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Reactive pozzolana from Indian clays—their use in cement mortars

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Abstract

Studies were undertaken to produce reactive pozzolana i.e. metakaolin from four kaolinitic clays collected from different sources in India. The metakaolin produced from these clays at 700–800 °C show lime reactivity in between 10.5 to 11.5 N/mm^2 which is equivalent to commercially available calcined clay Metacem-85. The microstructure of the metakaolin has been reported. The effect of addition of metakaolin up to 25% in the Portland cement mortars was investigated. An increase in compressive strength and decrease of porosity and pore diameter of cement mortars containing metakaolin (10%) was noted over the cement mortars without metakaolin. The hydration of metakaolin blended cement mortars was investigated by differential thermal analysis (DTA) and scanning electron microscopy (SEM). The major hydraulic products like C-S-H and C_4AH_{13} have been identified. Durability of the cement mortars with and without metakaolin was examined in different sulphate solutions. Data show better strength achievement in cement mortars containing 10% MK than the OPC mortars alone.

Keywords: Hydration; Amorphous; Calcium silicate hydrate (C-S-H); Metakaolin; Mortar

1. Introduction

For high workability and proper strength development for use in marine and mass construction works, blended cements are used. Blended cements are Ordinary Portland Cement (OPC) with which pozzolanic materials such as calcined clay, shales, fly ash, or silica fume are admixed with small quantity of gypsum with or without slag. The pozzolana content in OPC can range from 10% to 25%. Portland Pozzolana Cement (PPC) is recommended for use in place of Ordinary Portland Cement in all types of construction. The presence of mineral additions in blended cements gives distinct change of paste composition. The cement paste contains low $Ca(OH)_2$, high C-S-H phase with continuous pores which lowers the permeability of the cement concrete. Such properties provide high durability to blended cements in aggressive media.

Apart from fly ash, other pozzolanic materials in use are volcanic glass, opal, kaolinite-type clay, illite-type clay, montmorillonite type of clay, clay with vermiculite, zeolites, and hydrated oxides of aluminium. There is a evidence that lime pozzolana mixes had become fairly widespread throughout Europe by the 17th century [1]. Utilization of calcined clay pozzolana in the last couple of decades has essentially been linked with construction in seawater and dams in countries like Brazil, Denmark, France, England, USA, and in India and Egypt [2]. In India burnt clay is called as ‘Surkhi’. Its use with lime is famous in many ancient structures in India. Despite historical significance, the use of calcined kaolinitic or illitic clays as a pozzolanic additive for the modern cement and concrete is not very popular. This could be due to relatively higher cost of calcined kaolin or metakaolin compared to other pozzolanic materials such as fly ash and, finally, divided silica. Nevertheless, the utilization of metakaolin as a mineral admixture for cement and concrete is a well-documented practice. Metakaolin has been found to improve mechanical strength, reduce the transport of water and salts through the concrete, and prevent alkali aggregate reaction from occurring [3–6].

Metakaolin has also been used for making cementitious materials called as hydroceramics i.e. ceramic-like materials

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synthesized from a solid aluminosilicate and an alkali-rich solution at low temperature, <100 °C. It has been reported that metakaolin of high lime reactivity (6–7.5 MPa) can be produced by thermal decomposition of kaolin, a naturally occurring clay basically containing kaolinite [Al_2O_3.$Si_2O_5(OH)_4$] mineral and trace of silica and other minerals which can be blended with high quantity of fly ash (over 45%) lime and industrial gypsum to form strong binder of low leachability [7,8]. The use of calcined kaolin i.e. metakaolin has been reported to effectively improve the resistance to sulphate attack in OPC.

India is endowed with large deposits of kaolin. Currently it is being used as a filler in paint, rubber, plastic, chemical, medicines, and ceramic industries. The kaolin has not been exploited for the production of reactive pozzolana. Metakaolin has been found to improve mechanical strength, reduces the transport of water and salts through the concrete, and prevents alkali aggregate reaction from occurring.

Researches have been carried out at CBRI, Roorkee, to produce reactive pozzolana i.e. metakaolin from four kaolinitic clays collected from different sources in India. The metakaolin were produced by heating the clays at 700–800 °C. The lime reactivity of the metakaolin was determined as per relevant Indian Standards. The microstructure of the metakaolin is reported. The effect of addition of metakaolin up to 25% on the compressive strength, porosity, and pore size diameter was studied in the Portland cement mortars. The hydration of metakaolin blended cement mortars with age was investigated by differential thermal analysis (DTA) and scanning electron microscope (SEM) to identify the major hydraulic products. The durability of cement mortars with and without MK was studied in different sulphate solutions up to a period of 1 year. The findings of these studies are discussed in this paper.

