Thermally-Activated-Kaolin-Based Admixture for High-Performance Blended Cements

Addition of thermally activated kaolin to cement, even regular-grade cement and concrete, improves compressive strength and significantly decreases production expenses.

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There is an ongoing interest in the use of selected clay minerals, including kaolinites, in the construction industry. A recent development comprises the application of metakaolin as an artificial pozzolanic additive for concrete.[1–7] The strength and durability of conventional cement-based materials can be significantly improved using thermally activated kaolin (TAK) additives.[1–8] Such additives are conventionally manufactured by firing high-grade purified kaolinite at 650–850°C according to[8,9]

$$2SiO_2 + Al_2O_3 + 2H2O \xrightarrow{650\text{–}850^\circ C} 2SiO_2 + Al_2O_3 + 2H_2O\uparrow$$

The main beneficial effect of metakaolin in concrete and cement is related to its high pozzolanic activity, i.e., the ability to react with the portlandite ($Ca(OH)_2$) that is released during the hydration of portland cement.[1–8] The application of superfine metakaolin particles results in a microfiller effect and improves the packing of the cement matrix. The microbearing effect is provided by the flaky particles of metakaolin, which result in better sliding of more coarse cement particles and, therefore, facilitating the flow of the system.

Furthermore, metakaolin improves the morphology of the interface zone between the cement matrix and the aggregate surface.[5–8] Light and attractive color shades as well as improved strength and durability make metakaolin-based additive a vital component of modern architectural concrete.[1,6,9]

Shvarzman et al.[8] have demonstrated that useful properties of metakaolin are preserved even at a small content (as low as 30%) of kaolinite in the raw mix.[8] Based on this study, it has been proposed that the clays that contain >35% kaolinite can be directly used to manufacture the pozzolanic additives using thermal activation that eliminates the expensive stage of beneficiation.[9] Realization of such an approach can significantly decrease production expenditures related to intermediate wet beneficiation and subsequent drying of the raw kaolin.

Furthermore, the waste streams generated during these stages also can be eliminated. Consequently, TAK, which is differentiated from metakaolin that is made from purified kaolin, can be made available at a significantly decreased cost. This makes it feasible as an additive in regular-grade cement and concrete. The properties of such a product definitely can be tailored to provide improved strength and durability.

