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STUDIES ON CEMENTITIOUS MATERIALS
Part II. Natural and Artificial Hydraulic Limes

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Hydraulic lime can be produced by calcining limestones available from the quarries abondoned by cement factories as well as by firing a mix of limestone and clay. The effect of substituting the two categories, viz. natural and artificial hydraulic limes, into standard cement has been studied by comparing the compressive strength of mortars prepared from cement as well as the mixes. It has been found that the two types of hydraulic limes may substitute 30 % and 50 % of Portland cement respectively in masonry mortars.

Key words: Cementitious materials; Natural hydraulic lime; Hydraulic lime.

INTRODUCTION

Hydraulic lime may be broadly classified as being intermediate between fat lime and Portland cement [1-2]. While fat lime, described in an earlier paper [3], is obtained from relatively pure limestones and dolomitic limestone, hydraulic lime is derived from argillaceous limestone or cement rock whose calcined product contains a high percentage of silicates. The latter possesses mild hydraulic properties which suggest its hardening under water with the passage of time. Unlike cement, it contains considerable amount of free lime and magnesia which are responsible for the observed slaking in water. Compared with cement, they contain smaller quantities of silica, alumina, iron oxide and magnesia which are intermediate between those in Portland cement and limestone used for fat lime manufacture [4].

The degree of the hydraulicity of these limes varies considerably and using this as an index, have been classified into three different grades, viz. feeble, moderate, and eminent hydraulic limes [5]. Feebly hydraulic lime has low cementing properties if used in bulk or as mortar. It hardens on the surface during the course of time by absorbing carbon dioxide from air and has itself no cementing value [6]. Eminent hydraulic lime approaches hydraulic and natural cement in hydraulicity and cementing properties which are superior to feebly hydraulic lime but are feeble as compared with ordinary Portland cement. However, its blending with the latter gives a cementing material with the desired strength and hydraulicity.

Hydraulic lime can be produced by mixing clay having high silica, alumina and magnesia with limestone or lime in a predetermined proportion and calcining balls or granules of the powdered mixture at 850-1000°. The product h.. cementing properties due to the formation of complex calcium silicates and aluminates during calcination [7]. Large quantities of hydraulic lime of eminent grade have been successfully used on Karachi Harbour works and on major irrigation projects in Sind as these mortars gain strength when subjected to continual water storage conditions. This material has a superior performance record in resisting the chemical attack of salt water compared with Portland cement in coastal and saline areas [8].

Hydraulic lime continues to be a significant building material in European countries. The one in use in France has 21 to 31 % silica content and cementation index: 0.84 to 1.56. In Germany the lime contains 7 to 12 % silica having cementation index: 0.43 to 0.58 and accounts for about 28 % of the annual building lime shipments of the country [9].

EXPERIMENTAL

Three samples of limestone, namely, A, B and C were collected from three different sites of Murli Hill which is an abondoned quarry of National Cement Factory at Karachi. Sample D is artificial hydraulic lime prepared in these Laboratories by mixing clay from Gadap (Dist. Karachi) containing SiO_2 69.90 %, Al_2O_3 18.4 % and MgO 11.1 % with limestone of Saeedpur (Dist. Hyderabad) having CaO 54.9 %. The results shown for sample D are an average of over 10 samples prepared, powdered, granulated and calcined. Calcination was carried out in the traditional vertical gas fired kiln at temperatures of 850-1000°.

The samples were slaked by the batch method [10]. The unslaked residue removed by screening was found to be in the range of 3 to 4 %. The hydrated lumps were pulverized mechanically and blended into the lime samples. Dry hydrated limes capable of mixing with water to any desirable consistency but literally dry for packing in paper bags were prepared in closed circuit systems to prevent recarbonation [11].

Chemical analyses and determination of slaking and settling rates of the limes were carried out by methods described earlier [3].

Samples A, B, C and D were used in hydrated, dry and powdered form, with fineness to pass 200-mesh sieve for making substituted lime cement mortars. 10 to 70 % of the parent ordinary Portland cement was substituted by each of the hydrated lime. Standard mortars of Portland cement and of the four limes were prepared by mixing them with sand in the ratio of 1:2.75.

The compressive strength of plain mortars of cement, the four limes and substituted cements were determined at the age of 7 and 28 days in accordance with ASTM specifications.

RESULTS AND DISCUSSION

Chemical analysis of the four lime samples after slaking, listed in Table 1, shows that they all contain 60-64 % CaO and 18-27 % argillaceous material and indicates their hydraulic nature. Samples A and B contain higher amounts of alumina than C and D which have almost twice as much silica than the former. Since silicates determine the hydraulic nature of cementitious materials [12], the analytical data are indicative of the better hydraulic properties of samples C and D.

