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Influence of chemical and phase composition of mineral admixtures on their pozzolanic activity

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The influence of the chemical and phase composition of different mineral admixtures on pozzolanic activity was studied. Local kaolin clay, activated kaolin clay, porcellanite, activated porcellanite, pumice, fly ash, silica fume and ground quartz were used as components of blended binders for various mortars. Thermal treatments were performed as a means for activation of the minerals. The phase transformations during heat treatment were studied by XRD and DTA/TGA. The pozzolanic activity of these materials as a function of heat treatment parameters was investigated.

Introduction

The desire to improve the performance of cement-based products has led to an increased of use pozzolanic admixtures.[1,2] Pozzolana is a natural or artificial material containing silica and/or alumina in a reactive form.[3] Natural materials usually do not require any further treatment apart from grinding. Artificial pozzolanas are the products of chemical modifications and/or phase transformation of materials originally having no or only weak pozzolanic properties.[4]

The general term 'activity of additive' covers two properties: (a) chemical activity (usually pozzolanic activity); and (b) microfiller effect. The pozzolanic activity is the ability to react with portlandite, $Ca(OH)_2$, in the presence of an excess of water. It depends on the nature of the pozzolana and, in particular, on the quality and quantity of the active phases, type of treatment, Si/Al molar ratio, the lime/pozzolana ratio of the mix, water to binder ratio, curing conditions and specific surface area.[5,6] Microfiller effect depends mainly on the shape and size of particles, particle size distribution and specific surface area.[7] Silica fume is one of the most effective and widely used additives. However, the utilisation of silica fume is accompanied with the transportation difficulties and its cost is relatively high. These restrict a wider application of silica fume in construction in countries where it is not produced locally, such as Israel.

Therefore, attempts were made to develop effective mineral admixture produced from local materials, such as kaolin clay and porcellanite, and they are reported here. The pozzolanic properties of clay materials and porcellanite can be changed dramatically by heat treatment. The study was based on heat treatment of several materials and evaluation of their final properties. The properties of different heat-treated materials were studied in comparison with the pure (standard) kaolin.

The main objectives of this research were to determine the activity of various materials, with emphasis on local raw materials, by considering: (a) the influence of mineral, chemical and phase composition on the admixtures activity; and (b) the effect of the heat treatment.

Materials and methods

An ordinary Portland cement (ASTM Type 1) was used throughout this work. Materials with high content of alumina and silica such as kaolin clay (local material), standard kaolin (Spectrum Chemical, CP, USA), Metamax (high reactivity metakaolin, Engelhard Corporation, USA), coal fly ash (produced at the Hadera Power Plant), local material of sedimentary

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origin rich in silica and calcium such as porcellanite and materials rich in silica such as pumice (Lava Mining and Quarrying Co, Greece), silica fume (Retard, Israel) and ground sand were used as additives. The last two additives have the same chemical composition (silica), but different morphology and physical properties. The mineral and chemical compositions of the materials and their specific surface area are listed in Tables 1, 2 and 3, respectively.

Samples of standard kaolin, kaolin clay and porcellanite were heat-treated for 5 h at different temperatures in the range of 500–750°C in air. After the heat-treatment the samples were quenched in air to room temperature to avoid the crystallization of the amorphous metakaolin.

Changes in mineral and phase composition and in specific surface area were studied by XRD (Philips PW 1720, CuK radiation), DTA/TGA (simultaneous Differential Thermal and Thermogravimetry Analysis, Setaram TG 92-16.12) and BET (N_2 adsorption-desorption at 77K, Monosorb, Quantachrom) methods. The pozzolanic activity (strength activity index) of the samples was determined according to ASTM C311 and European Standard EN-450. The test for the pozzolanic activity is considered to be a suitable means for evaluating the strength contribution potential of the mineral admixture.

Table 1. Mineral composition of additives (% wt.)

Material	Minerals
Standard kaolin	Kaolinite
Metamax	Metakaolinite ∼ 85%, Quartz ∼ 13%
Kaolin clay	Kaolinite ∼ 75%, Quartz ∼ 23% Anatase ∼ 2%
Porcellanite	Opal ∼ 50%, Clay minerals ∼ 5–15%, Calcite ∼ 25–45%, Quartz ∼ 10%
Ground sand	Quartz

The strength activity index is the ratio of the compressive strength of standard mortar cubes, prepared with 80% reference cement plus 20% additive by mass, to the compressive strength of standard mortar cube prepared with reference cement only, tested at the same age. The water to binder ratio was 0·48.

