Pergamon

Cement and Concrete Research 32 (2002) 1717–1724

CEMENT AND CONCRETE RESEARCH

Cementitious properties of metakaolin–normal Portland cement mixture in the presence of petroleum effluent treatment plant sludge

N.J. Saikia[a], P. Sengupta[a], P.K. Gogoi[b], P.C. Borthakur[a,*]

[a]Regional Research Laboratory, CSIR, Jorhat, Assam 785 006, India
[b]Department of Chemistry, Dibrugarh University, Dibrugarh, Assam 786 004, India

Received 8 January 2002; accepted 3 May 2002

Abstract

The physicochemical characteristics of cocalcined kaolin and petroleum effluent treatment plant (ETP) sludge and its effect on the technological and hydration characteristics of cement have been presented. Conductivity measurements indicate that both the sludge ash (SA) and cocalcined kaolin–sludge mixtures in aqueous medium are reactive in nature. The rate of hydration was investigated by determining the combined water (CW) and $Ca(OH)_2$ content in the hydration products. The hydration products were characterized by FTIR spectrophotometric method and XRD analysis technique. The rates of hydration of cement containing cocalcined kaolin–sludge mixtures are comparatively higher than the others. Blended cements with improved technological properties may be prepared by replacing 20% cement with cocalcined kaolin–sludge mixtures containing up to 30% sludge.

Keywords: Blended cement; Metakaolin; Oil field effluent treatment plant sludge; Pozzolana; Waste management

1. Introduction

The production of cement is a highly energy consuming process. Different types of waste materials are increasingly used in production of cement [1,2]. Utilization of these materials for the purpose not only eliminates the problems associated with their disposal but also results in cement of improved properties.

Calcined clay is one of the earliest known pozzolanic materials. It is even used today in places devoid of industrial wastes like fly ash, granulated blast furnace slag, etc. Kaolin is widely distributed in nature and the use of metakaolin (MK) in blended cement production has been well established [1]. The calcination temperature of kaolin and the properties of MK produced from it depend on the physicochemical characteristics of the clay and the nature and amount of impurities associated with it.

Petroleum effluent treatment plant (ETP) produces a voluminous sludge, containing hydrocarbon more than the permissible level (3%) for safe disposal by land filling. The sludge in combination with a clayey soil may be used in production of building materials, wherein the hydrocarbon present in the sludge partly meets the fuel requirements in the burning process [3]. The sludge ash (SA) is slightly pozzolanic in character but it alone is not suitable as a mineral admixture for cement [4]. It was earlier reported that the hydration characteristics of MK–lime system might be improved if the kaolin is cocalcined with sludge [5].

This communication reports the physicochemical characteristics of cocalcined kaolin–sludge mixtures and its effect on the technological and hydration characteristics of normal Portland cement (NPC).

2. Experimental

2.1. Materials

The sludge was collected from the ETP of Lakwa oil field, situated in Assam, in the northeastern region of India. It was dried at 100±5 °C and ground before use. Kaolin, in powder form, marketed by English India Clay Company, India and cement clinkers produced by Bokajan Cement Factory (Cement Corporation of India) were used. The

* Corresponding author. Tel.: +91-376-337-0117; fax: +91-376-337-0011.
E-mail address: pcborthakur@yahoo.com (P.C. Borthakur).

0008-8846/02/$ – see front matter
PII: S0008-8846(02)00865-7

clinkers were ground in a laboratory ball mill to around 300 m^2/kg fineness and mixed with 4% gypsum to prepare NPC. Mixtures containing the dry sludge and kaolin in the mass ratios of 10:90, 20:80, 30:70, and 40:60 were prepared and homogenized. The sludge, kaolin, and sludge–kaolin mixtures were separately calcined in the presence of a sufficient amount of air in an electrically heated chamber furnace maintaining heating rate of ~10 °C min^{-1}. The samples were kept at 750 °C for 1 h and then allowed to cool to room temperature in the furnace and stored in airtight containers in a desiccator. Blended cements containing 20% (w/w) MK, SA, and cocalcined kaolin–sludge mixtures were prepared and homogenized in a ball mill. The compositions of the cocalcined kaolin–sludge and cement samples are given in Table 1.

2.2. Procedure

The chemical composition of the samples and blended cements were determined by standard analytical methods. The calcined products were analysed by FTIR technique using a Perkin Elmer System 2000 FTIR spectrometer. The conductivities of MK, SA, and cocalcined kaolin–sludge mixtures were determined in aqueous medium by suspending the solid in distilled water maintaining a solid/water ratio of 1:50 (w/v) using an automatic conductivity meter.

The Ca^{2+} and OH^- ion concentrations in the NPC and various blended cements were determined by extracting the same with distilled water maintaining a solid/water ratio of 1:50 (w/v) and titrating against standard EDTA and HCl solutions, respectively. Maximum care was taken to avoid carbonation.

