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Hydration behaviour of lime–co-calcined kaolin–petroleum effluent treatment plant sludge

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Abstract

Petroleum effluent treatment plant (ETP) sludge contains hydrocarbons and its ash is pozzolanic in character. The hydrocarbon may be utilized in the calcination of clay. The present communication reports on the hydration behaviour of lime–metakaolin mixtures produced in the presence of the sludge. The hydration products were characterized by using FTIR, TG, DTA and XRD methods. Use of sludge in metakaolin preparation increases the initial hydration rate and enhances the production of C–S–H or C–A–S–H gel. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Metakaolin; Lime; Hydration; Petroleum effluent treatment plant sludge

1. Introduction

Blended cements are produced by intermixing/intergrinding different amounts of various supplementary cementing materials and Portland cement. The blending materials may be either pozzolanic in nature like fly ash, calcined clay, silica fume, rice husk ash, etc. or having latent hydraulic activity like granulated blast furnace slag (GBFS) [1]. The performance of blended cement in many respects is superior to Portland cement.

Calcined clay is one of the earliest known pozzolanic materials and it is still in use in many places devoid of industrial wastes like fly ash, GBFS, etc. Metakaolin produced by thermal activation of kaolinite clay in the temperature range of 650–800 °C is an established pozzolana. It is an 'ultrafine,' highly reactive pozzolana similar in properties to condensed silica fume. Metakaolin is chemically different from many other pozzolanas as it has a very high alumina content and its reaction products with $Ca(OH)_2$ (CH) include C–S–H, C–A–S–H gel, C_2ASH_8 and C_3AH_6 [2,3].

Waste sludge produced in effluent treatment plants (ETP) in oil fields contains various amounts of inorganic and organic materials. The latter comprises of hydrocarbons and other organic substances like polyphenols and their amounts are very often more than the permissible level (3% hydrocarbon) [4] for safe disposal by land filling. Therefore, the sludge is hazardous in nature and its disposal is a problem. The disposal problem may be eliminated by utilizing it in the preparation of ceramic bodies like brick [5]. The present communication reports on the hydration behaviour of lime–kaolin mixtures calcined in the presence of the sludge.

2. Experimental and methods of investigation

The sludge was collected from the ETP of Lakwa oilfield, Assam, India. It was dried at 100 ± 5 °C and then ground. Kaolin, marketed by the English India Clay Company, India, and analytical grade $Ca(OH)_2$ were used in this study. Kaolin–sludge mixtures containing 10% and 20% sludge were prepared. The kaolin and the mixtures were mixed with $Ca(OH)_2$ in the lime:mixture ratio of 6:4 and homogenized in a laboratory size ball mill. These lime mixtures were calcined at 750 °C for 1 h in an electrically heated chamber furnace in air atmosphere and stored in a CO_2-free atmo-

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Table 1
Oxide compositions of clay, sludge ash and clay–sludge mixtures

Oxides	Metakaolin (%)	Sludge ash (%)	SC 1(%)	SC 2 (%)
SiO_2	53.02	18.98	49.62	46.22
Al_2O_3	43.24	48.12	43.73	44.21
Fe_2O_3	0.40	1.30	0.49	0.58
CaO	0.53	25.04	2.98	5.43
MgO	0.52	0.56	0.52	0.53
Na_2O+K_2O	0.20	1.05	0.29	0.37
SO_3	–	2.68	0.27	0.54
LOI	1.03	–	0.93	0.82
Free CaO	–	1.20	0.85	1.05

SC 1 and SC 2 = co-calcined sludge–kaolin mixtures containing 10% and 20% sludge, respectively.

sphere. The calcination temperature was fixed based on the dehydroxylation temperature of kaolin, sludge and lime as determined from thermal analysis. The chemical analysis of metakaolin, sludge ash and co-calcined kaolin–sludge mixtures were done by standard analytical methods [6].

