The Effect of Activated Qatari Attapulgite Clay Admixture on The Mechanical Properties and Hydration Kinetics of Ordinary Portland Cement

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ABSTRACT

In the Arabian Gulf countries, Concrete durability is currently of major concern as even recent concrete construction (10 to 15 years) has shown an alarming degree of deterioration. The Gulf environment is extremely aggressive and is characterized by severe geomorphic climatic conditions, severe ground and ambient salinity, and high temperature-humidity regimes. Coupled with these difficult natural conditions are the problems of aggregates, inadequate specifications, inappropriate construction practices and lack of skilled manpower. The deterioration in the Gulf region is of an accumulative nature and due to that the total over all deterioration is said to be in a complex way. Qatar is one of the Arabian Gulf countries, therefore it is effected by the formidable problem of concrete durability. This paper provides an effective practical attempt to deal with the problem. The author produced mixes of blended cement using an original Qatari artificial pozzolana. The pozzolana was made by firing Attapulgite clay at 800 C. Portland cement/artificial pozzolana pastes were made using an initial water/solid ratio of 0.40 and hydrated at room temperature for various time intervals. The hydration characteristics of the hardened pastes were studied and related to their load bearing (compressive strength) values, combined water and free lime contents. The results could be useful as a prediction of the performance characteristics of the mixes.

Key words: pozzolana, Attapulgite activated clay, blended cement, portland cement.

INTRODUCTION

Concrete is considered as a composite material consists of aggregate particales embedded in cement paste, which is the active part in this composite. The addition of pozzolana to concrete results in higher strength, lower permeability and reduced early heat of hydration (1-3). The enhancement in the properties of concrete is attributed to the pozzolana reactions taking place between the oxides originating from the pozzolana (mainly SiO2) and the hydration products of OPC [mainly Ca(OH)2] (4). pozzolanic reactions are characterized by the following, the reactions are slow and therefore the rates of strength development will be accordingly slow as well as the reaction is lime-consuming instead of lime-producing, which has an important bearing on the durability of the hydrated past to acidic environments (5). The pozzolanic reaction products are very efficient in filling up large capillary space, thus improving many intrinsic properties of the matrix (6). Firing temperature used in activating the clay to produce artificial (burnt clay) pozzolana (7,8) is one of the factors that effect the rate of blended cement hydration, blended cement containing Attapulgite activated clay is effected in the same manner (9). In ageneral, it can be said that, independently of the well known conditions to be fulfilled by any concrete to resist better whatever type of chemical attack, neither high early strength cement nor ordinary portland should be used for concrete resisting sulfate attack, owing to the two more important mechanisms of deterioration: lime leaching and expansive sulfoaluminate formation, depending on the nature and composition of the cement (10). Sulfate resisting cements: blast-funnace slag or pozzolanic should be used (10). The importance of the age of test pieces (or that of real concrete) i.e, the degree of hydration and hardening as well as the influence of testing conditions has been revealed by studies made in many countries, conclusion were drawn. In general pozzolanas behave as inerts at early ages in hard thermal and weathering conditions and that explains the abnormal result observed (11). So the hardining rate of the cement as well as it's curing conditions as factors determing the early strength, have a great influence on the performance of the cement, independently of it's chemical nature, this is the reason why some slag cements show sometimes a worse behavior, and also why the performance of pozzolanic and slag cements specially, is better the long the curing period in adequate curing conditions (12) (13).

EXPERIMENTAL

The starting materials used were ordinary Portland cement (OPC) and Qatari Attapulgite clay, for which the chemical analyses are shown in "**Table I**&**II**". The Attapulgite clay was activated by firing at 800 C and grinding up to 75µm (9). Different mixtures were prepared by mixing the Portland cement with the thermally treated clay at 800 C. Twelve mixes of different ratios of burnt clay/Portland cement were used namely 5/95, 10/90, 15/85, 20/80, 25/75, 30/70, 35/65, 40/60, 45/55, 50/50, 70/30, and 80/20 by weight. Cubic moulds 1x1x1 inch were used for moulding, the moulds were cured at 100% relative humidity at room temperature for 24 hours, then demoulded and cured under moist cotton in 100% relative humidity at room temperature up to 180 days. The cement pastes were made by using a water/solid ratio of 0.40 by weight. The specimens were cured for various hydration periods of 1, 3, 7, 14, 28, 90 and 180 days. After each time interval of hydration the compressive strength tests were determined and the hydration reaction of the hardened cement paste was stopped (14-16) then the samples were dried and kept in a desiccator. Compressive strength measurements were carried out on the fresh specimens of the hardened cement pastes after curing for various ages. Non-evaporable water (Wn) and free lime contents determinations were done on the dried specimens. Compressive strength measurements were determined using two cubic specimens of the hardened cement pastes cured at 100% relative humidity up to 180 days. Two cubes from each mix having the same age were used for compressive strengths measurements. The results are expressed in N/mm^2. Kinetics of hydration were studied by the determination of chemically combined water (Wn), calculated on the ignited weight basis, and free lime contents in the hardened cement pastes, determined by the solvent extraction method (9).

