio of 0.6, as shown in Table 2. The setting times (initial and final) showed significant increase as the percent replacement of PG was increased. The initial setting time ranged from 100 to 560 min for pastes prepared at 0 and 100% PG replacement of OPC, respectively, whereas the final setting time exceeded 1440 min at 100% PG replacement of OPC. Higher initial and final setting times resulted for mortar mixtures prepared using PPC. The increase in the setting time can be due to impurities (mostly from phosphate) and the possible retardation of cement hydration due to the presence of anhydrite. The increase in pastes expansion with further replacement of PG is referred to formation of more ettringate. The latter causes significant expansion, especially in saturated PPC.

3.2. Mechanical properties of PG mortar

Figs. 1, 2, and 3 show the compressive, flexure, and tensile strengths, respectively, of mortar mixes prepared at a 0.6 w/c ratio using OPC and NS at different percentages of PG replacement, after being cured for 3, 7, and 28 days in the laboratory air and in a moist room at 23°C. It can be observed that the compressive, flexural, and tensile strengths decreased as the percentage of PG was increased. This behavior is observed at all testing ages and for both curing conditions. It is also observed that in the range of 0 to 20% PG replacement, the moist curing method gave higher compressive strength than that of air-dry curing method, after which the opposite took place. On the other hand, the tensile and flexural strengths of mortars cured in air were higher than corresponding values of those cured in a moist condition at all percentages of PG replacement.

The consistent and marked difference in tensile strength between moist and air cured specimens, which is not apparent for compressive strength values, is mostly due to differences in moisture gradient developed between the surface and the interior of mortar specimens for the two types of curing regime. Flexural testing in particular is very sensitive to surface condition. This is referred to the fact that tensile stresses developed in the surface layers, due to the differential shrinkage, can produce significant reduction in the tensile strength, whereas the development of compressive strain would cause the opposite. Considering this fact and

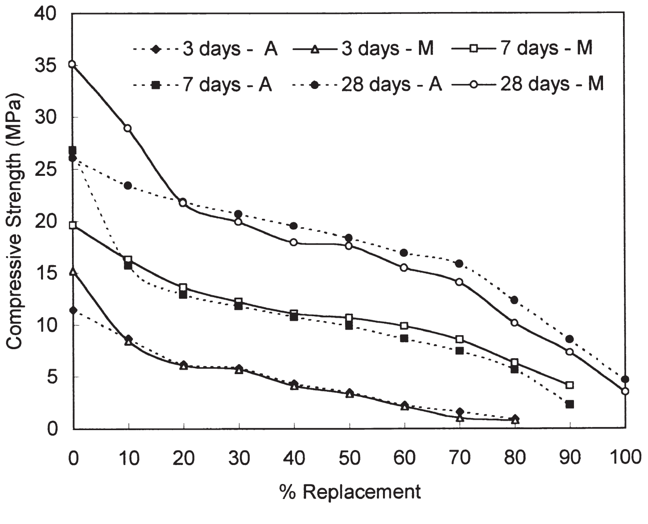

Fig. 1. Effect of PG replacement of OPC on the compressive strength of mortars with NS after being cured for 3, 7, and 28 days in moist and dry conditions.

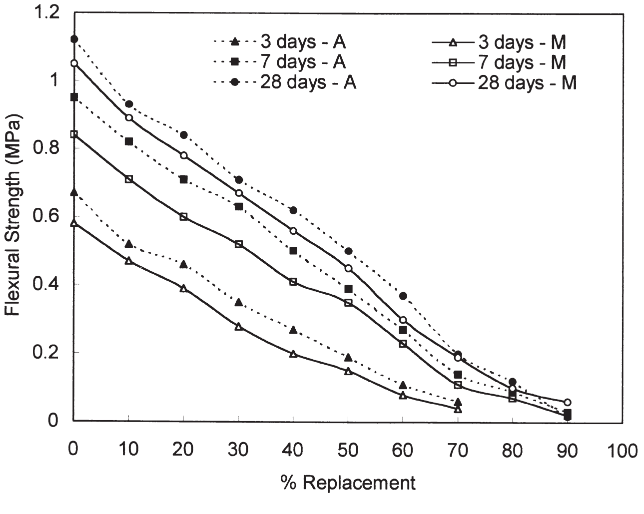

Fig. 2. Effect of PG replacement of OPC on the flexural strength of mortars with NS after being cured for 3, 7, and 28 days in moist and dry conditions.

