Pergamon

Cement and Concrete Research 33 (2003) 405–416

CEMENT AND CONCRETE RESEARCH

The effect of dehydroxylation/amorphization degree on pozzolanic activity of kaolinite

A. Shvarzman[a,*], K. Kovler[a], G.S. Grader[b], G.E. Shter[b]

[a]*Faculty of Civil Engineering, National Building Research Institute, Technion-Israel Institute of Technology, Haifa 32000, Israel*
[b]*Faculty of Chemical Engineering, Technion-Israel Institute of Technology, Haifa 32000, Israel*

Received 2 April 2002; accepted 19 August 2002

Abstract

The effect of heat treatment parameters on the dehydroxylation/amorphization process of the kaolinite-based materials such as natural and artificial kaolin clays with different amounts of amorphous phase (metakaolin) was investigated. The procedure for quantitative estimation of amorphous phase in the heat-treated kaolinite materials was developed. The process of dehydroxylation/amorphization of kaolinite was characterized by DTA/TGA with mass-spectrometry and X-ray powder diffraction. The influence of the heat treatment temperature and content of the amorphous phase on pozzolanic activity was studied. Finally, the relationships between the chemical activity, activity strength index and the amorphous phase content were found and discussed. The results obtained are important for an optimization of the process of the metakaolin large scale production and it's use as an active pozzolanic admixture.

Keywords: Metakaolin; Heating; Dehydroxylation; Amorphization; Pozzolanic activity; Thermal analysis

1. Introduction

The desire to improve the performance of cement-based products has led to an increased use of pozzolanic additives. The use of calcined clays as pozzolanic admixtures for cement has been known since the time of the Romans. The harnessing of calcined kaolinite clay (metakaolin) as a pozzolanic additive for modern cement and concrete has become very popular in recent years [1–8]. Metakaolin, $Al_2Si_2O_7$, is an amorphous product of the kaolinite dehydration, which exhibits strong pozzolanic activity.

Metakaolin is not by-product, contrary to the most often used mineral admixtures such as silica fume and fly ash. Usually, one of the methods of the production of amorphous metakaolin is carefully controlled heat treatment of kaolin at 700–800 °C. The thermal transformations of kaolinite have been a subject of a large number of investigations, showed that the heat treatment parameters such as temperature, heating rate and time, as well as the cooling parameters in the end of production cycle significantly influence the dexydroxylation process.

The major quantitative criterion for performance a kaolinite evaluating at heat treatment is a degree of the material dehydroxylation (D_{TG}) [9] calculated from the sample weight loss as follows:

$$D_{TG} = 1 - (M/M_{max}) \quad (1)$$

where M and M_{max} are residual and maximum weight loss, respectively.

The dehydroxylation of pure kaolinite in ambient atmosphere results in the weight loss of 13.76%, which corresponds to the composition $Al_2Si_2O_5(OH)_4$ and $D_{TG} = 1$. The degree of dehydroxylation, designated as D_{IR} [9], can be also characterized by Fourier transform infrared spectroscopy (FTIR) based on calculating from IR absorptions spectrums which reflected the molecular changes during heating.

The process of dehydroxylation is followed by kaolinite transformation from the crystalline to amorphous phase. It was shown earlier [10] that both amount and type of the amorphous phase could influence the activity of additives. The general term "activity of additive" covers two properties: (a) chemical activity (usually pozzolanic activity) and

* Corresponding author. Tel.: +972-4-8292-875; fax: +972-4-8324-534.
E-mail address: cvasia@tx.technion.ac.il (A. Shvarzman).

0008-8846/02/$ – see front matter © 2002 Elsevier Science Ltd. All rights reserved.
PII: S0008-8846(02)00975-4

Table 1
Mineral composition of admixtures

Material	Minerals
Standard kaolin	Kaolinite
Local kaolin clay	Kaolinite ~ 75%, quartz ~ 23%, anataze ~ 2%

Table 3
Specific surface area of admixtures

Materials	Specific surface area (m^2/g)
Standard kaolin	15.9
Local kaolin clay	18.3

(b) microfiller effect. The pozzolanic activity is defined as the ability to react with portlandite, $Ca(OH)_2$, in the presence of an excess of water.

The pozzolanic activity depends on a number of factors, the most significant of which seem to be the chemical and mineralogical composition of the additive, amorphous phase content, the degree of dehydroxylation, specific surface area, content of $Ca(OH)_2$ in the cement paste, the admixture content and water to binder ratio in the material [11]. It is known that pozzolanic activity of metakaolinite is strongly related to the crystallinity of the original kaolinite. According to Kakali et al. [12], well ordered kaolinite is transformed into less reactive metakaolinite.

Both direct and indirect methods are used for the measurement of chemical activity defined as lime reactivity of pozzolans. Direct methods are based on measuring the amount of lime reacted with additive. Indirect methods are based on monitoring the strength development occurring with time or on monitoring of lime depletion, for example, by measuring the electrical conductivity or resistivity [13].

The main objective of this study is to investigate the effects of the dehydroxylation degree and the amorphous phase content on the additive activity and to develop the technique for quantitative estimation of amorphous phase in heat-treated kaolinite materials.

2. Materials and methods

2.1. Sample preparation

The cement used throughout this work was ASTM Type I, ordinary Portland cement. The admixtures included:

- kaolin clay (local material, Negev Minerals, Israel);
- standard kaolin (CP, Spectrum Chemical., USA);
- artificial kaolinite materials with different content of amorphous phase.

Table 2
Chemical composition of admixtures (wt.%)

Main oxides	Standard kaolin	Local kaolin clay
SiO_2	56.17	59.34
Al_2O_3	41.67	37.68
Fe_2O_3	0	1.86
TiO_2	2.16	1.12

The artificial materials were prepared by adding a certain amount of powdery amorphous kaolinite to local kaolin clay with consequent thorough mixing. These mixes included the different content of amorphous phase (7.5%, 15%, 22.5%, 45% and 75%). The amorphous kaolinite was previously obtained by annealing local kaolin clay at 700 °C for 5 h. The materials chemical compositions (presented by manufacturers), mineral composition, specific surface area and the particle size distribution are listed in Tables 1–4, respectively.

In order to study the development of amorphous phase as a function of temperature, samples of standard kaolin and local kaolin clay were heat-treated in the air for 5 h at different temperatures in the range of 400–700 °C. After heating the samples were quenched to room temperature at ambient conditions to avoid crystallization of amorphous metakaolin.