The mortars were mixed with a pan mixer and cast as cube samples of 50-mm size. The samples were demolded after 24 h and cured in lime-saturated water at 20°C until testing at 1, 7, 28 and 90 days.

Results and discussion

Thermal behaviour of kaolinite

The DTA/TGA curves and the X-ray diffraction patterns for heat-treated (at 700°C) and untreated kaolin clay are presented in Figs 1 and 2.

Kaolin is a dioctahedral 1:1 layer silicate mineral. The thermal transformation of kaolinite has been the subject of many investigations.[8–12] It is known that the dehydroxylation of kaolinites at ambient conditions results in a mass loss of about 14%. The loss corresponds to transition of $SiO_2 \cdot 2Al_2O_3 \cdot 2H_20$ to $SiO_2 \cdot 2Al_2O_3$ and is associated with a well-defined endothermic DTA peak and sharp weight loss in the TGA curve between 450 and 600°C (Fig. 1(a)). The exact temperatures of this transition depend on the crystallinity and the particle size of kaolinite powders. The endothermic effect corresponds to a new disordered phase, metakaolin, $Al_2Si_2O_7$. The dehydroxy-

Table 2. Chemical composition of Portland cement and additives (% wt.)

	Portland cement	Standard kaolin	Kaolin clay	Metamax	Fly ash	Pumice	Porcellanite	Ground sand	Silica fume
SiO_2	19·38	56·17	59·34	52·18	44·28	70·55	57·91	99·5	85 ÷ 10
Al_2O_3	4·30	41·67	37·68	43·36	32·06	12·24	2·04	0	
Fe_2O_3	1·95	0	1·86	0·25	4·91	0·89	0·8	0	
TiO_2	0·38	2·16	1·12	4·21	1·89	0	0·1	0	
CaO	64·8	0	0	0	7·65	2·36	31·07	0	
MgO	1·09	0	0	0	2·11	0·1	1·75	0	
Na_2O	0·19	0	0	0	0·4	3·49	1·23	0	
K_2O	0·25	0	0	0	0·6	4·21	0·37	0	
SO_3+Cl	1·92	0	0	0	3·95	0·03	2·35	0	
P_2O_5	0	0	0	0	0	0	2·38	0	
SiO_2/Al_2O_3 molar ratio		2·29	2·70	2·05	2·35	9·8	48·27		

Table 3. Specific surface area of additives (m^2/g)

Standard kaolin	Kaolin clay	Activated kaolin clay	Metamax	Fly ash	Pumice	Porcellanite	Activated porcellanite	Ground sand	Silica fume
15·9	18·3	14·8	11·6	2·3	0·4	30·4	8·9	0·9	18·0