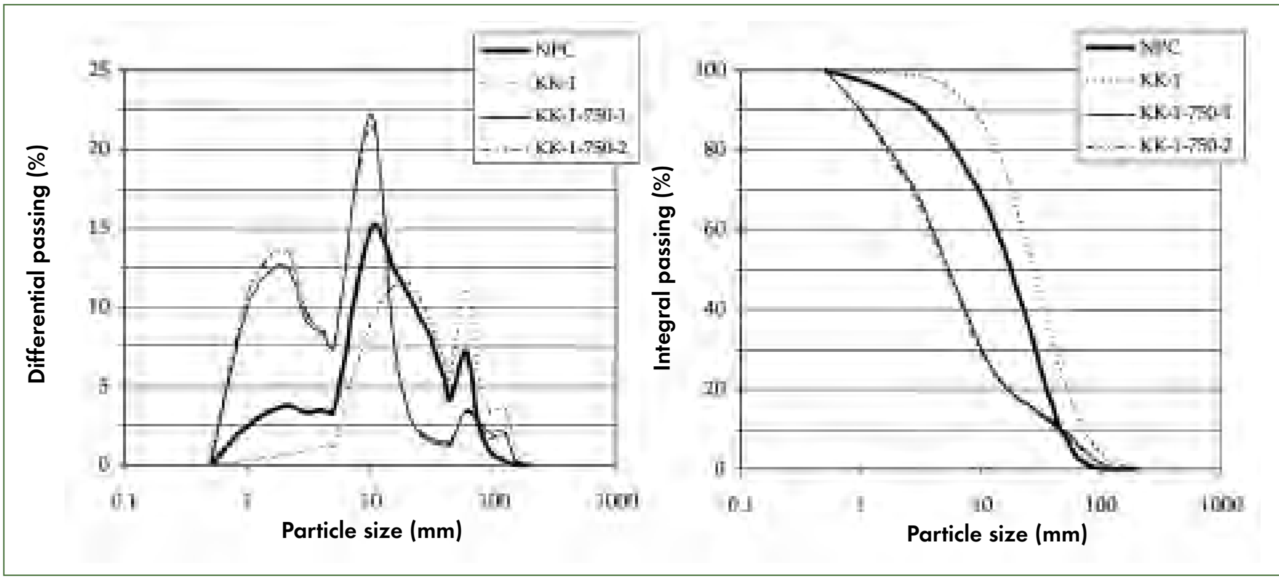

Fig. 1 Particle-size distribution of investigated materials.

To verify this proposal, an extensive research program that involves five R&D and educational institutions (METU, LAU, TCMA, MTA, TECHNION) has been initiated and supported by the Scientific and Research Council of Turkey (TUBITAK).[9]

Research Significance

Metakaolin is a well-known additive for improvement of concrete strength and durability. Application and performance of metakaolin is well documented in the scientific literature. However, there are limited references to the performance of cement and concrete additives based on low-grade or unprocessed kaolin. Therefore, the preliminary investigation of strength, microstructure and other performance parameters of cement containing TAK has been considered important. This research addresses such an evaluation.

Materials Used

Raw kaolin (KK) from Kütahya Kızılçukur quarry, Turkey,[10,11] and reference portland cement CEM-I 42.5 (NPC; corresponding to ASTM type I) were used in the research program. The chemical composition of these materials was analyzed using X-ray fluorescence (XRF) (Table 1). The kaolin contained a high concentration of Al_2O_3 (31.5%) and a relatively low concentration of SiO_2 (55%) according to the XRF analysis.

The raw kaolin was predominately composed of kaolinite and quartz, as determined using X-ray diffractometry (XRD), scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS).[10] The results of differential thermal analysis–thermal gravimetry (DTA-TG) investigation demonstrated the presence of the dehydroxylation endotherm at 580°C with characteristic weight loss of 9.2% that corresponded to 73.6% of kaolinite.[10]

Notations Used

The following notations are used to distinguish the investigated samples.

- **NPC is reference portland cement;**
- **KK is raw kaolin, from Kütahya Kızılçukur;**
- **KK-1 is TAK based on KK and activated for 1 h at 750°C;**
- **KK-2 is TAK based on KK and activated for 2 h at 750°C;**
- **KC is blended cement containing 20% of KK;**
- **KC-1 is blended TAK cement containing 20% of KK-1;**
- **KC-2 is blended TAK cement containing 20% of KK-2.**

Research Program

The experimental program involved three main tasks:

• Investigation of thermal activation of kaolin at 750°C for various time periods (0, 1 and 2 h);

Table 1 Chemical Analysis of Materials Used

	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	TiO_2 (%)	CaO (%)	MgO (%)	SO_3 (%)	K_2O (%)	Na_2O (%)	MnO_2 (%)	P_2O_5 (%)	LOI (%)
NPC	19.78	5.25		3.24	63.45	1.21	2.45	0.72	0.32			1.6
KK	55.0	31.5	0.3	0.1	0.1	<1.0		<1.0	<1.0	<1.0	0.2	10.85

Table 2 Physical Properties of Investigated Kaolin and TAK

Performance characteristic	NPC	KK	KK-1	KK-2
Blaine specific surface area (m^2/kg)	356	422	474	489
Median size (μm)	22	26	15	14
Whiteness (%)		77.6	81.5	82.4

- Investigation of properties (fineness, particle-size distribution, whiteness and morphology (using SEM)) of obtained TAK; and
- Investigation of properties (setting times, soundness, microstructure development (using SEM) and compressive strength (pozzolanic activity)) of blended TAK cement.

