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Characterization and evaluation of the pozzolanic activity of Egyptian industrial by-products

I: Silica fume and dealuminated kaolin

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Abstract

Silica fume (SF) and dealuminated kaolin (DK) from Egyptian sources have been characterized chemically and mineralogically, and a comparative study of their reactivities toward lime were conducted using isothermal conduction calorimetry and an accelerated chemical method. The kinetics of SF–lime and DK–lime reaction were investigated in suspension. Unreacted lime and combined water were determined as function of time, and the hydration products were identified with X-ray diffraction (XRD) and SEM combined with EDX. DK has a much higher surface area (90.5 m^2/g) than SF (18.6 m^2/g) and exhibits much higher pozzolanic activity, especially during early hydration. A low-density sponge-like CSH was formed, from both SF and DK at low lime contents (20% CH), and a more dense CSH was formed at higher lime contents (40% CH). © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: By-products; Silica fume; Dealuminated kaolin; FTIR; Pozzolanic activity; Calcium silicate hydrates; Conduction calorimetry

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1. Introduction

Environmental pollution, including the generation of waste by-products from different industrial sectors, is a serious problem in Egypt. These include, air-cooled slag, silica fume (SF), and dealuminated kaolin (DK), which is produced by the ferric aluminum sulfate industry. Traditional approaches to building in Egypt indicate cement users not to be aware of the quality and benefits of blended cements containing these materials. Consequently, further research is necessary to illustrate the economic, environmental, and structural benefits to their use. Because of this, there is a currently great interest in exploiting the pozzolanic and cementitious properties of these materials by incorporating them in building products.

According to ASTM C595, a pozzolan is defined as "a siliceous or siliceous and aluminous materials which in itself possesses little or no cementitious value but in the presence of moisture, chemically react with calcium hydroxide at ordinary temperature to form compounds possessing cementious properties" [1]. Pozzolanic activity is an index of the extent of the lime–pozzolan reaction [2,3]. Although there are many methods for pozzolanic activity assessment using chemical or physical tests [4,5], many of the standard specifications emphasize strength as the primary means for assessing the pozzolanic activity [1,6]. It is well known that blended cement strength is more strongly dependent on the type, microstructure, and pore size distribution of the hydration products than on the extent of the lime–pozzolan chemical reaction [3,7,8]. These factors are effected by mix design and curing conditions and thus, can be controlled. Therefore, the extent of lime–pozzolan reaction is a primary factor in assessing the suitabilities of the different materials as pozzolans.

Determination of the pozzolanic activity with certainty is a complex problem [14,15]. Many techniques have been developed to investigate lime–pozzolan reactions at early ages of hydration. These include isothermal conduction calorimatery [9,10] and conductivity or resistivity measure-

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ments [11–13]. In addition, useful information can be obtained from investigating reactivity with lime and the modification of microstructure as a result of both the lime–pozzolan reaction and the cement–pozzolan reaction.

The aim of this research is to characterize several Egyptian industrial by-products from the chemical and mineral viewpoint and evaluate their reactivities toward lime. This is the primary step in a project to investigate the utilization of these and other by-products in different building materials. Pozzolanic activity was studied using an accelerated chemical method and isothermal conduction calorimetry. In the accelerated chemical method, the lime–pozzolan reaction is followed with time in suspension. Under these conditions, the amounts of lime combined with the pozzolan reach appreciable values within relatively short times and the reaction products, in particular, the hydrated phases containing Al_2O_3, are sufficiently well crystallized to be identified by X-ray diffraction (XRD) [16]. Such characterization enables the analysis of the hydration phenomena and permits a comparison of the reactivities of the pozzolans.

2. Materials and methods

SF was obtained from Ferrosilicon Edfo, Egypt. DK was obtained from Egyptian Shaba, Egypt. It is produced as a waste by-product of aluminum extraction from calcined kaolin by sulfuric acid. Daily production is about 100 tons of wet material, and a large amount has been stored at the factory. Both SF and DK were characterized by wet chemical analyses, XRD, IR, and SEM. The surface areas were determined by BET analysis. Calorimetric studies were performed to compare their heats of reaction with 20 and 40 wt.% lime. In isothermal calorimetry, approximately 3 g of water were inoculated into an equivalent mass of a reactant powder that had been placed in a copper sample cup and placed within the calorimeter cavity. The cups were sealed with plastic film to minimize evaporation of water. Each reactant was allowed to equilibrate separately to 25°C, prior to mixing. The water was equilibrated in a syringe and when equilibrium had been achieved the plastic film was penetrated and the water injected over the solids. The rates of heat evolution, d*Q*/d*t* in milliwatts per gram of pozzolana, were measured and recorded using a computer data acquisition system. Integration of the areas under the rate curves allowed calculation of the total heats evolved.