2. Experimental

2.1. Raw materials

Four samples of kaolinitic clay collected from Amrapali (Maharastara), Bikaner (Rajasthan), and Bhuj (Gujarat) of chemical compositions (Table 1) were used to prepare pozzolana. Cement from Gujarat Ambuja Cements Ltd. was used for mortar studies.

Table 1
Chemical composition of clay samples

Constituents (%)	Amrapali (White)	Bikaner (Black)	Bhuj (Grey)	Amrapali (White)
SiO_2+insoluble in HCl	53.2	50.9	52.1	54.0
Al_2O_3+Fe_2O_3	44.9	43.1	42.6	44.0
CaO	0.02	0.05	0.09	0.02
MgO	–	0.08	1.02	0.06
SO_3	0.27	0.01	0.02	0.08
Na_2O+K_2O	0.50	0.26	0.22	0.31
Loss on ignition	3.20	4.90	3.60	3.55
pH (10% slurry)	6.40	6.20	6.20	6.30
Sp.Gr.	2.59	2.60	2.51	2.64

Table 2
Lime reactivity of metakaolin

Metakaolin (MK)	Lime reactivity (N/mm^2)	IS : 1344 Limits
MK-1	10.52	
MK-2	9.35	
MK-3	7.91	
MK-4	9.60	Min. 4.0
Metacem-85	11.26	

2.2. Preparation of metakaolin

The clay samples were crushed to the size of 0.25 to 0.5 in. and heated at 600, 700, and 800 °C for a period of 2.0 h, cooled and ground to pass 75-μm IS sieve (equivalent to specific surface area 500–550 m^2/kg (Blaine). The calcined clay/metakaolin, thus produced was tested for lime reactivity as per IS: 1727–1967 [9].

2.3. Preparation of cement mortar, its testing, and evaluation

5 cm×5 cm×5 cm cubes of mortar were cast using metakaolin and standard triple graded sand in the proportion 1:3 by weight at 105±5% flow. After 24-h moist curing, the cubes were demoulded and cured in water till testing.

2.4. Hydration of cement–metakaolin mixture

The ordinary Portland cement was partially substituted by metakaolin (burnt at 800 °C) with 5, 10, 15, 20 and 25 wt.%. The cement pastes were prepared using the standard consistency with water cement ratio 0.30%. The cubes were broken and ground to pass 150-μm sieve for differential thermal analysis (DTA) and scanning electron microscopy (SEM) tests.

The cement mortars were moulded into 2.5 cm×2.5 cm×2.5 cm cubes at normal consistency and hydrated for different periods, crushed and soaked in acetone and then placed in a vacuum oven at 60 °C to remove acetone and dried for 48 h. The cement mortars were reduced to 3 mm in size for pore-size distribution and porosity using a "Pore sizer 9320" mercury intrusion porosimeter (Micromeritics) with a maximum mercury intrusion pressure of 210 MPa.

3. Results and discussion

3.1. Lime reactivity of metakaolin

The metakaolin produced by heating the kaolin retains the similar composition of acidic and basic oxides as of kaolin except a decrease in loss of ignition content (0.30% to 0.90%). The fineness of the metakaolin was