For measurement of pH, 4-g mixture was mixed with 40-ml distilled water in a glass beaker and stored in a CO_2-free atmosphere. After 30 min, the pH was measured by using a digital pH meter. The pH of lime–metakaolin (12.5) and lime–metakaolin produced in the presence of 10% sludge (12.6) is approximately the same, but for lime–metakaolin mixture produced in the presence of 20% sludge it is slightly higher (13.1). Pastes were prepared by mixing the calcined mixtures with distilled water maintaining water:solid ratio 1:1 in a porcelain mortar for ~5 min. The pastes were immediately transferred to polythene bags and then placed in a desiccator at ambient temperature. The mixtures were allowed to hydrate for different periods. The hydration was arrested by grinding about 5 g of the pastes with a mixture of acetone and methanol (1:1) for 5 min. in a porcelain mortar. These were then washed several times with acetone and methanol mixture. Finally, the samples were dried at 65 ± 5 °C for 2 h and stored in an airtight plastic container in a CO_2-free atmosphere.

The thermal curves (DTA and TGA) of the hydration products were taken in a TA instrument, model STD 2960, simultaneous DTA TGA. A total of 10–15 mg of the samples was heated in a platinum crucible in a nitrogen atmosphere up to 1000 °C, maintaining 10 °C/min heating rate and using calcined α-Al_2O_3 as the reference material. The FTIR spectra of the samples were taken in a Perkin Elmer System 2000 FTIR spectrometer by the KBr disc method and XRD patterns in a Jeol X-ray diffractometer, model ZDX-11P3A, using Cu K_α radiation.

The rates of hydration of the mixtures were measured by determining the CH as well as the chemically combined water (CW) content from the TG curves. The weight loss in the temperature range of 420–550 °C was taken as the loss due to CH. The CW was calculated from the total loss in 100–1000 °C minus loss due to $Ca(OH)_2$ and $CaCO_3$. The loss in the temperature range of 600–750 °C was taken as the loss of due to $CaCO_3$.

3. Results and discussion

Chemical analysis (Table 1) reveals that the sludge ash sample is relatively poor in SiO_2 and rich in Al_2O_3, Fe_2O_3, CaO and K_2O+Na_2O compared to the metakaolin. 10 and 20 wt.% replacement of kaolin by sludge slightly lowers the total Al_2O_3, SiO_2 and Fe_2O_3 content but it is well within the requirement (> 70%) stated in ASTM for a natural pozzolana [7]. Sludge ash and calcined sludge–kaolin mixtures contain small amount of free lime.

The CH contents (Fig. 1) of the co-calcined kaolin–sludge–lime mixtures after hydration are lower than those from metakaolin–lime mixtures and decrease with the amount of sludge. The CH contents of the 1-day hydration products of the co-calcined mixtures prepared using 20% sludge is much lower than that prepared using 10% sludge or without the sludge but at 28 day, it is approximately same for all the mixtures.

The trend in the change of the amount of CW in the pastes (Fig. 2) of different compositions is the opposite of the change in the CH contents. It increases with increase of curing time as well as with the amount of replacement of kaolin by sludge in the compositions. The amount of CW in the 1-day hydration products of the mixture containing 20% sludge is the highest (15.33%) but at 28 days all the mixtures contain approximately the same amount (~26.5%). The change in CH and CW in the hydration products of the mixtures suggests that utilization of the sludge in the calcination of kaolin enhance the early hydration rate of a metakaolin–lime mixture.

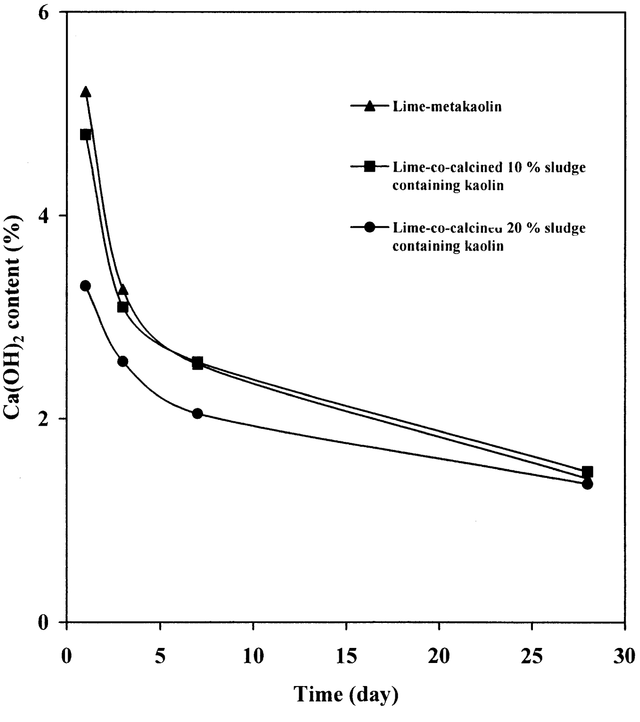

Fig. 1. $Ca(OH)_2$ contents in different hydrated products.