2.2. Sample characterization

The High Resolution Scanning Electron Microscopy (HR SEM) was performed using a digital scanning electron microscope, Zeiss and Leica, LEO 982, for he observation of microstructure. The specific surface area (SA) was determined by the single point BET method via nitrogen adsorption/desorption at 77 K (Micromeritics, Flowsorb II, USA). The mineral and phase composition were studied by XRD (Philips PW 1720, CuK_α radiation). The weight change, energetic transformations and a gas evolution under elevated temperature were observed by simultaneous Differential Thermal and Thermogravimetric Analysis (DTA/TGA-Setaram TG 92-16.12, France) with on-line Mass Spectrometry (MS—Quadruple mass spectrometer—Thermostar 200, Balzers, Switzerland-Luxemburg). During DTA/TGA/MS analysis the samples were heated at a rate of 5 °C min^{-1} to a maximum temperature of 1000 °C in air flow of 30 cc/min. The particle size distributions were

Table 4
Particle size distribution of local kaolin clay and standard kaolin

% <	Particle size (μm)	
	Standard kaolin	Local kaolin clay
10	0.82	0.53
25	1.48	1.02
50	2.63	2.17
75	4.21	3.84
90	5.81	5.35

measured in water suspension using a laser analyzer Coulter LS230 (Coulter, USA).

2.3. Pozzolanic activity

The pozzolanic activity (strength activity index) of the samples was determined according to ASTM C311 and European Standard EN-450. A test for the pozzolanic activity is considered to be a suitable means of evaluating the strength contribution potential of a mineral admixture.

The strength activity index was determined as 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 mixed with a pan mixer were 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.

2.4. Chemical activity

Chemical activity, i.e., the ability to react with portlandite, $Ca(OH)_2$, in the presence of an excess of water, was determined indirectly—using the results of the compressive test of the paste cube specimens made with 50% portlandite plus 50% additive by mass. The water to solid ratio in the paste specimens was 0.9.

The pastes mixed with a pan mixer were cast as cube samples of 25-mm size and cured in air (RH = 65%, at 20 °C) until demolding. The samples were demolded after 6 days and then cured in humidity room (RH = 100%, at 20 °C) until testing at 7, 14, 28 and 90 days.

3. Results and discussion

3.1. Thermal behavior of kaolinite

It is known that kaolinite is a dioctahedral 1:1 layer silicate mineral with well-formed six-sided flakes, frequently with a prominent elongation in one direction [14,15]. This typical microstructure was observed for standard kaolin used in the present work (Fig. 1).

The results obtained by the DTA/TGA/MS for pure standard kaolin and kaolin clay are presented in Figs. 2 and 3. The TG curves and the X-ray diffraction patterns for kaolin clay before and after the heat treatment at different temperatures are shown in Figs. 4 and 5. The TG-curves for untreated and annealing samples of standard kaolin clay and for untreated artificial materials based on local kaolin clay doped with different contents of amorphous phase are shown in Figs. 6 and 7, respectively.

The thermal transformation of kaolinite has been the subject of many investigations [16–21]. It is also known that the dehydroxylation of kaolinites in normal atmospheres results in a mass loss of 13.76%, which corresponds to the transition of $SiO_2{\cdot}2Al_2O_3{\cdot}2H_20$ to $SiO_2{\cdot}2Al_2O_3$. A strong endothermic effect in the range from 450 to 600 °C (the exact temperature interval depending on the crystallinity and particle size) is typical for most kaolinites. The well defined endothermic peak (Fig. 2a) associated with this effect corresponds to the formation of a new disordered phase—metakaolin ($Al_2Si_2O_7$) via dehydroxylation route followed by effluent of water as shown by MS (Fig. 2b). The dehydroxylation process of kaolinite is preceded by a "predehydroxylation" state in the range of 80–150 °C where the evolution of a small amount of water was detected (Fig. 2b). Between 900 and 1100 °C, the exothermal formation of crystalline phases, like spinel and mullite ($Al_6Si_2O_{13}$), where silica is

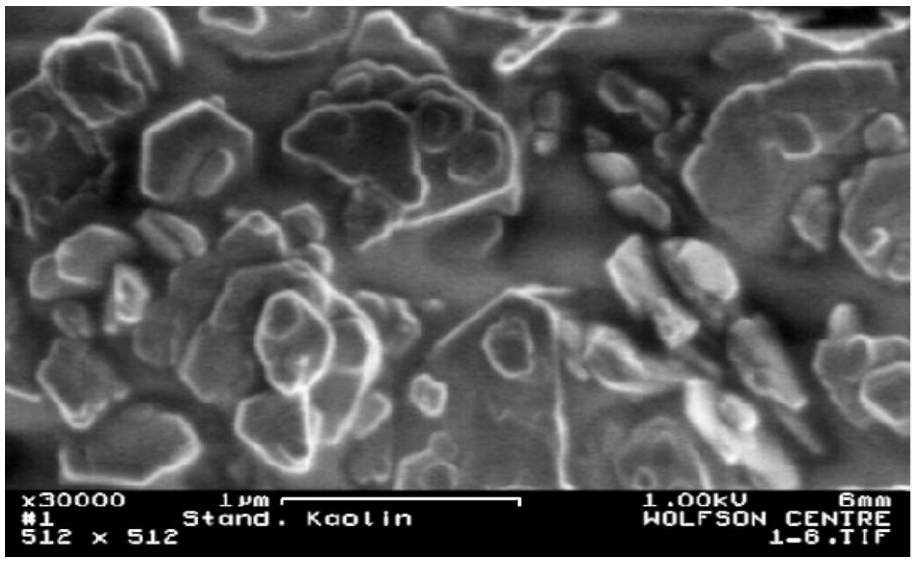

Fig. 1. HR-SEM micrograph of the pure standard kaolin.

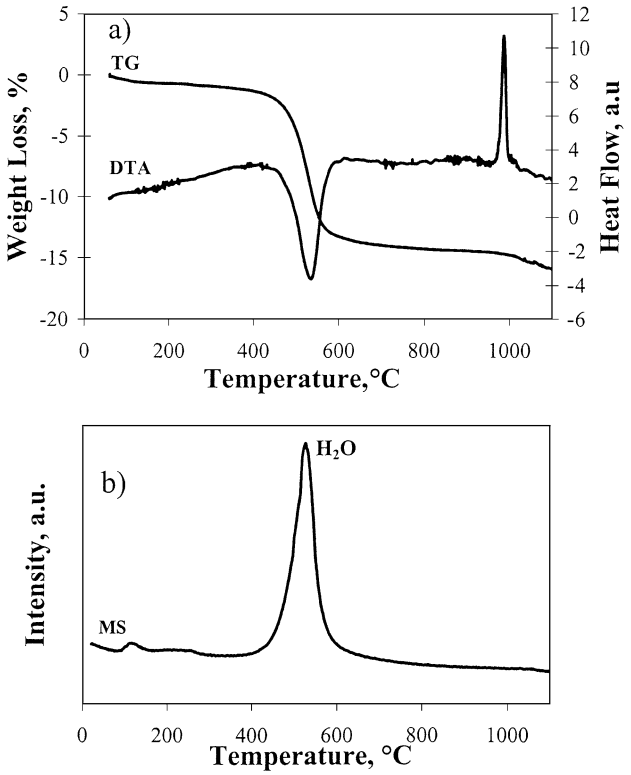

Fig. 2. DTA/TGA curves (a) and (b) MS pattern of effluent water for untreated pure standard kaolin.

totally or partly segregated, is characterized by exothermic peak on DTA curve and insignificant weight loss on the TGA curve (see Figs. 2 and 3).

