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THE INFLUENCE OF POZZOLANIC MATERIALS ON THE DURABILITY OF GLASS FIBRE REINFORCED CEMENT COMPOSITES

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ABSTRACT

The objective of the investigation was to evaluate the effectiveness of pozzolanic materials to improve durability of glass fibre reinforced cement composites manufactured by premix technique. The pozzolanic materials included silica fume, fly ash and metakaolin, a product of thermal treatment of locally available kaolin. Four point bending tests were performed to evaluate the strength and the flexural toughness of the composites, both in the short term and after accelerated aging in warm water. Scanning electron microscopy was also applied to identify effects of pozzolanic additives on durability of glass fibres in cement matrix. A replacement of 10% of cement by metakaolin resulted in a high level of long-term flexural strength and retention of large portion of strain hardening behaviour of composites.

INTRODUCTION

Dispersed glass fibres can provide significant enhancement of mechanical properties of cement-based composites. Both strength and toughness improvements provided should be stable over the design life-time of elements or structures. Intensive studies of glass fibre reinforced cement composites (GFRC) revealed various measures to improve durability of such composites, e.g. use of high-zirconia glass fibres, acrylic polymers or special cements [1]-[3]. However the most promising and economically justified approach is to gain as much as possible by the use of pozzolanic materials, e.g. [4], [5]. Majority of relevant publications concern the GFRC composites made using the spray-up technique, while the premix technique, although important for the industry, has not been investigated extensively yet.

The objective of this study is to compare the effectiveness of various pozzolanic materials in increasing the strength and the toughness of GFRC composites manufactured using premix technique. The toughness of GFRC is considered as the energy absorption capacity in bending ([6], [7]) and also in terms of the deformation capacity (the strain at rupture) according to the standard [8]. The major thrust of this phase of research was to assess potential benefits of the pozzolanic materials, in particular a pozzolana obtained by thermal activation of locally available kaolin.

EXPERIMENTAL

Pozzolanic materials

Apart from common pozzolanic materials, like fly ash and silica fume, the investigation included a pozzolana obtained by thermal activation of kaolin (Table 1). Results of DTA analysis of thermal treatment of kaolin between 20°C and 1100°C is shown in Figure 1. According to the results, the range of temperatures 550-900°C corresponds to the range between the effect of endothermic reaction of dehydroxylation of kaolinite and the exothermal effect due to recrystallization of amorphous phase. Metakaolin is present in this temperature range.

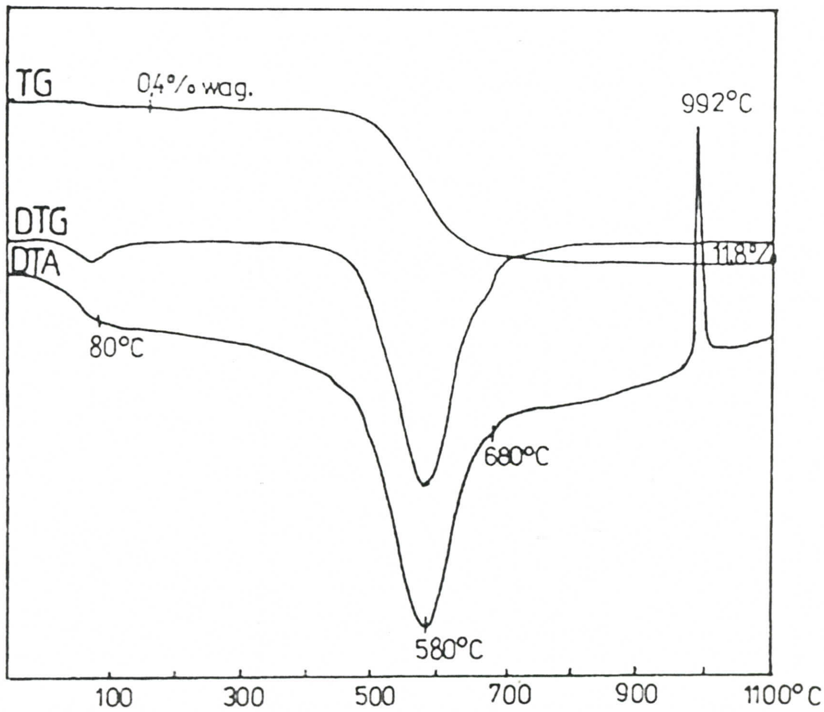

Figure 1 DTA analysis of kaolin

Table 1 Chemical composition of kaolin

Component	Content in % by weight
SiO_2	52.0
Al_2O_3	33.5
Fe_2O_3	0.5
Fe_2O_3 soluble in HCl	0.1
TiO_2	0.5
CaO	0.4
MgO	0.2
K_2O	0.8
Na_2O	0.08
loss on ignition	11.6

