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Cementitious binder from fly ash and other industrial wastes

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Abstract

In this paper, investigations were undertaken to formulate cementitious binder by judicious blending of fly ash with Portland cement as well as by admixing fly ash with calcined phosphogypsum, fluorogypsum, lime sludge, and chemical activators of different finenesses. The effect of addition of calcined clay in these types of binders was studied. Data showed that cementitious binders of high compressive strength and water retentivity can be produced. The strength of masonry mortars increased with the addition of chemical activators. The strength development of binders takes place through formation of ettringite, C-S-H, and C_4AH_{13}. The binders are eminently suitable for partial replacement (up to 25%) of the cement in concrete without any detrimental affect on the strength. The results showed that fly ash can be used in the range from 45% to 70% in formulating these binders along with other industrial wastes to help in mitigating environmental pollution.

Keywords: Fly ash; Cement; Waste management; Ettringite

Large quantities of industrial by-products are produced every year by chemical and agricultural process industries in India (Table 1). These materials have dual problems of disposal and health hazards. By-products such as phosphogypsum, fluorogypsum, and red mud contain harmful impurities that interfere with the normal setting and hardening of building materials from which they are produced. Among various industrial wastes produced so far, the utilization of fly ash, phosphogypsum, fluorogypsum, lime sludge, red mud, and mine tailings is important to saving the environment from quick degradation.

Fly ash is a major solid industrial waste. It occupies a considerable amount of land and pollutes air and water sources. The disposal of fly ash is an environmental problem, as fly ash discharged on land may quickly spread far. Fly ash has been utilized successfully in the production of various building materials, such as Portland pozzolana cement [1], lime-pozzolana mixtures [2], lime-fly ash cellular concrete [3], fly ash-sand-lime bricks [4], clay fly ash bricks [5], and precast building units [6]. Activated slag-fly ash blends were developed to form non-Portland cements or blended cements having strength properties at par with ordinary Portland cement for use as masonry cement [7]. In some countries, fly ash is processed further by classification techniques to obtain uniform grain size distribution [8]. There are considerable data reported on the durability of concrete produced using slag and fly ash [9]. A new binder with high strength, good volume stability, and excellent water resistance has been developed using fly ash, fluorogypsum, and Portland cement as the main raw materials [10].

Recently, a ternary mix known as Fal-G comprising fly ash, lime, and gypsum has been in production in small quantities in India for use as construction material [11]. In addition to fly ash, phosphogypsum, fluorogypsum, and lime sludges are the important industrial wastes generated as by-products from the phosphatic fertilizer plants, hydrofluoric acid units, and sugar, paper, acetylene, soda ash, tanneries, and ammonium sulfate fertilizer manufacturers. There have been reports on the utilization of these wastes for making cementitious binders and building products [12,13].

To reduce pollution and disposal of these industrial wastes, there is an urgent need to develop useful building materials from them. With this view, investigations were undertaken to produce cementitious binders by blending the fly ash with Portland cement as well as by suitably proportioning the fly ash with calcined phosphogypsum, fluorogypsum, lime sludges, and chemical additives. The influence of calcined clay in the formulation of these cementitious binders was investigated. Various physical properties of the cementitious binders at different finenesses were studied. The correlation between strength development and the formation of hydraulic products was established with the help of differential thermal analysis. The suitability of cementi-

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Table 1
Production of agricultural-industrial wastes in India

No. Sl. wastes	Source	Availability (Million tons/annum)
1. Fly ash	Thermal power plants	65.0
2. Blast furnace slag	Iron and steel industry	10.0
3. Lime sludge	Paper, sugar, fertilizer, acetylene, chromium industry, tanneries, soda ash	5.0
4. Phosphogypsum	Phosphoric acid fertilizer	5.0
5. Fluorogypsum	Hydrofluoric acid industry	0.2
6. Red mud	Aluminium industries	2.0
7. Ferro alloy and other metallurgical slags	Ferro Chrome Ferro manganese and ferrosilicone alloys and smelting of zinc and copper	3.5
8. Cement kiln dust	Cement industry	5.0
9. Mine tailings	Zinc, copper, gold, iron ore beneficiation plants	5.5
10. Cinder	Thermal power plants and railways using lump coal	3.0
11. Water works silts	Water works	>10.0
12. Lime kiln rejects	Lime kilns	Large quantity
13. Coal washery rejects	Coal washeries	Large quantity
14. Rice husk	Rice shellers	>30.0
15. Bagasse	Sugar industries	5.25
16. Jute stick	Jute industry	2.05
17. Ground nut shell	Ground nut oil mills	5.75
18. Cotton sticks	Cotton plantation	10.05
19. Saw mill waste	Saw mill and wood Based panel industries	2.0