To study their pozzolanic activities, the materials were mixed with 20 and 40 wt.% of lime [$Ca(OH)_2$]. Five gram amounts were added to 75 ml of decarbonated distilled water (W/S = 15) in polyethylene bottles. The mixtures were periodically shaken by a mechanical shaker at 0.5, 1, 3, 5, 7, and 28 days. The progress of the reactions was followed by analyzing the solid phases after separation by filtration through sintered glass filters. The hydration reaction was stopped by immersing the solid phase in about 100 ml of a (1:1) methanol/acetone mixture and stirring magnetically for 30 min. The solid samples were then filtered off, washed with methanol, and dried at 105°C for 24 h. The dried samples tested for free lime, using the modified Franke method [17], tested for combined water and examined by XRD and SEM.

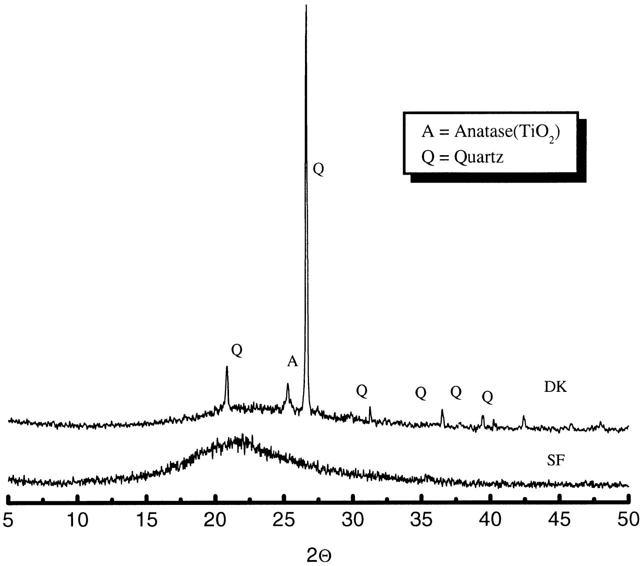

Fig. 1. XRD of SF and DK.

Table 1
Chemical composition of SF and DK

	SiO_2	CaO	Al_2O_3	Fe_2O_3	MgO	TiO_2	Na_2O	K_2O	SO_3	LOI	Total
SF	96.2	0.013	0.914	1.444	0.383	0.01	0.252	0.272	0.00	1.04	100.6
DK	74.93	0.00	9.08	0.96	0.157	3.80	0.113	0.052	1.466	9.25	99.82

XRD analyses were performed using an automated diffractometer (Scintag, Sunnyvale, CA), at a step size of 0.02°, scan rate of 2° per min, and a scan range from 4° to 60° 2θ. A single beam infrared spectrometer (FTIR) (MB100, Bornem/Hartmann and Braun, Quebec City, Canada) was used, and spectra were obtained over the wave number range of 400–4000 cm^{-1} at a resolution of 3 cm^{-1}. The KBr (Spectroscopic grade, Aldrich Chemical, Milwaukee, WI) drifts technique was used with a KBr/sample ratio of 100:1.

3. Characterization of the raw materials

The chemical analyses of SF and DK, after drying at 105°C for 24 h, are given in Table 1. The X-ray diffractograms of SF in Fig. 1 show it to be completely amorphous, exhibiting only a very broad scattering peak. The BET surface area is about 18.8 m^2/g. SEM investigation of the raw SF showed that individual SF spheres agglomerate to form larger particles. The mineralogical composition of DK as identified from XRD, as shown in Fig. 1, reveals it to