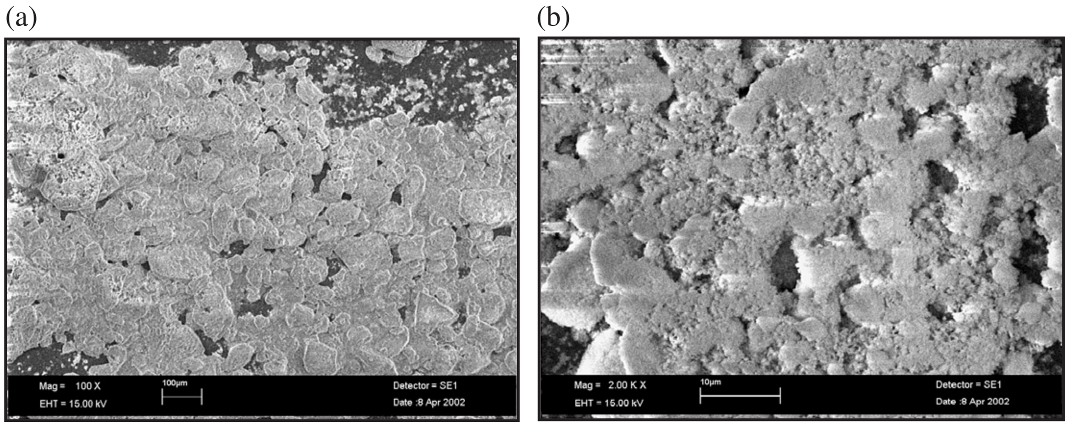

Fig. 1. SEM photographs of metakaolin sample (a) MK-1 and (b) Metacem-85.

in the range of 0.50% to 3.0% retained over 325 mesh (45 μm) sieve which is close to the fineness of the Metacem-85.

The lime reactivity of the calcined clays or any pozzolana is studied by determining their capacity to react with lime in presence of water. The lime reactivity of the metakaolin produced from the four samples of the clays was determined as per IS: 1727–1967 [9]. The results are reported in Table 2. Data show that all the metakaolin samples develop high strength values that the minimum specified value of 4.0 N/mm^2. The metakaolin sample MK-4, however, attained lime reactivity close to the lime reactivity of the commercial reactive pozzolana namely Metacem-85. The high reactivity of the metakaolin samples may be attributed to their amorphous structure as observed by their SEM. The SEM photographs of the metakaolin MK-1 and that of Metacem-85 are shown in Fig. 1. Data show that rounded bodies of high surface area showing reactive centres for the lime interaction can be seen in detail. It can be seen that both MK-1 and Metacem- 85 pozzolanic materials have the similar amorphous structure. The major factor in producing the metakaolin for use as a supplementary material, or the reactive pozzolana is to complete the dehydroxylization (removal of lattice water) process without any over calcination. Heating of kaolin beyond a definite temperature may form a sintered product not fit for use in cement and concrete. Hence, overheating of the kaolin has to be avoided in order to get reactive pozzolana.

Table 3
Properties of cement-metakaolin mortars

Composition (By wt.%) OPC–metakaolin (MK-1)–sand	Compressive strength (N/mm^2)			Water-retentivity (%)
	3 days	7 days	28 days	
100:0:3	7.9	8.55	11.8	15.5
95:5:3	10.6	11.8	15.3	45.6
90:10:3	9.2	11.92	17.5	56.6
85:15:3	9.5	10.86	14.1	51.2
80:20:3	10.6	11.6	12.12	48.2
75:25:3	9.4	11.70	13.54	47.1

3.2. Effect of metakaolin in cement mortar

The effect of replacement of cement with the metakaolin on the properties of cement mortar is reported in Table 3. An increase in compressive strength of cement mortar was noticed with the addition of metakaolin over the cement mortar without metakaolin. Maximum gain of strength was found at 10% replacement of OPC with the metakaolin.

The gain in strength of OPC–metakaolin mixture may be attributed to the following mechanism. When water is added to the OPC–metakaolin mixture, then lime concentration is high. The silica and alumina go into solution quickly, reacting to form two products, tetracalcium aluminate hydrate and calcium silicate hydrate. Both are precipitated as soon as saturation is approached. Results showed that addition of metakaolin prolonged initial and final setting times of cement.

$$\underset{\text{Metakaolin}}{Al_2O_3 \cdot 2SiO_2} + \underset{\text{Lime}}{5\,Ca(OH)_2} + \underset{\text{Water}}{19H_2O} \rightarrow \underset{\text{Tetracalcium aluminate Hydrate}}{Al_2O_3 \cdot 4CaO \cdot 19H_2O} + \underset{\text{Calcium silicate Hydrate}}{CaO \cdot 2SiO_2}$$

3.3. Porosity and pore-size distribution

The results of mercury intrusion porositometer are summarized in Table 4. The results show at all the curing periods, the pore size, and the porosity decreased. It can be

Table 4
Average pore diameter and porosity of cement mortars

Curing period	Average pore diameter (μm)		Total porosity (%v/v)	
	OPC–10% MK	OPC mortar	OPC–10% MK	OPC mortar
3 days	0.0266	0.0371	15.22	21.11
7 days	0.0252	0.0362	15.10	18.10
28 days	0.0187	0.0342	13.38	16.58
90 days	0.0176	0.0336	11.20	13.40