Table 2 Amount of CaO bounded per 1g of pozzolana determined using DTA

Type of pozzolana	Amount of CaO [mg]
silica fume	335.5
fly ash	96
prototype metakaolin	161
metakaolin of reference	236

The process of calcination of kaolin was performed in laboratory conditions at 800°C during 1h. Figure 2 presents diffraction pattern of both raw material (a) and the product (b). A SEM image of metakaolin obtained by thermal treatment of kaolin is shown in Figure 3.

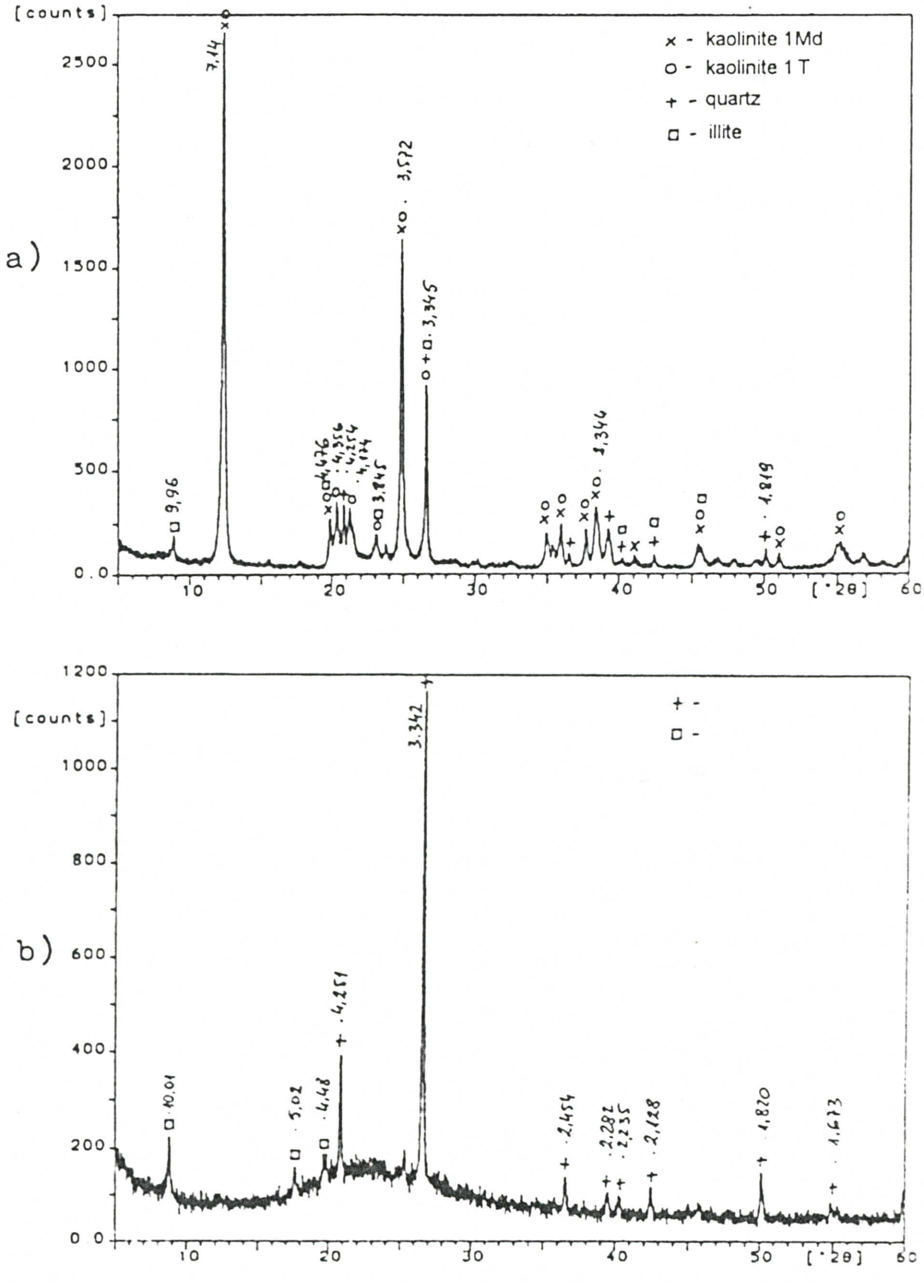

Figure 2 Diffraction pattern of kaolin: raw (a), after thermal treatment (b).

The phase analysis revealed that the product of calcination is metakaolin in amorphous phase. Reflections specific for kaolinite disappear and the background is increased for 2θ from 15 to 35°C, that indicates an appearance of amorphous phase and slight reflections for quartz and illite.

Pozzolanic activity