The hydration characteristics of the various cement compositions were determined by following the method described earlier [5]. Pastes were prepared by mixing the cement compositions with distilled water maintaining solid/water ratio of 1:2 (w/v) in an agate mortar for ~5 min. The pastes were immediately transferred to polythene bags and then stored in a desiccator at ambient temperature for hydration to various periods. Hydration was arrested by grinding about 5 g of the pastes with a mixture of 1:1 acetone/methanol for ~5 min in an agate mortar. It was filtered using a Buchner funnel, washed several times with acetone and methanol mixture, dried at 65±5 °C for 2 h, sealed in polythene bags, and then stored in a desiccator.

The rates of hydration of the cement compositions were measured by determining the $Ca(OH)_2$ (CH), as well as chemically combined water (CW) in the pastes. The CH content was determined by ethylene glycol method as described in Indian standard [6]. The CW was calculated from the total loss in 100–1000 °C minus the loss due to CH and $CaCO_3$. The latter was calculated from the weight loss in the temperature range 600–850 °C. Triplicate experiments were done for estimating these parameters.

The hydrated products were characterized by FTIR and XRD techniques. The FTIR spectra were taken in a Perkin Elmer System 2000 FTIR spectrometer using KBr pellet method. The XRD patterns of the samples were taken in a JEOL X-ray diffractometer, model ZDX-11P3A, using Cu K_α radiation.

The setting times and water requirements of the cementitious mixtures were measured by Vicat needle penetration method as described in Indian standard methods [7]. The compressive strengths were determined on 2.5 cm×2.5 cm× 2.5 cm mortar cubes prepared using 1:3 ratio of the cementitious compositions and graded sand [7]. The water-to-cement ratios (W/C) were maintained in the range of 0.36–0.47 to achieve similar degree of flow. The cubes were cured for 24 h in an air atmosphere at room temperature and then in water until the determination of compressive strengths. Three specimens were tested for compressive strength.

3. Results and discussions

3.1. Characterization of mixtures

The oxide compositions of MK, SA, and cocalcined sludge–kaolin mixtures are shown in Table 2. The free lime content in the SA is high. However, in the cocalcined kaolin–sludge mixtures, it is quite low, possibly due to solid-state reactions of the CaO-bearing components in the sludge with the silica and alumina components of the clay.

The FTIR patterns of the kaolin, MK, SA, and cocalcined kaolin–sludge mixtures are shown in Fig. 1. The kaolin exhibits characteristics bands at 3694, 3625, 1107, 1031, 918, 788, 756, 542, 471, and 428 cm^{-1} [8]. The intensities of the bands in the 3600–3700-cm^{-1} region are sharp indicating well crystallinity of the kaolin. The 750 °C-heated kaolin (MK) does not exhibit peaks due to kaolin but a new broad peak at 800-cm^{-1} region indicating destruction of kaolin structure and formation of MK [9]. MK formation leads to change of octahedrally coordinated Al^{3+} in kaolin into tetrahedral

Table 1
Composition of the cocalcined kaolin–sludge and cement mixtures

Mixtures	Compositions
MS1	co-calcined 10% sludge containing kaolin mixture
MS2	co-calcined 20% sludge containing kaolin mixture
MS3	co-calcined 30% sludge containing kaolin mixture
MS4	co-calcined 40% sludge containing kaolin mixture
Control	NPC
CM	20% MK in NPC
CMS1	20% cocalcined 10% sludge containing kaolin mixtures in NPC
CMS2	20% cocalcined 20% sludge containing kaolin mixtures in NPC
CMS3	20% cocalcined 30% sludge containing kaolin mixtures in NPC
CMS4	20% cocalcined 40% sludge containing kaolin mixtures in NPC
CS	20% SA in NPC

Table 2
Oxide compositions of MK, SA, cocalcined kaolin–sludge mixtures, and cement (wt.%)

Material	SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO	SO_3	Na_2O+K_2O	Free lime (g/1000 g)
MK	53.53	44.85	0.54	0.40	0.52	–	0.52	–
SA	18.93	48.12	25.04	1.30	0.56	2.68	1.05	7.12
MS1	50.07	45.18	2.99	0.49	0.53	0.27	0.35	0.84
MS2	46.61	45.50	5.44	0.58	0.53	0.54	0.43	1.45
MS3	43.15	45.84	7.89	0.67	0.53	0.80	0.51	2.02
MS4	39.69	46.16	10.34	0.76	0.54	1.07	0.59	3.79
Cement	18.25	6.24	62.05	3.87	3.45	3.05	0.67	0.32

Al^{3+}. The spectra of the cocalcined kaolin–sludge mixtures exhibit some new weak bands in the 600–900-cm^{-1} region. This is attributed to some new phases formed due to solid-state reactions of Ca^{2+}, Al^{3+}, Fe^{3+}, etc. ions of the SA with the silica and alumina of the clay. The SA exhibits sharp peak at around 1420 cm^{-1} due to calcium carbonate but its intensity is quite low in the cocalcined kaolin–sludge mixtures.

