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Physico-chemical and cementitious properties of sludge from oil field effluent treatment plant

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Abstract

Sludge generated in the effluent treatment plants (ETPs) of oil fields contain calcite, clay and other inorganic materials as well as hydrocarbon oil. The amount of the latter is often more than the permissible level for safe disposal by landfilling. The thermoanalytical characteristics of the sludge generated in the ETP of Lakwa oil field, Assam, India were investigated by using TG, DTG, DTA, XRD, FTIR techniques and chemical methods. The lime reactivities of the sludge ash and the physical properties of blended cement containing the ash were evaluated. Decomposition of calcite starts from above 550°C and it is succeeded by several solid state reactions involving CaO and aluminosilicates forming new phases. Gehlenite ($Ca_2Al_2SiO_7$) has been identified as one of the products and it forms above 750°C. Sludge ash prepared at 750°C consumes considerable amount of lime but it is not suitable for preparation of blended cement.

Keywords: Blended cement; Thermal treatment; Physical properties; Waste management

1. Introduction

Gainful utilization of waste materials generated in different industries is important from the points of ecology, economics and conservation of nonrenewable resources. Many waste materials like municipality sludge, steel dust wastes, granulated blast furnace slag, red mud, etc., find use in the manufacture of various types of building materials [1–4].

In the petroleum industry various types of waste materials are generated. The wastewater produced during the production of crude petroleum contains dissolved inorganic constituents, suspended clay and other related materials besides emulsified hydrocarbons. It is treated with lime and alum in effluent treatment plants (ETP) before discharging the clear water into the environment. In the process, a voluminous sludge, often containing hydrocarbon more than the permissible limit for safe disposal by land filling ($<3\%$) is produced. The petroleum industry is therefore confronted with the disposal problem of the huge amount of accumulated sludge produced over the years in the ETPs. The ETP at Lakwa oil field, situated in the northeastern region of India, produces about 120 m^3 sludge/day. Incineration of the sludge, utilization of the sludge for brick making, etc., are some of the possible ways to overcome the disposal problem [5,6]. Attempts were also made to utilize the sludge as an admixture in Portland cement. But the presence of large amounts of water and oil as well as large-sized solid materials in it restricts homogenization of the mixture. Therefore, an attempt has been made to utilize the sludge ash as mineral admixture in cement. The physicochemical characteristics of the sludge, the lime reactivity of its ashes prepared at various temperatures and the physical properties of blended cement containing the most reactive ash are presented in this communication.

2. Experimental

The sludge sample, collected from the ETP of Lakwa oil field, was in the form of slurry. It was dried in an oven at 100 ± 5°C before subjecting to characterization. The chemical analysis of the sample was done by standard

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analytical methods [7]. The hydrocarbon oil present in the sludge was separated by extraction with toluene. The thermoanalytical curves of the sludge were obtained in a computerized TA instrument (model STD 2960, simultaneous DTA and TGA), under dynamic air flow at the rate of 100 ml/min. Approximately 10–25 mg of the sample were heated in a platinum crucible at the heating rate of 10°C/min up to 1200°C, using calcined α-Al_2O_3 as the reference material.

Ash samples were prepared by heating the sludge taken in platinum crucible in a chamber furnace at air atmosphere for 1 h at different temperatures from 250°C onwards up to 950°C at an interval of 100°C.

XRD patterns of the samples were obtained by using 1 nm filtered Cu Kα radiation in a Jeol X-ray diffractometer, model JDX-11P3A. FTIR spectra were recorded in KBr disc and in the range of 500–4000 cm^{-1}, using Perkin Elmer system 2000 FTIR spectrophotometer.