To determine the pozzolanic activity, DTA method was applied. Material consisting of cement and pozzolana (proportion 9:1) was mixed with water using w/c=0.4. The samples were kept in 40°C for 14 days and then the hydration process was stopped. The amount of calcium hydroxide in a sample was determined by the endothermic effect due to decomposition of calcium hydroxide and related loss of weight. By comparing these values with the amount of calcium hydroxide produced during hydration of portland cement, a calculation of CaO amount bounded by 1 gram of pozzolana was performed (Table 2).

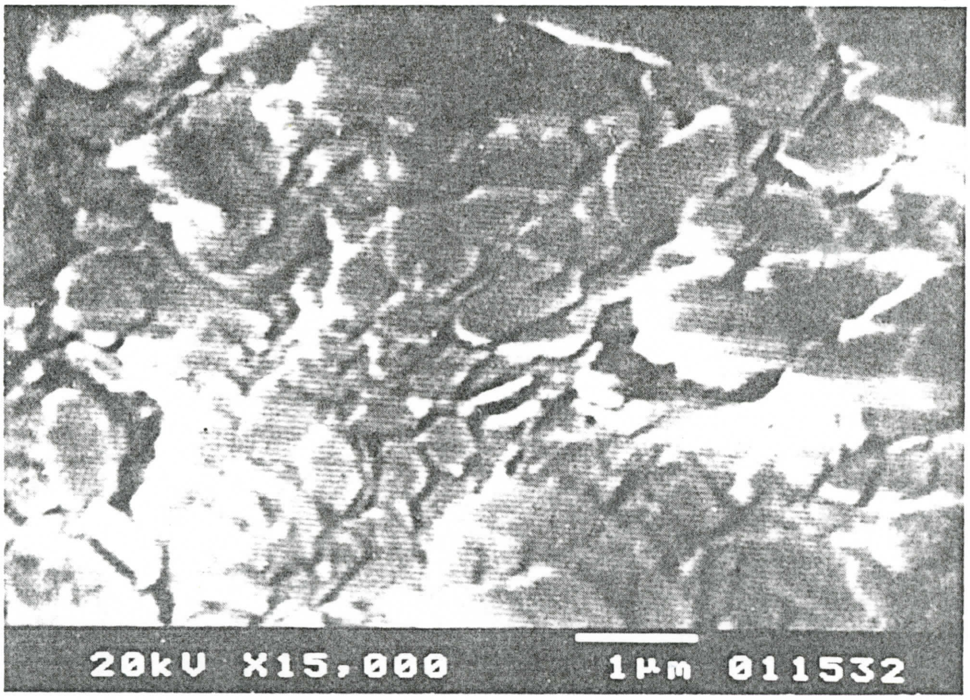

Figure 3 SEM image of metakaolin obtained at the temperature of 800°C.

Specimens

For manufacturing GFRC specimens the following materials were used: portland cement, quartz sand, chopped glass fibre 12mm long, superplasticizer and pozzolana. Types of fibres used were of high-zirconia AR glass and E glass. The amount of pozzolana used was to replace 10% of cement. An applied water-to-binder ratio, including cement plus pozzolana, was kept at constant level of 0.36.