RESULTS & DISCUSSION

1. Mechanical Properties

The load bearing (compressive strength) results of the hardened Portland cement/burnt clay pastes, investigated in the present study which are given in "**Table III**", and graphically represented as a function of the hydration age in "**Fig 1**", indicate some interesting characteristics, that could be summarized as follows: For all the hardened pastes, the compressive strength data of the hardened pastes indicated a continuous increment at all stages of hydration process from one day up to 180 days of hydration except for the hardened pastes containing 5, 10, 20, 50 and 70 % burnt clay. During the intermediate stages of hydration (7 Days), 5 and 10 % hardened pastes, showed some regression in compressive strength. The regression in the strength values are mainly attributed to the crystallization of the initially formed hydrates, having stronger binding forces and/or their transformation into other hydration products having weaker binding forces. On the other hand, richer mixtures, which contained 50 and 70 %

pozzolana, showed the same behaviour as 5 and 10 % mixtures at the later age of hydration (28 Days). The 20 % behaved in the same manner at 90 days. The free lime released, as a result of hydration of Portland cement undergoes a reaction with the pozzolana to give calcium silicate hydrates which contribute strongly to the compressive strength of these cured specimens (17,18,19), and the formation and the later stabilization of the initial hydration products, which act as binding centers between the unhydrated cement, and burnt clay grains. Comparing the results obtained for the compressive strengths of Portland cement/artificial pozzolana pastes in this study and that of the neat Portland cement pastes, it was obvious that the early strength values were lower in the case of the pozzolanic cement pastes than those of the neat Portland cement pastes. The early strength values are mainly due to the reduction in compressive strength that is observed, a result which might be associated with the transformation of the stable initial hydrates into other hydrates having a metastable character at the time of their formation. The stabilization and later accumulation of these second hydrates, having a relatively low lime content, accounted for the consequent development in compressive strength at the later ages of hydration. The interaction between the initially formed high lime hydrates and the unhydrated parts of pozzolana lead to the formation of low lime hydrates when only minor amounts of free lime are detected (19).

2. Hydration Kinetics

i. Combined Water Content

The results of non-evaporable (chemically-combined) water contents, (Wn %) are given in "**Table IV**" at various ages of hydration for the hardened pastes made from the pozzolanic cements obtained by burning attapulgite clay at 800 C, and graphically represented in "**Fig 2**" has been used as a measure of the degree of hydration (19). For all of the hardened pastes, there appeared a continuous increment in the combined water content with increasing age of hydration up to the final stages of the hydration (180 Days) for almost all the hardened pastes, and this is due to the reactions which takes place during these stages. During the early stages of hydration, the hydraulic reactivity of the artificial pozzolana made of burnt clay depends on the burning (firing) temperature. It was found that the hydraulic reactivity of the clay burnt at 800 C is high. Obviously, a rapid hydraulic interactions between Portland cement and artificial pozzolana takes place after one day of hydration at room temperature leading to noticeable amounts of combined water contents. Later, the 'Wn' contents increase gradually with age of hydration up to the final stages of hydration for almost all the hardened pastes investigated. The hydraulic reactivity of the artificial pozzolana increases with increasing proportions of Portland cement in the solid mixture, achieving it's peak at 95% OPC.

ii. Free Lime Content

The results of free lime (CaO %) content of the hardened Portland

Cement/pozzolana pastes are given in “**Table V”**, reflect negligible amounts at all ages of the hydration reactions. Therefore, the complete consumption of all of the free lime released as a result of Portland Cement hydration indicates a higher hydraulic reactivity of the burnt clay. Evidently, the free lime contents given in Table are underestimated values due to the increased salinity of the pozzolanic cement mixtures which affect the extraction of free lime by the solvent extraction method used in this study.

