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POZZOLANIC PROPERTIES OF BURNT CLAYS

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Some surface clays from the areas surrounding Lahore and some clays from Mianwali have been investigated for producing pozzolanic materials. Differential thermal analysis was carried out to determine the nature of clay mineral. Optimum burning temperature for each clay was determined through a series of firing tests and subsequent checking for pozzolanic properties by lime-reactivity test. Compressive strength values were compared with Portland cement mortars.

Key words : Pozzolana, Burnt clays, Pozzolanic cement.

INTRODUCTION

Pozzolana is the name given to natural or artificially manufactured materials which, though not cementitious in themselves, contain constituents which will combine with lime at ordinary temperature in the presence of water to form stable insoluble compounds possessing cementing properties. The artificial pozzolanas are mainly products obtained by the heat treatment of natural materials such as clays, shales, certain silicious rocks and pulverised fuel ash (fly-ash). The modern term "Pozzolana" is derived from the ancient term pozzolana which referred to a volcanic ash found near pozzuoli, Italy (near Vesuvius and the Bay of Naples). Such materials have been extensively used by builders for their most magnificient and durable structures from antiquity to the present day. On the basis of investigations [1-10] carried out especially after the second World War, the chemistry of pozzolana has been clarified and we now know the scientific basis for the manufacture of artificial pozzolana. Lime-pozzolan mortars can be used in certain types of construction and have definite advantage over Portland cement mortars. The use of pozzolana as part replacement of cement improves certain properties of mortars and concrete, such as plasticity and workability, reduces bleeding and segregation, increases impermeability, lowers heat of hydration and affords increased resistance to sulphate attack and alkali aggregate reaction. From a structural engineer's point of view these changes in properties mean a better bond, smoother surfaces, uniformity of quality and improved appearance of the finished structure.

The economic and quality-wise merits of lime-pozzolana and the mixtures of pozzolana with Portland cement are sufficient incentives for working in the direction of investigating such raw materials as can be used for the production of artificial pozzolana. We have selected some clays from the area surrounding Lahore with the idea that resources close to the centres of construction activity should be exploited. The selection of clays from Mianwali area has the aim of utilizing such clay deposits which are not useful for more important industries such as ceramics or refractories. The selected clays have been investigated for their mineral content and the optimum calcination temperatures. The pozzolanic activity so developed has been checked by lime reactivity test.

EXPERIMENTAL

Materials used . Surface clays from 'Kahna Kachha/ Jeea Bugga' (No:1) and PCSIR Campus Lahore (No:2) were selected for the study. In addition to these, two calcareous clays (stone forming clays) were collected from 'Jeea Bugga' and 'Kahna Kachha' areas (No: 3 & 4). Two kaolinitic clays from Mianwali clay-mines area were selected (No: 5 & 6). These clays were not useful for ceramic or refractory purposes.

Chemical and mineralogical analysis . Chemical analysis was carried out according to standard silicate analysis using classical methods. The results are presented in Table 1.

Differential thermal analysis and thermogravimetric analysis was carried out on a Hungarian Derivatograph at a heating rate of 10^{o} per min.

Calcination of clays . Clay samples were dried in an electric oven and ground to pass through 25-mesh BS sieve. Samples were divided into the required number of fractions for calcining at various temperatures from 400^{o} to 1000^{o} These fractions were fired at specified temperatures for 3½ hr in an electric muffle furnace and cooled to furnace. The calcined samples were ground in a dry ball mill to pass through a 200-mesh sieve. Ground samples were

Table 1. Chemical analysis of the clays under study.

Sr.No.	Loss/Ignition	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	$Na_2O + K_2O$	TiO_2	Soluble
1.	12.15	57.43	23.37	4.75	o.82	0.19	0.73	0.80	0.84
2.	12.56	56.92	23.76	5.56	0.73	0.21	0.84	0.75	0.72
3.	26.05	34.41	16.23	3.51	19.25	0.26	0.62	0.32	0.36
4.	25.96	34.51	15.96	3.75	19.08	0.21	0.57	0.48	0.28
5.	12.05	53.20	28.03	3.64	0.74	0.23	0.90	0.53	0.47
6.	12.05	23.18	28.35	3.69	0.52	0.23	0.85	0.48	0.41

sealed and stored in high density polythene bags till the clays were tested for lime-reactivity.