Soluble calcium was determined by suspending approximately 0.3 g of the samples in 50 ml distilled water in a stoppered conical flask, allowing to stand the suspension for 24 h with intermittent shaking followed by titration with EDTA. The lime reactivities of the ash samples were determined by following the procedure as reported earlier [8]. The ash samples (0.3 g) were suspended in 50 ml saturated lime solution in a stoppered conical flask, kept in CO_2 free atmosphere for 18 h and the amount of residual lime was calculated. Blended cements containing ordinary Portland cement and sludge ash (5 and 10 wt.%) were prepared and the physical properties of the cement samples were determined by following Indian standard methods [9]. The setting times were measured by the Vicat needle penetration method. The expansions were determined by the Le Chetelier method. The compressive strengths were determined on 2.5 × 2.5 × 2.5 cm mortar cubes prepared using 1:3 ratio of the cementitious compositions and graded sand and maintaining water to cement ratio in the range of 0.36–0.47 (to achieve similar degree of flow). The cubes were cured for 24 h in air atmosphere at room temperature and then in water till determination of compressive strengths. The compressive strengths were an average of three specimens. The free lime contents of the cement mixes were determined by following the ethylene–glycol method as described in Indian standard methods [10].

Table 1
Characteristics of ETP Lakwa sludge

Sample	Component	Amount present (wt.%)
Sludge (as received)	Hydrocarbon	4.80
	Water	88.20
	Inorganic matter	7.00
Dried sludge	Inorganic matter	59.32
	Hydrocarbon:	
	Asphaltene	0.35
	Resin	26.50
	Wax	8.50
	Heavy oil component	64.00

Table 2
Compositions and properties of sludge ash and cement

Constituents	Sludge ash (wt.%)	Cement (wt.%)
CaO	25.04	65.04
MgO	0.56	3.45
Al_2O_3	48.12	6.24
Fe_2O_3	1.30	3.87
SiO_2	18.98	15.14
SO_3	2.68	3.38
K_2O+Na_2O	1.05	0.67
Insoluble material	–	0.47
Loss on ignition	0.56	2.11
Specific gravity (g/ml)	2.43	2.74
Blain's fineness (cm^2/g)	4365.53	3352.31

3. Results and discussions

3.1. Characterization of sludge

3.1.1. Oxide compositions

The composition of the sludge is shown in Table 1. The oxide compositions of sludge ash (prepared at 750°C) and normal Portland cement are shown in Table 2. The water content of the sludge is very high. The sludge contains 4.8% and 7.0% hydrocarbon and inorganic material, respectively. The sludge ash mainly contains Al_2O_3, CaO and SiO_2.

3.1.2. Water-soluble calcium

Fig. 1 shows the amount of water-soluble calcium in the sludge and the ash samples prepared at 550°C, 650°C, 750°C, 850°C and 950°C. The amount of water-soluble

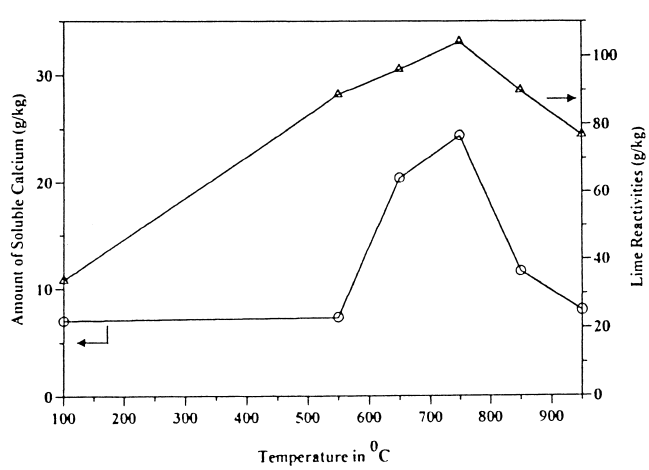

Fig. 1. Water-soluble calcium (–○–) and lime reactivities (–△–) of 1 h heat-treated sludge.