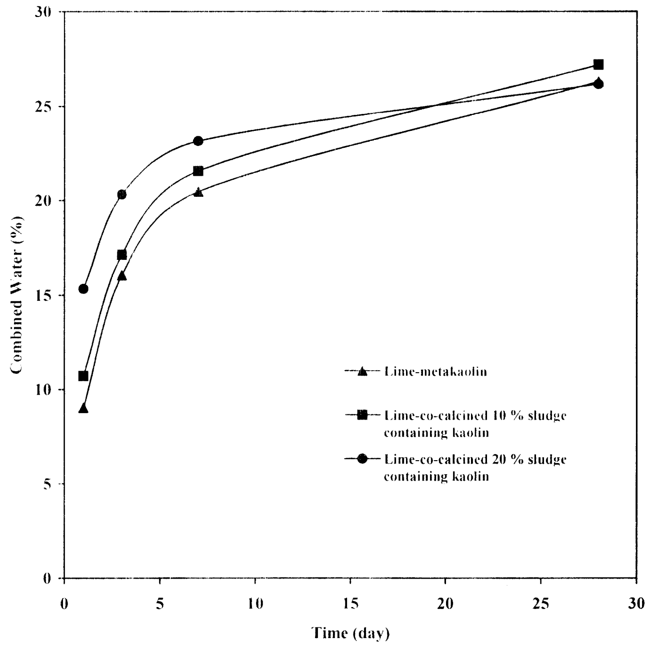

Fig. 2. Combined water content in different hydrated products.

The thermograms (TG and DTA) of the hydrated pastes of different compositions (lime–metakaolin mixtures produced alone and in presence of the sludge) cured at room temperature for various periods are presented in Figs. 3 and 4. The endotherms in the DTA curves, at the temperature ranges of 425–550 and 600–750 °C accompanied with weight loss as exhibited by corresponding TG curves are due to dehydroxylation of $Ca(OH)_2$ or portlandite and decomposition of $CaCO_3$, respectively. The endotherms observed in the DTA curves in the temperature regions of 100–150, 150–220 and 220–310 °C, accompanied by breaks in the TG curves are due to C–S–H or C–A–S–H gel, gehlinite hydrate or strätlingite (C_2ASH_8) and hydrogarnet series (C_3AH_6), respectively [2,3].

The weight loss in the 1-day hydration products of co-calcined lime–kaolin–sludge mixtures in the temperature range of 100–150 °C as calculated from the TG curve are higher (2.31% for 10% and 3.79% for 20% sludge) than that without the sludge (1.89%), indicating higher amount of C–S–H or C–A–S–H gel in these mixtures. The DTA curves of the 1-day hydration products of the co-calcined