Lime-reactivity test. Calcined clay was thoroughly mixed with slaked lime, Ravi sand (–20 + 100) and water in the following proportions by weight :

Clay	3 parts
Slaked lime	1 part
Sand	12 parts
Water	2.75 parts.

A sufficient quantity of the above mixture was shaken in every case in a wooden mould $(2\frac{1}{2}'')^3$/brass mould $(1\frac{1}{2}'')^3$ for 10 min. on an Endecott test sieve shaker. Extra material from the top of the mould was removed with a sharp knife. The moulds containing the samples were placed immediately in a humidity oven at 30° and kept there overnight. The oven was switched on 2 hours before the moulds were placed in it. After 24 hr the specimens were stripped off the moulds, marked for identification and kept under water for 7 and 28 days at 30°. Accelerated curing was done of some specimens at 50° for 8 days.

The compressive strength of the blocks was determined on an Avery 5-ton capacity testing machine. Portland cement-sand mixtures (1:3) were similarly tested for comparative results.

RESULTS AND DISCUSSION

A great deal of work has been done to understand the pozzolanic activity of burnt clays and it has been found that the main cause of this activity is the reaction of amorphous silica and alumina with $Ca(OH)_2$ to form calcium aluminate and calcium silicate or calcium aluminium silicate. Consequently those clays which comprise of minerals capable of producing amorphous silica and alumina when subjected to thermal treatment prove useful raw materials. Such minerals are usually secondary mineral, e.g. kaolinite, montmorillonite, and nontronite. Primary minerals such as feldspar and quartz do not contribute towards pozzolanic activity. The extent of pozzolanic activity of a clay therefore depends on the content and amount of secondary minerals. The optimum temperature of calcination to yield maximum pozzolanic activity differs with the type of major minerals and impurities contained in a clay. Chemical analyses of clays under investigation are presented in Table I. Chemical analysis alone can be a rough guide only. Free iron oxide is known to enhance the pozzolanic activity although the mechanism is not clear. Similarly higher amounts of silica are expected to increase pozzolanic activity. Impurities in general, when these are not the primary minerals, lower slightly the optimum calcination temperature because they catalyse the decomposition of secondary clay minerals. The clays were subjected to differential thermal analysis and thermogravimetric analysis. The results are presented in Figs. 1-12. It is clear that most

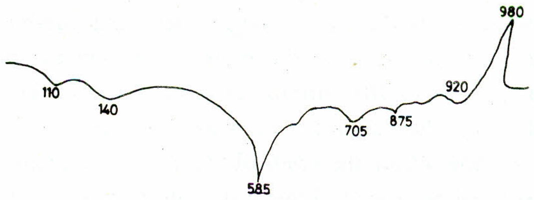


Fig. 1

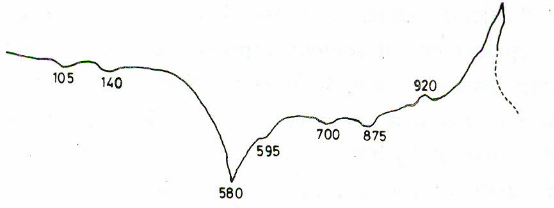


Fig. 2

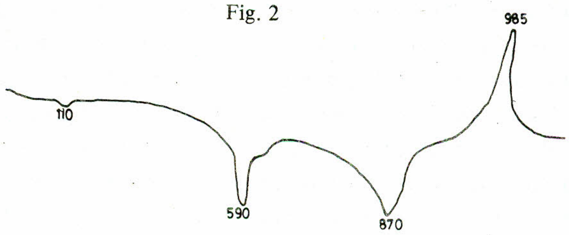
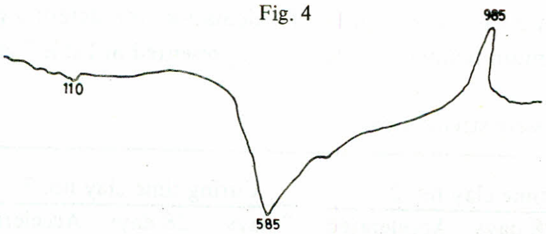


Fig. 3

Fig. 4



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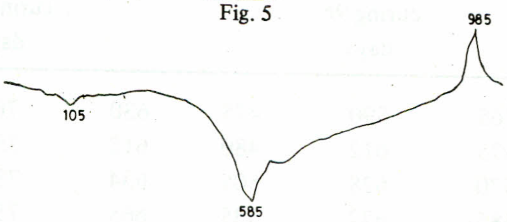


Fig. 6

Fig. 1-6. Differential thermal analysis (DTA).

