HYDROTHERMAL REACTIONS BETWEEN LIME AND AGGREGATE FINES

I. EXPERIMENTAL CONDITIONS FOR STRENGTH IMPROVEMENT USING SATURATED STEAM AT ATMOSPHERIC PRESSURE

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SUMMARY : A comparison of the compressive strength has been made through hydrothermal reactions of lime and silica sand. Various additives, such as china-clay, Na_2CO_3, $CaSO_4$, $2H_2O$, slate, fire-clay and Na_2SiO_3 have been employed in order to get the higher strength. The compressive strengths and mineralogy were determined for various mixtures of lime and aggregate fines autoclaved at a steam pressure of 0.1 MPa (100°C) for 6, 12, 18, 24 and 48 hours. A maximum strength of 25.0 MPa was recorded after 48-hours reaction between 80% silica sand, 15% lime and 5% china clay, whereas if the reactants are only silica sand (85%) and lime (15%), they lead to lower 48-hours strength (11.3 MPa). The cementitious product identified was calcium hydro-silicate.

Key Words : Hydrothermal reactions, compressive strength, mineral additives, atmospheric pressure.

INTRODUCTION

The production of portland cement in developing countries is often limited by the high consumption of energy necessary to manufacture the clinker. But some trumps are available in these countries, for example :

- no necessity of a high-cost housing.

- disposal of large quantities of local natural raw materials (clays, laterites, limestone, gypsum) which are interesting sources to manufacture low-cost building material (10).

- disposal of solar energy which can partially supply the fuel, coal or gas consumption if the preparation of particular hydraulic binders (gypsum plaster, pozzolanic cement) or building materials (autoclaved sand-lime bricks) does not need a high level of temperature (T<900°C).

This paper reports a comprehensive study on the reactions of the locally available silica sand and lime. Various other indigenous aggregates, e.g. china-clay, Na_2CO_3, $CaSO_4$. $2H_2O$, slate, fire-clay and Na_2SiO_3 have also been incorporated in order to improve the strength of the product. Hydrated calcium silicate (CSH, where C stands for CaO, and S and H represent SiO_2 and H_2O respectively) the main product in all cases, which is a strong and durable cementing agent.

A detailed comparison of the compressive strengths is also presented.

EXPERIMENTAL AND RAW MATERIALS

The experimental procedure involves the following steps :

1. Representative samples of the aggregates, with the exception of the silica sand, were ground to pass B.S. No. 150 sieve (100 µm).

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2. The ground silica sand aggregate was treated differently, only 47% being ground to pass the B.S. No. 150 (100 μm) sieve while the rest was used as coarse (200-300 μm).

3. Different dry mixes of hydrated lime and each of the aggregate fines were prepared, in different proportions by weight of lime to aggregate.

4. Cylindrical specimens of 3.8 cm diameter by 5.1 cm in height were molded at a pressure of 30.7 MPa after the requisite amount of moulding moisture had been added.

5. The amount of water for all the mixes was almost 8% by weight of total solids.

6. Specimens were processed for 6, 12, 18, 24 and 48 hours in an autoclave at a steam pressure of 0.1 MPa (100°C), these periods being chosen so that a study of the rate of reaction between lime and the aggregates could be made.

7. At the conclusion of each autoclaving period, the specimens were removed and placed in a desiccator to cool and were retained under dry CO_2 free conditions until they were needed for further examination.

8. The cylindrical specimens were tested for compressive strength, the crushed materials being saved for mineralogical examination.

9. It was quartered down to obtain a representative sample, which was ground to pass a B. S. No. 150 sieve.

10. The product was analyzed by X-ray powder diffraction (cu Ka radiation) and infrared spectroscopy the materials were pelleted with potassium bromide.

Table 1: Chemical composition of various indigenous aggregate fines (%).