The X-ray diffraction analysis was performed for both untreated kaolin clay and kaolin clay, which were heat-treated at $T=500$, 570 and 700 °C (Fig. 5). Diffraction peaks corresponding to kaolinite decreased after calcination at $T=500$ °C and disappeared at temperatures above 570 °C. In the range from 570 to 700 °C the remaining peaks were attributed to quartz and anataze. It can be concluded from the DTA/TGA and XRD results that the process of kaolinite dehydroxylation is accompanied by its amorphization. Finally, after dehydroxylation at 570 °C, kaolin was entirely transformed to amorphous phase (Fig. 5).

3.2. Influence of the heat treatment temperature on the degree of dehydroxylation

The degree of dehydroxylation was calculated for different untreated and heat-treated (at $T=400$, 450, 500, 570 and 700 °C) kaolin clay and also for standard kaolin (heated at $T=450$, 500, 600 and 700 °C). The relationships between weight loss determined by TGA, the degree of dehydroxylation and the heat-treatment temperature are presented in Figs. 8 and 9, respectively.

The heat-treatment temperature range in the graphs of weight loss as well as the dehydroxylation degree of kaolinite materials was divided into three characteristic Regions A, B and C (Figs. 8 and 9). In the Region A, kaolin clays showed relatively low differences in weight loss (of about 1–2%) for the samples treated in the range of 20–430 °C. In the same region, the dehydroxylation degree (D_{TG}) did not exceed 0.18. In contrast, in the Region B (430–570 °C) both the D_{TG} increased sharply to 0.95 and the weight loss drastically changed by about 10%. Finally, in Region C, (570–700 °C) insignificant changes of weight loss and D_{TG} were again observed. At the end of this region (at 700 °C) kaolinite was fully dehydroxylated, i.e., the degree of dehydroxylation achieved its maximum ($D_{TG}=1$) and no weight loss for this sample was detected.

3.3. Quantitative analysis of the amorphous phase in heat-treated kaolinite materials

In general, thermal behavior of kaolinite clays may be characterized by different methods, such as differential thermal analysis, thermodilatometry, IR spectroscopy, differential scanning calorimetry, emanation thermal analysis, thermogravimetry, X-ray diffraction, X-ray spectropscopy and the radial electron density distribution technique [22–24]. As was shown before for kaolinite, and in the present work for local kaolin clay (Fig. 5), the dehydroxylation process should be accompanied with amorphization of kaolinite and usually such a transition is affected by the heat-treatment conditions. In this connection, the necessity of quantitative determination of the amorphous phase as a function of calcination temperature becomes important for explicit evaluation of annealed kaolinite based materials. For the quantitative estimation of the amorphous phase we

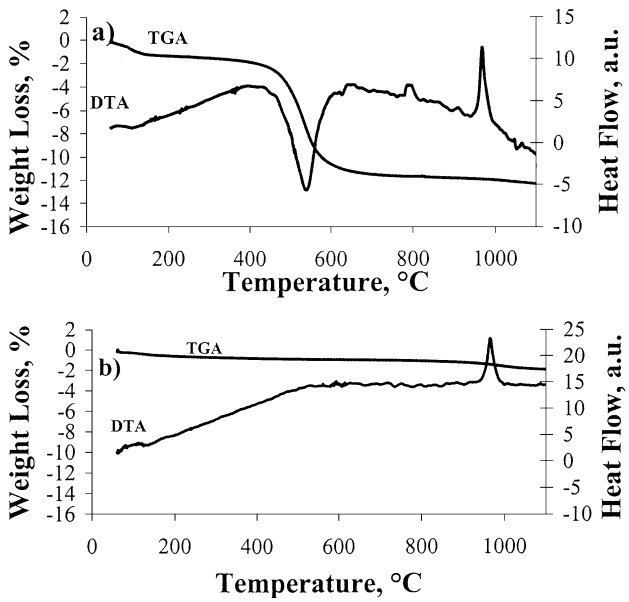

Fig. 3. DTA/TGA of (a) untreated and (b) heat-treated at 700 °C local kaolin clay.

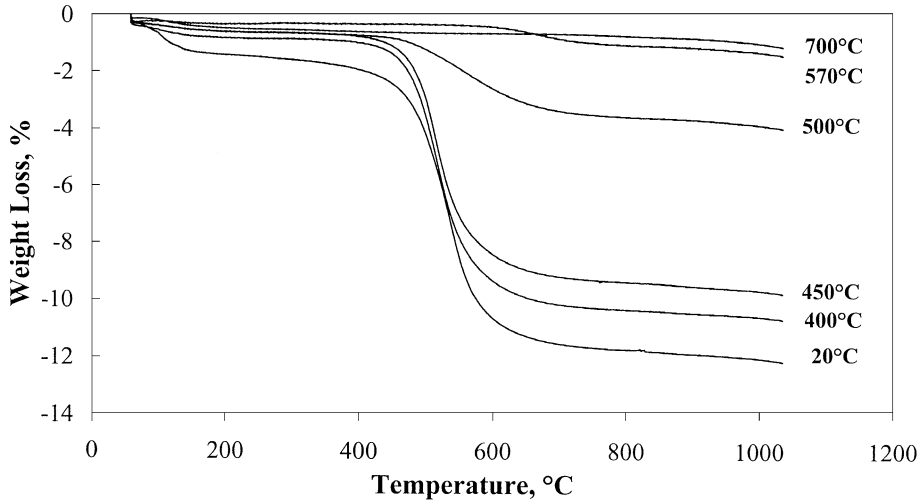

Fig. 4. TG-curves of local kaolin clay before heating (20 °C) and after heating at different temperatures for 5 h.

propose the methods based on the DTA/TGA and XRD analysis combination. For kaolinite clays contained different concomitant compounds stable in the temperature range of kaolinite → metakaolinite transformation the following procedure were developed and used:

(1) XRD test is performed in the beginning to determine the phase composition of the initial material before calcinations. If the sample contains kaolinite as the main and secondary components, which do not decompose in the range 400–700 °C, the following subprocedures should be executed.

(2) DTA/TGA test is performed to obtain the pattern of heat flow and weight loss (WL) under elevated temperature up to 1000 °C in air for untreated clays. The determined values of the sharp weight loss associated with characteristic strong endoeffect in the range of 400–600 °C are the initial data for the next stage of the procedure. This value of WL is designated below as a specific weight loss (SWL).

(3) Calculation of the kaolinite content in initial material using the TGA data, in particular the SWL, and establishing the relationships between SWL, calcination temperatures and amorphous phase content.