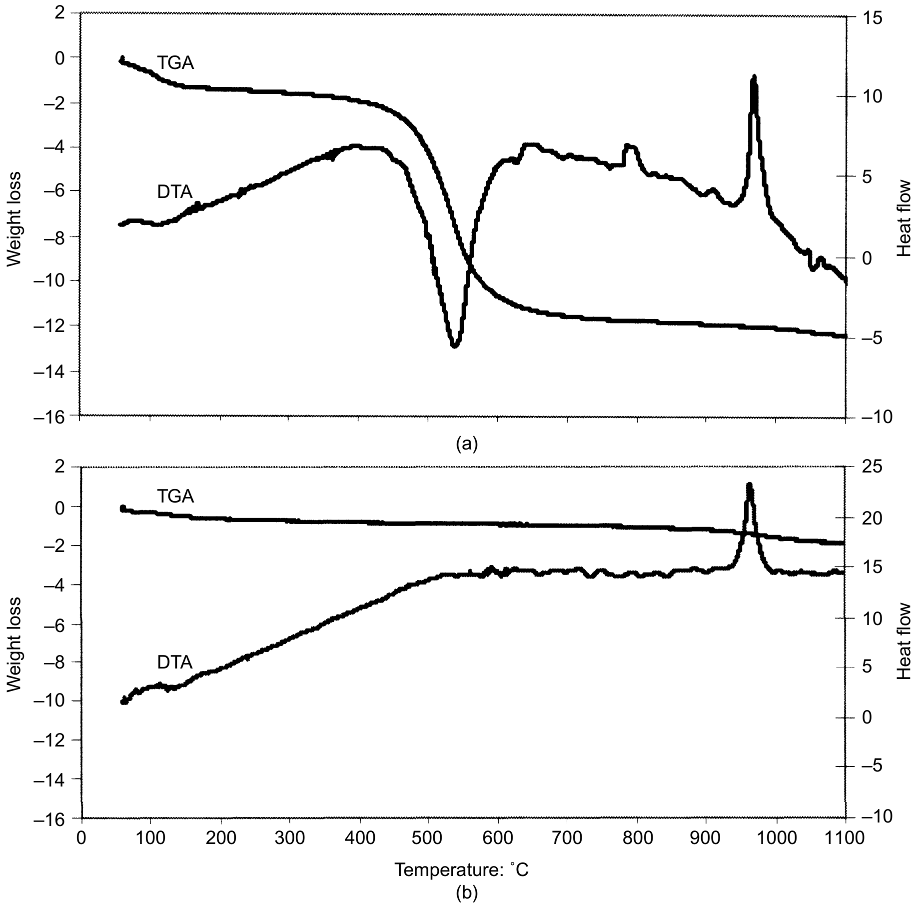

Fig. 1. Results of thermal analysis (TGA/GA/DTA) for: (a) untreated; (b) heat-treated kaolin clay

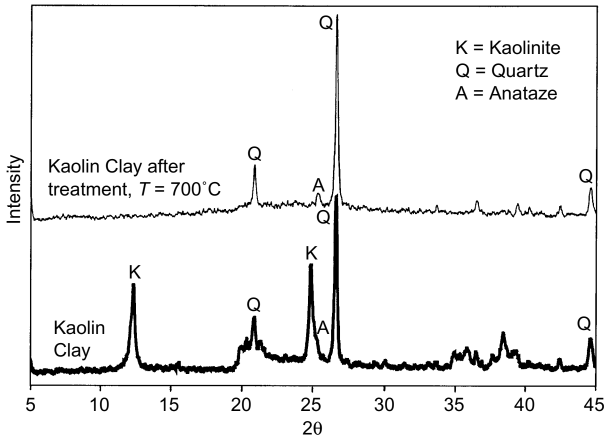

Fig. 2. X-ray diffraction patterns of heat-treated and untreated kaokaolin clay

lation process of kaolinite is preceded by a 'predehydroxylation' state in the range of 80–150°C. Between 900 and 1100°C, the exothermal formation of crystalline phases, such as spinel and mullite ($Al_6Si_2O_{13}$), where silica is totally or partly segregated, is characterised by exothermic peak on DTA curve without weight loss (see Fig. 1).

The XRD was performed for both untreated and treated at 700°C kaolin clay (Fig. 2). All the diffraction peaks corresponding to kaolinite disappeared after thermal activation, and the remaining peaks were attributed to only quartz and anatase. The strong endothermic peak and sharp weight loss in the range 450–600°C disappeared in the TGA/DTA curve (Fig. 1(b)).

Thus it may be concluded from the DTA/TGA and XRD that, after dehydroxylation of kaolin at 700°C, the kaolinite was completely transformed to an X-ray amorphous phase (metakaolinite).

Influence of heat treatment

The influence of the heat treatment was studied separately for standard kaolin containing ~100% of kaolinite, kaolin clay containing ~75% of kaolinite and porcellanite.

The results of the strength activity index for kaolinite-based materials are shown in Fig. 3. As can be seen from this data, after heat treatment at 500–700°C the pozzolanic activity was dramatically increased. This