Composition	Silica sand	Slate	Gypsum	Fireclay	China-clay
SiO_2	98.90	63.22	2.25	42.68	45.44
Fe_2O_3	0.07	6.56	Nil	1.55	0.80
Al_2O_3	0.33	19.10	0.71	38.49	38.52
TiO_2	Nil	Nil	-	2.90	0.16
MnO	Nil	-	-	-	-
P_2O_5	Nil	-	-	-	-
SO_3	-	-	44.10	-	-
CaO	0.10	0.90	30.98	-	0.08
MgO	trace	1.10	1.14	0.08	0.08
Na_2O	Nil	0.72	0.40	0.28	0.66
K_2O	0.03	3.33	0.20	0.49	0.14
L.O.I.	0.50	5.02	1.58	-	-
H_2O	-	-	19.22	14.07	14.20
Total	99.93	100.01	100.58	100.54	100.08
Mineral	qurtzite	quartz chlorite biotite feldspar pyrite haematite	selenite gypsite	kaolinite	kaolinite

RESULTS AND DISCUSSION

1. Strength development

The dependence of the compressive strength on the autoclaving time is shown in Figures 1a, 1b, 2a, 2b, 3a, 3b and 4 for the various moulds investigated.

a. Sand - Lime Mixture : As shown in Figures 1a and 1b, it appears that sand which contains almost 99.0% SiO_2 (Table 1) reacts with $Ca(OH)_2$ leads to a cementatious materials of variable compressive strength. Obviously, the strength shows a gradual increase with the time of autoclaving and also with the quantity of lime. It first increases with addition of lime up to 20% followed by a decrease with 25% lime content and finally again an increase is recorded when the lime content in the reaction mixture is 30%.

A maximum strength of 25.8 MPa is obtained after 48 hours autoclaving and 30% $Ca(OH)_2$ (silica sand/$Ca(OH)_2$ =2.3). The initial increase in the compressive strength is mainly attributed to the formation and later stabilization of the initial hydration product. However, with 25% lime contents a reduction in the compressive strength occurs which might be due to the well crystallization of the initial hydrates and/or their partial transformation into other hydrates. Later, the new formation of inner hydration products causes a marked increase in the compressive strength as a result of the increase in the total contents of the binding centers in the specimen (1).

Figure 1a: Compressive strength as a function of autoclaving time.

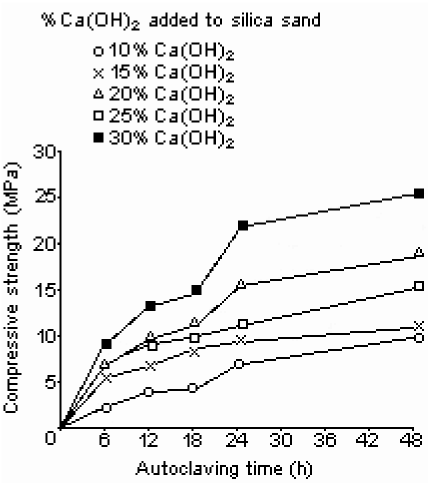


Figure 1b: Variation of 6-48 hours compressive strengths versus % $Ca(OH)_2$ added and SiO_2 sand / $Ca(OH)_2$ ratio.

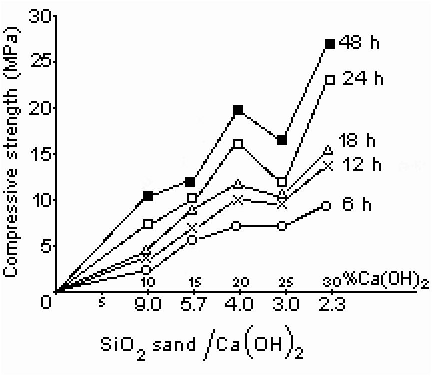


Figure 2a: Compressive strength as a function of autoclaving time.