Table 2 showing the slaking rate of the lime samples suggests that the slaking time for samples C and D is higher than that of A and B. This may, as indicated above, be

Table 1. Chemical analysis of portland cement and hydraulic limes*

S. No.	Constituents analysed	Portland cement %	Hydraulic lime sample % A	B	C	D
1.	Loss on ignition	1.48	20.53	17.87	18.40	9.51
2.	SiO_2	22.18	7.32	9.38	13.32	17.48
3.	CaO	63.96	61.38	61.03	60.49	63.50
4.	Al_2O_3	6.06	7.18	6.99	3.93	5.12
5.	Fe_2O_3	4.21	0.39	0.41	0.40	0.49
6.	SO_3	1.05	0.25	0.90	0.98	0.69
7.	MgO	1.41	3.04	3.23	3.41	3.04

*A, B and C = Natural hydraulic limes; D = Artificial hydraulic lime.

Table 2. Slaking and settling rates of natural and artificial hydraulic limes.

S. No.	Sample	Slaking rate	Settling rate (ml/24 hr)
1.	A	9.0	26.0
2.	B	10.5	26.5
3.	C	12.5	28.5
4.	D	15.0	24.5

attributed to their higher silica content. The settling rate of the hydrated limes also recorded in Table 2 shows that it is almost similar for the four samples except for sample C which may be due to its lower alumina and slightly high magnesia content [13].

Compressive strength data of the plain mortars and substituted dry hydrated lime-cement samples recorded in Table 3 indicate that Portland cement blended with 60 % samples C and D have an average compressive strength(psi) of 550, 641, 975 and 1183 at 7 and 28 days respectively which is higher than for A and B as also shown by Fig. 1. This, as suggested above, may be due to the

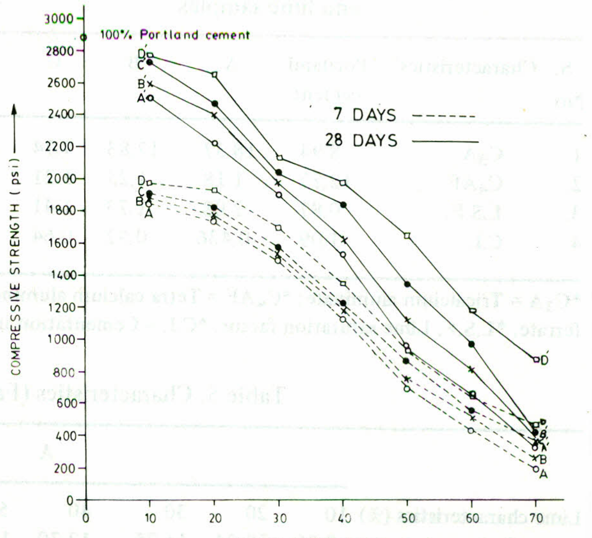

Fig. 1. Compressive strength of hydrated hydraulic lime – OPC mortars.

relatively higher siliceous nature of samples C and D which is also borne out by the compressive strength data of their plain mortars recorded in Table 3. While the standard cement-sand mortars has a compressive strength of 2030 and 2880 psi at 7 and 28 days respectively, the ASTM standard specification for masonry cements, C-91, requires a minimum strength of 500 psi at 7 days and 900 psi at 28 days. For lime pozzolan the strength requirement

Table 3. Compressive strength (psi) of hydrated hydraulic lime-cement mortar.

	A							B						
% Lime substituted	10	20	30	40	50	60	70	10	20	30	40	50	60	70
7 days	1850	1740	1500	1133	700	425	191	1880	1780	1540	1191	750	505	255
28 days	2510	2225	1908	1530	950	658	325	2600	2400	1977	1633	1066	808	391
	C							D						
% Lime substituted	10	20	30	40	50	60	70	10	20	30	40	50	60	70
7 days	1900	1820	1570	1220	860	550	362	1980	1925	1700	1250	941	641	450
28 days	2725	2480	2041	1841	1350	975	616	2770	2650	2324	1983	1650	1183	875

Compressive strength (psi) of standard Portland cement-sand mortar: 7 Days = 2030 psi
28 Days = 2880 psi

Compressive strength (psi) of standard lime-sand mortars:

	7 Days	28 Days
A:	. 75	190
B:	120	355
C:	135	375
D:	430	550

Table 4. Characteristics* (factors) of portland cement and lime samples.

S. No.	Characteristics	Portland cement	A	B	C	D
1.	C_3A	8.94	18.37	17.83	9.74	12.74
2.	C_4AF	12.77	1.18	1.25	1.21	1.49
3.	L.S.F.	0.87	2.08	1.73	1.41	1.14
4.	C.I.	1.09	0.436	0.52	0.64	0.81

*C_3A = Tricalcium aluminate; *C_4AF = Tetra calcium alumino ferrate; *L.S.F. Lime saturation factor; *C.I. = Cementation index.

according to ASTM C109-63 after 7 and 28 days remains 600 psi at temperatures of 54° and 23° respectively. These data, therefore, suggest that the lime-cement mixes of upto 50 % substitution for A and B and 60 % for C and D have acceptable compressive strength for masonry mortars.