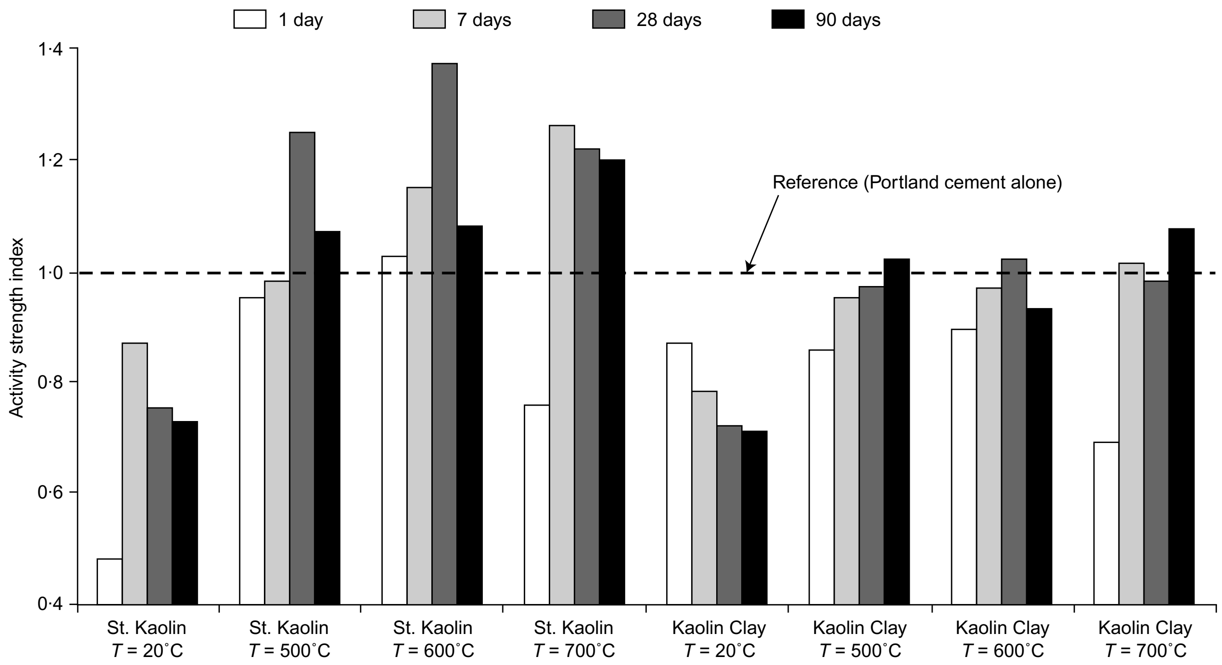

Fig. 3. Activity strength index of kaolin materials (standard kaolin and kaolin clay mortars)

increase is associated with the transformation of kaolinite into an amorphous phase (metakaolin). Untreated standard kaolin and kaolin clay show decrease of the activity strength index between 28 and 90 days. Untreated standard kaolin and kaolin clay have crystallite structure and are not able to react with portlandite and may serve as microfiller only, less contributing to the strength. The phenomenon of the strength decrease might be also an indication for a swelling process characteristic of clay materials.

A temperature effect on the strength activity of porcellanite is shown in Fig. 4. Although untreated

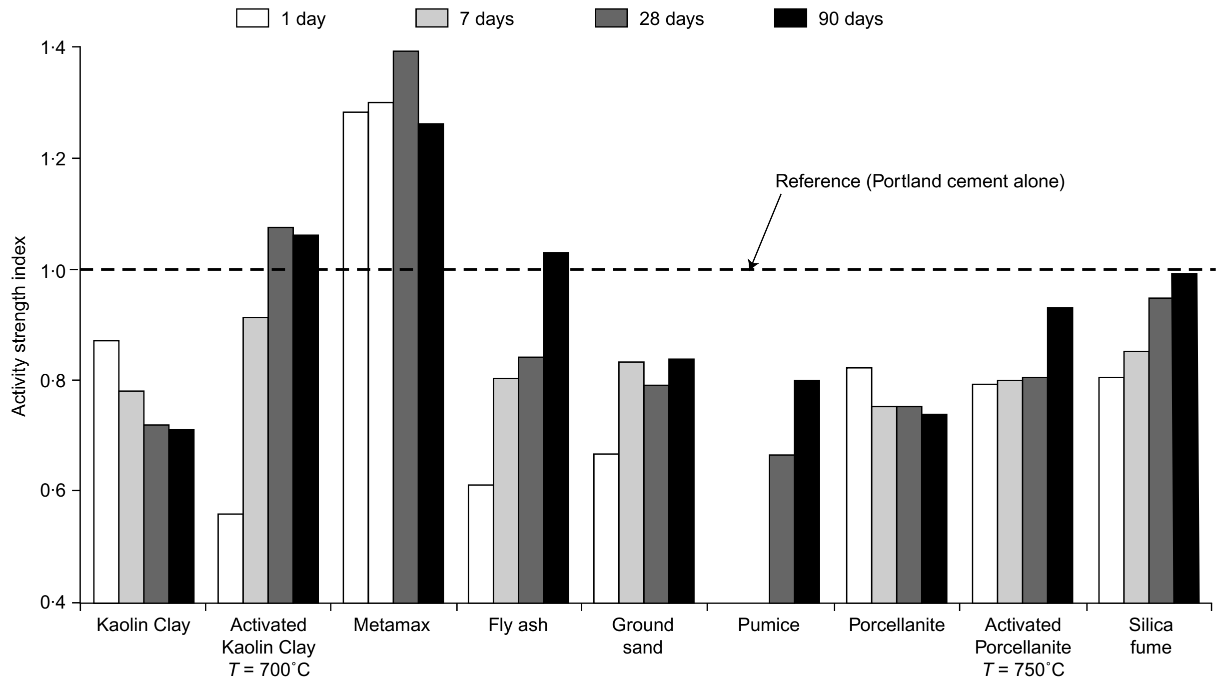

Fig. 4. Activity strength index of kaolin materials in comparison with fly ash, pumice, activated porcellanite, silica fume and ground quartz