The electrical conductivities of the suspensions of MK, SA, and cocalcined kaolin–sludge mixtures in water are shown in Fig. 2. The electrical conductivity of MK is very low and remains constant for a long duration. On the other hand, the conductivity of the SA is quite high and it increases with time, indicating gradual solubilization and ionization of some ash constituents. The conductivities of MK increase when it is calcined in the presence of sludge, but it is less than that of the SA. The slopes of the conductivity curves, i.e., the rate of conductivity rise with respect to time of the SA and cocalcined kaolin–sludge mixtures initially show a decreasing trend. This indicates that the lime liberated from the cocalcined kaolin–sludge products and SA combines with some reactive components presents in the mixtures.

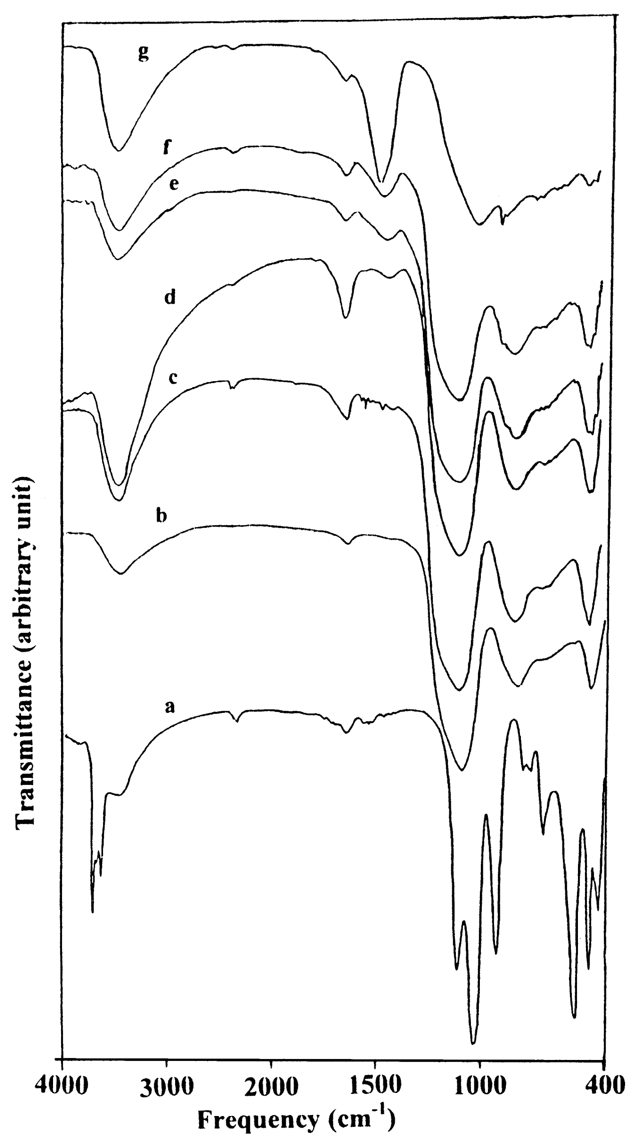

Fig. 1. FTIR spectra of (a) kaolin, (b) MK, (c) MS1, (d) MS2, (e) MS3, (f) MS4, and (g) SA.

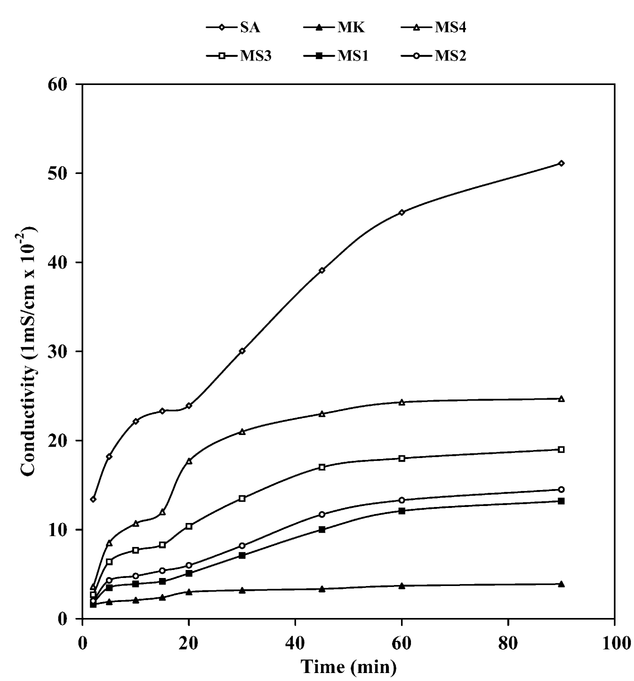

Fig. 2. Electrical conductivities of suspensions containing different pozzolans.