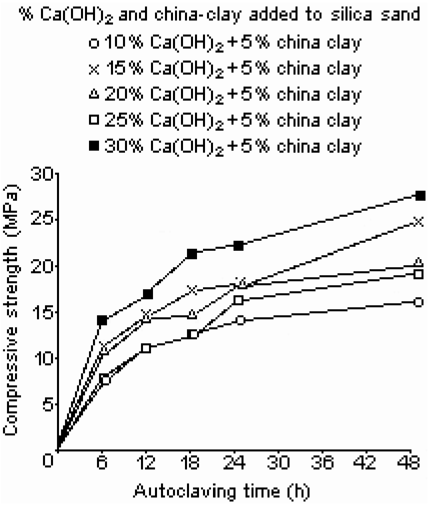
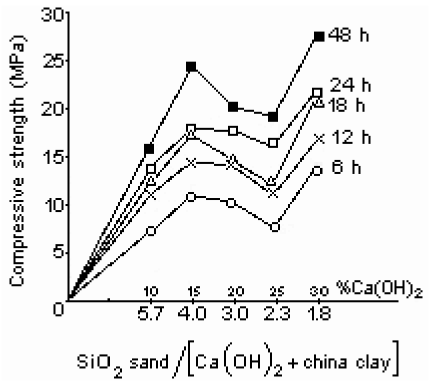


Figure 2b: Variation of 6-48 hours compressive strengths versus % $Ca(OH)_2$ added and SiO_2 sand / [$Ca(OH)_2$ + china clay] ratio.



The above results are consistent with earlier findings (14) that with the contact of siliceous particles with cement solution OH^-, Ca^{++}, Na^+, K^+ are adsorbed on the silica surface. The adsorption of OH^- provokes the dissolution of silicium atom on silica surface while Ca^{++} is adsorbed more strongly so first it reacts with dissolving silica to form CSH (C=CaO; S= SiO_2; H=H_2O).

The following reaction has been proposed (5) for the chemisorption of $Ca(OH)_2$ on the surface of silanol groups which has been confirmed by different workers (2, 3, 6).

$SiO_{2(s)}+C^{++}(Qq)+2{:}H\text{-}(Qq)\rightarrow n_1CaO.\ SiO_2\ \ n_2\,H_2\,O(s)$

b. Sand - Lime - China Clay Mixture : The hydrothermal reaction data of the mixture are presented in Figures 2a and 2b. As evident there is an abrupt increase in the compressive strength and a higher strength of 25.0 MPa is recorded after 48 hours autoclaving reaction of 15% $Ca(OH)_2$ and 5% china clay with 80% silica sand [silica sand/Ca(OH)2 + china-clay)=4.0] which is comparable to the maximum strength (25.8 MPa) obtained in the preceding sand-lime reaction with 30% lime contents (Figures 1a and b). Again there is a decrease in the strengths with 20% and 25% lime contents in the mixtures respectively, whereas a maximum strength of 28.1 MPa is recorded with 48-hours autoclaving, 30% Ca(OH)2 and 5% china-clay [sand/(Ca(OH)2+china-clay) =1.8].

Figure 3a: Compressive strength as a function of autoclaving time.

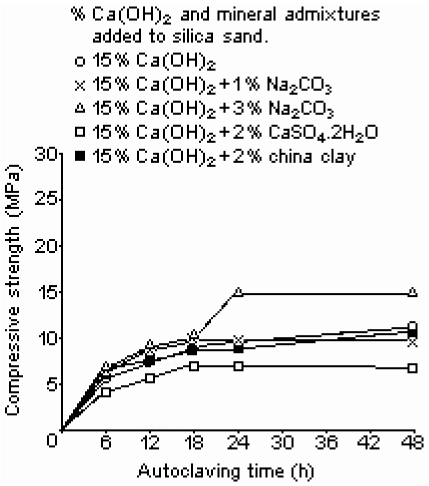
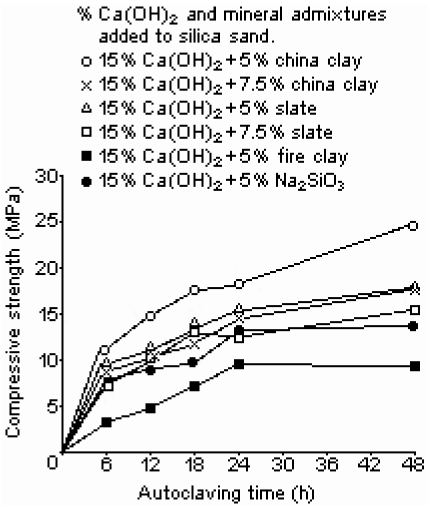


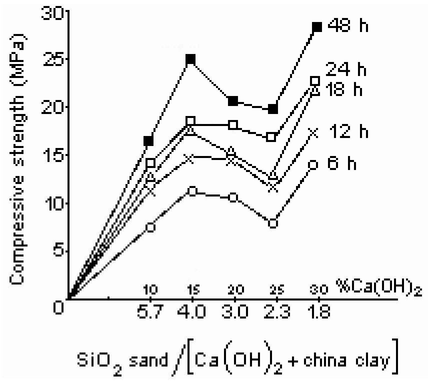
Figure 3b: Compressive strength as a function of autoclaving time.