tious binder for making masonry mortars and concrete was examined.

1. Experimental

1.1. Raw materials

Fly ash, OPC, fluorogypsum, phosphogypsum, lime sludges, and clay of chemical compositions given in Table 2 were used as raw materials for making the cementitious binders. The clay was calcined at 700°C for 1.5 h to produce pozzolana conforming to Indian standard specification IS 1344-1981, specification for calcined clay pozzolana.

1.2. Preparation and testing of cementitious binders

The cementitious binders were prepared by blending the ground fly ash and Portland cement to specific surface areas of 300, 400 and 500 m^2/kg (Blaine) in different proportions. Replacement of fly ash with OPC up to 25.0% (by mass%) was studied. In addition to fly ash-OPC binders, the cementitious binders were prepared by blending the ground fly ash, fluorogypsum, OPC, hydrated lime sludge, and a chemical activator in the proportion 60:10:15:15:1, followed by intergrinding to a fineness of 500 m^2/kg (Blaine) (designated as binder A). In other binder composition designated as binder B, the ingredients were mixed using fly ash, fluo-

Table 2
Chemical composition of fly ash, OPC, fluorogypsum, phosphogypsum, lime sludge, and calcined clay

Constituents (%)	Fly ash	OPC	Fluorogypsum	Phosphogypsum	Lime sludge	Calcined clay
P_2O_5	—	—	—	1.40	3.6	—
F	—	—	1.2	0.51	1.0	—
Organic matter	—	—	—	0.30	—	—
Cl	—	—	—	0.10	0.10	—
$Na_2O + K_2O$	0.76	—	—	0.07	0.16	—
SiO_2	62.90	22.50	0.67	1.25	3.1	53.09
$R_2O_3(Al_2O_3 + Fe_2O_3)$	28.35	9.60	0.61	0.70	0.50	46.01
CaO	1.50	61.50	40.44	32.20	52.0	0.29
MgO	0.80	2.65	Tr.	Tr.	0.31	0.60
SO_3	0.20	1.75	56.0	44.0	0.16	—
LOI	1.50	2.00	0.62	19.48	41.00	—
$CaSO_4 \cdot 2H_2O$	—	—	—	94.60	—	—
pH	—	—	2.50	5.0	11.0	—

Basis: oven-dried temperature (42–105°).

Table 3
Properties of cementitious binder prepared from fly ash and OPC at 27°C and > 90% relative humidity

Materials (by mass%)		Fineness (m^2/kg)	Consistency	Compressive strength (MPa)				Bulk density (kg/m^3)			
FA	OPC	(Blaine)	(%)	1 day	3 days	7 days	28 days	1 day	3 days	7 days	28 days
90	10	300	38.2	0.4	0.8	1.0	1.9	1130	1300	1410	1440
		400	32.0	0.6	1.3	1.7	5.0	1148	1520	1550	1580
		500	33.3	1.0	1.7	2.5	5.7	1148	1520	1550	1580
85	15	300	37.1	0.6	1.1	2.3	5.0	1138	1410	1420	1450
		400	32.0	1.1	1.8	2.9	8.0	1148	1490	1570	1520
		500	33.3	1.2	2.6	4.3	10.1	1147	1500	1620	1650
80	20	300	37.3	1.2	3.3	4.7	12.9	1131	1330	1440	1440
		400	30.3	1.6	5.1	8.8	15.1	1155	1620	1660	1630
		500	32.4	1.8	5.8	9.3	20.1	1162	1650	1690	1700
75	25	300	36.3	1.9	3.8	6.0	15.7	1150	1360	1390	1400
		400	30.3	2.1	5.5	9.8	21.0	1559	1660	1650	1670
		500	31.4	2.2	5.9	13.8	22.1	1167	1680	1720	1730

FA: fly ash; OPC: ordinary Portland cement.

rogypsum, lime sludge, calcined clay, and chemical activator in a ratio of 50:10:20:20:1.0 (by mass%).

