LIMESTONE AS A RETARDER AND FILLER IN LIMESTONE BLENDED CEMENT

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Received 8. 4. 1994

In this investigation, four blended cement pastes were made from Portland cement and limestone by using the suitable water of consistency of each paste. The influence of limestone replacement was studied through the determination of non-evaporable water content, free lime content, total porosity, compressive strength and pH value for each blended cement paste. The blended cements were compared with the ordinary Portland cement. The pH values increase with the increase of limestone addition as well as with curing time. Also, the addition of limestone enhances the rate of hydration as measured from the combined water contents. In the light the results obtained, blended cement pastes and mortars can be made by the addition of limestone up to 20 % giving reasonable mechanical properties and suitable passivation of reinforcing steel in the concrete.

INTRODUCTION

The debate on whether or not it should be permissible to allow the addition of limestone to Portland cement clinker is currently ongoing in most countries. In the United States there is a proposal to modify ASTM specification for Portland cement (C 150) to allow up to 5% limestone to be interground with cement clinker into Portland cement. In Canada, the Canadian Standards Association, under CAN3 - M83, now allows up to 5% addition of limestone for normal Portland cement, so long as the limestone is of a quality for the manufacture of the cement [1].

Proponants point to studies indicating that a 3 % to 5 % addition of limestone to Portland cement either increase structural properties of the concrete or has no effect [2]. Since cement kilns are located on or near limestone deposits, the substitution of a material that is both cheaper than gypsum and does not have to be transported long distances to the kiln is economically appealing. Results of laboratory and plant grinds with partial substitution of limestone for gypsum show that a definite reaction between limestone and Portland cement clinker occurs. The product shows acceptable performance in all areas except very early strength. False set properties are dramatically reduced.

The possibility of substituting $CaCO_3$ for gypsum in Portland cement was explored by Bensted [3]. Up to 5 % substitution had no deleterious effect on setting or strength development in the particular system. During the early hydration period, the sulphate ions had greater control over setting than the carbonate ions, although calcium carboaluminate hydrates were also formed. Gradent and Ollivier [4] have also noted the formation of $C_3A.CaCO_3.11H_2O$ in hydrated Portland cement in the presence of $CaCO_3$.

It was reported [5] that tricalcium aluminate reacts with calcium carbonate to from high and low carbonate forms of calcium carboaluminate hydrates in such the same manner as C_3A reacts with gypsum to form high and low sulphate forms of calcium sulphoaluminate hydrates. Their refractive indices and x-ray patterns are similar to the high and low calcium sulphoaluminate hydrates.

The effect of ground limestone and reagent quality $CaCO_3$ on the compressive strength of Portland cement was compared with the corresponding effect of two pozzolanic fillers and one noncalcareous CaF_2 [6]. Fillers affect strength through their accelerating effect on the cement hydration. This effect is essentially the same for all the fillers errespective of their chemical composition. Further tests are being carried out to show that the use of fillers is associated with an increased rate of hydration.

It is reported that [7] the addition of 5 to 25 % limestone to Portland cement enhances the formation of $Ca(OH)_2$ at early ages probably because it provides nucleation sizes for its growth. The addition of 25 % limestone influences both the size and distribution of regions of $Ca(OH)_2$. Addition of limestone fillers enhances the formation of hydration rims of C-S-H surrounding C_3S particles.

The effect of completely substituted gypsum by limestone as well as increasing amounts of limestone on the workability, the setting and the hardening of limestone filled cement was studied.

EXPERIMENTAL

The materials used in this investigation were Portland cement clinker, limestone and gypsum provided by National cement, Tebbin, Egypt. The chemical oxide composition of Portland cement clinker is found to be : SiO_2, 20.21 %;Al_2O_3, 5.23 %; Fe_2O_3, 3.58 %; CaO, 64.52 %; MgO, 2.76 %; SO_3, 1.57 % and I.L., 0.26 % and that of limestone was found to be: SiO_2, 5.08 %; Al_2O_3, 1.81 %; Fe_2O_3, 0.78 %; CaO, 48.37 %; MgO, 2.20 %; SO_3, 0.59 % and I.L., 40.18 % while that of gypsum: SiO_2, 10.72 %; Al_2O_3, 2.76 %; Fe_2O_3, 1.56 %; CaO, 35.43 %; MgO, 1.59 %; SO_3, 21.11 %; and I.L., 26.32 %.