3.2. Cementitious properties

The Ca^{2+} ions present in the water extracts of the cementitious compositions hydrated for various periods are shown in Fig. 3. The Ca^{2+} ion concentrations for all the samples initially show an increasing trend, followed by a decreasing trend, and finally an increasing trend. The initial increase in concentration is due to dissolution of Ca^{2+} ions from the materials and the decrease in concentration is attributed to reaction with silica and alumina present in the mixtures forming initial hydrated products. The increase in Ca^{2+} ion concentration at later stages (after 24 h) is due to liberation of Ca^{2+} ions due to hydration of the clinker phases. The Ca^{2+} ion concentrations of the blended cement compositions are always lower than the control. This is partly due to the decrease of the amount of cement content in the mixtures and also due to the pozzolanic reactions between the liberated Ca^{2+} ions with reactive components of pozzolana. The Ca^{2+} ions concentration of the cementitious mixtures containing sludge is lower than that containing MK alone. This indicates that calcination of kaolin in the presence of sludge enhances the pozzolanic activity of the MK.

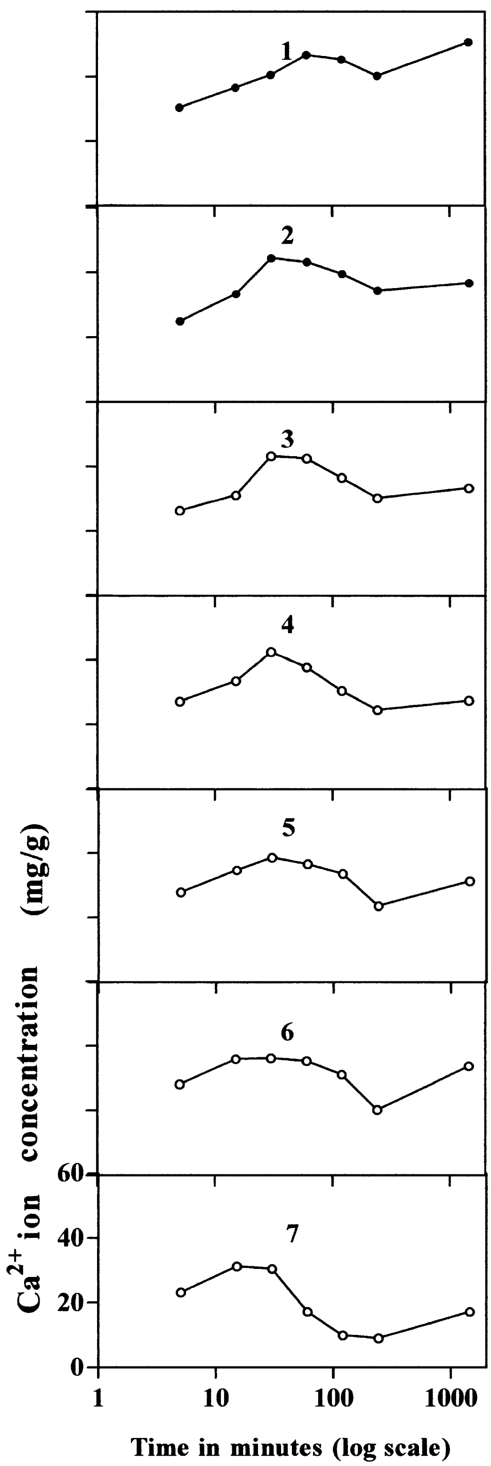

Fig. 3. Ca^{2+} concentrations in the water extracts of the cementitious compositions: (1) control, (2) CM, (3) CMS1, (4) CMS2, (5) CMS3, (6) CMS4, and (7) CS.

Table 3
CH and CW contents in the cement pastes

Compositions	CH content (%)				CW content (%)			
	2 days	7 days	15 days	28 days	2 days	7 days	15 days	28 days
Control	4.31	6.23	9.05	5.12	5.21	8.76	14.21	23.45
CM	3.21	5.15	7.21	2.32	5.43.	9.45	16.33	25.32
CMS1	3.20	4.03	6.01	2.01	6.75	9.25	16.30	25.43
CMS2	2.45	3.21	4.32	1.23	7.02	9.63	19.47	26.54
CMS3	2.10	2.94	2.21	1.01	8.57	10.21	22.44	26.61
CMS4	2.05	2.75	3.67	3.45	6.23	8.95	16.56	20.12
CS	2.21	3.10	4.23	4.81	5.21	5.34	14.91	18.56

The change of OH^- concentrations of the extracts with time (not shown) also exhibits similar trend. It initially exhibits an increasing trend followed by a decreasing trend for sometimes and then increases again. The results can be explained similarly as that for Ca^{2+} content in mixtures.