porcellanite contains amorphous SiO_2 (~50% of opal), it is an inert material from the standpoint of pozzolanic activity. However, after heat treatment at 750°C the pozzolanic activity increases considerably and achieves 0·93 at 90 days (see Fig. 4). We suggest that this result is connected with transformation of clay minerals (~5–15%, see Table 1) to amorphous phases, as it was described by Grim.[8] It leads to increases in the total amount of amorphous part, to above 50%, followed by enhanced pozzolanic activity.

Influence of heat treatment on specific surface area

Specific surface area only is not a characteristic for identification of structure and chemical composition of any particular clay mineral, since it is a function of morphological parameters, such as particle size and its distribution, particle shape, the presence of microcracks and meso- and micropores in the samples. To follow the change of materials morphology during heat treatment, the surface area (SA) was measured at each stage of processing. The measured SA for untreated and heat-treated kaolin-based materials are presented in Table 4.

The data in Table 4 show a tendency for SA to increase with temperature of heat treatment of standard kaolin up to 700°C. In the range below 500°C the effect of temperature is negligible, while the heating above 500°C resulted in increase of the SA by about 10%. It correlates well with TGA/DTA data relative to temperature interval of amorphization (Fig. 1). At the same time, the change in SA with temperature for kaolin clay containing both kaolinite and quartz is different: SA achieves a maximum value of about 17 m^2/g at 600°C, but thereafter decreases. A similar trend was obtained in He *et al.*[6]

Influence of specific surface area, chemical and mineralogical composition of admixture

The results of strength activity index for kaolin admixtures compared with those of fly ash, pumice, porcellanite, silica fume and ground quartz are presented in Figs 4 and 5.

It is known that the pozzolanic activity depends on a number of factors,[1–4] the most significant of which seems to be the chemical and mineralogical composition of the additives, specific surface, content of $Ca(OH)_2$ in the cement paste, the admixture content and water to binder ratio of the mix.

Table 4. Specific surface area of kaolin-based materials

Temperature (°C)	Sepcific Surface Area (m^2/g)	
	Standard kaolin	Kaolin clay
Untreated	15·9	18·3
500	16·0	15·6
600	17·2	16·7
700	17·4	14·9

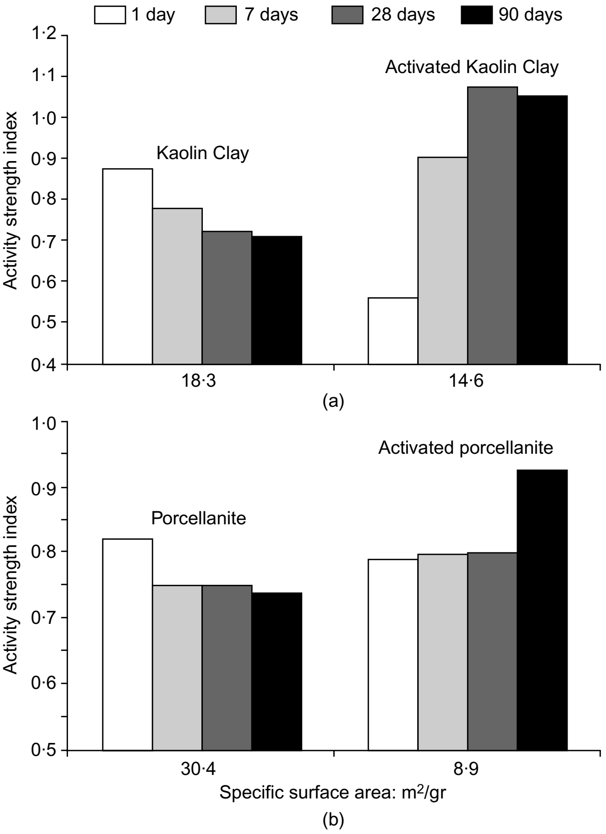

Fig. 5. Relationship between specific surface area and activity strength index: (a) untreated and heat-treated kaolin clay; (b) untreated and heat-treated porcellanite

In general correlations between the pozzolanic activity index and specific surface area are not observed. Comparing the SA-values of the same material, before and after activation (Fig. 5), it can be seen that the influence of SA on the pozzolanic activity index is observed only for very early age (1 day), when the pozzolanic admixture acts mostly as a microfiller and pozzolanic properties are not developed yet. For example, at the age of 1 day the activity strength index of non-treated kaolin clay with SA = 18·3 m^2/g is higher than that of treated kaolin clay with SA = 14·6 m^2/g, whereas the activity of the mature mixes (older than 1 day) does not depend on SA. A similar trend can be seen for porcellanite before and after activation (see Fig. 5(b)).