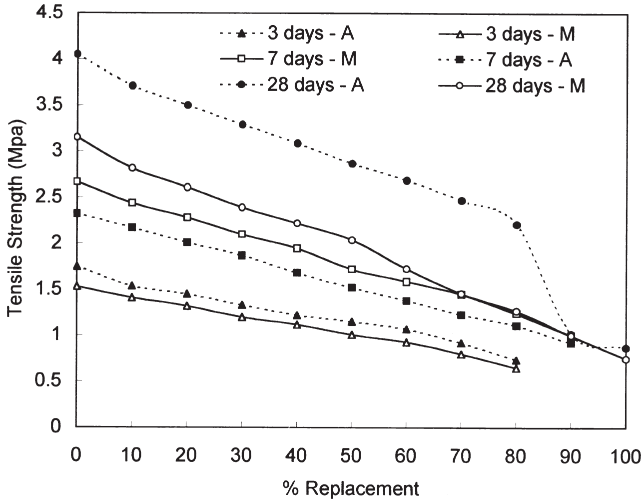

Fig. 3. Effect of PG replacement of OPC on the tensile strength of mortars with NS after being cured for 3, 7, and 28 days in moist and dry conditions.

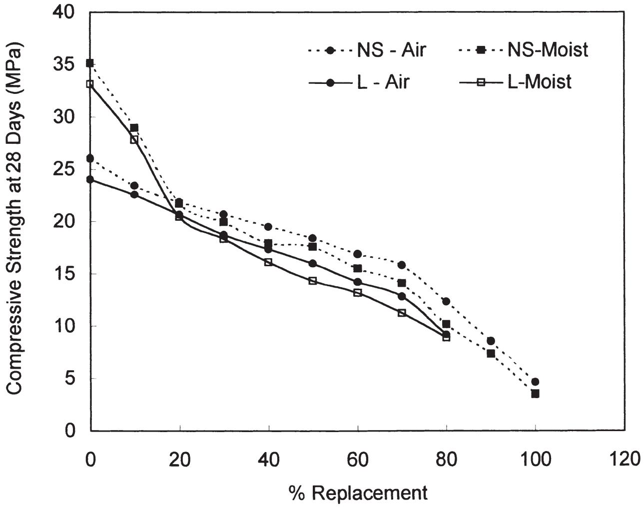

Fig. 5. Effect of PG replacement of OPC on the compressive strength of mortars prepared using NS and L and cured for 28 days in moist and dry conditions.

that the moisture gradient changes over curing time (in air) and according to the position, at which specimens were stacked on the laboratory shelves, the distribution of produced shrinkage stress varies over time. This apparently explains the behavior of flexural strength of mortars cured in air compared to those cured in moist condition over curing time. As for compressive strength, that reduction of moisture (in mortars) led to higher obtained compressive strength due to the weakening of the inner hydraulic pressure of the pore water: The latter usually causes pressure on the mortar internal pore structure, thus contributing to more cracking upon loading. The reduction in the compressive, flexural, and tensile strengths with replacement of PG can be referred to the combination of lower reacting cement content, lower cementing value of hydrated gypsum, possible retardation of cement reaction due to the presence of anhydrite, and retardation of cement hydration due to the presence of impurities (mostly from phosphate).

