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Effect of Various Additives on the Hydration of Perlite-Gypsum Plaster and Perlite-Portland Cement Pastes

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Perlite is a volcanic glass which forms a light-weight cellular aggregate when ground and heated to about 1000° C. It is used in the production of light-weight masonry blocks and concrete in the building industry as well as in insulation, fire protection, agriculture and pharmacology. In this study, the effects of admixtures such as lime, sodium citrate and various superplasticizers on the hydration of perlite-gypsum plaster, perlite-white Portland cement and perlite-blended Portland cement mixtures were investigated by measurement of flexural and compressive strengths and by DTA-TG. It was found that the addition of lime caused pozzolanic reactions and, consequently, increased strength in gypsum plaster-perlite mixtures; however, sodium citrate was found to have negative effects. On the other hand, the use of superplasticizers in perlite-Portland cement pastes resulted in reduced water/cement ratios and an excessive decrease in strength.

Introduction

Perlite is a volcanic glass containing more than 65 per cent silicon-oxide. It can be utilized as a ground or swelled product and in prefabricated elements. Perlite has crystalline water in its structure. When ground and heated to about 1000 °C, it forms a light-weight cellular aggregate ¹.

It is used primarily in the USA as a loose filler material or as light-weight aggregate or in mortar for its favorable insulating and acoustical properties, and in fireproofing false ceilings. Other areas of utility include agriculture and pharmacology.

Turkey is an important perlite producer in the world, with abundant reserves. Recently, perlite use in Turkey has been concentrated on the building industry for insulation and fire protection and the production of light-weight panels². In addition, expanded perlite is being used in agriculture as a water adsorbent.

When perlite is mixed with Portland cement, it undergoes pozzolanic reactions and the possibility is reduced of an alkali silica reaction, which is known to be caused by the use of amorphous siliceous aggregates with high-alkali Portland cements. They can react with alkalis in the pore solution when concrete is exposed to wetness or humidity. The reaction product in an alkali silicate gel may cause the expansion and consequent distruption of concrete. On the other hand, in the same conditions, the same materials, when they are in

finely divided form, can react with calcium hydroxide obtained upon the hydration of dicalcium silicate and tricalcium silicate in cement. It is not the pozzolanic reaction which reduces alkali-silica reactions, but the consumption of lime upon pozzolanic reactions. Therefore, the expansion of concrete due to the alkali silica reaction reduces and the quality of the concrete is improved in the long term by pozzolanic reactions ^{1,3}.

Superplasticizers are used to increase the workability of cement mixes formulated at lower water-to-cement ratios (w/c) and to produce concretes of high strength. Commercial superplasticizers are mainly based on either sulphonated melamine formaldehyde or sulphonated napthalene formaldehyde. Triethanolamine is used to accelerate the setting of cement pastes⁴.

Urhan has reported the study of the devolopment pozzolanic and alkali silica reactions and late expansion of expanded perlite aggregate concretes by measurement of length changes, water porosity and mechanical strengths, and by SEM (Scanning Electron Microscope) observations of perlite concretes exposed to different curing ^{1,3}.

In this study the effects of admixtures such as lime and sodium citrate and various superplasticizers on the hydration of perlite-plaster, perlite-white Portland cement and perlite-blended Portland cement mixtures were investigated by measurements of flexural and compressive strengths, and by DTA-TG.

Experimental

The chemical composition and particle size distribution of expanded perlite (PR) obtained from the Etibank Perlite Plant in Cumaovası are shown in Table 1 and Table 2, respectively. White Portland cement (WPC) and blended Portland cement (BPC) were obtained from the Ladik Cement Factory. Lime, ordinary commercial gypsum plaster (OCP) and chemical reagents were obtained at various markets. The chemical analysis of perlite was conducted according to TS 687⁵.

| Component | % wt. | Component | % wt. |
|--------------------|-------|-------------------|-------|
| SiO_2 | 72.60 | Na ₂ O | 2.77 |
| $\mathrm{Al_2O_3}$ | 12.15 | K ₂ O | 5.20 |
| $\mathrm{Fe_2O_3}$ | 1.04 | SO_3 | _ |
| CaO | 0.67 | Cl ⁻ | 0.02 |
| MgO | 0.96 | Loss on Ignition | 1.31 |

Table 1. The chemical composition of expanded perlite (PR)

Table 2. The analysis of sieve of expanded perlite (PR)

| Sieve(mm) | On sieve, % wt. | Sieve(mm) | On sieve, % wt. |
|-----------|-----------------|-----------|-----------------|
| 2.000 | 0.40 | 0.080 | 3.69 |
| 1.60 | 5.63 | 0.060 | 4.04 |
| 1.000 | 21.06 | 0.045 | 9.01 |
| 0.200 | 30.82 | 0.032 | 6.01 |
| 0.090 | 15.05 | | |

Cement and OCP control tests were carried out according to TS 24 and TS 370, respectively, without sand. Cement test prisms $(4 \times 4 \times 16 \text{ cm})$ were prepared using tap water and solutions containing various superplasticizers at different concentrations according to TS 24 and cured in tap water at $20^{\circ}\text{C}^{6,7}$. The water/cement ratio was 1.39 for cement mixtures. Flexural and compressive strength values of prisms were reported as the average of 3 and 6 separate measurements, respectively.