Cementitious binders were prepared in which fly ash was blended with 25% calcined clay pozzolana (by mass%). These binders were prepared by blending the ground fly ash with calcined clay and other ingredients such as phosphogypsum plaster/fluorogypsum, hydrated lime sludge, OPC, and chemical activators to a fineness of 500 m^2/kg (Blaine).

The cementitious binders were cast into 2.5 × 2.5 × 2.5 cm cubes at normal consistency for compressive strength. The cubes were cured in water at 27 ± 2°C for 28 days and tested for strength and bulk density values. The compressive strength of mortar of the cementitious binders with and without addition of chemical activators was studied using binder and sands of fineness modulus 1.26 and 1.82 in proportions of 1:3, 1:4, and 1:5 by mass at 105 ± 5% flow. The

Table 4
Effect of $CaCl_2$ activator on the properties of fly ash–OPC binders at 27°C and > 90% relative humidity

Materials (by mass%)		$CaCl_2 \cdot 2H_2O$	Fineness (m^2/kg)	Consistency	Compressive strength (MPa)				Bulk density (kg/m^3)			
FA	OPC	(by mass%)	(Blaine)	(%)	1 day	3 days	7 days	28 days	1 day	3 days	7 days	28 days
90	10	1.0	300	39.0	0.1	0.4	0.4	0.6	1260	1310	1340	1350
		2.0	300	38.0	0.3	0.5	0.8	1.1	1350	1360	1380	1380
		1.0	400	32.6	0.2	0.5	0.6	0.5	1570	1553	1550	1560
		2.0	400	32.6	0.4	0.6	0.9	0.9	1550	1610	1630	1600
		1.0	500	32.3	0.6	0.8	1.0	2.1	1650	1650	1680	1690
		2.0	500	31.4	0.4	0.8	1.4	3.6	1650	1660	1730	1690
85	15	1.0	300	37.3	0.7	1.2	2.3	5.1	1290	1320	1330	1340
		2.0	300	37.4	0.8	1.5	2.4	5.9	1340	1370	1390	1440
		1.0	400	32.0	1.2	2.0	3.9	9.1	1550	1560	1590	1600
		2.0	400	31.4	1.2	2.8	4.0	9.8	1520	1560	1640	1650
		1.0	500	32.7	1.2	2.6	4.5	11.6	1680	1680	1700	1680
		2.0	500	32.7	1.6	5.6	8.2	15.7	1730	1700	1700	1710
80	20	1.0	300	37.3	0.6	3.9	5.2	13.0	1390	1390	1400	1420
		2.0	300	37.1	1.1	3.2	5.5	13.6	1430	1440	1450	1470
		1.0	400	32.0	1.7	5.2	8.9	16.3	1430	1530	1560	1570
		2.0	400	32.7	1.7	5.4	9.2	17.9	1470	1570	1570	1580
		1.0	500	31.4	2.0	5.8	9.4	20.2	1720	1740	1760	1720
		2.0	500	31.4	2.8	6.4	11.3	21.7	1690	1716	1720	1700
75	25	1.0	300	36.3	2.0	3.9	4.6	14.3	1420	1460	1520	1530
		2.0	300	36.3	2.2	3.9	5.4	14.5	1380	1420	1450	1480
		1.0	400	32.0	2.1	5.8	10.0	21.2	1490	1500	1510	1530
		2.0	400	32.6	2.4	6.2	11.4	23.0	1410	1480	1550	1540
		1.0	500	31.1	1.8	6.0	11.9	22.7	1720	1750	1650	1760
		2.0	500	30.7	3.4	7.8	14.2	24.4	1630	1650	1750	1680