The premix process was used for manufacturing GFRC specimens: plates 225x320x15mm were cut into specimens 50x225mm. Out each group of six specimens three were tested at this age and remaining three were then stored in accelerated aging conditions and tested after aging. The accelerated aging procedure was a warm water immersion at 50°C during 56 days, as described in [1]. Using an acceleration factor based on Arhenius law one can estimate this aging period as roughly equivalent to 15 years of natural exposure in middle-European climate.

Mechanical testing and microstructural observations

The flexural testing procedure corresponded to ASTM C 947. The four point bending tests, over the span of 200mm, were performed using Instron servohydraulic testing machine at constant rate of cross-head displacement of 0.5 mm/min. During testing the measurements of the bending load, the net deflection at midspan were performed and acoustic emission counts were recorded. The data storage was achieved using a PC based acquisition system developed in ASYST environment.

Microstructural observations of fracture surfaces of specimens were conducted using SEM JFM 5400, equipped with X-ray microprobe.

TEST RESULTS AND DISCUSSION

Examples of flexural load-deflection curves for selected specimens are shown in Figures 4 and 5. A significant influence of pozzolana type on flexural behaviour of specimens is observed.

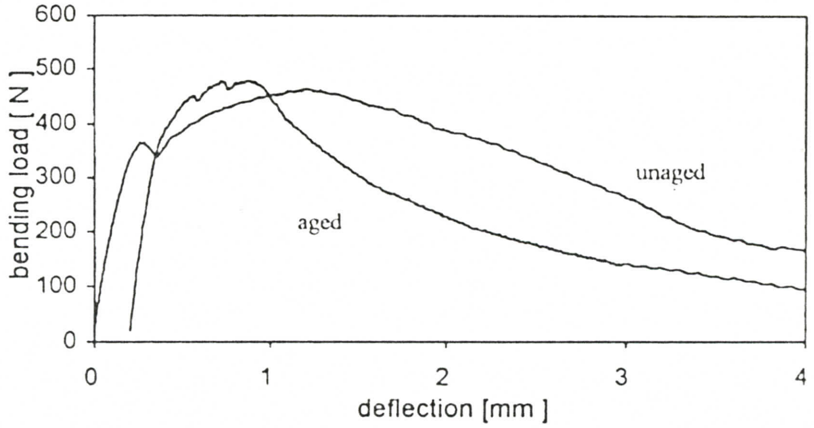

Figure 4 Examples of load-deflection curves for GFRC containing metakaolin and AR glass fibres.

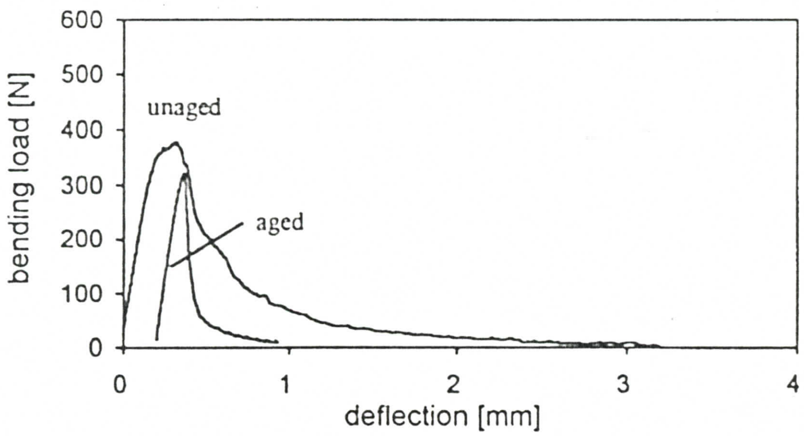

Figure 5 Examples of load-deflection curves for GFRC containing metakaolin and E glass fibres.

In order to quantify the effects of pozzolana type as well as age of specimens the flexural behaviour was analyzed using strength data (MOR - the modulus of rupture) and deformation data (u_m - the deflection at maximum load). The load-deflection curves were also integrated numerically to calculate the work of fracture as an absolute measure of the toughness of composites. The work of fracture was determined up to the point of the maximum load, W_m, since this measure is found very sensitive to test variables. Using the deflection data the deformation at rupture ϵ_m was calculated as follows:

$$\epsilon_m = \frac{108}{23} \cdot \frac{u_m \cdot h}{l^2}$$

where h denotes the thickness of specimen and l is the span, according to European Standard [8]. Such a measure of deformability of GFRC materials has been recently introduced into a common design practice.