DTA-TG curves were obtained simultaneously with a Rigaku TG-8110 thermal analyzer and a TAS 100 thermogravimetric analyzer in a nitrogen atmosphere (80 ml/min). The heating rate was 20° C/min. Al₂O₃ was used as a reference.

Results and Discussion

OCP-PR Mixture

The mixing ratios (by volume) and strengths of OCP-PR with and without lime mixtures are given in Table 3. The compressive and flexural strengths of plaster-perlite mixtures gradually increased depending on the amount of binder gypsum plaster.

| Mixture | Composition by | 28 days flexural | 28 days compressive |
|---------|--------------------|------------------|---------------------|
| No | volume | strength, Mpa | strengths, MPa |
| E1 | 1 OCP+5 PR | 0.6 | 1.8 |
| E2 | 1 OCP+4 PR | 0.7 | 2.0 |
| E3 | 2 OCP+3 PR | 1.8 | 5.3 |
| E4 | 3 OCP+4 PR | 2.5 | 6.9 |
| E5 | 4 OCP+4 PR | 2.9 | 9.2 |
| *EG | *1 OCP+4 PR | *1.2 | *1.1 |
| E7 | 2 OCP+3 PR+1 Lime | 2.1 | 6.3 |
| E8 | 2 OCP+3 PR+2 Lime | 1.7 | 4.5 |
| E9 | 1 OCP+3 PR+1 Lime | 1.4 | 2.2 |
| *E10 | *2 OCP+3 PR+1 Lime | *1.1 | *2.8 |

Table 3. The composition and strengths of plaster-perlite-lime mixtures

When lime was added to mixtures containing OCP and PR at the same proportions, their strengths increased slightly according to the devolopment of the pozzolanic reactions between PR and lime. The E7 mixture, containing 2 OCP 3 PR and 1 lime by volume, had the highest strength values.

Because of the decreasing solubility of OCP and the delay of its setting time, E6, and E10 mixtures hydrated by 0.1 per cent sodium citrate solution had lower strength values than mixtures hydrated by water alone⁸. In the E10 mixture, lime and sodium citrate precipitated as calcium citrate with an inactive matrix effect. Therefore, the reduction of compressive strengths of lime containing mixtures (approximately 40%) was lower than that of limeless ones (45%).

The DTA-TG curves of PR, OCP and the hydrated E7 mixtures (for 28 and 90 days) are shown in Figure 1. The endothermic peaks at 135°C and 440°C in the curves of DTA-TG of OCP and E7 mixtures (for 28 days) were attributed to the dehydration of gypsum and Ca(OH)₂ ^{8,9}. In the curve of the E7 mixture (for 90 days), the short and broad peak at around of 600°C was due to the formation of calcium silicate hydrates. The peak at 718°C was attributed to the decomposition of CaCO₃, formed by the reaction of lime and atmospheric CO₂ ¹⁰. While there was a lime peak at 440°C in the DTA-TG curve of the E7 mixture on the 28th day, the peak disappeared on the 90th day because of the lime consumed by pozzolanic reactions. It was concluded that the calcium silicate hydrates which occur by pozzolanic reaction between PR and lime increase the strengths of lime containing mixtures³.

^{*}Mixing solution contains 0.1 per cent sodium citrate by weight.

| Table 4. The composition and strengths of WPC-PR and BPC-PR containing various superplasticizers mixtures | |
|---|--|
| | |

| Composition by | Superplasticizer | 28 days flexural | 28 days compressive |
|----------------|------------------|------------------|---------------------|
| volume | solutions, % wt. | strength, Mpa | strength, MPa |
| 1 WPC+4 PR | _ | 3.3 | 11.3 |
| 1 BPC+4 PR | _ | 1.6 | 7.2 |
| 1 WPC+4 PR | 0.1 TEA | 1.3 | 4.0 |
| 1 WPC+4 PR | 0.2 TEA | 1.4 | 4.6 |
| 1 WPC+4 PR | 0.3 TEA | 1.3 | 4.5 |
| 1 WPC+4PR | 0.5 TEA | 1.2 | 4.3 |
| 1 BPC+4 PR | 0.1 TEA | 1.1 | 3.5 |
| 1 BPC+4 PR | 0.2 TEA | 1.1 | 3.5 |
| 1 BPC+4 PR | 0.3 TEA | 1.1 | 3.0 |
| 1 BPC+4 PR | 0.5 TEA | 1.0 | 3.5 |
| 1 BPC+4 PR | 0.1 SNF | 2.3 | 4.4 |
| 1 BPC+4 PR | 0.2 SNF | 1.6 | 4.2 |
| 1 BPC+4 PR | 0.3 SNF | 1.5 | 4.1 |
| 1 BPC+4 PR | 0.2 CLS | 1.2 | 4.7 |
| 1 BPC+4 PR | 0.4 CLS | 1.2 | 4.6 |
| 1 BPC+4 PR | 0.6 CLS | 1.1 | 3.4 |