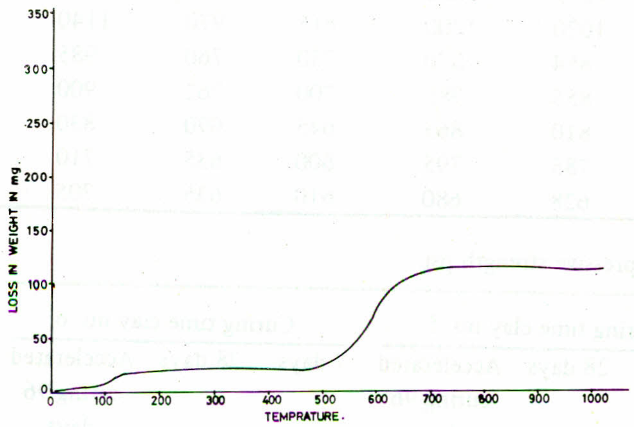
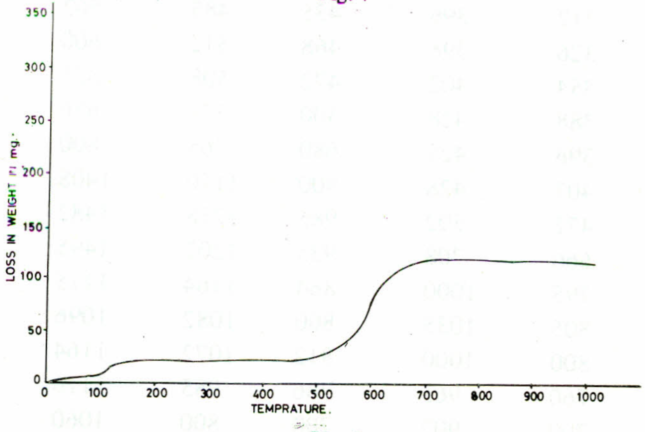


Fig. 7



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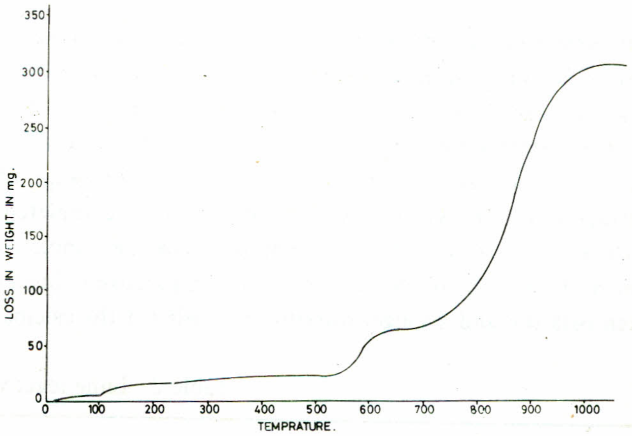

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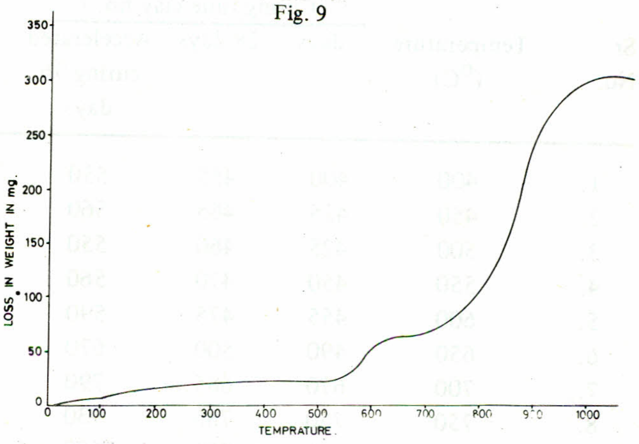