Mixture Proportioning

The properties of four cements were investigated. These included the NPC and composite cements with 20% of KK or TAK. The mortars were designed using a sand/cement ratio (S/C) of 3.0 and water/cement ratio (W/C) of 0.5 according to EN 196, ASTM C109, ASTM C311 and ASTM C349.[12–14]

Preparation of Specimens

Prior to its use in the research program, KK was preground in a ball mill for 60 min, and the remaining coarse particles were removed using a screen on a 90 μm sieve. KK was thermally activated in a muffle furnace at 750°C for 1 and 2 h, which resulted in the TAK samples KK-1 and KK-2, respectively.

The composite cements with 20% of kaolin were obtained by dry intermixing in a standard laboratory mixer. This process represented the industrial approach applied by many cement companies.

The investigated mortars were produced following EN 196.[15] The mortars were cast into three-gang (40 × 40 × 160 mm) prism molds and were compacted in accordance with EN 196. Cement pastes were prepared at W/C = 0.3 using the same mixing and molding method for SEM investigations.

Curing of Specimens

After the compaction procedure was completed, the molds were placed in a humidity cabinet for 24 h at a relative humidity of 95% and a temperature of 20 ± 1°C). The specimens then were removed from the molds and kept in water until the testing age.

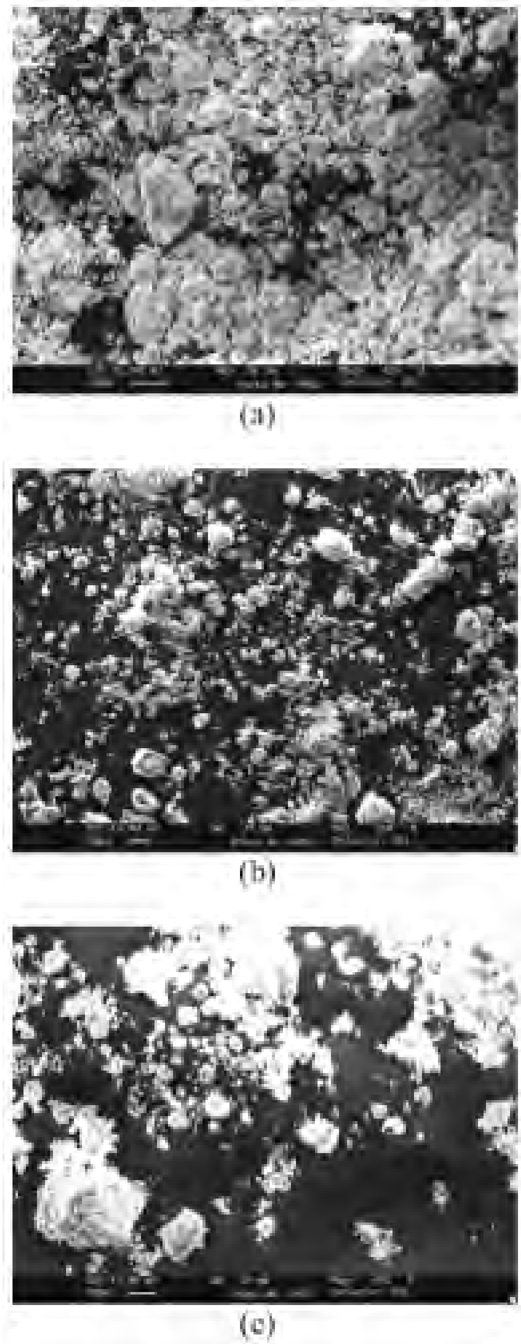

Fig. 2 SEM observations of kaolin morphology: (a) raw kaolin; (b) KK-1; and (c) KK-2.

The cement pastes prepared for SEM investigations were cured for 7 and 28 d at 20 ± 1°C. After the curing period, the fractured specimens were dried, treated with acetone and coated with a thin layer of gold.

Tests Performed

The particle-size distribution of the investigated cements was measured using laser diffraction analysis (Model Masersizer, Malvern Instruments, Malvern, U.K.). The resulting particle-size distribution and other characteristics of investigated materials (i.e., cement, kaolin and TAK) were summarized (Fig. 1 and Table 2).