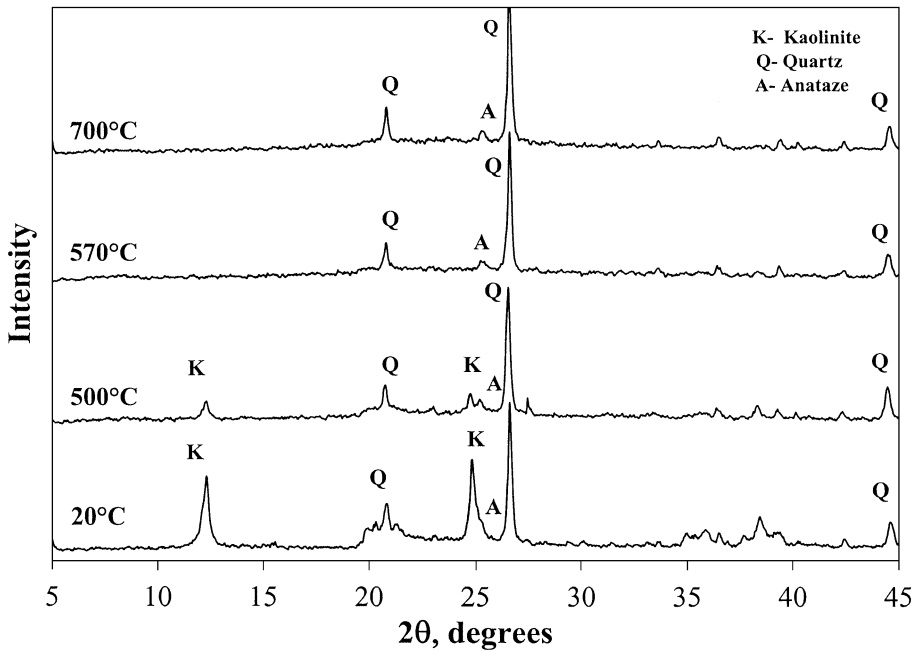

Fig. 5. X-ray diffraction patterns of local kaolin clay before heating (20 °C) and heat-treated at different temperatures for 5 h.

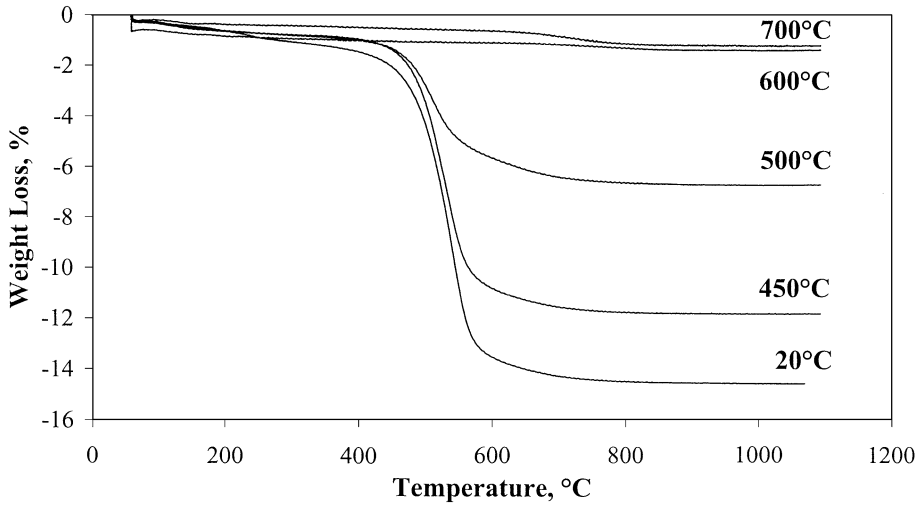

Fig. 6. TG-curves of standard kaolin before heating (20 °C) and after heating at different temperatures for 5 h.

For example, the SWL for standard pure kaolin is known to be 13.76%, i.e., this material contains 100% of kaolinite. After the heat treatment at $T = 700$ °C it had been transformed into metakaolinite completely and negligible WL only was detected (Fig. 6). The annealed material in this case is completely amorphous phase—metakaolin.

In the special case when the secondary phase is unstable in the range of 400–600 °C and the weight loss overlaps with kaolinite SWL, obtaining of the TGA data for all pure phases is necessary and a simple system of relevant equations has to be solved.

In the present work this methodology was applied to investigation of numerous kaolinite-based samples. The artificial kaolinite materials with different content of amorphous phase were prepared (see Section 2.1) and the DTA/TGA tests were conducted (Fig. 7). The DTA parts of these experiments are omitted in Fig. 7 due to the detailed explanation of a similar pattern in paragraph 3.1, see (Figs. 2 and 3). As shown in Fig. 7, the SWL changed regularly with amorphous phase content at all calcination temperatures. The relationship between amorphous phase content and the SWL for local kaolin clays is defined as linear function (Fig. 10). The constant 75.6 in linear equation is actually the content of pure kaolinite in local kaolin clays (75 wt.% in Table 1). It can be seen that the slope of the curve for local kaolin clay is essentially equal to that of standard kaolin. This fact proves an assumption that in clays the active component responsible for the value of SWL is kaolinite and this value is independent of the nature of other inert secondary compounds. Based on the liner regressions in Fig. 10 on one hand, and on the data for SWL (Fig. 8) on the other hand, the amorphous phase content as the function of heat treatment temperature was calculated and shown in Fig. 11 for local kaolin clays

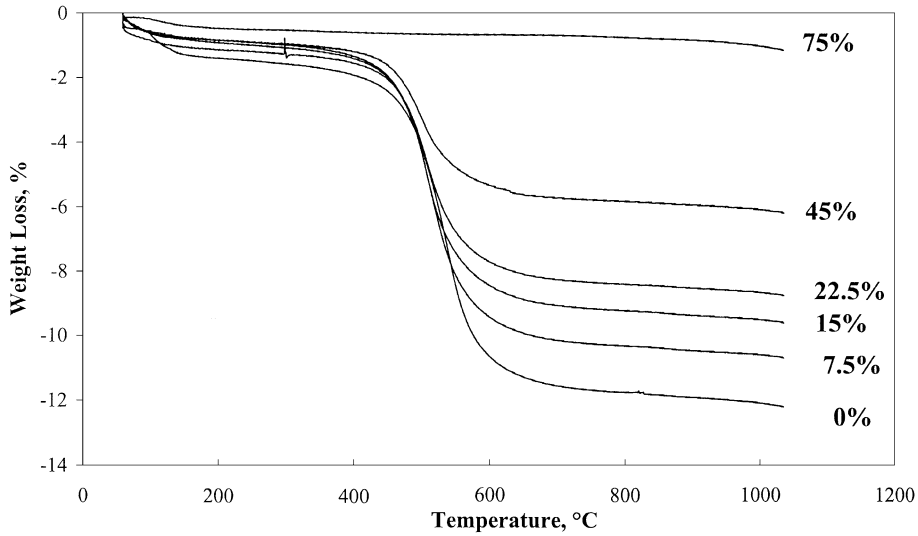

Fig. 7. TGA-curves of untreated local kaolin clay doped with different amount of amorphous phase (wt.%).