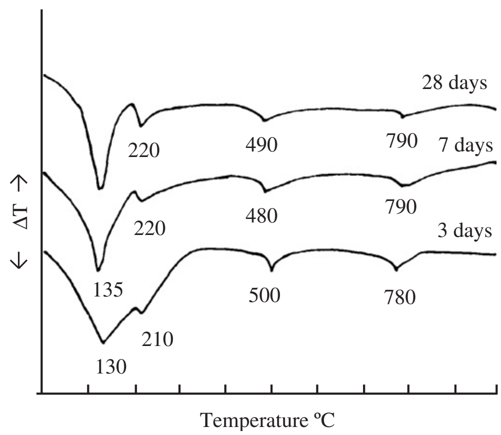

Fig. 2. Differential thermograms of OPC–metakaolin mix hydrated for different periods.

seen that the cement mortars containing 10% metakaolin possess lower values of pore diameter and porosity than the plain cement mortars. This amply demonstrates the higher pore structure refinement for the cement mortars containing metakaolin. These findings corroborate the results of Khatib and Wild [10] and Frias and Carbera [11].

Hydration of OPC–metakaolin mixtures were monitored by DTA and SEM. DTA of hydrated cement showed (Fig. 2) formation of endotherms of major hydraulic products such as C-S-H(1) (130–135 °C), hexagonal calcium aluminate hydrate (C_4AH_{13}) (180–200 °C), and $Ca(OH)_2$ (480–500 °C) due to their decomposition reactions. The endotherms at 750–770 °C is due to decomposition of calcium carbonate ($CaCO_3$). An increase in peak areas of C-S-H(1) and C_4AH_{13} was observed with increase in metakaolin up to 10%.

SEM (Fig. 3) showed formation of dense subhedral to euhedral crystals of C-S-H(1) and C_4AH_{13} interspersed with short length ettringite at 3 days (a) of curing. Appearance of partially hydrated amorphous SiO_2 and Al_2O_3 can also be seen. At 7 and 28 days of hydration (b and c), well-crystallized CSH(I) formed. With the increase in curing period (d), well-developed euhedral CSH(I) crystals with little unhydrated metakaolin are formed. The formation of these crystals is responsible for increase in strength of OPC–metakaolin mortar than the plain OPC mortar. Replacement of metakaolin with silica fume (up to 5%) did not show appreciable improvement in compressive strength of the cement.

3.4. Durability of OPC–metakaolin mortars

The durability of cement mortar and concrete in sulphate atmosphere is significant from the point of view of their use in marine and industrial environment.