The above data are also supported by factors calculated from chemical analysis of Portland cement, the four lime samples and the substituted mortars. The limitation of chemical composition for Portland cement is that its lime saturation factor (LSF) should be in the range of 0.66-1.02 (BS 12 : 1958). LSF for the lime samples recorded in Table 4 is not within the limits of Portland specifications. However, it may be seen from Table 5 that on substitu-

Table 5. Characteristics (Factors) of substituted lime-cement mixtures.

	A							B						
Lime characteristics (%)	10	20	30	40	50	60	70	10	20	30	40	50	60	70
C_3A	9.89	10.84	11.75	12.70	13.70	14.61	15.51	9.89	10.73	11.58	12.52	13.48	14.28	15.15
C_4AF	11.61	10.49	9.33	8.18	6.96	5.81	4.65	11.61	10.49	9.33	8.17	6.87	5.80	4.68
L.S.F.	0.95	0.98	1.05	1.13	1.22	1.33	1.46	0.92	0.97	1.02	1.08	1.15	1.23	1.33
C.I.	0.99	0.96	0.91	0.83	0.76	0.69	0.63	1.03	0.97	0.92	0.86	0.80	0.75	0.69
	C							D						
Lime substituted characteristics (%)	10	20	30	40	50	60	70	10	20	30	40	50	60	70
C_3A	9.02	9.09	9.17	9.26	9.36	9.42	9.48	9.32	9.69	10.08	10.45	10.88	11.22	11.58
C_4AF	11.61	10.49	9.33	8.17	6.99	5.84	4.68	11.64	10.55	9.42	8.27	7.11	5.99	4.86
L.S.F.	0.91	0.94	0.98	1.02	1.07	1.12	1.19	0.89	0.92	0.94	0.96	0.99	1.01	1.04
C.I.	1.04	1.00	0.95	0.91	0.87	0.82	0.77	1.06	1.03	1.00	0.97	0.95	0.92	0.89

tion with OPC it approaches the specified range on 20 and 30 % substitution by samples A and B and 40 and 60 % substitution by samples C and D indicating the superiority of the latter.

Cementation index (silica modulus) of Portland cement, natural and artificial hydraulic limes and the values on 10 to 70 % substitutions have also been recorded in Tables 4 and 5. From the arbitrary classification of cementation index, viz, Feeble: 0.30-0.50, Moderate: 0.50-0.70 and Eminent: 0.70-1.1 (14), sample A may be classified as feeble B and C as moderate and sample D as eminent in hydraulic nature which is in accordance with the gradual increase in silica from 7 to 17 % in samples A to D as given by Table 1.

Table 5 shows that on 70 % substitution, samples A and B become moderate in their hydraulic character while C and D remain eminent. The difference in the cementation index of the latter at 10 and 70 % substitutions is lower than that for A and B. This is supported further by the compressive strength data listed in Table 3 as C and D meet the ASTM standard for mortars upto 60-65 % substitution whereas for A and B this limit is at 50 to 55 %. Since C and D have higher silica content, lime combines with silica and alumina at 950-1100^o to form silicates and aluminates in the CaO-SiO_2-Al_2O_3 complex which possesses pronounced hydraulic settling properties with water and hence there is a resultant increase in their compressive strength. At temperatures of 850-900^o, relatively little silica and other impurities combine with the lime. At higher temperatures of 950-1100^o, the uncombined impurities in hydraulic limestone are increasingly absorbed and result in the formation of mono-and dicalcium silicates CS and C_2S and aluminates.

Factors like tricalcium aluminate C_3A and tetracalcium aluminoferrite C_4AF act as flux and thus facilitate the combination of lime and silica by reducing the temperature of the reaction. Tetracalcium aluminoferrite adds to the strength on long standing while calcium silicates is responsible for high early strength. Higher calcium silicates and lower C_3A and C_4AF may be responsible for a gain of only approximately 400 psi by samples A and B on 30 to 40 % substitution in OPC. C gains just as much strength on 60 % substitution and D does so at 70 %. Sample D is, however, within the range of acceptable compressive strength at 50 % substitution because of a gain of 700 psi between 7 and 28 days storage in water.

In Karachi and its suburbs, limestone for the production of lime having good hydraulic properties is available in abundance. Local cement factories are already utilizing some of it with low LSF in the manufacture of Portland cement. This study reveals that abandoned quarries, like Murli Hill, having still sizeable deposits of high LSF limestone, could become a dependable source for producing hydraulic limes with adequate cementing properties and these could substitute upto 60 % of Portland cement in masonry mortars. In the light of energy considerations, it is particularly important that alternative cementitious material should be given a fair trial. Use of hydraulic lime produced by processes already known could, therefore, be retrieved both by producing hydraulic lime and using OPC-lime mixes.

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