Fig. 10

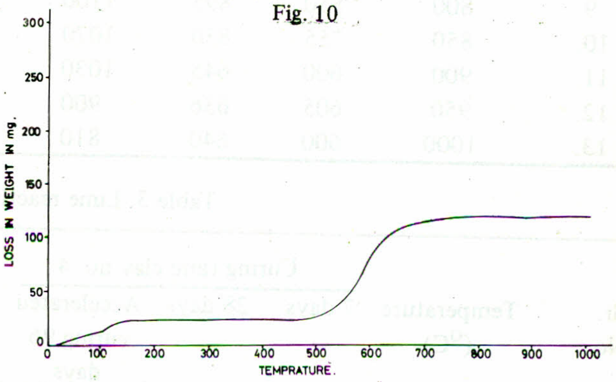

Fig. 11

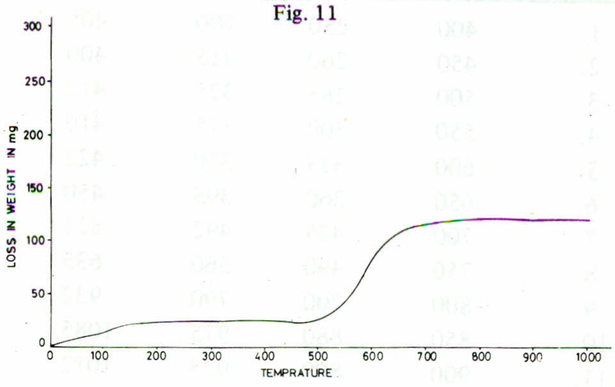

Fig. 12

Figs. 7-12. Thermogravimetric analysis.

of surface clays contain kaolinite as the major clay mineral. Stone forming calcarious clays contain sufficient amount of calcium carbonate in addition to the clay mineral. D T A curves determine exactly the temperature of decomposition of clay minerals and T G A curves give the range of temperature in which the decomposition is completed. These curves show that the decomposition can be completed in a short time if we calcine at a comparatively higher temperature and a longer duration is needed if the calcination is done at a relatively lower temperature. Inspite of all this the optimum calcination temperature has to be determined by practical firing tests since the pozzolanic activity of the clay depends upon the nature of free silica. In using high temperatures there is a possibility of some recrystallisation which can decrease the pozzolanic activity. Low calcination temperatures may leave the decomposition incomplete. The results of calcination for determing the optimum temperature have been presented in Table 2 and 3.

Table 2. Lime reactivity compressive strength psi.

Sr. No.	Temperature (°C)	Curing time clay no. 1			Curing time clay no. 2			Curing time clay no. 3		
		7 days	28 days	Accelerated curing 96 days	7 days	28 days	Accelerated curing 96 days	7 days	28 days	Accelerated curing 96 days
1.	400	400	455	550	470	565	590	475	630	760
2.	450	425	465	560	460	575	612	480	615	750
3.	500	425	460	550	495	570	628	505	634	755
4.	550	450	470	560	500	585	622	535	665	755
5.	600	455	475	590	510	600	635	670	680	790
6.	650	490	500	670	910	1030	1245	880	956	1175
7.	700	670	685	790	920	1095	1280	885	980	1160
8.	750	750	785	930	910	1070	1200	815	970	1140
9.	800	850	895	1100	735	854	1070	730	760	985
10.	850	755	830	1070	730	855	985	700	762	900
11.	900	600	645	1030	720	810	865	645	690	830
12.	950	605	636	900	700	785	795	600	635	710
13.	1000	600	640	810	610	628	680	610	635	705

Table 3. Lime reactivity compressive strength psi.