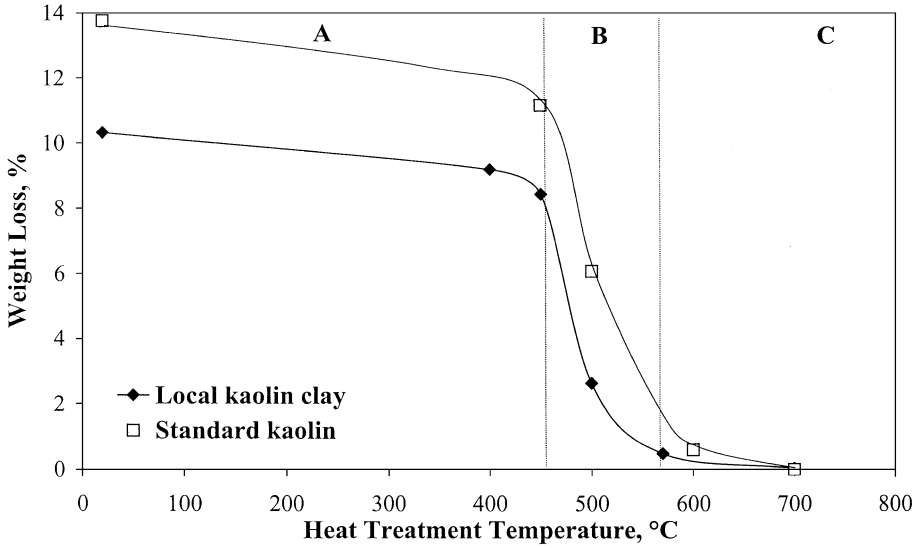

Fig. 8. Weight loss of local kaolin clay and standard kaolin heat-treated at different heat treatment temperatures.

and standard kaolin. These graphs were used hereafter as calibration curves for quantitative evaluation of the amorphous phase amount in materials treated for 5 h. For other durations of treatment the appropriate calibration curves should be obtained.

3.4. Influence of the amorphous phase content on chemical activity

The influence of the amorphous phase content on chemical activity was investigated in the pastes containing portlandite and both untreated and heat-treated kaolinite-based materials (local kaolin clay, standard kaolin, Metamax). This effect is shown by data for compressive strength as a function of the amorphous phase content in kaolin admixtures (Figs. 12 and 13).

As can be seen from Fig. 12, pastes containing less than 20% amorphous phase showed very low strength and hence could be considered as inert materials from the standpoint of pozzolanic activity. For example, the paste containing ~20% amorphous phase at the age of 7 days had compressive strength of 3.3 MPa only.

After 7 days of curing at 65% relative humidity it had changed to 100%. It can be seen that compressive strength significantly decreased (0.5 MPa at the age of 14 days). At the same time, the compressive strength of the pastes, containing more than 20% amorphous phase and cured in similar conditions, dramatically increased with time (Figs.

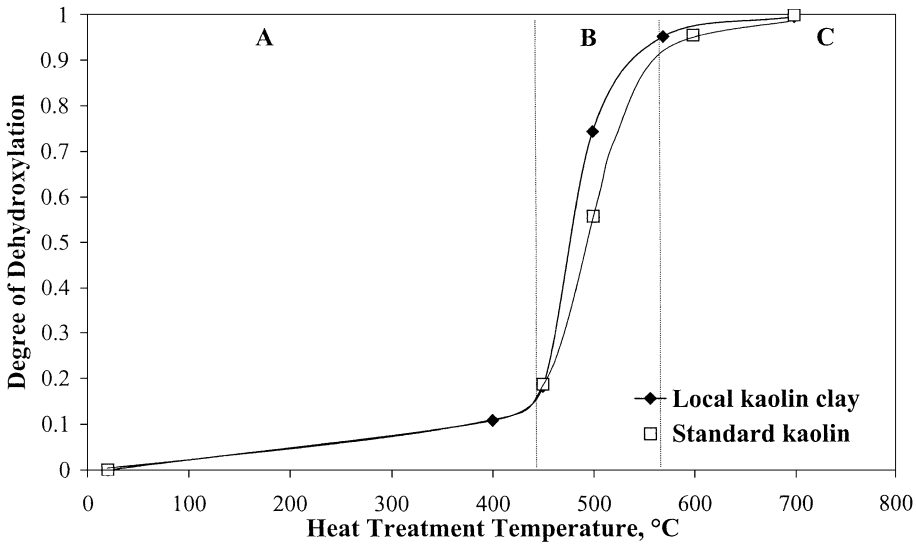

Fig. 9. Degree of dehydroxylation of local kaolin clay and standard kaolin heat-treated at different temperatures.

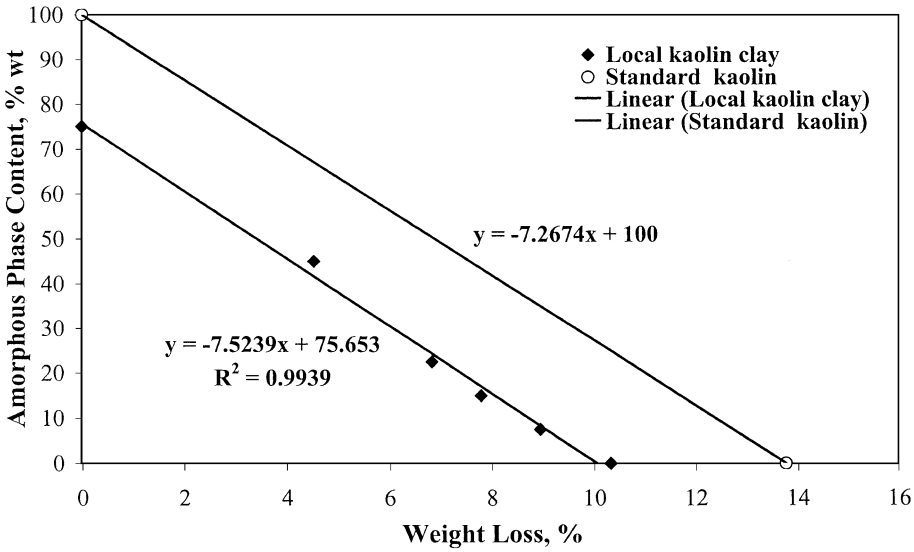

Fig. 10. Relationships between SWL and amorphous phase content in local kaolin clay and standard kaolin.

12 and 13). As an example, the paste containing 100% amorphous phase showed compressive strength of 13 MPa at the age of 14 days and 26 MPa at 90 days. In general, the positive effect of amorphous phase on the compressive strength and consequently on the chemical activity, was readily observed.

Local kaolin clay containing 23% of quartz shows about half as much of the standard kaolinite clay strength (Figs. 12 and 13). This material shows a dramatic increase of compressive strength with time only until the age of 28 days, while the increase of strength was detected for pure kaolinite clay in mature age. In addition, a significant difference in chemical activity of these materials is well represented by graphs of the compressive strength development rate, as shown for samples with 56% of amorphous phase (Fig. 14). The strength of the standard kaolin was developing at a threefold rate compared to local kaolin clay at age of 14 days. At this age, the rate of strength development for both materials was maximal, but for standard kaolin the strength increased much more intensively than in the kaolin clay material. It can be seen from Fig. 14 that such intensive strength growth was observed in a very short aging time, while the rate for kaolin clay changed slightly. It can be suggested that the difference in activity, described in this paragraph, resulted from the distinction in the initial powders morphology and the surface feature of materials made with the same contents of amorphous phase.