CONCLUSIONS

From the results of this investigation the following conclusions could be derived:

1. Activation of the Qatari Attapulgite clay by grinding up to 75 m and igniting at 800 C is suitable for the production of blended cements with certain optimum conditions.
2. The author suggests that the suitable working ratios for the production of blended cement using ordinary Portland cement and the Qatari Attapulgite clay activated at 800 C are 5-35 % burnt clay.

REFERENCES

[1] Larbi, Heron, 38(1) , 1-69 (1993).

[2] Saad, Ph.D. thesis, Ain Shams University, (1996) .

[3] Saad, S.A bo-El-Enien, G.B. Hanna, M.F. Kotkata, Cem. Concr. Res., 26(10), 1479-1484 (1996).

[4] Saad, S.A. A bo-El-Enein and G. B. Hanna, Cem. Concr. Res., 27(9), 1307-1312 (1997).

[5] Escalantz-Garcia and J.H. sharp,Cem. Concr. Res.,28(9),1245-1257(1998).

[6] Escalantz-Garcia and J.H. sharp, Cem. Concr. Res., 28(9), 1259-1274 (1998).

[7] A.F. Galal, E.E. Hekal, Kawkab Kh.Al-Noaimi and S.A. Abo-El Enein, Prog.12th inter. Conf. Cement microscopy,U.S.A., April 2-6,280–302(1990) silicate industrials9-10,149-154(1992).

[8] F. Galal, E.E. Hekal, KawkabKh. AL-Noaimiand S.A. Abo-EL Nein, Prog.12th international Conf. Cement.

[9] Kawkab Kh. AL-Noaimi, Qatar Univ. Sci. Journal, Jun.5 (2001).

[10] Building Researeh Station-UK- Digest no.95 (1968),.

[11] H. Kremser, Zement-kalk-Gips, 21(3), 134-137(1968).

[12] A. Meyer, Beton 24(7), 261-264(1974).

[13] M.A. Samarai, Magaz. Concr. Res., 28, no 96, 130-142(1976).

[14] A.S. Taha, H. El-Didamony, S.A. Abo-El-Enein, H.A. Amer.Zement-Kalk-Gips; 34, 351-353, (1981).

[15] H. El-Didamony, M.Y. Haggag and S.A Abo-El-Enein, Cem. Concr. Res, 8, 351-358 (1978).

[16] S.A Abo-El-Enein, M. Daimon, S. Ohsawa and R. Kondo, Cem Concr Res 4, 229-312 (1974).

[17] S.A. Abo-ElEnein, E.E.Hekal, M Abdel-Khalik, F.I. El-Hosiny, Il Cemento, 87, 47-160 (1990).

[18] S.A. Abo-El Enein, M.A Shater and M.Nowar, il Cemento, 78, 137-144 (1981).
[19] E. El-Shimy, T.A Osman, M.A Shater, S.A. Abo-El-Enein, Arabic Building Materials and the Economical Challenges Conference, P. 205-209, Cairo, Egypt, April(2000).

Table I: Chemical Analysis of the Pure Ordinary Portland Cement

	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	SO_3	Cl^-	Loss on Ignition
	20.72	3.02	4.43	63.18	2.99	2.68	Nil	1.50
Free CaO	0.60							
SR	2.69							
AR	1.47							
LSF	0.94							
LCF	0.93							
C3S	55.51							
C2S	17.61							
C3A	6.64							
C4AF	9.18							
	Specific Surface Area						337 m^2/Kg	
	Setting Time Initial						160 minutes	
	Setting Time Final						200 minutes	
	Le Chatlier Expansion						1 mm	
	Compressive Strength (3 Days)						34.8 MN/mm^2	
	Compressive Strength (28 Days)						53.1 MN/mm^2	

Table II: Chemical Analysis of the Attapulgite Clay

	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	SO_3	Cl^-	Loss on Ignition
	48.60	5.25	12.81	10.60	4.07	0.93	0.20	11.70
	K_2O		Na_2O		P_2O_5		TiO_3	MnO
	3.77		1.32		0.10		0.67	0.04

Table III: Load Bearing Values (kN) for Different Mixes of Clay Fired at 800□C / Ordinary Portland Cement