Four dry mixtures were made from limestone replacement of 5, 10, 15 and 20 % by weight of P.C. clinker. Each blend was ground in a steel ball mill till the surface area reaches 3000 ± 50 cm^2 g^{-1}. The samples were kept in air tight containers until the time of paste preparation. Each dry mixture was homogenized for one hour in a porcelain ball mill using two balls. The mixing was carried out on the cement powder with the water of consistency of each mix. The water of consistency, the initial and final setting time of the blended cements were determined using a Vicat apparatus [8,9]. The mixing of the paste was carried out with the water of consistency, the moulding, curing and the stopping of hydration was described elsewhere [10].

The mortars were prepared by mixing the blended cement clinker with sand with ratio 1 : 3 and water ratio of 10 % by weight. The mortars were moulded into cubes having internal dimensions of 7.07×7.07×7.07 inch. The same curing procedure was followed as that of cement paste.

Compressive strength, total porosity and *pH* value were measured for each blended specimen. The kinetics of hydration was followed by the determination of free lime [11] and chemically combined water at the interval times of hydration. The combined water content is the ignition loss of the hydrated paste at any time minus the loss of the anhydrous blend. The *pH* value was determined for the hardened pastes at all ages. The dried paste was ground to pass 90 μm sieve. 50 g of the paste was put in 250 ml distilled water and stirred by magnetic stirrer for three minutes. The *pH* value was measured in the suspension by an Orion Ion-Analyzer Model 920 A equipped with a combination glass-calomel electrode.

RESULTS AND DISCUSSION

The results of water of consistency percent and setting time of the blended cement pastes are graphically represented as a function of limestone replacements in Figure 1. The values show that the percentage water of consistency of the blended cement paste, generally, increases with the amount of the limestone. This may be attributed to the capacity of limestone to absorb water. Also, the addition of limestone may increase the plasticity of the mix which needs more water for workability. There is a small difference between Portland cement and blended cement with 5 % limestone.

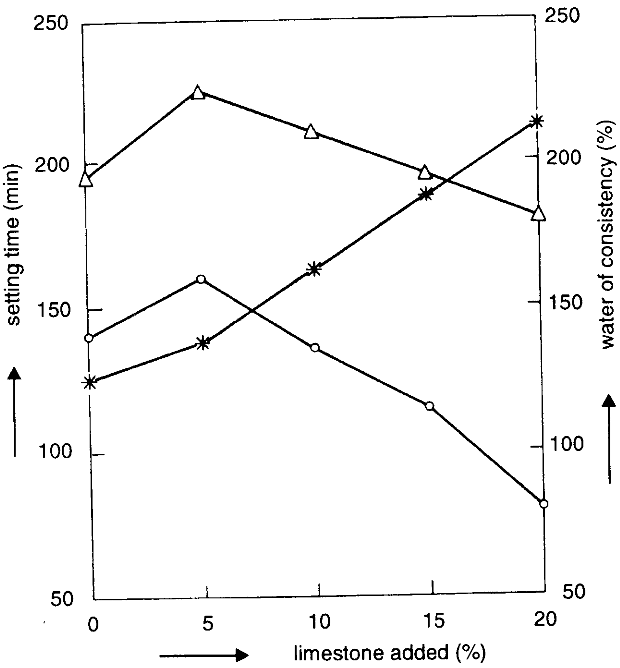

Figure 1: Initial, final setting time and water of consistency of blended cement pastes.
o - Init. sett., Δ - Fin. sett., * - W. cons.

Figures 2a and 2b illustrate the chemically combined (nonevaporable) water (W_m, %) and free lime (CaO, %) contents for all the blended cement pastes as a function of curing time. Obviously, the chemically combined water contents and the free lime contents increase with increasing the curing time as well as with the addition of limestone. The increase in the chemically combined water is due to that the addition of limestone fillers probably enhances the formation of hydration rims of C-S-H surrounding C_3S particles because they increase the rate of hydration of C_3S. Evidently, P.C. clinker which contains 20 % limestone has more ratio of hydrated calcium silicates which have high chemically combined water contents. Also, as the hydration proceeds, the