It was found (Fig. 15) that the compressive strength (σ_c) of kaolinite-based materials is a linear function of the

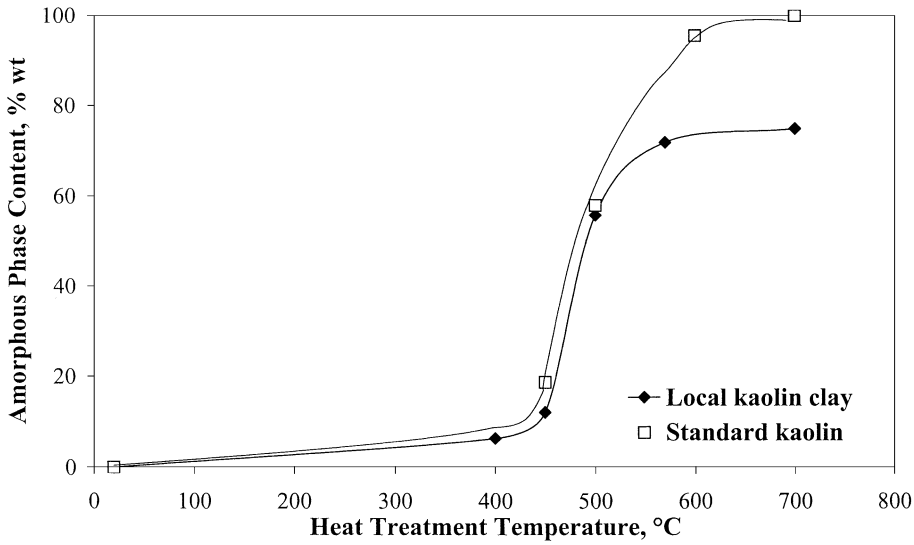

Fig. 11. Effect of heating temperature on the amorphous phase content in local kaolin clay and standard kaolin.

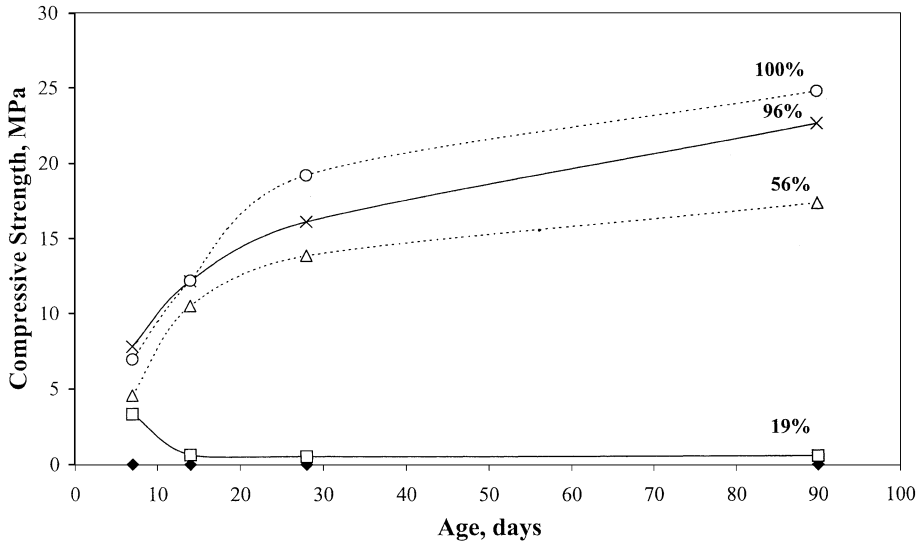

Fig. 12. Compressive strength versus age for standard kaolin paste with different amorphous phase content.

amorphous phase content (AP_c) for samples with more than 50% of metakaolinite. These relationships are described by following equations for age of 90 days:

$$\sigma_c = 0.154AP_c - 8.650 \quad \text{(standard kaolin)} \tag{2}$$

and

$$\sigma_c = 0.26AP_c - 8.242 \quad \text{(local kaolin clay)} \tag{3}$$

The reason of that the linear function was observed only in range of $\sim 50-100\%$ of amorphous phase is not clear and this fact should be investigated in another work.

3.5. Influence of the heating temperature and content of the amorphous phase on the activity strength index

The mortars containing both untreated and heat-treated kaolin based materials were investigated after calcination at $T = 400$, 450, 500, 570, 600 and 700 °C. A major part of this investigation was the quantitative evaluation of the effect of amorphous phase content and the dehydroxylation degree on the activity strength index (ASI) for different ages.

The values of strength activity index vs. amorphous phase content for kaolin admixtures at different ages are presented in Fig. 16. As can be seen from Fig. 16a, there is

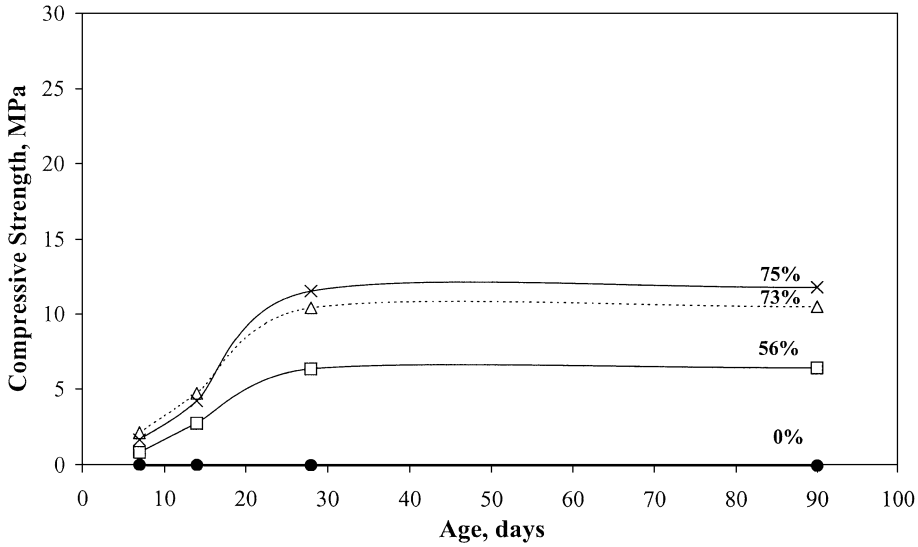

Fig. 13. Compressive strength versus age for local kaolin clay pastes with different amorphous phase content.