Mix Proportions	1 Day	3 Days	7 Days	14 Days	28 Days	90 Days	180 Days
5 / 95 %	10.60	18.50	18.20	34.80	36.40	42.20	50.80
10 / 90 %	25.0	25.0	16.0	15.4	18.7	23.9	29.3
15 / 85 %	14.50	20.10	24.50	25.50	25.40	31.90	34.97
20 / 80 %	10.10	10.50	14.40	22.70	24.10	22.60	25.50
25 / 75 %	12.30	18.50	26.50	25.50	30.80	32.40	41.84
30 / 70 %	8.30	11.40	13.80	20.40	23.0	26.70	24.10
35 / 65 %	7.80	19.40	22.0	22.2	24.40	32.0	34.0
40 / 60 %	7.30	17.4	19.6	23.2	20.9	25.0	25.5
45 / 55 %	7.50	15.1	15.4	21.0	21.4	24.8	27.1
50 / 50 %	5.30	14.9	18.1	20.1	17.1	24.5	19.0
70 / 30 %	1.50	5.50	9.00	13.00	14.50	15.50	16.0
80 / 20 %	1.5	5.5	9.0	13.0	14.5	15.5	16.0

Note **: X 1.6 = compressive strength values**

Table IV: Free Lime (%) for Different Mixes of Clay Fired at 800□C / Ordinary Portland Cement

Mix Proportions	1 Day	3 Days	7 Days	14 Days	28 Days	90 Days	180 Days
5 / 95 %	0.00	0.00	0.00	0.00	0.00	0.00	0.00
10 / 90 %	0.00	0.01	0.03	0.01	0.03	0.02	0.09
15 / 85 %	0.00	0.00	0.00	0.00	0.00	0.00	0.00
20 / 80 %	0.00	0.00	0.00	0.00	0.00	0.12	0.02
25 / 75 %	0.67	1.31	2.10	0.02	0.95	0.03	0.02
30 / 70 %	0.00	0.00	0.00	0.00	0.00	0.00	0.00
35 / 65 %	0.00	0.00	0.00	0.01	0.23	0.04	0.00
40 / 60 %	0.00	0.00	0.00	0.00	0.00	0.00	0.00
45 / 55 %	0.00	0.00	0.00	0.00	0.00	0.00	0.00
50 / 50 %	0.00	0.00	0.00	0.00	0.00	0.00	0.00
70 / 30 %	0.00	0.00	0.00	0.00	0.00	0.00	0.00
80 / 20 %	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table V: Combined Water (%) for Different Mixes of Clay Fired at 800□C / Ordinary Portland Cement

Mix Proportions	1 Day	3 Days	7 Days	14 Days	28 Days	90 Days	180 Days
5 / 95 %	12.56	15.16	16.14	16.49	16.99	17.24	18.32
10 / 90 %	27.17	12.52	30.51	35.52	16.13	19.27	20.23
15 / 85 %	9.70	12.26	14.09	14.22	20.90	20.80	20.95
20 / 80 %	32.46	34.74	36.46	15.40	16.41	21.65	25.50
25 / 75 %	9.61	14.53	14.65	14.58	19.80	18.00	18.10
30 / 70 %	9.83	22.53	25.23	14.19	16.57	18.31	18.58
35 / 65 %	9.24	13.75	14.02	15.63	18.51	19.42	20.12
40 / 60 %	16.27	18.69	21.69	17.67	16.14	18.34	25.50
45 / 55 %	9.98	12.54	14.79	17.68	20.48	19.03	19.28
50 / 50 %	8.78	12.14	14.20	13.66	13.66	19.07	19.21
70 / 30 %	8.78	12.14	14.02	13.66	13.66	19.03	19.22
80 / 20 %	20.33	17.17	11.05	12.14	13.65	16.85	19.98