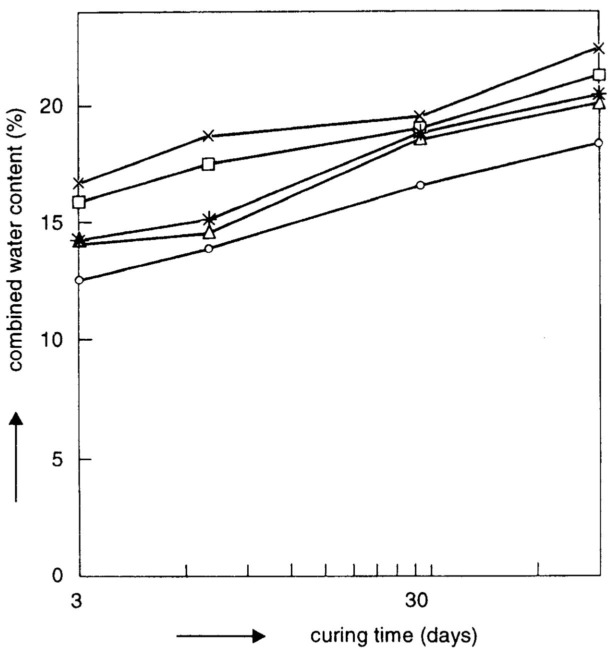

Figure 2a: Chemically combined water content of blended cement pastes
o - P.C., Δ - 5 % L.S., * - 10 % L.S., □ - 15 % L.S., x - 15 % L.S.

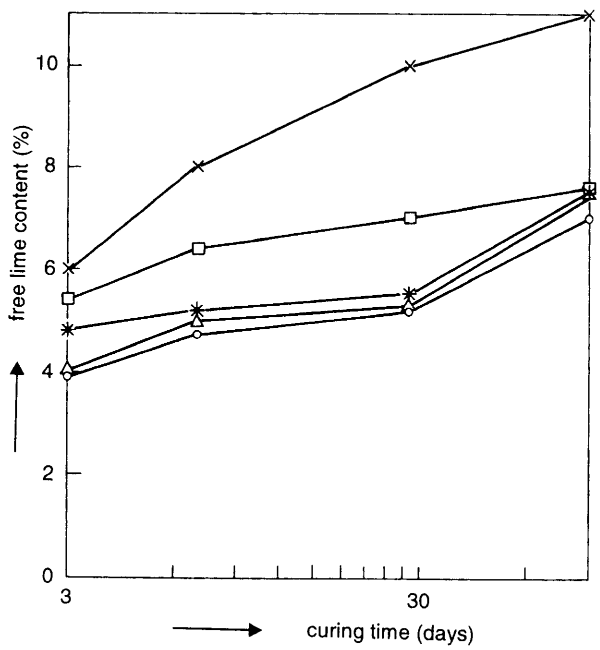

Figure 2b: Free lime content of blended cement pastes.
o - P.C., Δ - 5 % L.S., * - 10 % L.S., □ - 15 % L.S., x - 15 % L.S.

amount of carboaluminate hydrates increases which have higher combined water contents in comparison with the hydrated calcium silicates. The continuous liberation of lime during the hydration of P.C. clinker and leaching of Ca^{2+} from the limestone present in the masonry cement [12] lead to the increase of free lime content. The results illustrate that the limestone accelerates the rate of hydration of Portland cement, i.e. the combined water contents of Portland cement clinker with 5 % limestone; higher than that of ordinary Portland cement. Also, the liberated $Ca(OH)_2$ during the hydration of limestone blended cement pastes is higher than that of Portland cement and increases with the amount of limestone added.

The total porosity for all hardened cement pastes decreases as the curing time proceeds as shown in Figure 3. This is due to the filling up of a part of the available pore volume with the hydration products. Furthermore, the reaction between the C_3A in P.C. clinker and limestone to produce calcium carboaluminate hydrates $C_3A . CaCO_3 . 11\ H_2O$ or $C_3A . 3\ CaCO_3 . 32\ H_2O$