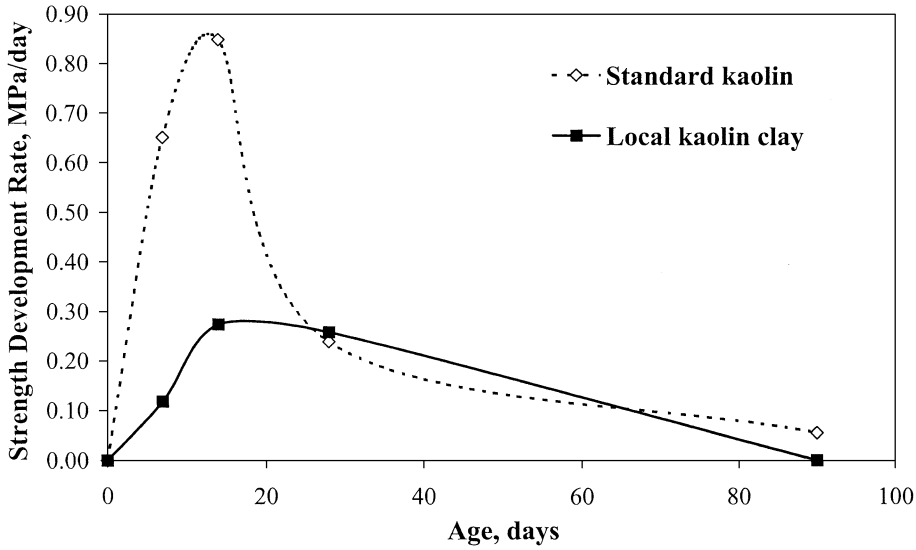

Fig. 14. Compressive strength development rate for local kaolin clay and standard kaolin with 56% of amorphous phase.

no clearly defined tendency in the changes of ASI for both materials. Therefore, it was concluded that the amorphous phase content has no affect on the pozzolanic activity index at early age of 1 day. However, the ASI of mature mixes (7, 28 and 90 days) depends significantly on the content of amorphous phase, as well as on the degree of dehydroxylation (see Fig. 16b–d). Kaolinite clay calcined at $T<450$ °C (Region A, Fig. 9) shows relatively low level of dehydroxylation and amorphization (the $D_{TG}<0.18$ and the content of amorphous phase is less than 20%). At these parameters the ASI was lower then 0.75 and therefore, according to ASTM 618, the samples obtained could be considered as inert material.

At the same time, a temperature rise from 450 to 570 °C (Region B, Fig. 9) resulted in a greater increase of D_{TG} from 0.18 to 0.95 and significantly intensified the amorphization process. In turn, a rise of amorphous phase content from 15% to 55% led to the sharp increase of activity strength index to the level of 0.85 and 1.23 for local kaolin clay and standard kaolin, respectively. The further gain of the temperatures above 570 °C associates with significant increase of amorphization and dehydroxylation degrees, which reached maximal values at 700 °C. But, at the same time, it was shown that the values of ASI did not essentially change in the interval of 570–700 °C. In other words, the increase of the amorphous phase content by over 55% does

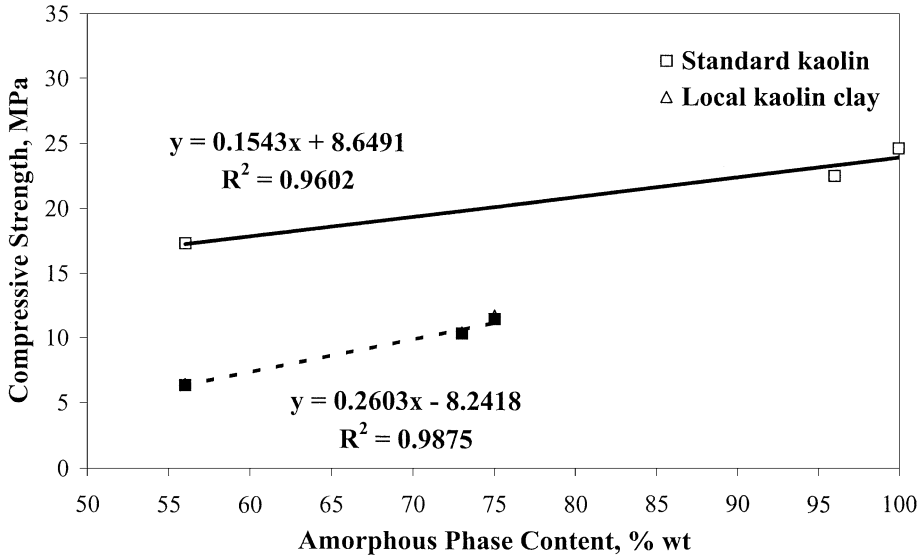

Fig. 15. Relationship between compressive strength and amorphous phase content of kaolin based materials for 90 days.

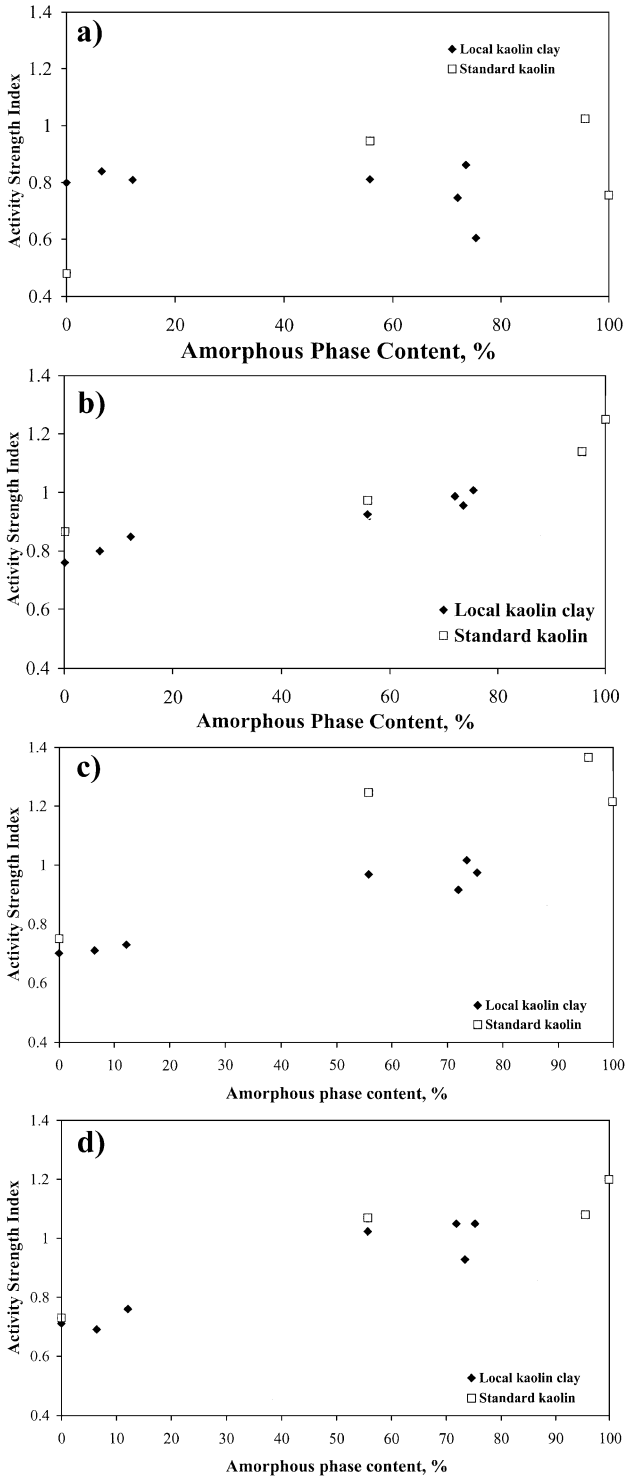

Fig. 16. Strength activity index vs. amorphous phase content of kaolin materials at ages of: (a) 1 day, (b) 7 days, (c) 28 days, (d) 90 days.

not lead to additional growth in the ASI, in contrast to the chemical activity. This phenomenon may be related to the $Ca(OH)_2$/admixture molar ratio, morphology of the untreated clay, water/binder ratio, the action of admixture as microfiller and probably to some other factors. The framework and volume of this paper is limited, therefore the effect of the above listed parameters is the subject of further studies.