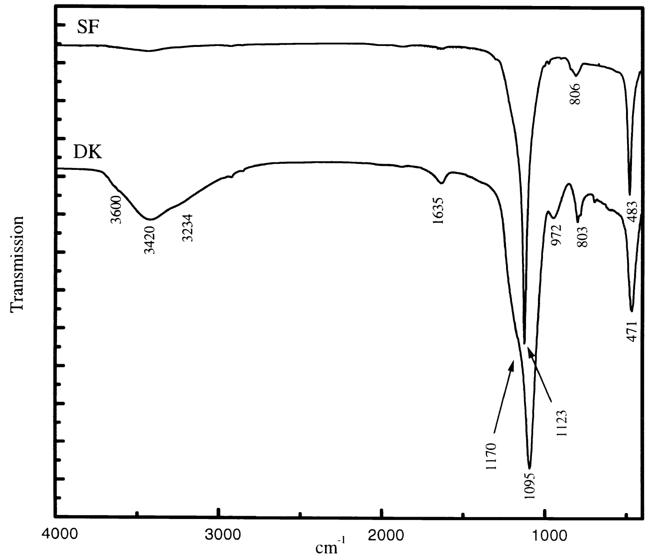

Fig. 2. FTIR spectra of SF and DK.

contain quartz, a small proportion of titanium oxide (anatase) and a considerable amount of amorphous material as indicated from the hump. Its BET surface area is about 90.5 m^2/g. SEM image analysis of the DK confirmed the presence of quartz and highly amorphous silica beside amorphous Al_2O_3. IR studies were conducted to identify the structure and nature of amorphous silica in both types of pozzolan. Unlike XRD, which provides information on long-range order in a material, vibration spectra are most useful in characterization short-range (interatomic) relationships in a matrix. Fig. 2 shows the FTIR spectra of SF and DK. The spectrum of SF shows the strongest absorbance bands at 1123, 806, and 483 cm^{-1}, characteristic of condensed silica [18]. The broad band centered at 1123 cm^{-1} is attributed to asymmetric stretching frequency of Si-O-Si, the band centered at 806 cm^{-1} is due to symmetric stretching of Si-O-Si, and the band at 483 is due to the bending frequency of O-Si-O [19]. The IR spectrum of DK shows a shift to lower frequencies for these three bands to 1098, 803, and 471 cm^{-1}, which indicates a lower degree of polymerization of the silica network. The frequencies of the Si-O-Si bands is an indication of the overall degree of polymerization of the silica network. In general, a lower frequency will correspond to a lower degree of polymerization [20]. DK spectrum also shows a band at 1170 cm^{-1}, due to the presence of sulfate ion [21] and at 972 cm^{-1} due to the Si-O stretching mode of nonbriding oxygens [22]. The former band also confirms the lower the degree of polymerization of silica in DK. The band characteristic for the silanol (Si–OH) groups, appears in DK in the 3660–3740 cm^{-1} region. The band at 1640 cm^{-1} is due to the H-O-H bending vibration of molecular H_2O and the broad band at 2800–3700 cm^{-1} is due to the stretching vibration of –OH groups in H_2O hydroxyls with a wide range of hydrogen bonding strengths [23].

The absorption bands account for the noticeable large loss on ignition (LOI) of DK, which results from the loss of hydrogen bonded water ($Si–OH:OH_2$) and the pyrolysis of silanol (Si–OH) groups, formed during acid leaching of metakaolin. The hydrogen bonded water may still persist in the silica gel until 200°C [24], and in some cases up to 500°C [25], if it is strongly hydrogen bonded to opposite sides of the pore walls.

4. Calorimetric study

Fig. 3A and B show the rates of heat evolution by isothermal calorimetry at 25°C for DK–lime and silica