The properties, i.e., setting times, soundness and compressive strength, of the developed cements were obtained using EN 196 (Table 3).[15] The mortar samples were tested at the ages of 7, 28 and 90 d for com-

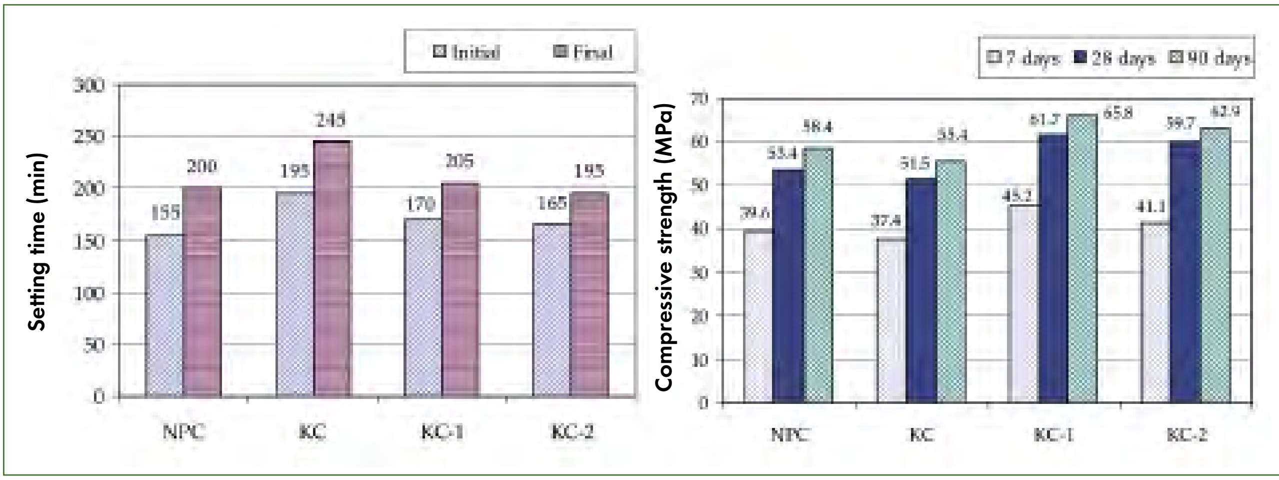

Fig. 4 Effect of TAK on cement performance.

pression. Compressive strength tests were conducted using the portions of prisms broken in flexure. Therefore, the compressive strength results reported are the average of six values.[15]

Microstructure observations of the cement paste specimens were performed at 7 and 28 d using SEM (LEO) operated at an accelerating voltage of 15 kV.

Table 3 Performance of Investigated Cements

Cement type	Setting time (min) Initial	Setting time (min) Final	Soundness (mm)	Compressive Strength (MPa) 7 d	Compressive Strength (MPa) 28 d	Compressive Strength (MPa) 90 d
NPC	155	200	1.0	39.6	53.4	58.4
KC	195	245	1.0	37.4	51.5	55.4
KC-1	170	205	0.0	45.2	61.7	65.8
KC-2	165	195	1.0	41.1	59.7	62.9

Particle-Size Distribution of TAK

The particle-size distribution of the investigated materials was observed using laser diffraction analysis (Fig. 1). The KK particles were larger than those of portland cement. The particle-size distribution of KK was characterized by a bimodal distribution. Because of its thermal treatment at 750°C and its recrystallization to metakaolin, the kaolin particles were significantly decreased in size (with a predominant size of 1–15 μm).

Because of this transformation, the Blaine specific surface area of TAK was much higher than that of KK (Table 2). The obtained TAK was characterized by a three-modal distribution (Fig. 1). Size decrease associated with such thermal treatment led to an increase in the whiteness of TAK from 77.6% for KK to 81.5 and 82.4% for samples KK-1 and KK-2, respectively (Table 2).

Morphology of TAK

The comparison of surface features and morphology of investigated KK and TAK samples was performed using SEM. KK particles were predominantly 5–50 μm, with obvious agglomerates around the quartz particles (Fig. 2(a)).