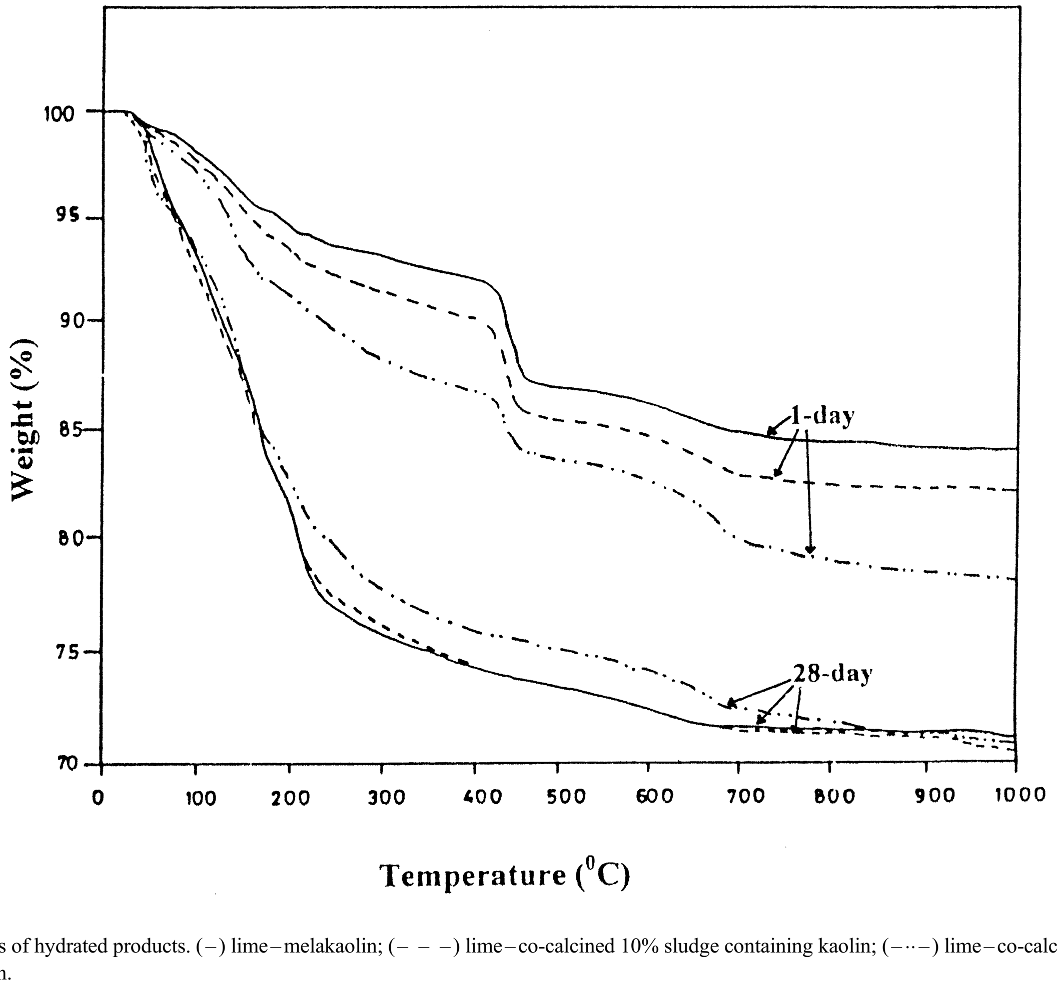

Fig. 3. TG curves of hydrated products. (–) lime–melakaolin; (– – –) lime–co-calcined 10% sludge containing kaolin; (–··–) lime–co-calcined 20% sludge containing kaolin.