At mature ages the activity strength index depends mostly on the chemical and mineralogical composition of admixture and on the content of amorphous phase.

The heat-treated at 700°C kaolin clay and Metamax have shown fast strength development at early ages at 1 and 7 days, but slower development after 28 days (Table 5 and Fig. 4). The initial higher reactivity can be explained by the formation of active alumina-containing phases at early ages.[3,4]

Table 5. Effect of amorphous phase on the mortars compressive strength

Additives	Amorphous phase content (% wt.)		Compressive strength (MPa)			
	Alumosilicate (metakaolinite)	Silicate	1 day	7 days	28 days	90 days
Reference (no additive)	–	–	11·3	35·7	49·4	56·4
Kaolin clay	–	–	9·9	24·4	35·2	38·5
Local kaolin clay, heat treated at 700°C	75	–	7·9	36·1	53·2	58·8
Metamax	85	–	14·5	46·7	68·7	70·1
Standard kaolin	–	–	5·4	30·9	37·1	41·2
Standard kaolin, heat treated at 700°C	100	–	10·3	55·4	57·5	67·6
Silica fume	–	90	11·2	34·8	47·2	54·5

At 1 and 7 day ages the fly ash and ground quartz specimens have shown almost the same pozzolanic activity, while after 28 days the pozzolanic activity of fly ash was higher. At 28 and 90-day ages, the activity strength index of mortars with fly ash was higher than that of the mortars made of activated porcellanite and silica fume. Ground quartz sand has had activity strength index higher than that of pumice (see Fig. 4). Surprisingly, activated porcellanite, in spite of the fact that it contains relatively large number of coarse particles (54% > 45 μm), has activity strength index similar to that of silica fume after 28 days.

Influence of the amount and type of the amorphous phase

It is well known that both the amount and type of the amorphous phase strongly affect pozzolanic activity.[1–6] The mortars made of Portland cement alone (reference), standard kaolin heat-treated at 700°C (containing 100% metakaolinite), untreated kaolin clay (75% kaolinite, 0% metakaolinite), kaolin clay treated at 700°C (75% metakaolinite), and Metamax (85% metakaolinite) were studied, and the results were compared with those of silica fume. The data obtained from compressive tests of mortars are summarized in Table 5.

It can be seen that there is a tendency of the compressive strength to increase with the content of amorphous phase, until the content of amorphous phase of ~85% is achieved.

It is clearly seen from both Fig. 4 and Table 5 that the type (chemical composition) of amorphous phase influences the activity of admixture as well. It can be concluded that pozzolanic activity strength index and absolute value of compressive strength of the materials containing amorphous alumosilicates (activated kaolin clay and Metamax) is higher than that of the silica fume mortar containing 90% of amorphous silica. This conclusion is valid for the used testing method (ASTM-311) of the determination of the pozzolanic activity strength index. It is interesting that the pozzolanic reactivity of metakaolin determined using another test method – the Chapelle test, was also found the highest among different pozzolanas, such as silica fume, fly ash and granulated blast furnace slag.[3]

Conclusions

(*a*) The heat treatment, chemical and mineralogical composition, specific area, amount and type of amorphous phase influence the pozzolanic activity of admixture.

(*b*) The specific surface area influence the pozzolanic activity index only at very early age (1 day), whereas the activity for older materials depends mostly on the chemical and mineralogical composition of admixture and on the content of amorphous phase.

(*c*) Thermal treatment at 500–700°C of standard kaolin and local kaolin clay used as admixtures for mortars results in a dramatic increase of the pozzolanic activity. Thermal treatment of porcellanite at 750°C increases its pozzolanic activity.

(*d*) Admixtures containing amorphous alumosilicates are more effective as pozzolanic additive than the amorphous silicate materials. For example, the pozzolanic activity index of silica fume is significantly lower compared to activated kaolin clay and Metamax.

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Discussion contributions on this paper should reach the editor by ???