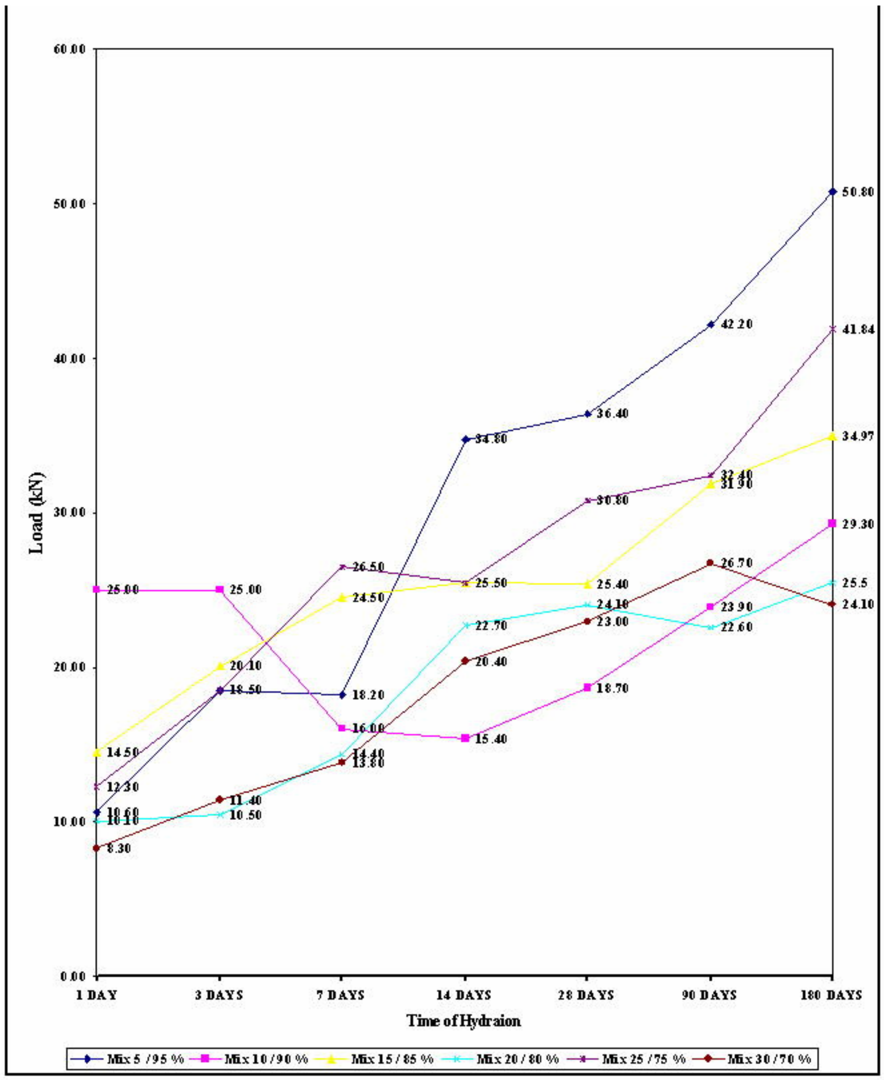

Fig. 1, a: Load Bearing (kN) for Different Mixes of Clay Fired at 800°C / Ordinary Portland Cement.