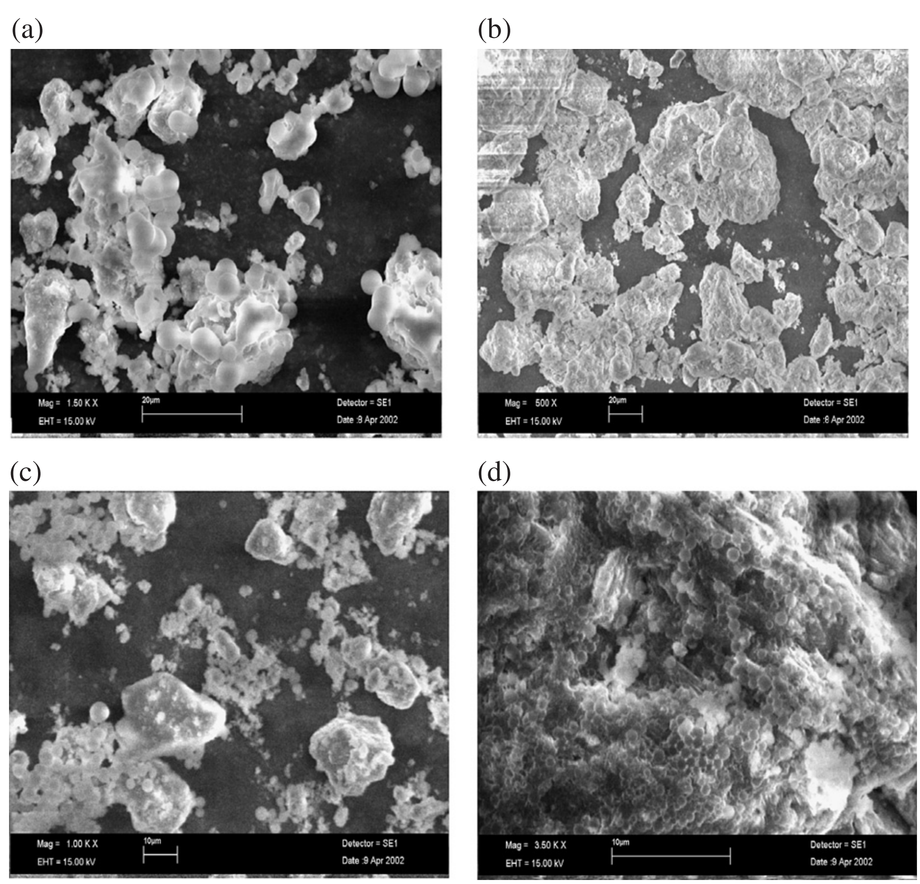

Fig. 3. SEM of OPC-metakaolin mixture hydrated for different periods: (a) 3 days, (b) 7 days, (c) 28 days, and (d) 90 days.

Table 5
Compressive strength of OPC–metakaolin mortars in sulphate solutions (OPC–MK–Sand : : 90–10(1)–3)

Sulphate solutions (%)	Compressive strength (MPa)					
	3 days	7 days	28 days	90 days	180 days	360 days
Na_2SO_4 (5%)	11.3	16.6	17.4	17.8	18.5	19.9
$(NH)_2SO_4$ (4%)	15.0	16.6	16.9	18.4	19.2	19.1
$MgSO_4$ (4%)	11.3	16.0	16.6	17.1	18.1	18.6
Na_2SO_4(2%)+NaCl (2%)	16.1	17.1	17.6	17.9	18.4	18.8
OPC–sand mortar (1:3)						
Na_2SO_4(5%)	10.9	12.7	16.0	17.2	17.8	19.1
$(NH)_2SO_4$ (4%)	11.0	12.9	13.8	13.9	17.1	17.6
$MgSO_4$ (4%)	11.1	12.2	15.1	16.1	16.5	17.2
Na_2SO_4(2%)+NaCl (2%)	13.2	13.6	15.2	15.8	16.1	16.6

Sulphate attack in cement mortars and concrete has been studied for many decades. It is believed that sulphate attack of portland cement is caused by chemical reactions between cement ingredients and sulphate ions from different sources [12,13] that helps in the formation of ettringite and gypsum, giving rise to excessive expansion, cracking, and strength loss. Typically these constituents are monosulphate hydrate (C_4ASH_{12}), calcium aluminate hydrate (C-A-H), and calcium hydroxide (CH). The sulphate attack can be contained when the C_4ASH_{12} and C-A-H are reduced or eliminated by either controlling C_3A content of the portland cement, or by substituting a portion of the portland cement with suitable blending material. The addition of blending materials such as pozzolana can effectively reduce the CH content of the hydrated OPC.

Thus, the durability of OPC mortars replaced with 10% Metakaolin was studied by immersing 28-day cured 2.5 cm×2.5 cm×2.5 cm cubes in different sulphate solutions. The strength of the OPC–metakaolin–sand mortar (1–3 by wt.) vis-à-vis plain cement–sand mortar in different sulphate solutions is listed in Table 5.

Data show when OPC was mixed with 10% metakaolin, the binder developed better strength values than the OPC mortars alone. This may be attributed to the formation of higher amount of CSH and C_4AH_{13} in the OPC–MK mix due to higher rate of reaction between amorphous silica and alumina of MK with the lime released from the cement. The higher reactivity of MK in OPC mortars may be due to its Al_2O_3 phases [14], which are associated in the formation of gehlenite (C_2ASH_8) and the crystalline C_4AH_{13} phase [15].

4. Conclusions

Indian kaolinitic clays are suitable for making reactive pozzolana. The pozzolana (metakaolin) produced by heating the clays at 800–850 °C showed high lime reactivity which is close to commercially available reactive pozzolana Metacem-85. The metakaolin can be used up to 10% as a replacement to ordinary Portland cement in the cement mortars without any reduction in strength, rather compressive strength was improved over the OPC mortars. The formation of increased amount of C_4AH_{13} and the CSH (I) can be responsible for higher strength development in OPC–metakaolin mortars than the plain OPC mortars. The OPC–metakaolin mortars (90:10 by wt.%) show better sulphate resistance than the OPC mortars owing to enhanced formation of CSH and C_4AH_{13} in former than latter. The use of metakaolin in cement mortars is recommended.

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