The CH contents in the cement pastes with respect to time are shown in Table 3. The CH content of all the pastes is high at the early ages. The CH contents in the blended cement compositions are always lower than the control. The high CH content in the 2-day hydration products is due to the liberation of Ca^{2+} ions from the clinker phases during hydration and the lower CH contents of the blended cement pastes is due to its consumption through pozzolanic reactions. The CH contents of the blended cements prepared using cocalcined kaolin–sludge mixtures containing up to 30% sludge are always lower than that containing MK alone. This indicates that kaolin, when calcined in the presence of a limited amount of sludge, results in MK of higher pozzolanic activity. The CH content in the 28-day hydration products of the blended cements prepared using cocalcined kaolin–sludge mixture containing 40% sludge and SA are slightly higher than the other compositions.

The chemically combined water in the hydration products of all the cement compositions (Table 3) increases with

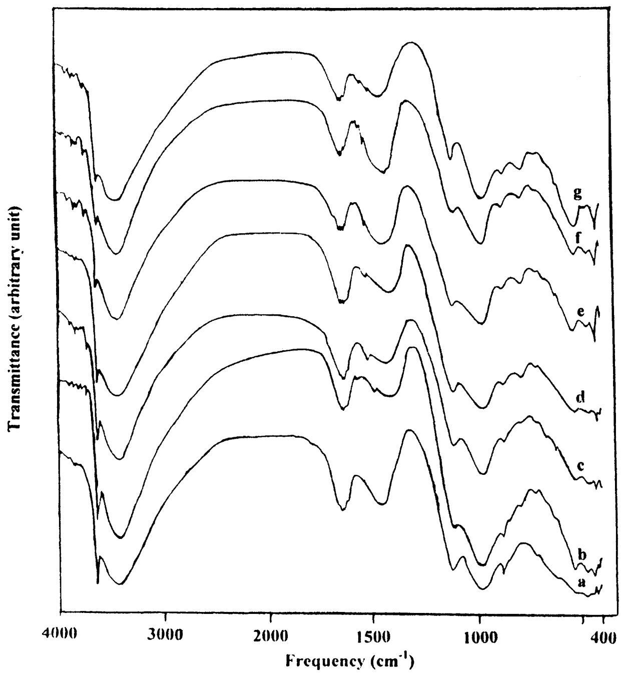

Fig. 4. FTIR spectra of 2-day hydration products of (a) control, (b) CM, (c) CMS1, (d) CMS2, (e) CMS3, (f) CMS4, and (g) CS.

increasing hydration time. The hydration products of the compositions containing cocalcined kaolin–sludge mixtures containing up to 30% sludge contain a high amount of chemically combined water than the control as well as MK-containing blended cement, indicating the presence of a high amount of hydrated products in these compositions.

FTIR patterns in the 400–4000-cm^{-1} region of the 2-, 7-, and 28-day hydration products of the cementitious mixtures are shown in Figs. 4–6. Different bands observed and their assignments [10–13] are shown in Table 4.

The 2-day hydration products of all the samples show characteristics peaks at 970 cm^{-1} due to C-S-H, and at ~3430 and 1640 cm^{-1} due to water. The samples show peaks at 1105 and ~420 cm^{-1}, indicating the formation of ettringite. The intensity of the peak at 3640 cm^{-1} due to CH is approximately same for the control and MK-blended cements. The intensity of the CH peak in the cocalcined kaolin–sludge and SA-containing blended cements is less than the other compositions. This corroborates the earlier findings that the pozzolanic activity of MK is enhanced when the clay is calcined in the presence of sludge. The bands at ~530 cm^{-1}, due to Al–O vibrations, is more intense in the blended cement containing MK than the control. The intensities increase further in the compositions containing cocalcined kaolin–sludge mixtures and SA, indicating the formation of a higher amount of C-A-H-type compounds.