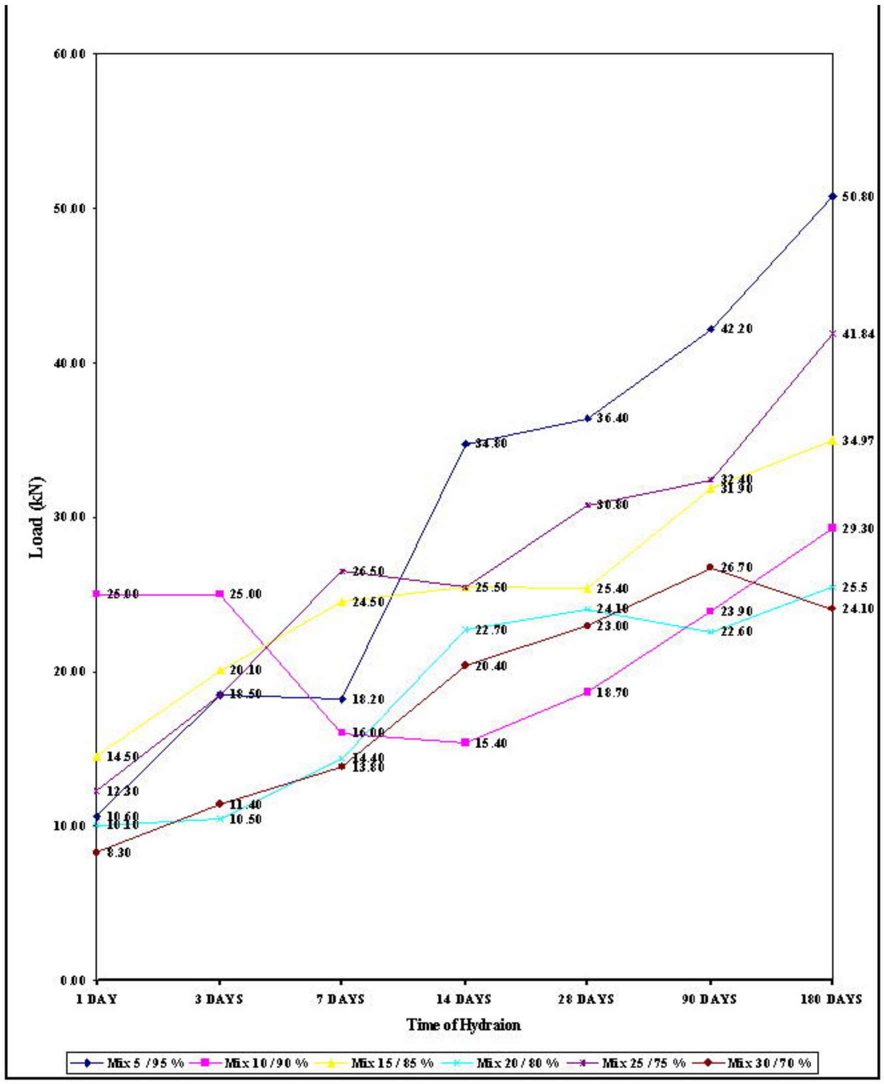

Fig. 1, b: Load Bearing (kN) for different Mixes of Clay Fired at 800°C / Ordinary Portland Cement