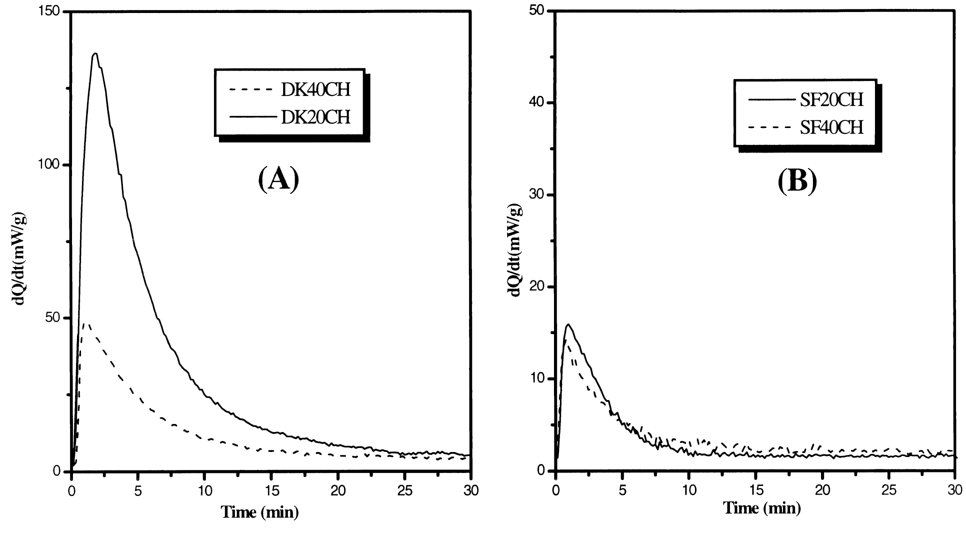

Fig. 3. Heat of reaction of DK–lime mixes (A), and SF–lime mixes (B) at 25°C.

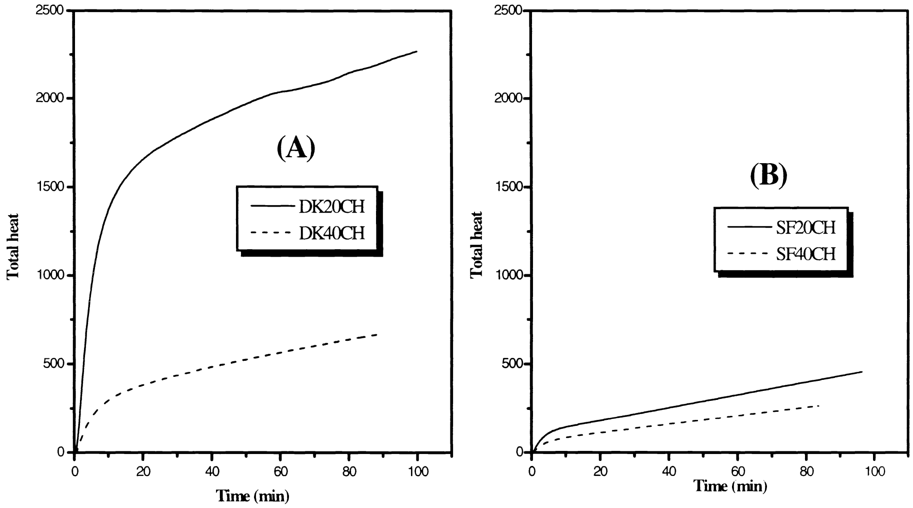

Fig. 4. Total heat of reaction of DK–lime mixes (A) and SF–lime mixes (B) at 25°C.

SF–lime mixes, respectively. Only single heat evolution peaks, which occur immediately after mixing, were observed. This heat cannot be explained by the effects of wetting and dissolution. Heat evolution is attributable to the lime–pozzolan reaction, which initiates as soon as mixing water added. The heat evolution peak of DK–lime is very high compared to those of SF (note the difference in scales between Fig. 3A and B). The difference between the accumulative total heats of DK and SF is seen in Fig. 4A and B. These results indicate the initial reaction rate greatly depends on the surface area of the pozzolanic material and the presence of hydrated silica (silanol groups), which are expected to act like a weak acid ($K_1 = 10^{-9.8}$) [26]. Weakly acidic sites are capable of a fast acid–base reaction with $Ca(OH)_2$, and total heat evolved will be the heat of reaction plus the heat of neutralization:

$$2Si_S - OH + Ca(OH)_2 \rightarrow (Si_S - OH)_2Ca + H_2O$$

The rates of heat evolution decrease at the higher lime contents for both SF and DK mixes, but the decrease is much higher in the case of DK. This indicates that the heat of reaction depends on the amount of DK, i.e., the number of silanol sites. This fact was confirmed by repeating the isothermal calorimetry measurements for DK–lime and SF–lime mixes, after ignition of the pozzolans at 800°C for 2 h, in order to remove the silanol groups. The results give a