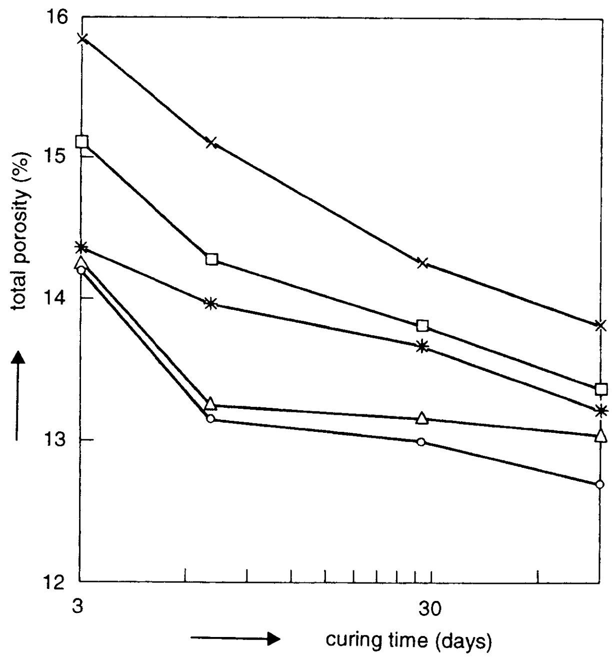

Figure 3: Total porosity of blended cement pastes
o - P.C., Δ - 5 % L.S., * - 10 % L.S., □ - 15 % L.S., x - 15 % L.S.

reduce the porosity owing to its high molar volume. Obviously, the hardened cement pastes which have high content of limestone (20 %) have higher values of total porosity. This is attributed to the high values of their initial porosities as controlled by their water of consistency.

The results of compressive strength of blended cement pastes cured at room temperature under tap-water and hydrated up to 90 days are graphically represented as a function of curing time in Figure 4. Obviously, the compressive strength values increase as the hydration proceeds for all of the hardened cement pastes up to 90 days. This is attributed to the formation and later accumulation of the hydration products within the available pore spaces giving the more strength. As the amount of limestone increases from 5 up to 20 % the corresponding strength values, decreases slightly. Therefore, it can be concluded that a blended cement from limestone can be made by the addition of fine limestone up to 20 % from the total amount of blended cement.

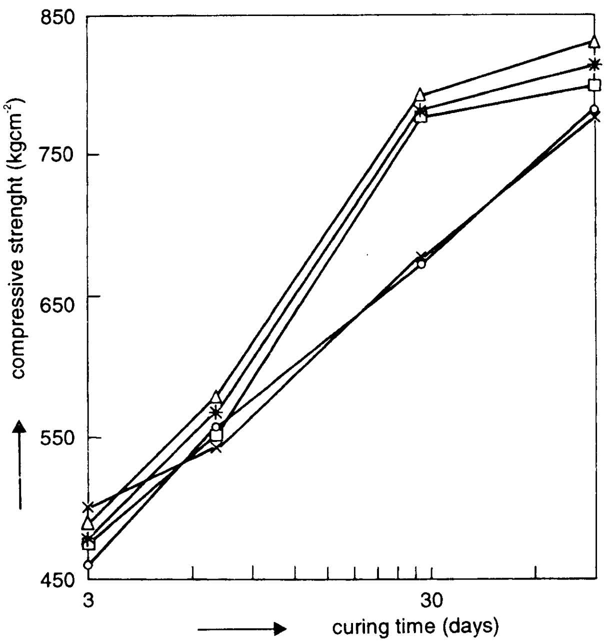

Figure 4: Compressive strength of blended cement pastes
o - P.C., Δ - 5 % L.S., * - 10 % L.S., □ - 15 % L.S., x - 15 % L.S.

The results of compressive strength of the blended cement mortars as a function of curing time are shown in Figure 5. Evidently, the compressive strength of the mortar shows the same trend of the hardened cement pastes. Blended cement mortars made from 20 % limestone give compressive strength slightly lower than the corresponding mortar made with 5 % by about 6.43 %. It can be concluded that blended cement mortars can be made by the addition of limestone up to 20 % with reasonable mechanical properties. The values of compressive strength of cement pastes as well as mortar containing up to 10 % limestone are nearly the same of ordinary Portland cement.

The *pH* values of the blended cement pastes are given in Table I. Obviously, the *pH* values increase for all cement pastes with the curing time and with the addition of limestone. Thereby, the blended cement containing more limestone is more suitable for the passivation of reinforcing steel in the concrete. The ordinary Portland cement pastes give lower *pH* values at all ages of hydration than those of limestone blended cement pastes.