Because of the thermal treatment at 750°C and subsequent recrystallization to metakaolin, the kaolin particles were separated from quartz and significantly smaller. The resulting TAK was characterized by particles predominantly 1–15 μm (Fig. 2(b)). SEM observations of KK-2 morphology demonstrated the presence of starlike agglomerates of low-density metakaolin (Fig. 2(c)).

Effect of TAK on Cement Properties and Microstructure

The replacement of cement with TAK at a dosage of 20% did not affect the final setting time of the blended cements (Fig. 2 and Table 3). The initial setting time of such cements was prolonged slightly. However, the addition of KK delayed setting of blended cements. The soundness of all investigated cements was at the same level of 1% for all the cements, except the blended cement with 20% of KK-1 additive (which had zero soundness).

Cement pastes hardened for 7 and 28 d were investigated using SEM (Figs. 3). NPC hydration showed that unhydrated clinker grains were surrounded by radiating fibers of C-S-H that resembled the pattern of type I C-S-H. Randomly oriented C-H crystals and prismatic ettringite crystals were widely dispersed throughout the paste (Fig. 3(a)). The microstructure of the NPC hydrated paste aged for 28 d included an amorphous gel that filled the spaces between the hydrated particles. In NPC pastes, the layered accumulations of C-H crystals of ~15 μm in width were intermingled throughout the paste (Fig. 3(b)).

SEM showed that the kaolin and TAK particles were well dispersed within the cement paste, which resulted in a dense structure with low porosity (Figs. 3(b)–(d)). There was visible densification around the TAK particles because of the pozzolanic reaction of TAK. This led to the formation of C-S-H. At the age of 7 d, the kaolin and TAK grains were already well covered with a pseudomorphic layer composed of hydration products. The matrix phase was composed mainly of short acicular outgrowths of C-S-H around the clinker grains and needle-shaped ettringite crystals (Figs. 3(e) and (g)). At the age of 28 d, the kaolin and TAK grains were well embedded into the matrix and were well connected throughout the C-S-H gel. Cement pastes based on TAK, especially cement with KK-1, were of higher density compared with reference cement and blended KK cement (Fig. 3).

Compressive Strength of Mortars

The 7 d compressive strength of KC-1 cement was the highest among the investigated cements, i.e., 45.2 MPa. The cement with KK-2 had a 7 d compressive strength of 41.1 MPa, which was approximately that of the strength of reference NPC (39.6 MPa). The cement with KK had the lowest 7 d compressive strength of 37.4 MPa (Table 3). Acceleration of strength development of TAK-cement aged for 7 d with optimized TAK (KK-1 of 14%) was explained by pozzolanic reaction and densification of the cement matrix (as also observed using SEM).

The compressive test results of investigated mortars (following EN 196) were summarized (Table 3 and Fig. 4). The best 28 d compressive strength of 61.7 MPa was obtained in cement KC-1 with TAK activated for 1 h (KK-1). This value was 15% higher than the strength of the reference cement. The cement with TAK activated for 2 h (KK-2) reached a 28 d compressive strength of 59.7 MPa, which was only slightly less than that for KK-1. The cement with KK had a 28 d compressive strength of 51.5 MPa, which was approximately that of the strength of reference NPC (53.4 MPa). The observed trend also was preserved at the age of 90 d with KK-1-based cement, which achieved the highest compressive strength of 65.8 MPa (or 13% higher than the reference).

Additional investigations may be necessary to explain and quantify the hydration mechanism and the long-term structural development of TAK cements that contain various amounts of TAK. Further research also is required to investigate the behavior of TAK cements in concrete as well as to investigate the durability of such materials. ■

Acknowledgments

This study was performed under TUBITAK Research Grant No. İÇTAG–680 in cooperation with a MTA research team represented by Dr. Mustafa Albayrak and Dr. Aydin Aras. Authors express their gratitude to Ipek Şener and Bahadir Erdogan for their help with preparation of the samples. Extremely useful comments of Prof. Konstantin Kovler are highly appreciated. The financial contributions of TUBITAK, TCMB, LAU, MTA, CONACYT, PROMEP and PAICYT are gratefully acknowledged.