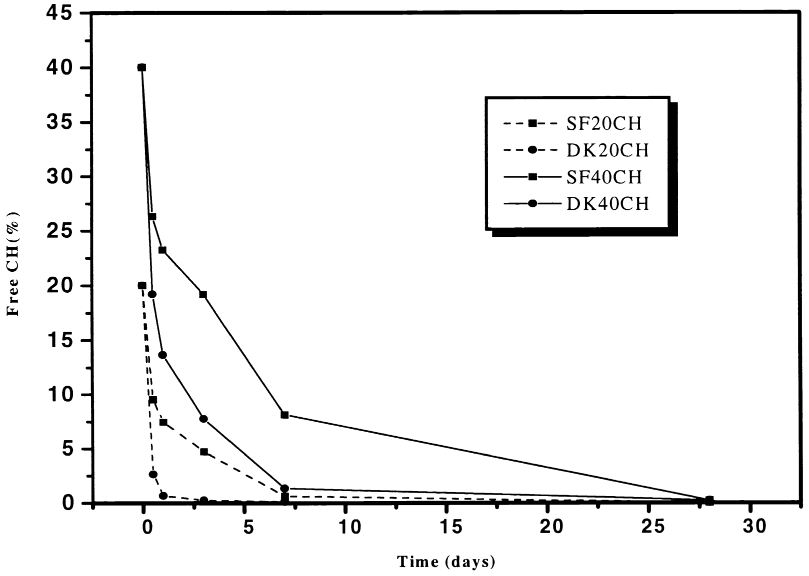

Fig. 5. Free lime contents at different times.

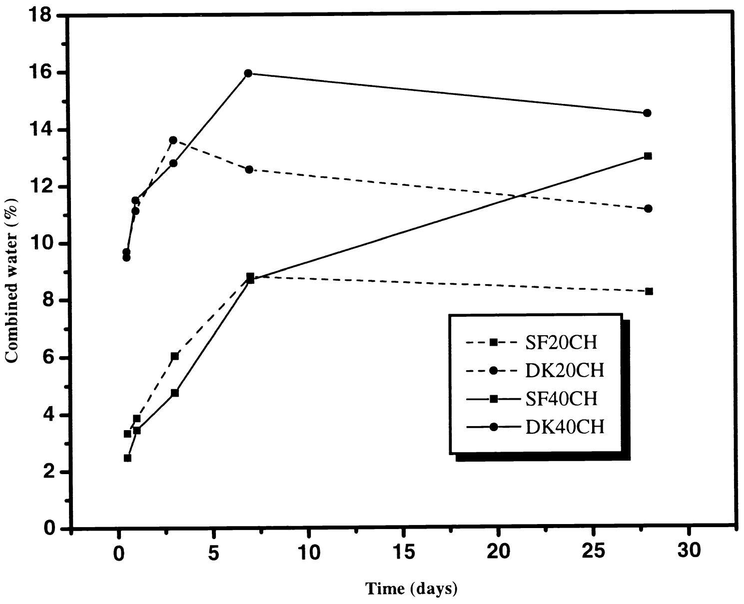

Fig. 6. Combined water contents at different times.

strong reduction in the heat of hydration of the DK mix with 20% lime, with nearly no reduction on the heat of hydration of the corresponding SF mix.

5. Pozzolanic activity in suspension

The changes in the free lime contents of SF–lime and DK–lime suspensions with time is shown Fig. 5. The results indicate that DK has higher pozzolanic activity than SF. Lime consumption in mix DK20CH is nearly complete in the first 12 h of reaction.

Combined (nonevaporable) water (Wn) was regarded as equivalent to the LOI of the dried sample, after making corrections for the loss due to the free lime. The changes in chemically combined water with time of hydration are shown in Fig. 6. The combined water contents will change as a result of two factors: the amount of hydration products formed and the type of the hydration products. As the reaction between lime and pozzolan proceeds, the combined water increases as a result of the increase in the amount of the hydration products. However, once the lime has been consumed, the combined water starts to decrease. This is due to the transformation of the initially formed high-lime