4. Conclusions

- The dehydroxylation process occurring during calcination of both standard kaolin and local kaolin clay at different temperatures was investigated. At the calcination temperatures below 450 °C kaolin clays show relatively low level of the dehydroxylation degree, less then 0.18. In the range from 450 to 570 °C the degree of dehydroxylation sharply increased to 0.95, and finally at the temperatures between 570 and 700 °C the kaolinite was fully dehydroxylated since the only moderate change of degree of dehydroxylation was observed in this range (from 0.95 to 1.0).
- It was found that the dehydroxylation is accompanied with the kaolinite amorphization, which affects the activity of additives. A method of qualitative evaluation of amorphous phase content (APC) in treated materials was developed and applied for characterization of the investigated samples.
- The effect of APC on chemical activity was demonstrated by data for compressive strength. The pastes containing less than 20% of amorphous phase can be considered as inert materials from the standpoint of pozzolanic activity. It was shown that chemical activity is a linear function of APC in its range of 50–100%. As an example, the graphs and equations described this relationship were presented for kaolinite materials aged for 90 days.
- It was shown that the activity strength index (ASI) of mature mixes (7, 28 and 90 days) depends significantly on APC, as well as the degree of dehydroxylation. In contrast to the chemical activity, the increase of APC by over 55% did not lead to additional growth in ASI. Therefore, even with the partial dehydroxylation of kaolinite accompanied with ~55% amorphization the material may be considered as very active pozzolanic admixture (according to ASTM 618). This finding seems to be extremely important for the industry looking for means to reduce energy demand during the production of metakaolin.

Acknowledgements

The authors kindly appreciate the valuable advice and help of Prof. Arnon Bentur during all the stages of the investigation. This work was supported in part by the Fund for the Promotion of Research at the Technion, by a joint grant from the Center for Absorption in Science of the Ministry of Immigrant Absorption and the Committee for Planning and Budgeting of the Council for Higher

Education under the framework of the KAMEA Program. The authors are grateful to Negev Minerals (Israel) for supplying the materials used as admixtures in this work.

References

[1] B. Sabir, S. Wild, J. Baj, Metakaolin and calcined clays as pozzolans for concrete: a review, Cem. Concr. Compos. 23 (2001) 441–454.
[2] M. Caldarone, K. Gruber, R. Burg, High-reactivity metakaolin: a new generation mineral admixture, Concr. Int. 16 (11) (1994) 37–40.
[3] M. Zhang, V. Malhotra, Characteristics of a thermally activated alumino-silicate pozzolanic material and its use in concrete, Cem. Concr. Res. 25 (8) (1995) 1713–1725.
[4] J. Khatib, S. Wild, Sulphate resistance of metakaolin mortar, Cem. Concr. Res. 28 (1) (1998) 83–93.
[5] F. Curcio, B. DeAngelis, Dilatant behavior of superplasticized cement pastes containing metakaolin, Cem. Concr. Res. 28 (5) (1998) 629–635.
[6] F. Curcio, B. DeAngelis, S. Pagliolico, Metakaolin as a pozzolanic microfiller for high performance mortars, Cem. Concr. Res. 28 (6) (1998) 803–811.
[7] D. Klimesh, G. Lee, A. Ray, M. Wilson, Metakaolin additions in autoclaved cement-quartz pastes: a ^{29}Si and ^{27}Al MAS NMR investigation, Adv. Cem. Res. 10 (3) (1998) 93–99.
[8] S. Wild, J. Khatib, L. Roosse, Chemical shrinkage and autogenous shrinkage of Portland cement-metakaolin pastes, Adv. Cem. Res. 10 (3) (1998) 109–119.
[9] H. Rahier, B. Wullaert, B. Van Mele, Influence of the degree of dehydroxylation of kaolinite on the properties of aluminosilicate glasses, J. Therm. Anal. Calorim. 62 (2000) 417–427.
[10] Lea's Chemistry of Cement and Concrete, Edited by Hewlett, 4th ed., Wiley, New York, 1998.
[11] A. Shvarzman, K. Kovler, I. Schamban, G. Grader, G. Shter, Influence of chemical and phase composition of mineral admixtures on their pozzolanic activity, Adv. Cem. Res. 14 (2002) 35–41.
[12] G. Kakali, T. Perraki, S. Tsivilis, E. Badogiannis, Thermal treatment of kaolin: the effect of mineralogy on the pozzolanic activity, Appl. Clay Sci. 20 (2001) 73–80.
[13] W. McCarter, H. Ezirim, Monitoring of the early hydration of pozzolan-$Ca(OH)_2$ mixtures using electrical methods, Adv. Cem. Res. 10 (4) (1998) 161–168.
[14] L. Berry, B. Mason, R. Dietrich, Mineralogy, 3rd ed., Freeman, San Francisco, 1983.
[15] R. Grim, Applied Clay Mineralogy, McGraw-Hill, New York, 1962.
[16] M. Murat, M. Driouche, Chemical reactivity of thermally activated clay minerals, Cem. Concr. Res. 18 (2) (1988) 221–228.
[17] R. Grim, Clay Mineralogy, 2nd ed., McGraw-Hill, New York, 1968.
[18] G. Baronio, L. Binda, Study of the pozzolanicity of bricks and clay, Constr. Build. Mater. 11 (1997) 41–46.
[19] D. Akolekar, A. Chaffee, R. Howe, The transformation of kaolin to low-silica X zeolite, Zeolites 19 (1997) 359–365.
[20] A. Gualtieri, P. Norby, G. Artioli, J. Hanson, Kinetic study of hydroxysodalite formation from natural kaolinites by time resolved synchrotron power diffraction, Microporous Mater. 9 (1997) 189–201.
[21] R. Torres, E. Basaldella, J. Marco, The effect of thermal and mechanical treatments on kaolinite: characterization by XPS and IEP measurements, J. Colloid Interface Sci. 215 (1999) 339–344.
[22] V. Balek, M. Murat, The emanation thermal analysis of kaolinite clay minerals, Thermochim. Acta 282 (1996) 385–397.
[23] M. Mayoral, M. Izquierdo, J. Andress, B. Rubio, Aluminosilicates transformations in combustion followed by DSC, Thermochim. Acta 373 (2001) 173–180.
[24] A. Gualtieri, M. Belloto, Modelling the structure of the metastable phases in the reaction sequence kaolinite-mullite by X-ray scattering experiments, Phys. Chem. Miner. 25 (1998) 442–452.