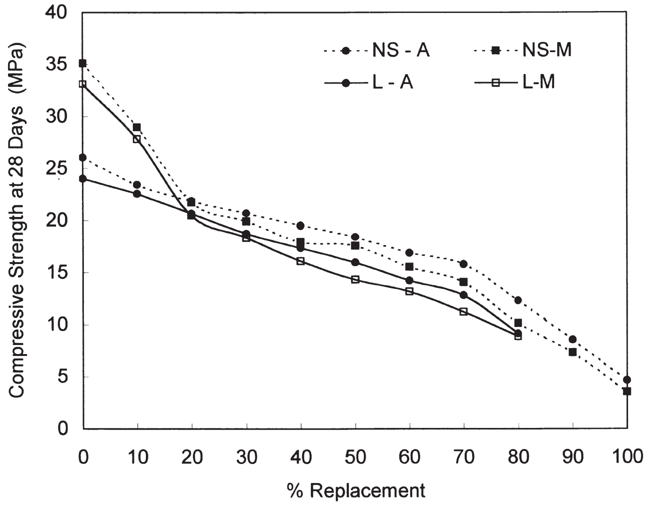

Fig. 4. Effect of PG replacement on the compressive of mortars prepared using OPC and PPC and NS after being cured for 28 days in moist and dry conditions.

Fig. 4 shows the compressive strength vs. percentage of PG replacement of mortar mixes prepared using PPC and NS and cured in air and moist conditions for 28 days. The trend is similar to that observed for mortars prepared using OPC, however, the obtained strengths are lower. Similar behavior was noticed for flexural and tensile strengths. This can be attributed to the reduction in the percent of OPC in the mortar mix (PPC contains 20% replacement of pozzolan), in addition to the fact that the curing temperature and period are not high and long enough, respectively, for an effective pozzolanic reaction to take place [11].

Fig. 5 shows the effect of aggregate type on the compressive strength of the mortar mix prepared using OPC. The compressive strength is lower for mortars prepared using limestone aggregate than those prepared using NS, but follows the same trend with curing time. Similar behavior was observed when the same mortars were tested for flexural and tensile strengths. This is probably is due to the difference in the water content between the two mixes; higher water content was needed for the mix with L, due to the L higher fineness, to achieve the same flow value of that with the NS.

Table 5
Percentage reduction in the strengths of mortars upon replacement of PG (28 days of air and moist curing)

	Compressive strength (MPa)		Flexural strength (MPa)		Tensile strength (MPa)	
% PG	Air	Moist	Air	Moist	Air	Moist
10	10–20	13–21	14–17	15–16	6–9	9–11
80	53–76	71–77	87	90–91	42–58	60–75

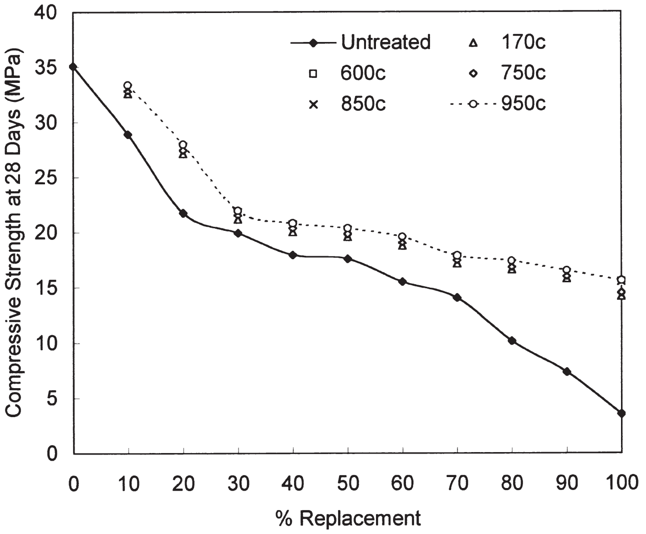

Fig. 6. Effect of purified PG replacement of OPC on the compressive strength of mortars with NS after being cured for 28 days in moist condition.