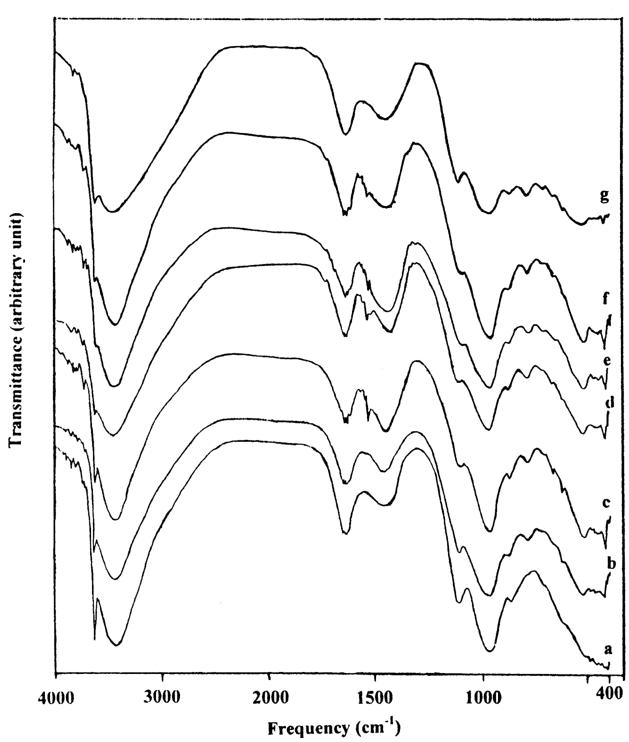

Fig. 5. FTIR spectra of 7-day hydration products of (a) control, (b) CM, (c) CMS1, (d) CMS2, (e) CMS3, (f) CMS4, and (g) CS.

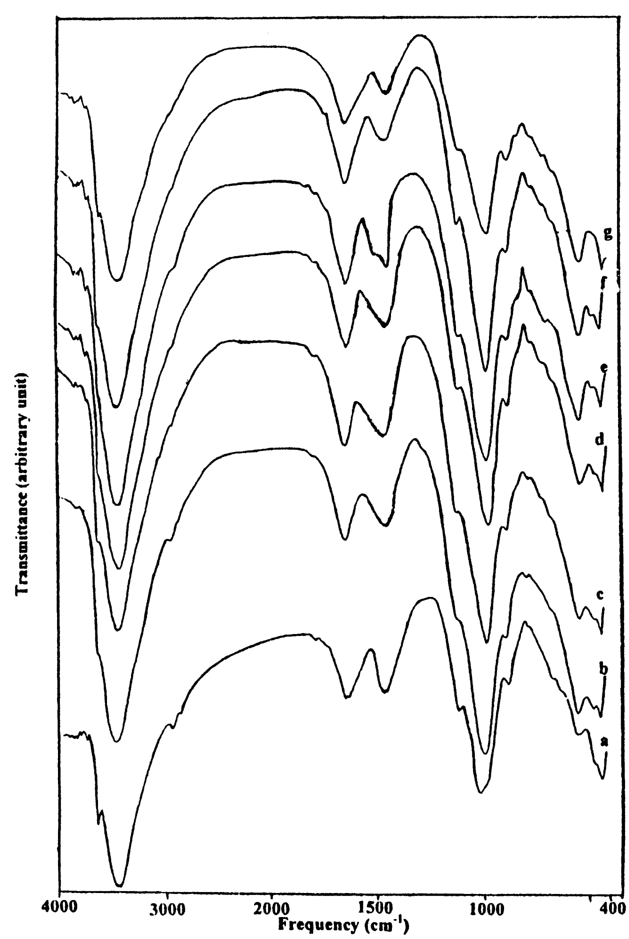

Fig. 6. FTIR spectra of 28-day hydration products of (a) control, (b) CM, (c) CMS1, (d) CMS2, (e) CMS3, (f) CMS4, and (g) CS.

Table 4
FTIR bands assignments of hydrated products

Wave number (cm^{-1})	Characteristics
3640	ν, OH^-, free CH
3430	$\nu_1+\nu_3$, H_2O
3011, 2965	ν_1, H_2O
1640	ν_2, H_2O
1430	ν_3, CO_3^{2-}
1105	ν_3, SO_4, $C_6A\bar{S}_3H_{32}$
970	ν_3, SiO_4, C-S-H
875	ν_2, CO_3^{2-}
821	ν, C-A-H
780	ν, C-A-H
716	ν_4, CO_3^{2-}
664	ν, Al–O, C-A-H
530	ν, C-A-H
460	ν, Al–O, C-A-H
420	ν_2, SO_4^{2-}, $C_6A\bar{S}_3H_{32}$

The intensities of the bands due to C-S-H (970 cm^{-1}), C-A-H (~530 cm^{-1}), and H_2O (~3430 and 1640 cm^{-1}) increase on prolonging the hydration time to 7 days or more due to increased formation of hydration products. The intensity of the peak due to CH (3640 cm^{-1}) in the 7-day or more hydration products of the control also increases indicating more hydration but in the blended cement it decreases indicating consumption of liberated CH due to pozzolanic reactions. The intensity of the CH peak is lowest for the composition containing cocalcined kaolin–sludge mixture containing 30% sludge.

The 28-day hydration products the control exhibit prominent band at 3640 cm^{-1}, indicating the presence of a considerable amount of CH. The intensity of this band is less in the hydration products of the blended cement containing MK and it decreases further in the products of compositions containing the cocalcined kaolin–sludge mixtures. The hydration products of the composition containing cocalcined kaolin–sludge mixture containing 30% sludge exhibits only a shoulder at 3640 cm^{-1}. Almost the entire CH, produced in hydration of the clinker phases, is therefore consumed by the pozzolana prepared by calcining the kaolin in the presence of 30% sludge. The intensity of the CH band in the hydrated products of the blended cement prepared using cocalcined kaolin–sludge mixtures containing 40% sludge and SA are found to increase on prolonging the hydration to 28 days indicating lower pozzolanic activity of the compositions.