The WPC-PR and BPC-PR Mixture

The composition by volume and the strengths of WPC-PR, BPC-PR and containing various superplasticizers at different proportion mixtures are given in Table 4. The compressive and flexural strength of WPC-PR mixtures were higher than those of BPC-PR since the Ca(OH)₂, arising from the hydration of WPC reacted with PR, converting to hydrate compounds ¹¹. In addition, the hydration of WPC developed quickly in proportion to BPC since the amount of clinker in the WPC-PR mixture was greater than in the BPC-PR mixture. The calcium hydroxide occurring by the hydration of BPC was consumed for pozzolanic reaction between lime and pozzolan. The activation of perlite was not performed completely and its strengths were lower than in the WPC-PR mixtures.

The DTA-TG curves of WPC-PR (for 28 and 90 days) and BPC-PR (for 28 days) mixtures are shown in Figure 2. The endothermic peaks around $100\text{-}200\,^{\circ}\text{C}$, and $900\,^{\circ}\text{C}$ were attributed to hydrated products (ettringite and calcium silicate hydrates), but the peak at $440\,^{\circ}\text{C}$ was due to calcium hydroxide 10,12 . The peak around of $680\,^{\circ}\text{C}$ was due to the decomposition of CaCO_3^{10} .

The DTA-TG curves of the BPC-PR and WPC-PR mixtures were similar to each other, but the lime peak in the WPC-PR mixture was higher than the peak of the BPC-PR mixture. On the 28th day, the WPC-PR and BPC-PR mixtures contained about 2.0 and 1.5 per cent lime, respectively.

The flexural and compressive strengths of triethanolamine (TEA) containing WPC-PR mixtures on the ^{28th} day were higher than those of the BPC-PR mixtures. The strengths of mixtures containing TEA were lower than those of mixtures with no TEA. An increase in TEA content did not cause any significant difference in the strength of the two types of mixture.

Using sodium sulphonated napthalene formaldehyde (SNF) and calcium ligno sulphonate (CLS) as superplasticizers caused a drastic drop in the strengths of BPC-PR mixtures. Generally, the strength of the mixtures was slightly decreased by increasing the amount of superplasticizer in the BPC-PR mixture.

The best results were obtained by using 0.2 per cent of CLS solution. However, it is expected that the use of superplasticizers lowered water/cement ratios and raised strengths ¹³. We concluded that a considerable amount of superplasticizer molecules and hydration water are absorbed in the pores of PR, which has a porous structure, and the devolopment of hydration is impeded. A significant delay in the setting of cement pastes by increasing superplasticizers content supports this idea.

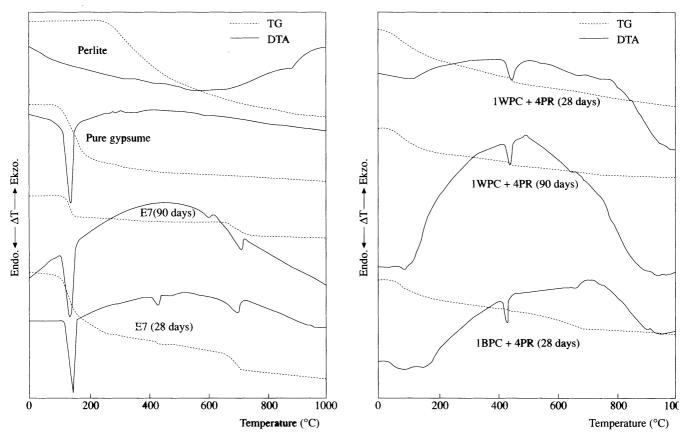


Figure 1. The DTA-TG curves of perlite, gypsum plaster and hydrated E7 mixture (for 28 and 90 days).

Figure 2. The DTA-TG curves at 28 and 90 days of WPC-PR and BPC-PR mixtures.

The greater strength of CLS containing mixtures may be explained by the consumption of Ca²⁺ ions during the hydration reactions. However, Na⁺ ions in SNF can not convert to hydrated binding compounds. Therefore, they have lower strength values. Consequently, the strengths decrease due to the delaying pozzolanic reactions and hydration of the clinker^{1,3}.

The results of the present study indicate the following:

- 1. The addition of lime to OCP-PR mixtures will cause an increase of strengths due to the devolopment of pozzolanic reactions between PR and lime. Lime may be used in OCP-PR mixtures as strength developing agent. The optimum mixing ratio may be 2 OCP, 3 PR and 1 lime by volume. The addition of sodium citrate has negative effects because it causes a reduction of strength.
- 2. It was concluded that calcium silicate hydrates were formed by the pozzolanic reaction between PR and WPC, but in the BPC-PR mixtures, the reactions were not sufficiently developed. PR can be used with WPC successfully. If PR is used with BPC, a small amount of lime must be added to the mixture for the activation of perlite.
- 3. It must be taken into consideration that the use of superplasticizers causes retardation of setting times and decreases the strengths of perlite-cement mixtures.

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