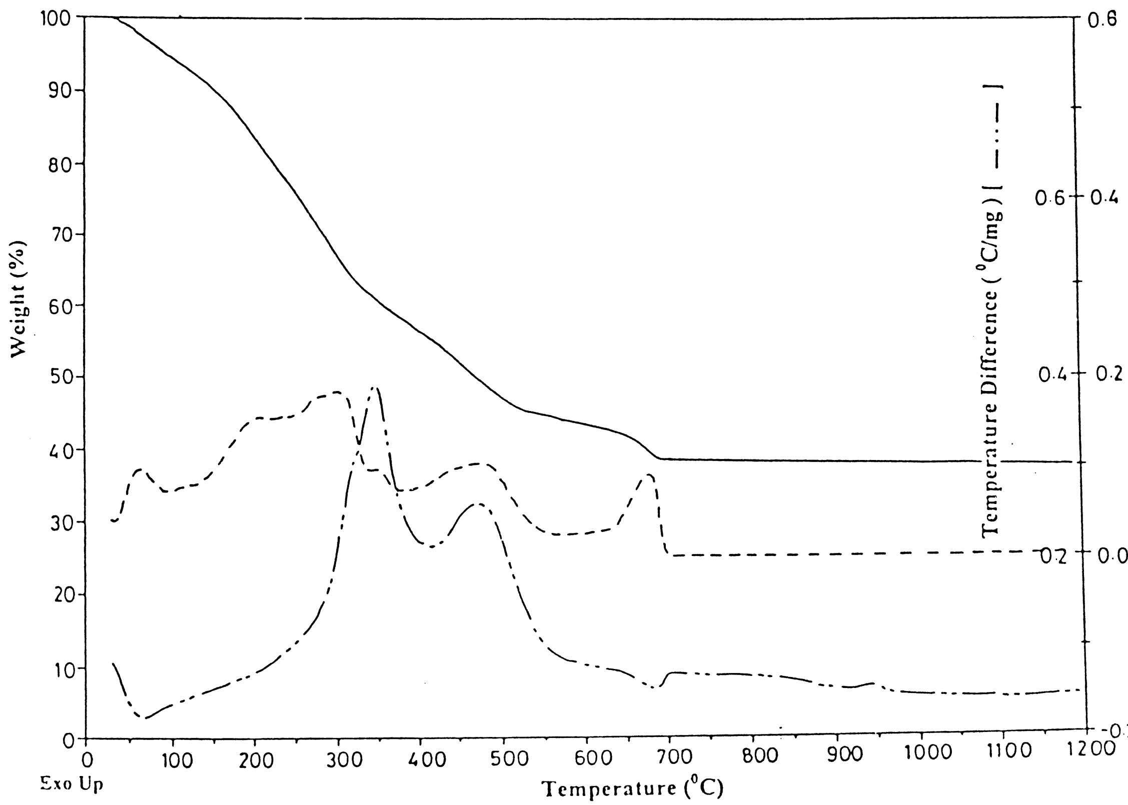

Fig. 2. Thermal curves of dried sludge: (–) TG, (– – –) DTG and (–··–) DTA.

calcium increases with increasing temperature up to 750°C and then decreases. The increasing trend is due to increase in decomposition of some calcium-bearing components present in the sludge forming CaO and the decreasing trend is due to fixation of the liberated lime in the form of more stable phase.

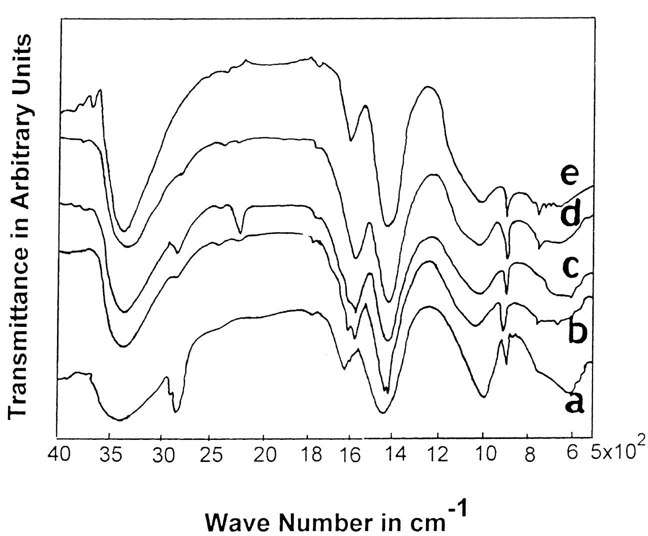

Fig. 3. FTIR spectra of sludge heat-treated for 1 h at different temperatures: (a) 105°C, (b) 250°C, (c) 350°C, (d) 450°C and (e) 550°C.