The XRD patterns of the 28-day hydrated products (not shown in the figure) of the cement samples are diffused due to the gel-like nature of the products. The control cement pastes shows peaks at d=2.63, 4.93, and 1.93 Å due to CH. The blended cement compositions containing 20% SA also shows a weak peak at 2.63 Å, indicating the presence of CH. The peaks due to CH could not be detected in the blended cement compositions containing MK and cocalcined kaolin–sludge mixtures. Possibly, the amount is too small and beyond the detection level of the instrument used. All the hydrated products exhibit peak due to calcite (d=3.03, 2.23, and 1.88 Å) and ettringite (d=9.56, 8.23, and 3.87 Å). The blended cement compositions containing MK and cocalcined kaolin–sludge mixtures show a peak at d=2.87 Å, which may be due to strätlingite.

Table 5
Physical properties of cementitious mixtures

Mixture	Specific surface (Blaine, cm^2/g)	Specific gravity (g/cm^3)	Weight/volume (g/l)
Control	3352	2.74	1624
CM	5675	2.68	1360
CMS1	4965	2.60	1332
CMS2	4616	2.55	1331
CMS3	4480	2.41	1321
CMS4	4012	2.40	1305
CS	3524	2.02	1295

The physical and technological properties of the cement samples are shown in Tables 5 and 6. Due to increased fineness of MK, the water requirement of the composition containing MK is higher than the control. The water requirements increase further in compositions containing cocalcined kaolin–sludge mixtures and SA and are due to presence of free lime (Table 5).

The initial and final setting times of the blended cements containing MK are more than the control. The setting times of the cements containing cocalcined kaolin–sludge mixtures decrease with increase of the amount of sludge. The cement containing SA sets immediately. The relatively short setting times of blended cements containing sludge is possibly due to the presence of relatively high amounts of Al_2O_3, Fe_2O_3, Na_2O, and $CaCO_3$ than the control as well as MK-blended cements.

The Le-chatelier's expansions of the blended cements containing MK and cocalcined kaolin–sludge mixtures containing up to 30% sludge is less and that containing cocalcined kaolin–sludge mixtures containing 40% sludge and SA are more than the control cement. The increase in expansion is due to presence of a high amount of free lime in the sludge.

The compressive strengths of the mortar cubes of different cementitious compositions at different ages up to 90 day are shown in Fig. 7. The cement compositions containing cocalcined kaolin–sludge mixture containing 30% sludge

Table 6
Water requirements, setting times, and expansions of the cement pastes

Sample	Water requirements (%)	Setting times (h:min.)		Expansion (mm) (Le-chatelier)
		Initial	Final	
Control	35.0	2:10	2:40	7.5
CM	43.0	3:12	3:50	4.5
CMS1	43.5	2:00	2:45	4.5
CMS2	44.5	1:58	2:03	4.0
CMS3	46.5	1:42	1:92	3.5
CMS4	48.0	1:33	1:12	8.0
CS	51.5	0:02	–	15.0