It is evident that if SiO_2 is partially replaced by Al_2O_3 a major constitment of china-clay a noticeable high strength is obtained. Furthermore, it has also been reported (7) that the solubility Al_2O_3 in alumina silicates is 30 times lower than that of SiO_2 but once dissolved, alumina reacts instantaneously with lime (4).

c. Sand-Lime with Different Mineral Admixtures : It is known (13) that finely divided siliceous materials (including clays, zeolites and diatomite) can react with free lime of cement leading to formation of hydrated products having binding properties. Small additions of basic materials like NaOH (11) are found to be good accelerators.

Figure 4: Compressive strength as a function of autoclaving time.



Figures 3a and 3b depict a comprehensive profile of the compressive strengths obtained with different admixtures of the sand-lime reaction. Various additives e.g., china-clay, slate, Na_2CO_3, Na_2Si_3 fire-clay and $CaSO_4$. $2H_2O$ have been incorporated in variable proportion in order to know their effect on the strength. 15% (W/W) lime has been used throughout while the 48 hours maximum strought (25.0 MPa) with 5% china- clay is consistent. Slate, Na_2CO_2, Na_2SiO_3 and fire-clay are giving lower compressive strengths whereas the presence of $CaSO_4$. $2H_2O$ has an adverse effect on the strength which might be of the reason that sulphate solution retards the formation of the hydrated calcium silicate product (8).

d. Effect of Na_2CO_3 and $CaSO_4.2H_2O$ on Sand-Lime-China Clay Mixture : It is known (12) that Na_2CO_3 is a good activator that can be used to get high strength hydrated calcium silicate products. In our study we tried to show the effect of Na_2CO_3 and also of $CaSO_4$. $2H_2O$ on the strength, when incorporated into sand-lime china-clay mixture (Figure 4). It can be concluded from the results presented in Figure 4 that the compressive strengths do not increase markedly in the presence of these additives and china clay alone is the most important activator when mixed with sand-lime mixture.

Characterization on the products

X-ray powder diffraction analyses were performed on the products which showed the higher compressive strength. In addition to the final material diagram, other patterns in intermediate samples taken throughout the reaction were recorded. During the early hours, the main line is detected at 2.98 Å, which is followed by the other two lines at 2.83 Å and 1.80 Å respectively. Te latter two lines, which are attributing to the C-S-H, become more intense on the completion of the reaction.

The products can be authenticated in the light of infrared spectroscopy results. It is known (9) that the amorphous silica gives characteristic bands at 1100 cm^{-1}, 805 cm^{-1}, 468cm^{-1}, attributed to the SiO and Si valence vibrations and to the SiO deformation vibrations, respectively.

During the course of reaction, it was observed that the 1100 cm^{-1} band was decreasing as the reaction proceeded. A new stretching mode was observed at 970 cm^{-1}, a characteristic of the C-S-H, which became more intense at later stage of the reaction.

CONCLUSION

High strength cementations products can be obtained from the reaction between silica sand and $Ca(OH)_2$ when treated hydro thermally. These materials are abundantly available in Pakistan. The compressive strength can be improved in the presence of some indigenous additives and it has been observed that the maximum strength is recorded when china-clay, slate, Na_2SiO_3, are incorporated in these reactions. On the other hand, Na_2CO_3, $CaSO_4 . 2H_2O$ and fire-clay do not increase the strength markedly, though the latter has a similar composition as china-clay (Table 1).

Hydrated calcium silicate, as identified by X-ray powder diffraction analysis and infrared spectroscopy is the main product in all the reactions studied.

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