3.1.3. Thermal characteristics

The thermal curves of the sludge are shown in Fig. 2. The low temperature exotherm (100–550°C) of the DTA curve accompanied by sharp weight loss as exhibited by the TG curve at low temperature indicates combustion of the hydrocarbon present in the sludge. The DTA curve exhibits an endotherm in the temperature region of 600–700°C, accompanied by sharp weight loss in the TG (4.90%) and DTG curves and is attributed to decomposition of calcium carbonate. The relatively low temperature of decomposition of $CaCO_3$ is possibly due to the presence of other inorganic constituents in the sludge as well as combustion of the hydrocarbon present in the sludge. The DTA pattern shows a weak exotherm with maximum at 934.5°C and is attributed to solid state reactions involving liberated CaO and other ash constituents.

3.1.4. Analysis of calcined products by X-ray and FTIR techniques

X-ray diffraction analysis (not shown in figure) shows that the sludge contain calcite (d = 3.034, 2.499, 2.285, 2.097, 1.915 and 1.878 Å) as the major phase together with various hydrated aluminosilicates (d = 9.830, 8.634, 4.135, 3.346 and 1.444 Å) and aluminum sulfate (d = 4.420 and 4.283 Å). The calcium carbonate is possibly formed due to the carbonation of hydrated lime added as a flocculent along with alum in the treatment of the effluent. The XRD pattern

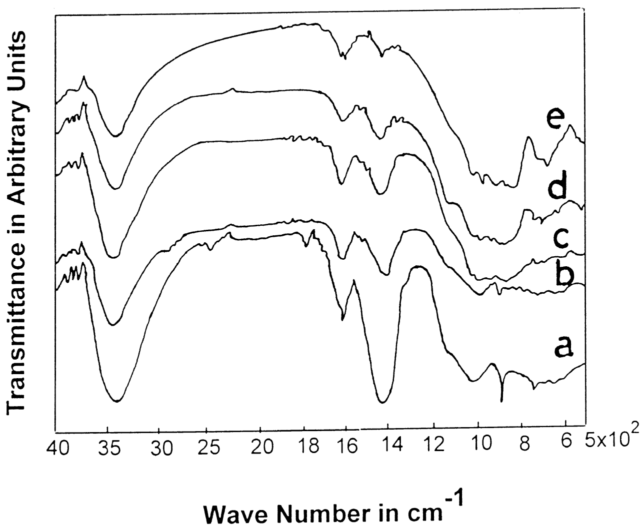

Fig. 4. FTIR spectra of sludge heat-treated for 1 h at different temperatures: (a) 550°C, (b) 650°C, (c) 750°C, (d) 850°C and (e) 950°C.

of the ash prepared at 550°C is comparable with the parent sludge. The intensities of the calcite peaks progressively decrease with temperature from 650°C and the peaks disappear in the 950°C-heated sample. The 750°C-heated sample does not exhibit peak due to hydrated aluminosilicates and aluminum sulfate, indicating decomposition of these compounds at or prior to this temperature. The sample exhibits some new peaks at d = 3.334, 2.778, 2.414 and 1.710 Å due to calcium oxide. The 850°C-heated sample exhibits new peaks at d = 2.846 and 2.434 Å, which become intense in the 950°C-heated sample. The latter sample exhibits an additional peak at d = 1.753 Å. The peaks at d = 2.846, 2.434 and 1.753 Å confirm the formation of gehlenite ($Ca_2Al_2SiO_7$) [PC-PDF Card No. 35-755]. Gehlenite forms in the system comprising of $CaO-Al_2O_3-SiO_2$ when the amount of Al_2O_3 relative to SiO_2 is high [11].