Table 3 presents a set of flexural data for GFRC composites containing various pozzolana. The four series of composites included AR glass fibres while just one series included E glass fibres. In Figure 6 the influence of the type of pozzolana on the flexural strength of GFRC composite is presented. Due to presence of the prototype metakaolin no loss of flexural strength was observed in the long term. The beneficial effects of pozzolanic materials observed for AR glass fibres do not exist for E glass fibres. Although an addition of silica fume and fly ash resulted in some increase of the flexural strength, after accelerated aging these effects were not present.

Table 3 Average flexural test results for unaged and aged specimens

Type of pozzolana and glass fibre	Unaged composites				Aged for 56 days in water of 50°C			
	Max. load [N]	MOR [MPa]	u_m [mm]	W_m [Nm]	Max. load [N]	MOR [MPa]	u_m [mm]	W_m [Nm]
none AR	457	9.6	2.27*)	1.17*)	481	8.8	0.53	0.22
silica fume,AR	506	10.7	0.99	0.43	346	7.3	0.42	0.11
fly ash AR	559	11.9	1.61	0.74	422	8.4	0.45	0.15
metakaolin AR	466	10.2	1.35	0.56	595	10.6	0.77	0.38
metakaolin E	366	6.9	0.29	0.07	328	5.8	0.14	0.03

*) large scatter

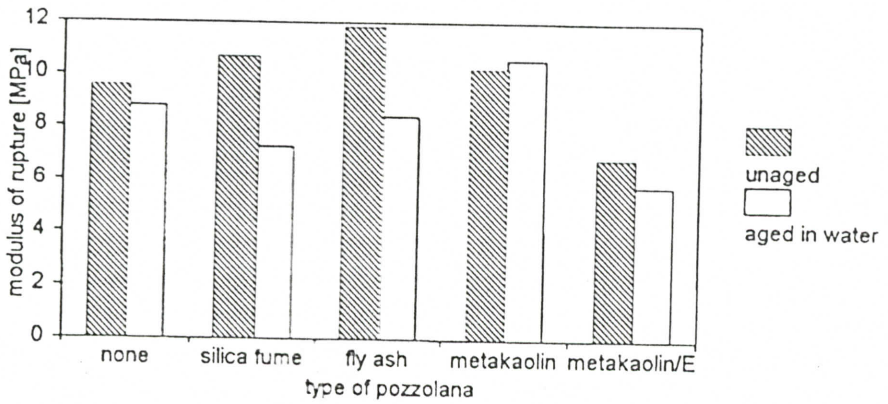

Figure 6 Influence of the type of pozzolana on the flexural strength (MOR) of GFRC composite.

The most important effect caused by tested pozzolanic materials was a significant change of the work of fracture W_m as well as the deformation at rupture ϵ_m. A comparison of the ϵ_m values for AR-GFRC and E-GFRC is shown in Figure 7. Even after aging the composites reinforced with high-zirconia glass fibres retained a large portion of pseudo strain-hardening behaviour, in contrast to brittle behaviour of the ordinary E glass composites.

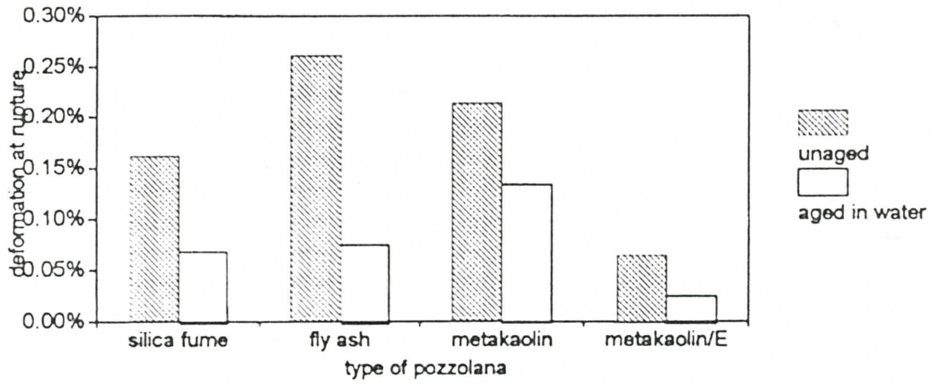

Figure 7 Influence of the type of pozzolana on deformation capacity (ϵ_m) of GFRC composites.