Table 5
Properties of cementitious binder

Binder designation	Consistency (%)	Setting time (h)		Compressive strength (MPa)				Bulk density (kg/m^3)			
		Initial	Final	1 day	3 days	7 days	28 days	1 day	3 days	7 days	28 days
A	35.6	0.30	4.25	6.9	9.7	13.6	32.8	1550	1560	1580	1650
B	37.5	1.24	5.30	8.0	18.6	23.7	36.9	1530	1660	1660	1670

Table 6
Composition of cementitious binders

Binder designation	Composition								
	Binder A2	Fly ash	Calcined clay	Plaster of Paris from phosphogypsum	Lime sludge	OPC	Fluorogypsum	$CaCl_2 2H_2O$	$Na_2SO_4 \cdot 10H_2O$
A1	—	60	25	—	—	15	—	2.0	—
A2	—	45	25	10	20	—	—	—	—
A3	—	40	25	—	20	—	15	—	1.0
A4	90	—	—	—	10	—	—	—	—

Table 7
Properties of cementitious binders

Binder designation	Consistency (%)	Setting time (h)		Compressive strength (MPa)				Bulk density (kg/m^3)			
		Initial	Final	1 day	3 days	7 days	28 days	1 day	3 days	7 days	28 days
A1	32.57	—	—	0.6	0.6	0.6	1.2	1460	1470	1520	1460
A2	37.0	2.21	5.10	11.1	19.1	21.9	27.2	1650	1740	1780	1650
A3	34.0	1.32	4.25	12.2	21.9	32.9	36.7	1850	1880	1870	1880
A4	38.3	—	—	9.8	17.6	21.9	24.0	1540	1570	1660	1600

mortar mix 1:3, binder-standard sand (triple graded) was cast as per IS 4031-1968, specification for physical tests of hydraulic cements. The concrete cubes (10 cm) were cast according to IS 516-1991, methods of test for strength of concrete using 15.0% and 25.0% replacement of Portland cement by the cementitious binder, gravel, and Badarpur sand (F.M.2.2) in proportions 1:2:4 and 1:3:6 at water-to-cement ratio of 0.5.

2. Results and discussion

2.1. Properties of cementitious binders

The properties of the cementitious binders containing fly ash and OPC mixtures with and without $CaCl_2$ activator are listed in Tables 3 and 4. Data show increase in strength and bulk density with increase in fineness and curing period in all the compositions. Highest compressive strength was achieved in the binder mix 75:25 (fly ash:OPC). The consistency of the binders in general was reduced, and the minimum consistency was recorded for the binder mix 75:25 (fly ash:OPC); hence, maximum attainment of strength was obtained (Table 3). With addition of $CaCl_2$ activator, the binder strength increased at the initial stage of curing, but 28-day strength was not affected appreciably (Table 4) compared to results given in Table 3. The results are contrary to the findings of Shi [14], who reported strong acceleration of strength at 28 days rather than at 3 and 7 days of curing. However, with addition of mixture of activators

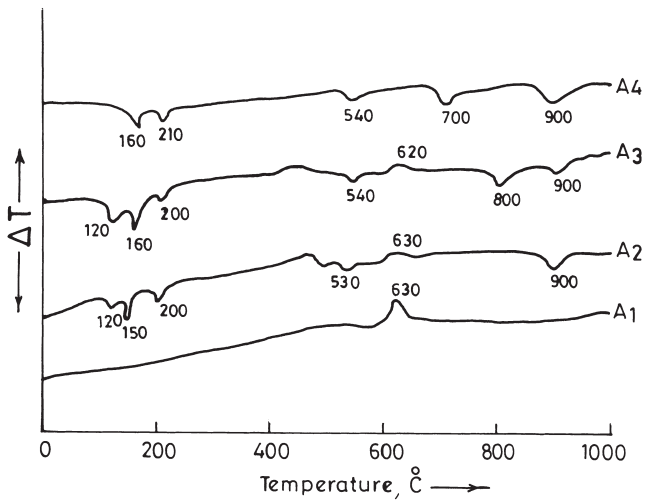

Fig. 1. Differential thermograms of cementitious binders hydrated for 28 days.