FTIR spectra of the dried and calcined sludge samples are shown in Figs. 3 and 4. The sludge exhibit bands at 1452, 875 and 728 cm^{-1} due to calcite, broad and diffused band at around 970 cm^{-1} due to Si–O–Al or Si–O–Si stretching vibration and broad band at around 3500 cm^{-1} due to absorbed water [12,13]. The samples exhibit sharp bands at 2922 and 2851 cm^{-1} due to aliphatic hydrocarbon and at around 1600 cm^{-1} which may be due to C=C vibration of aromatic ring and O–H stretching vibration due to absorbed water.

The intensities of the calcite peaks in the ash sample prepared at 550°C are comparable to those of the parent. These are much less in the samples prepared at 650°C and above temperatures. The 750°C-heated sample shows a new peak at 858 cm^{-1}, due to Si–O–Si vibration of $M_2^{2+}SiO_4$ [12]. The 850°C-heated sample also shows new peaks at 820, 728 and 678 cm^{-1}, assigned to vibration of Al–O in Al–O–Si tetrahedra [12]. The 950°C-heated sample does not show peaks due to calcite but new peaks at 975, 876, 662 and 535 cm^{-1} indicating formation of either $Al^{3+}M_2^{2+}(SiO_4)_3$-type aluminosilicates [M^{2+} is Fe, Ca] or polymerization of silicates containing different anions [12]. The decrease of the intensities of calcite peaks and appearance of new peaks in the samples heated to 750°C, 850°C and 950°C corroborate the earlier inference that decomposition of calcium carbonate in the sludge is succeeded by formation of new phases, involving CaO and aluminosilicates.

3.2. Cementing properties of sludge ash

3.2.1. Lime reactivity of sludge ash

The lime reactivity curve (Fig. 1) reveals that the sludge ash samples prepared at different temperatures consume considerable amount of lime and is attributed to the presence of reactive silica and alumina-bearing materials in the ash. The reactivity of the ash gradually increases with temperature of preparation of the ash up to 750°C and then falls, possibly due to gehlenite formation.

3.2.2. Physical properties of sludge ash–cement mixtures

The 3-, 7- and 28-day compressive strengths of the mortar cubes, setting times, water requirements and expansions of blended cements containing sludge ash prepared at 750°C are shown in Table 3. The data reveal that the water required for obtaining paste of standard consistency of the blended cements are higher than that of the neat cement and it increases with the increase of the amount of the ash. The initial and final setting times of the blended cements are less than the neat cement and these decrease with the increase of the amount of the ash and possibly due to high alumina content in the ash. The expansions of the blended cement samples containing 5% and 10% sludge ash are higher than the neat cement and is attributed to the presence of high free lime content in the sludge ash–cement mixes. The 3-day compressive strengths of the blended cement samples containing the ash are higher but at later ages lower than the

Table 3
Physical properties of cement and cement–sludge ash mixtures

				Setting times (h:min)		Compressive strengths (kg/cm^2)		
Mixture	Water requirements (%)	Expansion (mm)	Free lime (%)	Initial	Final	3-day	7-day	28-day
Cement	24.3	2.5	0.71	0:52	1:19	164.0	233.1	316.4
Cement + 5% sludge ash	29.0	3.0	2.35	0:38	0:58	179.6	159.4	90.7
Cement + 10% sludge ash	33.0	4.5	3.79	0:16	0:21	200.1	141.2	79.2

neat cement. Strength deterioration at later ages of the sludge ash–cement mixes is consistent with the expansion of the mix.

4. Conclusions

(1) The major inorganic constituents of the sludge are: Al_2O_3, CaO and SiO_2 and the predominant crystalline phase is calcite, which decomposes in a wide temperature range between 550–950°C. Decomposition of calcite is succeeded by many solid state reactions involving CaO, Al_2O_3 and SiO_2 at above 750°C and gehlenite is one of the products. Its amount increases with the increase of temperature up to 950°C. High amount of alumina relative to silica in the sludge favors gehlenite formation.

(2) The lime reactivity shows that the sludge ash is pozzolanic in nature and the most reactive ash may be obtained at 750°C, beyond which formation of gehlenite decreases the reactivity.

(3) Physical properties of blended cement indicate that the sludge ash as such is not suitable as a mineral admixture in cement.

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