Microstructural observations of fracture surfaces revealed a dramatic degradation of the E fibres in cementitious matrix, in spite of pozzolanic modification. Numerous pores are observed in fibre locations after accelerated aging (Figure 8). This image corresponds well to increased brittleness of such composites with age, and a decreased strength and deformation even at unaged state (see Figure 5 and Table 3).

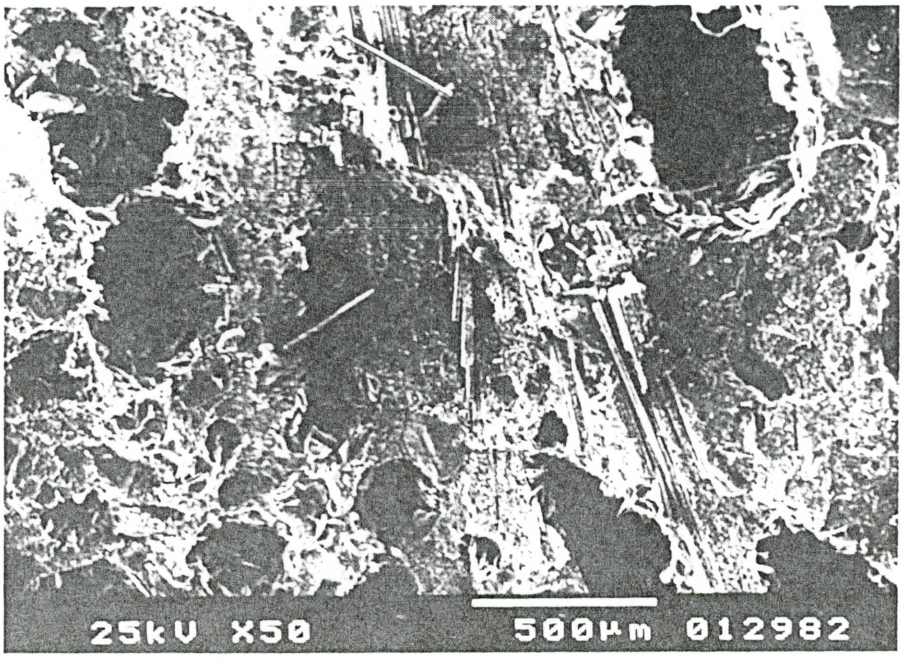

Figure 8 SEM image of GFRC composite containing E glass fibres, modified with metakaolin.

Figure 9 presents a microscopic image of AR-GFRC containing metakaolin, that exhibited no traces of fibre corrosion but so-called telescopic fracture of fibres. Observation at higher magnifications revealed slight traces of local fibre corrosion for GFRC containing fly ash and without pozzolana.

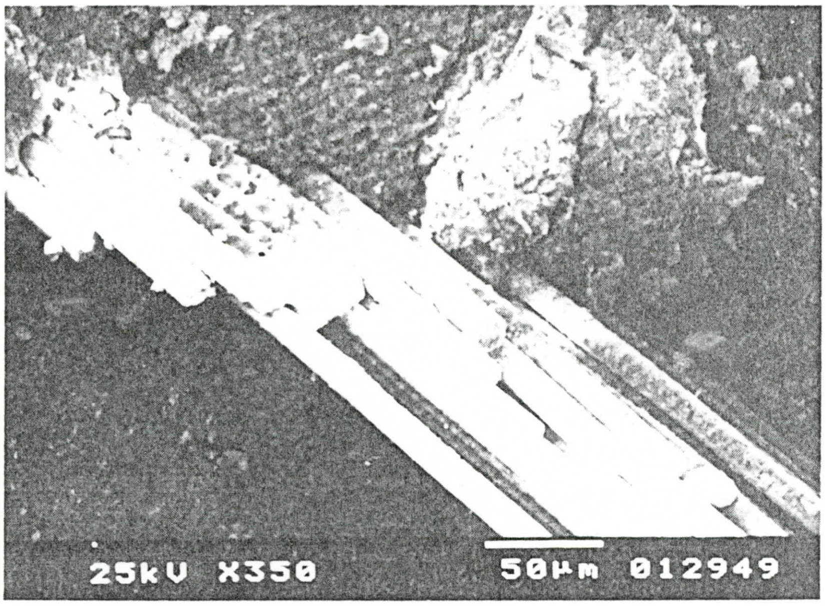

Figure 9 SEM image of GFRC composite containing AR glass fibres, modified with metakaolin.