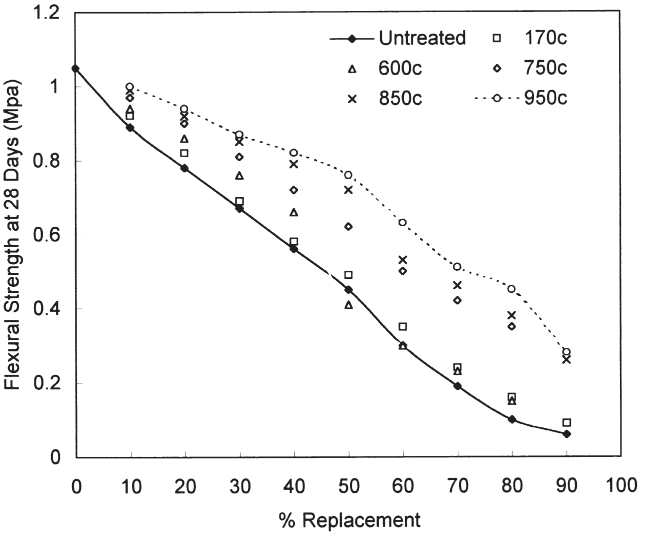

Fig. 8. Effect of purified PG replacement of OPC on the flexural strength of mortars with NS after being cured for 28 days in moist condition.

Generally, the compressive, flexural, and tensile strengths after 28 days of curing is reduced as the percentage replacement of PG is increased, regardless of the type of cement and/or sand. The reduction in the compressive, flexural, and tensile strengths at 10 and 80% replacements of PG are listed in Table 5.

3.3. Use of calcined PG

Figs. 6 and 7 show the compressive strength of mortars prepared using OPC at different percentage replacements of PG (calcined, not washed, and untreated) after being cured in air and moist conditions for 28 days, respectively. The curves indicate a significant increase in the compressive strength upon treatment of PG. The highest strengths were obtained at high calcination temperatures of 850 and 950°C. Similar behavior was observed for the same mortars when tested for flexural and tensile strengths after being cured in air and in moist conditions for 28 days: Figs. 8 and 9 show the behavior of those cured in moist conditions. At curing ages of 3 and 7 days compressive, flexural, and tensile strengths of same mortars showed similar percentage increases as those corresponding to 28 days of curing.

The effect of washing before heat treatment can be seen in Fig. 10. The results indicate that there is no significant difference between compressive strengths of mortars prepared using either washed or not washed heat-treated PG.

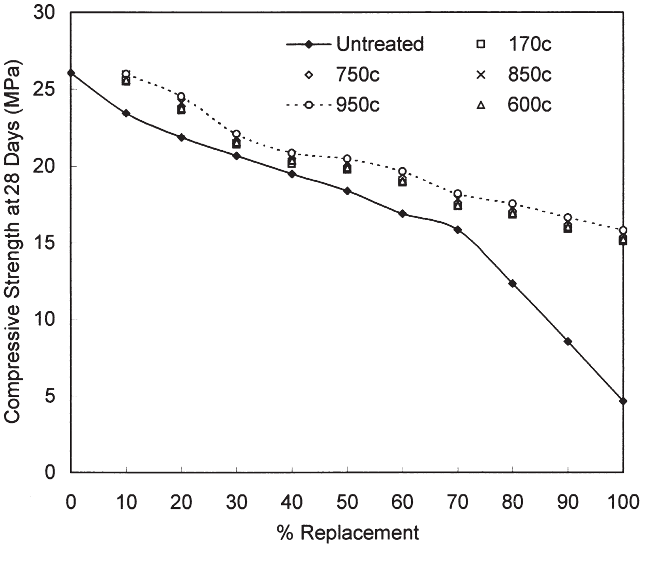

Fig. 7. Effect of purified PG replacement of OPC on the compressive strength of mortars cured for 28 days in dry condition.