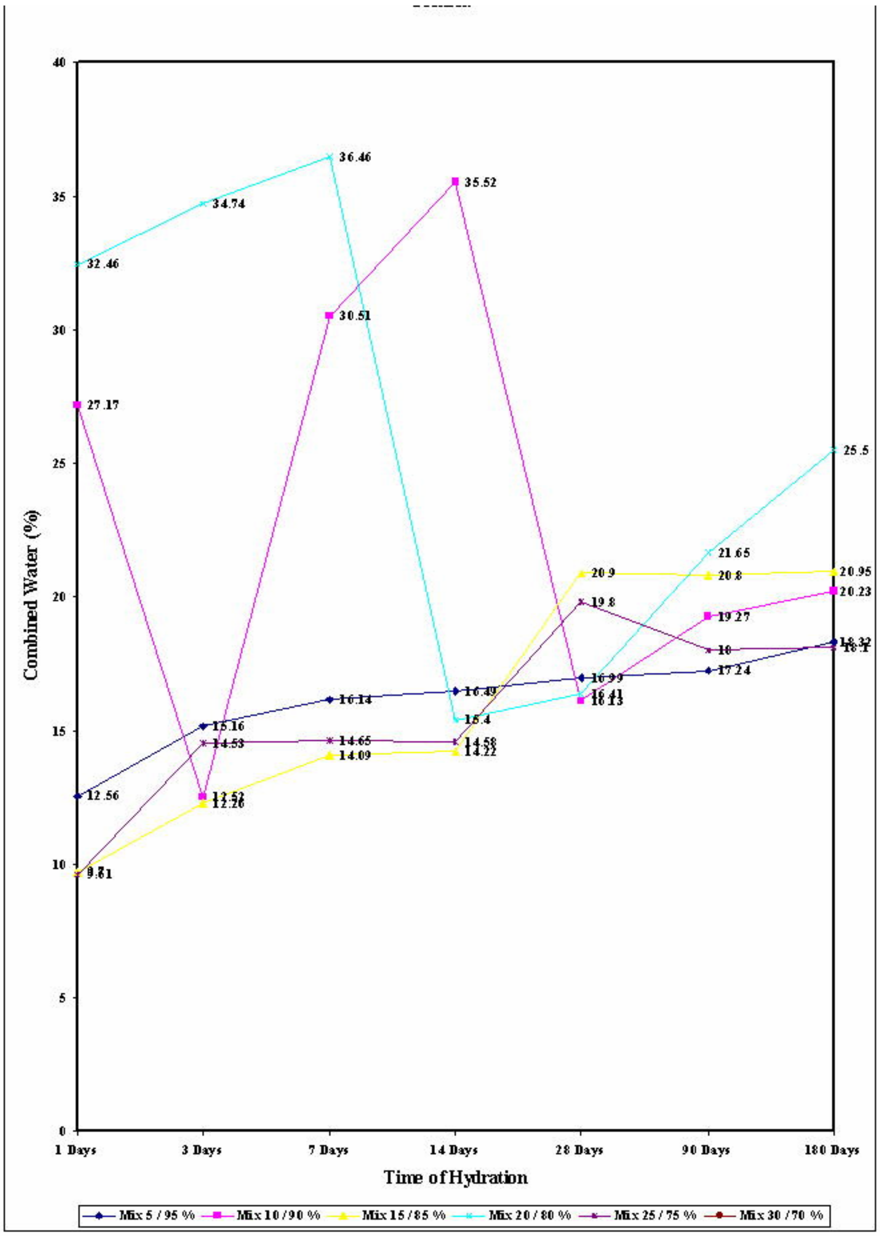

Fig. 2, a: Combined Water (%) of Different Mixes of Clay Fired at 800^{o}C / Ordinary Portland Cement

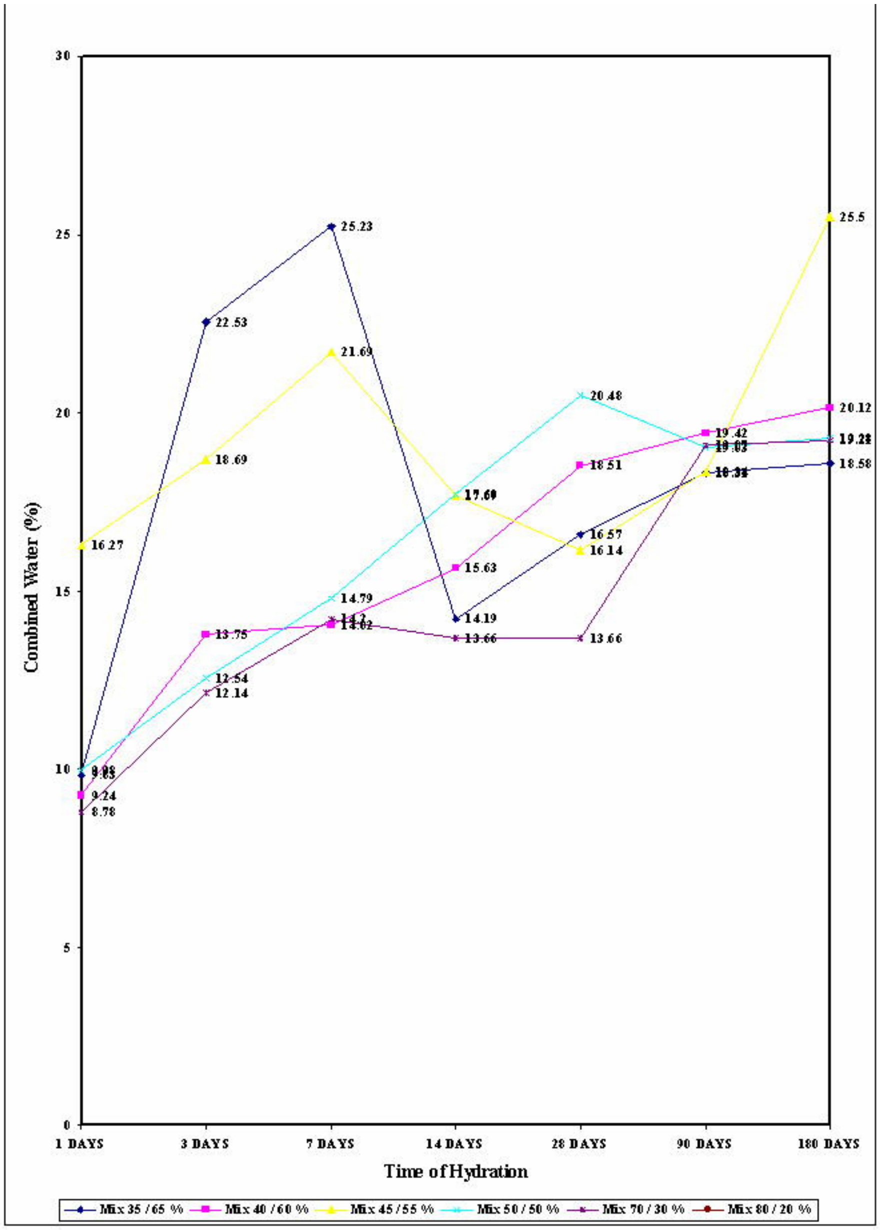

Fig 2, b: Combined Water (%) of Different Mixes of Clay Fired at 800^{o}C / Ordinary Portland Cement