In order to explain the role of metakaolin in increasing durability of glass fibre cement composites further microstructural observations were carried on, using a SEM with X-ray microprobe. This enabled the identification of phases formed during hydration of cement paste containing metakaolin. Such a hydration process involved a formation of aluminosilicate hydrates in thin plate-like forms engulfed with fine-crystalline phase of CSH (Figure 10). Analysis of test results suggests that in highly-alkaline environment of hardening cement paste the components of pozzolanic materials are subjected to hydrolysis, that is accompanied with a transition of silica and alumina ions to solution, and react with calcium ions forming CSH phase and hydrated calcium aluminate.

The test results showed that metakaolin was one of the most effective additive to increase durability of glass fibre reinforced cement composites. This beneficial effect observed for high-zirconia alkali-resistant glass fibres was absent for E glass fibres: even at the age of 28 days a significant drop in both strength and deformation capacity was observed. In spite of various types of metakaolin tested, after accelerated aging period the E glass fibres were totally degraded and hydration products were observed in pores appearing in fibre locations. This is contrary to results reported in [5], that covered as high fraction of pozzolana as 40% of the binder content.

CONCLUSIONS

The following conclusions could be drawn on the basis of presented results.

Among tested pozzolanic materials: silica fume, fly ash and metakaolin, the last one was the most efficient in increasing the durability of glass fibre reinforced cement composites made by premix technique. A replacement of 10% of cement by metakaolin resulted in a high level of long-term flexural strength and retention of large portion of pseudo-strain hardening behaviour.