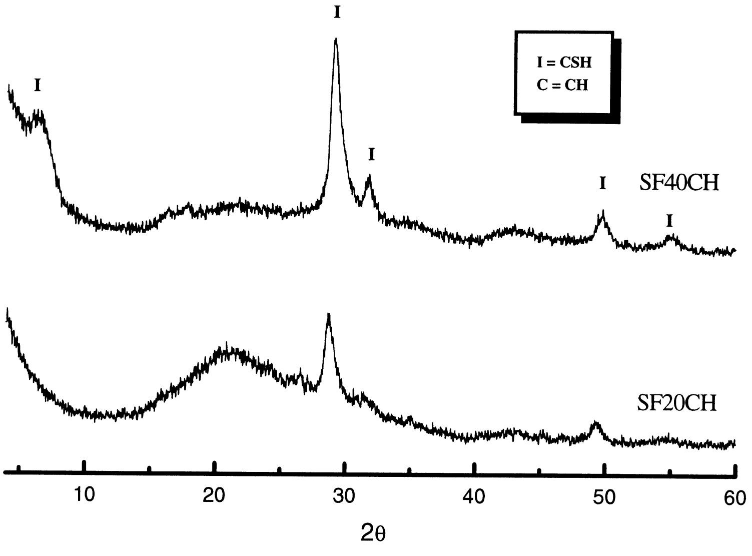

Fig. 7. XRD of SF–CH mixes hydrated for 28 days in suspension.

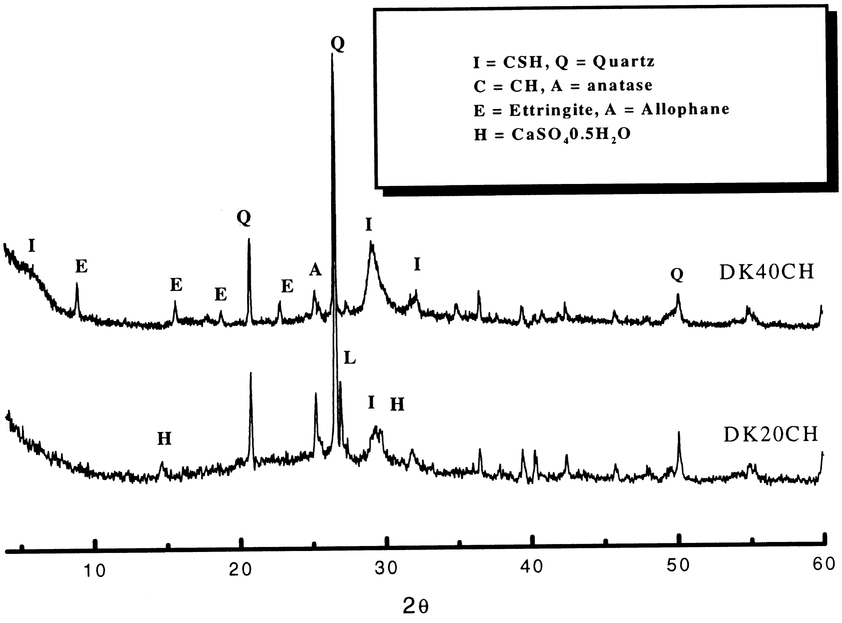

Fig. 8. XRD of DK–lime mixes hydrated for 28 days in suspension.

CSH with higher combined water content, to low-lime CSH, which has a lower combined water content [27]. In mix DK20CH, Wn starts decreasing at 24 h. Mix SF40CH shows no decline in Wn at the end of 28 days. This suggests free lime was not totally consumed in this period.

Generally, the DK mixes show higher amounts of combined water at all ages of hydration. This is due to the formation of aluminated phases, because DK contains a considerable amount of aluminum (Table 1).

XRD analyses were carried out at 28 days to identify the crystalline solid phases. The diffraction patterns are given in Figs. 7 and 8. XRD analyses of both SF mixes indicate the main phase to be CSH. The amorphous hump associated with the SF (centered at $2\Theta = 22°$) is reduced with the progress of hydration. The peak characteristic of CSH at $2\Theta = 28°$ increases. As expected in mix SF20CH (low lime), the SF amorphous hump is still clearly detected at 28 days, indicating that 20% CH is not enough for the consumption of all SF. XRD patterns of DK mixes shown in Fig. 8 confirm the higher reactivity of DK. Mix DK40CH shows the peak characteristics of ettringite ($C_6A\bar{S}_3H_{32}$) at 28 days. However, this phase is not present in the low-lime mix DK20CH. Based on the Al_2O_3 ratio in the DK, the presence of ettringite is surprising in that AFm formation would be expected.