Sr. No.	Temperature (°C)	Curing time clay no. 4			Curring time clay no. 5			Curing time clay no. 6		
		7 days	28 days	Accelerated curing 96 days	7 days	28 days	Accelerated curing 96 days	7 days	28 days	Accelerated curing 96 days
1.	400	250	300	405	245	312	396	435	485	562
2.	450	260	315	400	240	326	398	468	512	600
3.	500	285	325	412	295	354	402	472	508	625
4.	550	300	375	410	317	388	428	500	572	686
5.	600	315	370	422	333	396	425	680	765	800
6.	650	360	395	450	354	407	428	900	1170	1408
7.	700	435	492	525	408	472	502	985	1218	1482
8.	750	490	560	635	567	666	708	935	1202	1495
9.	800	700	790	932	680	795	1000	864	1164	1175
10.	850	880	975	1085	700	805	1035	800	1082	1096
11.	900	800	925	1012	690	800	1000	812	1072	1164
12.	950	760	910	985	685	760	965	786	985	1116
13.	1000	600	805	885	635	700	902	700	800	1060

Table 4. Compressive strength at the age psi.

Sr. No.	Temperature of Calcination (^{o}C).	28 days	3 months	6 months	13 months	36 months
1.	800	895	1100	1616	1920	2890
2.	700	1095	1280	1725	2035	2965
3.	650	956	1175	1664	1996	2932
4.	850	975	1085	1486	1835	2800
5.	850	805	1035	1385	1585	2766
6.	650	1218	1482	2275	2800	4424
Portland cement.	–	3550	–	–	–	5296

Table 5. L.R: psi values for accelerated curing (i.e. 50^{o}C after 8 days).

Clay No.	Optimum temperature of Calcination (^{o}C).	L.R. values PSI	
		Minimum	Maximum
1.	800	550	1100
2.	700	590	1280
3.	650	475	1175
4.	850	405	1085
5.	700	396	1035
6.	750	435	1482

The pozzolanic activity has been judged from compressive strength values obtained through lime-reactivity test. Calcarious clays did not need the addition of lime and these were tested with the addition of appropriate amount of sand. Compressive strengths were measured after seven days, 28 days. Accelerated curing for 8 days was considered to be equivalent to 96 days. Optimum calcining temperature for clay No. 1, 2, 3, 4, 5, 6 are 800, 700, 650, 850, 850, and 650^{o} respectively. Clay samples burnt at optimum temperatures were tested for their compressive strength after 28 days, 3 months, 6 months, strength values were compared with Portland cement blocks. The results are presented in Tables 4 and 5. After twenty-eight days the strength of pozzolana mixture is about 1/3 of that of Portland cement and attains about 4/5 of the strenght of Portland cement after 36 months.

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REFERENCES

1. ASTM, Designation 618, Ann. Book of ASTM Standards, Part 10, Philadelphia, Pennsylvania, 1976.
2. Milos Polivka, "Pozzolans and Their Use in Concrete", an address given before the structural Engineers Association of Northern California (1967).
3. A.K. Chatterjee, Pozzolanic activity and semiconductivity of fired Kaolin and Kaolinitic clays, Nature, **192**, 1180-1. (1961).
.4 Riccordo Sersale, "Problems of applied mineralogy constitution and reactivity of tuffs, pozzolan and ashes of the volcanic region of the calli Albaui", Revd. Soc. Mineral, Italy, **18**, 215-58 (1962).
5. Pozzolanic Clays of India, Their Industrial Fexploitation and Use in Engineering Works. Spec. Rep No. 1, Cent. Road Res. Inst.' New Delhi (1964).
6. K.M. Alexander Reactivity of ultrafine powders produced from silicous rocks, J.A.C.I., **32**, 557-69 (1960).
7. Morcello Del Guerra, The reactivity of natural and artificial pozzolanas, Ann. Chim. (Rome), **45**, 575-86 (1955).
8. Richard C. Mielenz, witle, Leslie P. Witle, and Glant Omzar J. , "Effect of calcination on natural Pozzolanas" Symp. on the use of Pozzolanic materials in Mortars and concretes, Am. Soc. Test. Mat. Spec. Tech Publ. No. 99, 43-91 (1950).
9. Goroyamag Uchi and Akihisa Kato. "X-ray study for evaluating the activity of Pozzolans", Semento Gijutsu Nenpo, **10**, 214-21 (1956).
10. M.L. Puri and N.R. Srinavasan, A note on the upto date position with regard to the use of Surkhi as a pozzolana, Indian Roads Congr., XXIII-2 (1958), 435.