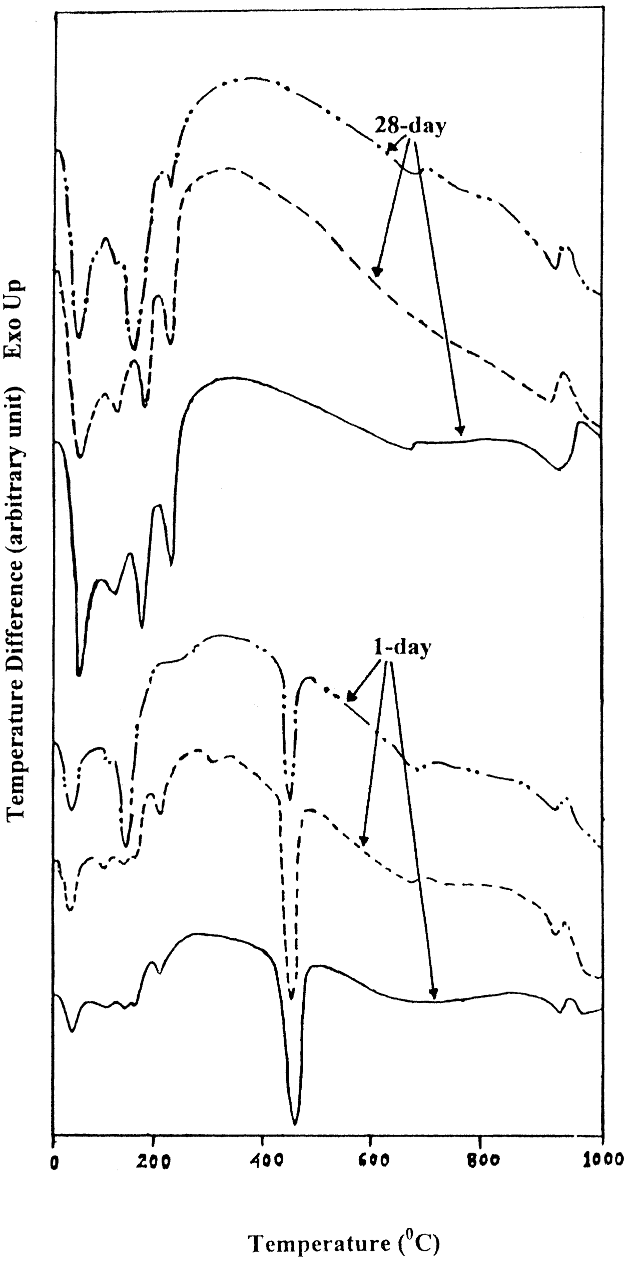

Fig. 4. DTA curves of hydrated products. (–) lime–metakaolin; (– – –) lime–co-calcined 10% sludge containing kaolin; (–···–) lime–co-calcined 20% sludge containing kaolin.

kaolin–sludge (10%)–lime mixture and metakaolin–lime mixture are comparable except that the former exhibits a weak endotherm at 298 °C due to the formation of hydrogarnet (C_3AH_6). The amount of C–S–H or C–A–S–H increases on increasing the sludge content to 20% in the mixture. The 1-day hydration products of this mixture however exhibit the peak due to hydrogarnet at 248 °C. The 28-day hydration products of this mixture exhibit a more intense peak at 148 °C with a weak inflexion at 111 °C due to C–S–H or C–A–S–H. The intensity of the peak due to strätlingite (C_2ASH_8) in the mixture containing 10% and 20% sludge increases in the 28 days hydration products with corresponding disappearance of the hydrogarnet peaks. The hydrogarnet possibly converts to strätlingite. Conversion of hydrogarnet to strätlingite was earlier observed in several systems like high alumina cement (HAC)–zeolite system, HAC–GBFS system, etc. [8,9]. Thus, replacement of 20% kaolin by sludge in the starting mixture leads to change in the nature of hydration products of the calcined mixtures with formation of higher amount of C–S–H or C–A–S–H gel.

The FTIR patterns of the 1-, 7- and 28-day hydration products of the mixtures in 400–4000 cm^{-1} range are shown in Fig. 5. Different band assignments are given in Table 2. [10–14]. The band at 3645 cm^{-1} is due to the str. vibns. of OH group of portlandite (CH). The peaks around 3454 and 1650, 1611 cm^{-1} are due to water. The bands at 1461 and 883 cm^{-1} are attributed to presence of calcite, possibly formed due to aeration of the pastes. The band at 970 cm^{-1} region is due to Si–O stretching vibration of C–S–H and at 1084 cm^{-1} is due to amorphous aluminosilicates.

In the 1-day hydration products, the intensity of the 970 cm^{-1} band increases with the increase of the amount of sludge in the mixture indicating increased formation of

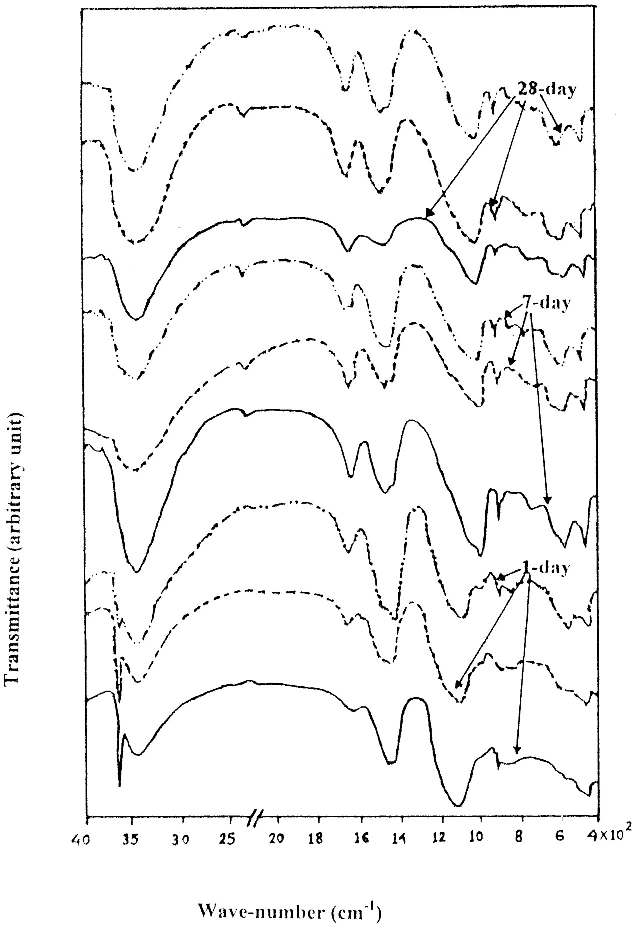

Fig. 5. FTIR spectra of hydrated products. (–) lime–matakaolin; (– – –) lime–co-calcined 10% sludge containing kaolin; (–···–) lime–co-calcined 20% sludge containing kaolin.