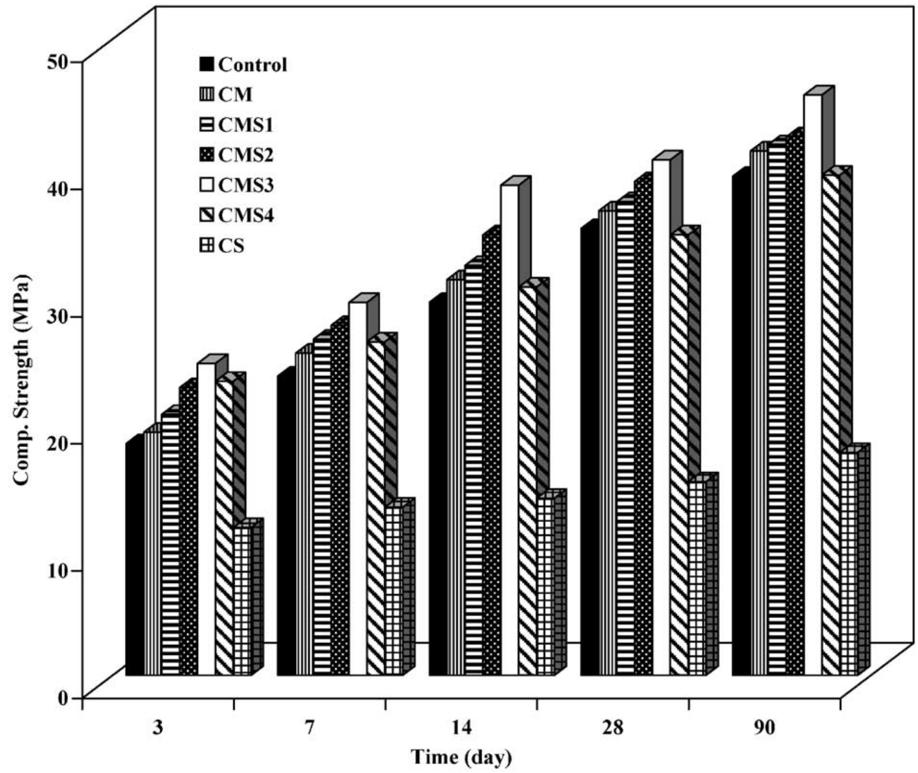

Fig. 7. Compressive strengths of the mortar cubes of different cementitious compositions.

exhibits the highest and that containing SA alone exhibits lowest compressive strengths at all ages. The poor strengths of the composition containing SA alone is attributed to high free lime and alkali metals oxides content in the SA [4]. The strengths of the cement compositions containing cocalcined kaolin—40% sludge are comparable with the control but lower than the MK-blended cement.

The high compressive strengths of the blended cements prepared using cocalcined kaolin–sludge mixtures containing up to 30% sludge is in confirmatory with the high amount of C-S-H, C-A-H, C-A-S-H, etc. materials in the hydration products. The presence of free CaO, alkali metals, and $CaCO_3$ up to a certain level in the blended cements may also enhance the compressive strengths [14].

4. Conclusions

The results can be summarized as:

1. Kaolin calcined in the presence of a limited amount of petroleum ETP sludge when used as a mineral admixture enhances the rate of hydration of cement.
2. The cocalcined kaolin–sludge mixtures increase the water requirements and decrease the setting times of the cements.
3. Blended cements with improved technological properties may be prepared by replacing 20% cement with cocalcined kaolin–sludge compositions containing up to 30% sludge.

Acknowledgements

The authors are grateful to Mr. P. Khound and Dr. R.K. Barua of this laboratory for recording the FTIR spectra and XRD patterns, respectively. The authors are also grateful to Dr. J.S. Sandhu, FNA, Director, RRL, Jorhat for his encouragement in the work.

References

[1] H.F.W. Taylor, Cement Chemistry, second ed., Thomas Telford, London, 1997, pp. 261–293.
[2] A. Demirbas, A. Aslan, Evaluation of lignite combustion residues as cement additives, Cem. Concr. Res. 29 (1999) 983–987.
[3] N.J. Saikia, P. Sengupta, D.K. Dutta, P.C. Saikia, P.C. Borthakur, Oil field sludge used to make brick, Am. Ceram. Soc. Bull. 79 (7) (2000) 71–74.
[4] N.J. Saikia, P. Sengupta, P.K. Gogoi, P.C. Borthakur, Physico-chemical and cementitious properties of sludge from oil field effluent treatment plant, Cem. Concr. Res. 31 (2001) 1221–1225.
[5] N.J. Saikia, P. Sengupta, P.K. Gogoi, P.C. Borthakur, Hydration behaviour of lime–co-calcined kaolin–petroleum effluent treatment plant (ETP) sludge, Cem. Concr. Res. 32 (2) (2002) 297–302.
[6] IS: 4032–1968 (Revised 1 985): Methods of Chemical Analysis of Hydraulic Cement (1st revision), Bureau of Indian Standards, New Delhi, 1985.

[7] IS: 4031–1968 (Revised 1988): Methods of Physical Tests for Hydraulic Cement (1st revision), Bureau of Indian Standards, New Delhi, 1988.
[8] M.J. Wilson (Ed.), Clay Mineralogy: Spectroscopic and Chemical Methods, first ed., Chapman & Hall, London, 1994, pp. 18–21.
[9] G. Kakali, J. Perraki, S. Tsivilis, E. Badogiannis, Thermal treatment of kaolin: the effect of mineralogy on the pozzolanic activity, Appl. Clay Sci. 20 (2001) 73–80.
[10] J. Bensted, S.P. Verma, Some application of infrared and Raman spectroscopy in cement chemistry: Part 3. Hydration of Portland cement and its constituents, Cem. Technol. 5 (5) (1974) 440–450.
[11] M.A. Trezza, A.E. Lavat, Analysis of the system $2CaO-Al_2O_3-CaSO_4{\cdot}2H_2O-CaCO_3-H_2O$ by FTIR spectroscopy, Cem. Concr. Res. 31 (2001) 869–872.
[12] H.F.W. Taylor, Cement Chemistry, second ed., Thomas Telford, London, 1997, pp. 190–191.
[13] J. Bensted, An infrared spectroscopic examination of high alumina cement and its hydration products, World Cem. 13 (2) (1982) 85–90 (March).
[14] H.F.W. Taylor, Cement Chemistry, second ed., Thomas Telford, London, 1997, pp. 289, 321.