Table 8
Properties of mortars

S1. no.	Proportion of mortars (by mass)		Compressive strength (MPa)	
	Binder	Sand	7 days	28 days
1		(F.M. 1.26)		
	1	3	2.8	6.3
	1	4	2.5	5.4
	1	5	1.1	4.5
2		(F.M. 1.82)		
	1	3	4.0	5.6
	1	4	3.7	5.3
	1	5	2.8	4.5
3		(Standard sand)		
	1	3	7.3	14.5
	IS 3466-1989 limits		Min 2.5	Min 5.0

F.M.: fineness modulus.

such as Na_2SO_4 and $CaCl_2$, no appreciable enhancement in strength of the cementitious binder was noted. The suitability of binder was examined for masonry mortars and found to comply with the requirements given in IS 3466-1988, specification for masonry cement.

The physical properties of cementitious binders A and B are listed in Table 5. It can be seen that the binder B developed higher values for strength and bulk density than binder A, probably because of the more alkaline environment in the latter than the former. The development of higher strength in these binders can be attributed to the formation of cementitious products (C-S-H, ettringite) due to interaction of the calcined clay with the hydrated lime sludge.

The composition of cementitious binders produced by replacing fly ash with 25% clay pozzolana and other materials and their properties are listed in Tables 6 and 7. It can be seen that binder A3 developed maximum strength and bulk density at a much faster rate than the other binders A1, A2, and A4. The strength development in these binders can be ascribed to the formation of C-S-H, ettringite ($C_3A{\cdot}3CaSO_4 \cdot 32H_2O$), and C_4AH_{13} compounds, which is amply demonstrated by differential thermal analysis. The thermograms (Fig. 1) shows endotherms at 120°C, 150°–160°C, 200°C, 530°–540°C, and 800°–900°C due to formation of ettringite, C_4AH_{13}, Ca $(OH)_2$, and $CaCO_3$, respectively. The intensity of C-S-H, ettringite, and C_4AH_{13} phases is more pronounced in binder A3 than the other binders, confirming development of higher strength in the former than the latter.

2.2. Properties of mortars

The compressive strength of masonry mortars prepared from the cementitious binders are listed in Table 8. Data show that mix proportions 1:3 and 1:4 binder-sand (fineness modulus 1.26 and 1.82) mortars comply with the strength requirements laid down in IS 3466-1988.

2.3. Role of cementitious binder in concrete

The compressive strength results of concrete cubes (10 cm) prepared with 15% to 25% replacement of cement with binder A3 are listed in Table 9. Data show that the compressive strength was reduced when replacing OPC with binder as compared to plain cement concrete. However, 28-day strength is much higher than the minimum specified strength of 15.0 and 10.0 MPa for the concrete mixes 1:2:4 and 1:3:6, respectively, as specified in IS 456-1988, code of practice for plain and reinforced concrete. Costwise these binders are cheaper than the Portland cement.

3. Conclusions

1. The cementitious binders can be produced by blending fly ash with OPC as well as by mixing fly ash, phosphogypsum plaster, fluorogypsum, hydrated lime sludge, OPC, calcined clay pozzolana, and chemical activator.
2. Ettringite, C-S-H, and C_4AH_{13} were identified as the major cementing compounds responsible for strength development in binders.
3. The cementitious binders are eminently suitable for use in masonry mortars and for making concrete.

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Table 9
Compressive strength of concrete

S1. no.	Mix proportion (mass %)				Compressive strength (MPa)	
	Cement	Binder (A3)	Sand	Coarse aggregate	7 days	28 days
1	85	15 (1)	2	4	16.8	26.9
	75	25 (1)	2	4	12.0	25.2
2	85	15 (1)	3	6	8.6	12.8
	75	25 (1)	3	6	5.8	11.3
3	1	—	2	4	19.0	30.7
	1	—	3	6	8.7	13.6

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