Mix DK20CH shows peaks characteristic of allophone ($Al_2O_3{\cdot}2SiO_2{\cdot}3H_2O$) and calcium sulfate hemihydrate ($CaSO_4{\cdot}0.5H_2O$). The former appeared due to the lack of

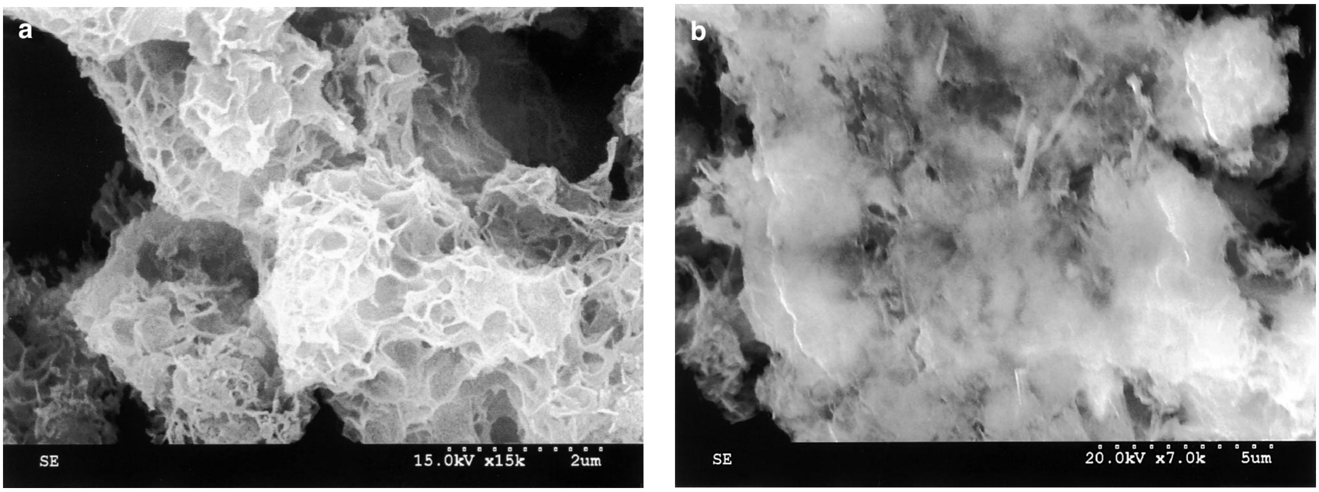

Fig. 9. SEM of (A) mix DK20CH and (B) DK40CH hydrated for 28 days.

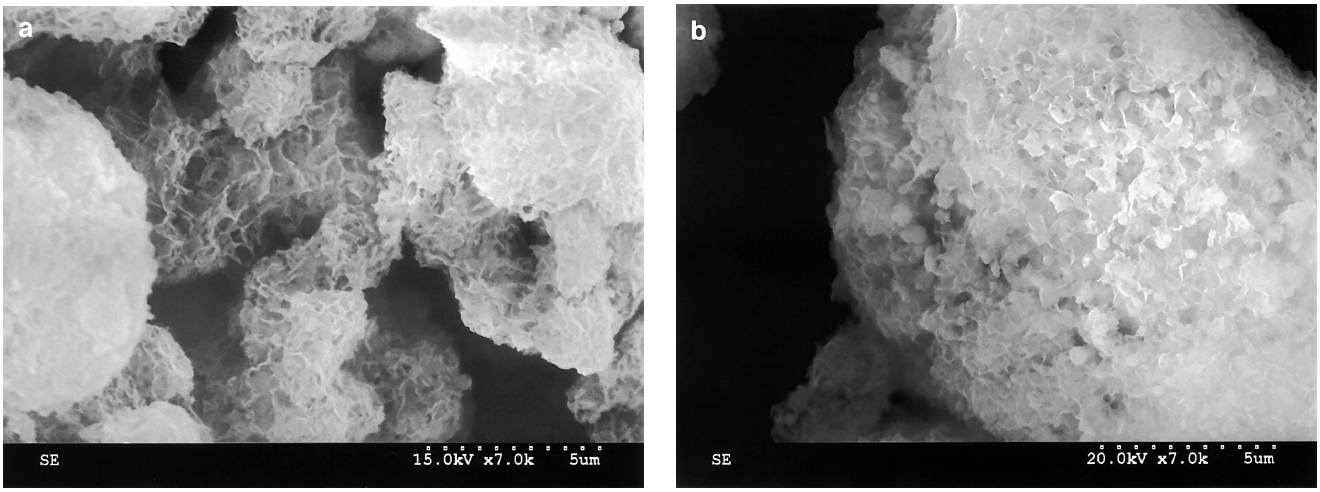

Fig. 10. SEM of (A) mix SF20CH and (B) SF40CH hydrated for 28 days.

calcium, the presence of reactive alumina and excess reactive silica. The latter appeared since the small amount of CSH formed cannot accommodate all the sulfate which precipitated as $CaSO_4 \cdot 2H_2O$, and converted to $CaSO_4 \cdot 1/2H_2O$ with drying at 105°C.