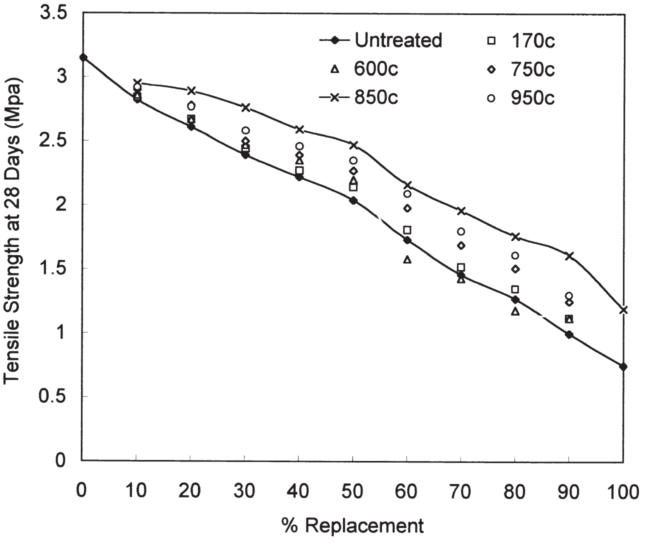

Fig. 9. Effect of purified PG replacement of OPC on the flexural strength of mortars with NS after being cured for 28 days in dry condition.

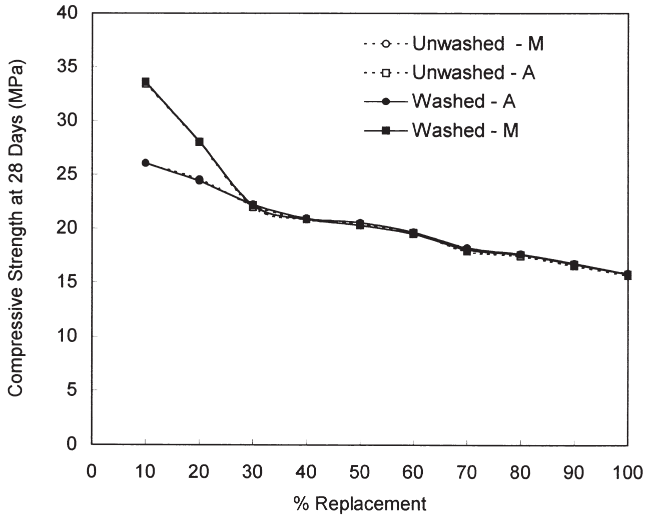

Fig. 10. Effect of the replacement of OPC by PG, calcined washed and not washed, on the compressive strength of mortars with NS after being cured for 28 days in moist and dry conditions.

Similar behavior is observed for mortars tested for flexural and tensile strengths at all curing ages.

The improvement in PG mechanical behavior in mortar clearly indicates a certain effect of the heat treatment on the cementing value of PG. The chemical analysis conducted on calcined PG indicates that heating at these temperatures has not resulted in volatilizing major oxides, such as SiO_2, CaO, and SO_3 as well: No major changes in the mineralogical composition of PG has taken place upon heat treatment. However, the X-ray diffraction showed transformation of bassanite and gypsum to anhydrite at calcination temperatures greater than 600°C. Therefore, the improvement in strength would be mostly related to the hydration of anhydrate to gypsum, which has relatively a good cementing value, rather than to changes in major oxides content or reduction in impurities. This is in agreement with the experimentally obtained LOI values. The reduction in the LOI of PG, calcined at a temperature equal to or greater than 600°C, is solely related to the loss in weight of gypsum (21% by weight) and bassanite (6.2% by weight) after dehydrated to anhydrite, rather than due to the loss of impurities during the ignition process (at 1500°C) performed to evaluate the LOI [12–13].

It should be indicated that longer curing periods should have been considered in investigating the influence of gypsum formation on the soundness of PG concrete and the possibility of dissolution of the calcium sulfate formed at high contents of anhydrite. Both factors are expected to result in a reduction of the strengths of the PG mortars over the long run.

4. Conclusions

Based on the results of the present investigation, the following conclusions may be drawn:

1. The strength of the mortar mixes decreased with replacement of cement with PG.
2. The soundness of pastes prepared using PPC and OPC was reduced with further increases in PG replacement.
3. The initial and final setting times increased upon replacing cement with PG.
4. Heat treatment (calcination) of PG (washed with water and not washed) used in replacing cement in the mortar mixes has resulted in improvement of the latter's mechanical properties compared to those of mortars prepared with untreated PG; the flexural strength showed the highest improvement, whereas the compressive strength showed the lowest. The percentage improvement in strengths was higher at higher percentages of PG replacement.
5. The curing method has affected significantly the strengths of the mortar specimens; mortars cured in a moist room showed lower strengths than those cured in air.

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