Table 2
FTIR vibrations of hydrated products

Wave numbers (cm^{-1})	Characteristics vibrations
3640	ν, OH^-; free $Ca(OH)_2$
3420	$\nu_1+\nu_3$, H_2O
1640	ν, H_2O
1440	ν_3, CO_3; calcite
1140	$2\times\nu_4$, SiO_4; C–S–H and/or ν_{asym} of Al–O–Si
1084	Amorphous aluminosilicates
1034	ν_3, SiO_4; tobermorite
970	ν_3, SiO_4; C–S–H, tobermorite
875	ν_2, CO_3; calcite
800	ν_{asym} of Si–O–Si
720	ν, CO_3; calcite and/or ν_{sym} of Si–O–Al
690	Al–O, AlO_4 tetrahedra; hydrogarnet
600	Free AlO_4; C–A–H
530	Al–O, AlO_6 octahedra; hydrogarnet or Ca–O of C–A–H

C–S–H gels. The calcined products of the mixture containing 20% sludge exhibit comparatively weak peak at 3645 cm^{-1} indicating consumption of higher amount of CH during hydration.

The intensity of the band at 970 cm^{-1} in all the hydrated products increases with hydration period indicating increased formation of C–S–H. The 7-day hydration products exhibit an additional peak at 1025 cm^{-1}, which may be due to formation of new C–S–H phase or transformation of C–S–H phase. The peak due to CH, which disappeared in metakaolin–lime hydration products after 7-day hydration, is observed as a weak shoulder in the co-calcined kaolin–sludge–lime mixture. The FTIR patterns of the 28-day hydration products of all the mixtures are almost the same.

The XRD patterns (not shown in the figure) of the hydrated products are diffused due to gel like nature of the hydrated products. The 1-day hydrated products of all the samples exhibit weak peaks due to portlandite, CH (d=2.63, 4.93, 1.93 Å). The CH peaks however could not be detected in 28-day hydration products possibly due to its low content (<1.5% as per Fig. 1). The major crystalline products observed in the 28-day hydrated products are strätlingite (d=4.17, 2.87, 2.37 Å) and small amount of calcite (d=3.05, 3.30, 2.73 Å).

Thus, from the above results, we found that kaolin calcined in presence of 10% sludge does not effect the nature of the hydration products but slightly increases the reaction rate. The replacement has not caused much change in the pH of the fluid but the amount of alkali metal oxides, alumina and free lime have changed as shown in Table 1. The presence of slightly higher amount of the latter components than in the pastes of lime–metakaolin generates additional amount of heat in the hydration process, which possibly increases the initial hydration rate. Kaolin calcined in presence of 20% sludge not only further increases the heat of hydration but also the pH of the solution. Consequently, the amount of dissolved silicate and aluminate species increases, which favoures the formation of higher amounts of C–S–H and C–A–S–H type gels [15].

Oilfield ETP sludge, due to association with hydrocarbon may be used in the calcination of kaolin. The metakaolin so produced possesses improved pozzolanic activity. Hydration of co-calcined kaolin–sludge–lime mixture favours formation of higher amount of C–S–H or C–A–S–H gel than metakaolin–lime mixture. This is important from the environmental point of view as these phases may immobilize different types of toxic metals [16]. However, more research is necessary to increase knowledge on the properties of this material.

4. Conclusions

The results can be summarized as follows:

1. The pozzolanic activity of metakaolin improves, when prepared in the presence of oil field ETP sludge.
2. The early rate of hydration of so produced metakaolin–lime mixture is greater with the formation of higher amounts of C–S–H or C–A–S–H gel than those produced in the absence of the sludge.
3. Presence of relatively high amount of alkali metal oxides, alumina and free lime in the sludge enhances the hydration reaction with increased formation of C–S–H, C–A–S–H gels.

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