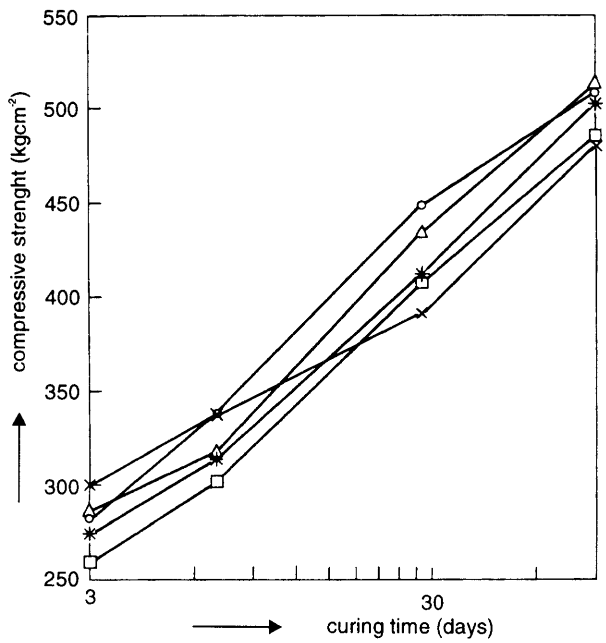

Figure 5: Compressive strength of blended cement mortar
o - P.C., Δ - 5 % L.S., * - 10 % L.S., □ - 15 % L.S., x - 15 % L.S.

Table I. *pH* values of blended cement pastes made from P.C. clinker with different percentages of limestone

Sample	3-days	7-days	28-days	90-days
P.C.	12.00	12.35	12.45	12.90
5 % L.S.	12.00	12.40	12.50	13.00
10 % L.S.	12.30	12.50	12.70	13.20
15 % L.S.	12.75	12.80	13.00	13.30
20 % L.S.	12.90	13.20	13.50	13.80

CONCLUSIONS

The following conclusions may be deduced from the above findings:

1 - The water of consistency of limestone blended cement increases with the increase of the amount of limestone. On the other side, the initial and final setting times decrease with the increase of limestone content. Also, Portland cement needs lower water of consistency and shorter setting times than the blended cements.

2 - Portland cement pastes give lower values of combined water and free lime than that of any blended cement paste at all ages of hydration. It can be concluded that limestone accelerates the hydration of Portland cement clinker.
3 - Addition of 5 % limestone instead of gypsum gives the same porosity and compressive strength. The increase of limestone increases the total porosity and decreases the compressive strength.
4 - The *pH* values of the blended cement pastes are higher than the ordinary Portland cement pastes at all ages of curing.

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Submitted in English by the authors

VÁPENEC JAKO ZPOMALOVAČ A PLNIDLO VE VÁPENCOVÉM SMĚSNÉM CEMENTU

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Protože se cementářské pece obvykle nacházejí nedaleko místa těžby vápence, je ekonomicky atraktivní možností částečná náhrada slínku materiálem, který je levnější než slínek nebo sádrovec, a nemusí se přepravovat na dlouhé vzdálenosti do cementárny. Předložená práce měla proto za cíl zabývat se použitelností vápence místo sádrovce jako regulátoru tuhnutí a zároveň plnidla při výrobě směsného cementu. Byly zjišťovány fyzikálně-chemické vlastnosti, kinetika hydratace, normální konsistence, počátek a konec tuhnutí, pevnost v tlaku, celková porozita, obsah volného vápna, a průběh hodnot *pH* výluhů z cementových kaší až do stáří 90 dnů. Výsledky pro běžný portlandský cement s obsahem 5 % sádrovce byly porovnávány s hodnotami získanými se směsným cementem obsahujícím 5, 10, 15 a 20 % vápence.

Výsledky ukazují, že vodní součinitel potřebný pro dosažení normální konsistence tohoto směsného cementu stoupá s obsahem vápence v něm obsaženým. Na druhé straně vyžaduje běžný portlandský cement nižší množství záměsové vody než směsný cement s 5 % vápence. Počátek a doba tuhnutí se rovněž zkracují se zvyšováním obsahu vápence. Mezi vlastnostmi běžného portlandského cementu a směsného cementu s 5 % vápence je malý rozdíl. Obsah vázané vody v zatvrdlém cementu a také obsah volného vápna se zvyšují s obsahem vápence ve směsném cementu, což je způsobeno aktivací hydratace portlandského cementu vápencem. Vápenec rovněž vyluhuje určité množství Ca^{2+}, a proto jsou hodnoty pH kaší směsných cementů vyšší než u kaší portlandského cementu, a dále se zvyšují se stoupajícím obsahem vápence. Směsné cementy s obsahem 5 až 10 % vápence vykazují téměř stejné počáteční i konečné pevnosti v tlaku jako běžný portlandský cement.