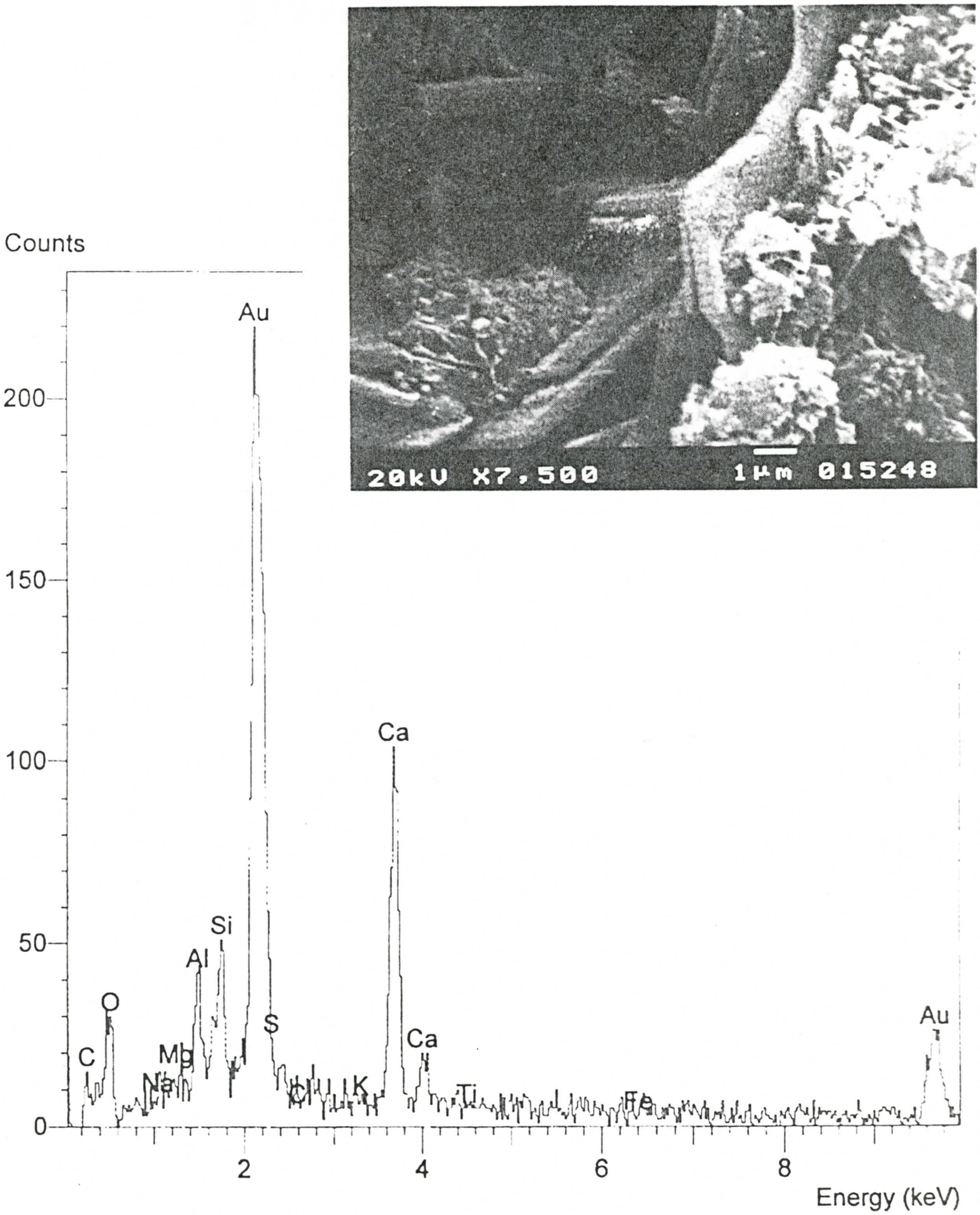

Figure 10 Hydrated alumino-sillicate in thin plate-like forms in cement paste containing metakaolin after 28 days of hydration

The level of the long term flexural toughness of GFRC, measured by the work of fracture, was greater by about 73% due to addition of metakaolin. Neither silica fume nor fly ash additions improved the flexural toughness and deformation capacity after accelerated aging.

Microstructural observations and X-ray microprobe tests suggest that in the environment of hardening cement paste the metakaolin is subjected to hydrolysis, that is accompanied with a transition of silica and alumina ions to solution; these ions react with calcium ions forming CSH phase and hydrated calcium aluminate. Such an influence of metakaolin on hydration process and formation of cement paste structure can be also beneficial for unreinforced mortar and concrete.

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REFERENCES

1. Litherland, K.L., Proctor, B.A., The effect of matrix formulation, fibre content, and fibre composition on the durability of glassfibre reinforced cement, Proc. Durability of Glass Fiber Reinforced Concrete Symposium, ed. S.Diamond, PCI, Chicago, 1985, 124-135.

2. Majumdar, A.J., Continuing development of GRC as a construction material, Journal of Materials in Civil Engineering, Vol.6, No.3, 1994, 335-340.

3. Molloy, H.J., Jones, J., Harmon, T.G., Glass fiber reinforced concrete with improved ductility and long term properties, Thin Reinforced Concrete Products and Systems, ed. P.Balaguru, ACI SP-146, ACI, Detroit, 1994, 79-90.

4. Glinicki, M.A., Vautrin, A., François-Brazier, J., Soukatchoff, P., Impact performance of glass fibre reinforced cement plates subjected to accelerated ageing. 9th Biennal Congress of GRCA, Copenhagen, June 14-17, 1993, I/1-10.

5. Péra, J., Dejean, J., Ambroise, J., Tuset, J., Amélioration de la durabilité des composites ciment/verre E par ajout de métakaolin, Textile Composites in Building Construction, Pluralis, 1990, Part.1, 191-202.

6. Mobasher, B., Shah, S.P., Test parameters for evaluating toughness of glass-fiber reinforced concrete panels, ACI Materials Journal, Vol.86, No.5, 1989, 448-458.

7. Brandt, A.M., Toughness of fibre reinforced cement based materials, Archives of Civil Engineering (AIL), XLII, 4, 1996, 471-493.

8. CEN, Test method for glass-fibre reinforced cement, prEN 1170-5, 1993.

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