Comparing the patterns from samples DK40CH and SF40CH shows the peaks characteristic of CSH to be less well defined in the DK mix than in the SF mix. This may be due to the incorporation of aluminum into the CSH structure [28]. In addition, the 002 basal reflection, which is the interlayer spacing, shifts to a smaller angle (larger d-spacing) in the DK40CH sample. It is not clearly known if SO_4^{2+} substitutes for Si in CSH or between the chain layers of the silicate tetrahedra.

An SEM investigation was carried on samples at the end of 28 days hydration. Mixes with 20% CH produce CSH having a sponge-like morphology, as shown in Figs. 9A and 10A for mix SF20CH and mix DK20CH, respectively. The CSH produced in mixes with 40% CH shows a denser microstructure as illustrated in Figs. 9B and 10B for mix SF40CH and mix DK40CH, respectively. The needle-like crystals typical of ettringite are present in mix DK40CH.

6. Conclusions

The kinetics of the pozzolanic reaction and the hydration products formed depend on the pozzolan and the proportion of lime. Calorimetric studies and chemical activity in suspension proved DK to be an excellent pozzolanic material. DK was much more reactive than SF, especially at early age of hydration. Dealumination of metakaolin by acid leaching, produces amorphous silica with a high surface area (90.5 m^2/g), this indicates the bases of high reactivity. It appears that the main effect of acid attack on metakaolin is the dissolution of the aluminum from its octahedral and tetrahedral sites and the formation of free silica. Chemical analysis and FTIR spectroscopy of DK revealed the features of the reaction between H_2SO_4 and metakaolin can be considered in terms of ion exchange and network hydrolysis mechanisms, as seen in other systems [29,30]. In an ion-exchange mechanism, the modifier cations associated with nonbridging oxygen atoms in siloxane groups or Al–O–M^+ sites are subject to ion exchange under strongly acidic conditions to form silanol (Si–OH) or Al–OH groups:

$$-Si_S - O \ldots M^+ \rightarrow^{H^+} -Si_S - OH + M^+$$

The consequence of ion exchange is that the siloxane and the remaining Al become hydroxylated as alkali or alkaline earth cations are leached. Aluminate ions, in general, will be further hydrolysed to Al^{3+} and other soluble species, living the hydroxylated silica. Also H_2SO_4 attack at high temperature may result in a network hydrolysis at bridging oxygen atoms by H_2O catalysed by H^+ [30–32], which leads to hydroxylation as follows:

$$Si - O - Si + H_2O \rightarrow^{H^+} Si_S - OH + HO - Si_S$$

This hydroxalated silica surface can hold water with hydrogen bonding as indicated from the IR spectra.

It has been shown that the metakaolin structure does not undergo extensive collapse during acid attack [33] and the free silica produced has the structure of silicates with unit sheets of large dimensions [34]. Suraj et al. [35] showed that Al^{3+} ions are removed from the lattice without disturbing its structure and revealing sites for substitution by other metal ions. Dimas et al. [34] showed that acid dealumination of kaolin causes an increase of its globular pore volume without an appreciable change in the mean pore size, resulting in a surface area increase to about 90 m^2/g. Due to the open porous structure of the residual silica and the presence of silanol (Si–OH) groups, it was expected that DK would have a high pozzolanic activity by allowing cations to penetrate easily. There is also a probability of fast cation exchange [35] since Sersale [36] and Uribe-Afif et al. [37] found that materials, containing zeolites capable of cation exchange, are more reactive than those containing vitreous constituents.

$$2\mathrm{Si_S}-\mathrm{OH}+\mathrm{Ca(OH)_2}\rightarrow(\mathrm{Si_S}-\mathrm{OH})_2\mathrm{Ca}+\mathrm{H_2O}$$

The high reactivity of DK suggests that it can be used in the production of bricks by blending with CaO at room temperature or can be used in the production of blended cement.

Acknowledgments

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