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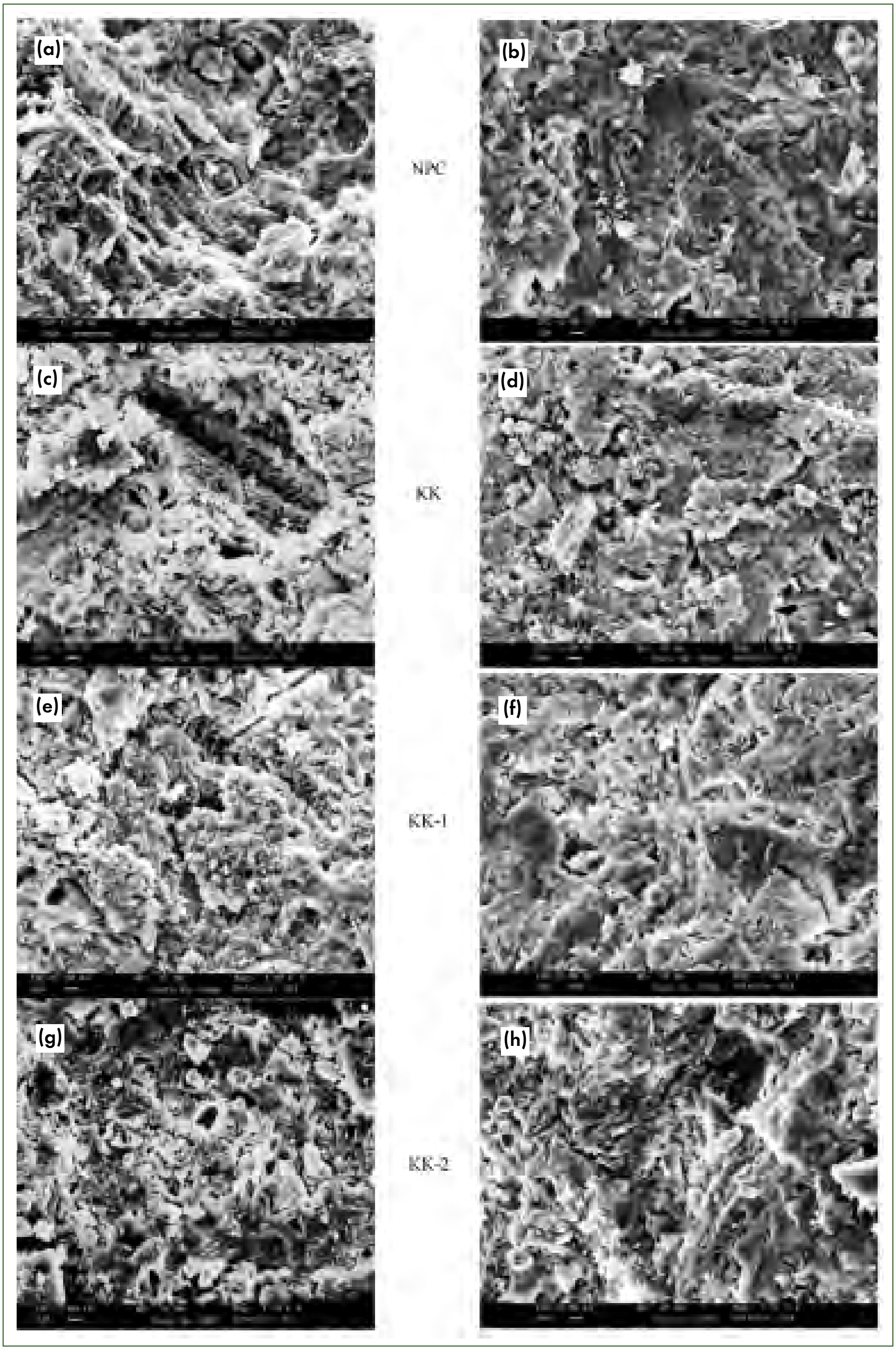

Fig. 3 Effect of TAK on cement paste microstructure at ((a), (c), (e) and (g)) 7 d and at ((b), (d), (f) and (h)) 28.