THE EFFECT OF MICA PARTICLES ON THE PROPERTIES OF COMPOSITES WITH A MATRIX OF GYPSUM-FREE PORTLAND CEMENT

Part 1

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Composites were prepared with a matrix of gypsum-free Portland cement, containing 2–10 wt. % of mica of various grain sizes and specific surfaces. The effect of mica was discussed in terms of the apparent viscosity of cement pastes, the time course of hydration reactions, the development of hydration heat, and compressive strengths. It was found that the different specific surface area of mica particles was capable of adsorbing various amounts of the aqueous solutions of the additives, thus markedly affecting the setting time and the apparent viscosity of the cement pastes. The phenomenon is also associated with the development of the heat of hydration which decreases with increasing mica content in the composite. All of the mica fractions tested decreased the compressive strengths of the composites prepared.

THEORETICAL

In recent years, cement composites with random-dispersed fibre reinforcement have found wide global application. It is claimed that fibres of both inorganic and organic origin improve impact strength, flexural strenght, durability, frost resistance and fire resistance of cement composites [1].

Till recently, asbestos fibres had been by far the most common type of such fibre, outstanding particularly by its high flexural strength. However, in view of the negative effects of asbestos on human health, suitable substitutes were seeked, and at one time found in glass fibres. Unfortunately, Portland cement reacts with water producing strongly alkaline compounds which tend to attack the fibres chemically. This process may eventually lead to complete disappearance of the fibres from the cement matrix.

For this reason, alkali-resistant glass fibres containing ZrO_2 were developed. Within a relatively short period of time, the decrease of flexural strength of these special fibres in cement composites stops, and the residual strength is then approximately constant, contrary to the case of using standard glass fibres which lose their performance properties completely [2].

Applications of metal fibres and particles, carbon, ceramic and organic fibres for these purposes has also been described [3]. However, their wider use is prevented by the costs which are higher than those of natural materials.

Cement composites reinforced with mica particles attract technologists because of their relatively availability, resistance to alkalies, and also for reasons of economy. Composites based on Portland and aluminate cements and reinforced with mica particles were studied by Beaudoin [4]. The author used mica of the phlogopite type, with particle sizes from 250 to 1400 μm, and a high-aspect ratio. His extensive studies resulted in the following conclusions [4, 5]:

1. The addition of mica flakes retards the hydration of Portland cement and reduces the compressive strength of the respective hardened cement pastes.
2. The increase in flexural strength and fracture toughness of cement pastes due to mica flake reinforcement depends on the volume of the flakes added and on matrix porosity, there being an optimum proportion at which better values were obtained in comparison with mica-free controls.

The results indicate that the lower the matrix porosity, the higher the flexural strength and the fracture toughness of the composite. It may therefore be assumed that by using a cement matrix of low porosity, such as provided e.g. by gypsum-free cement, one could attain high flexural strength and fracture toughness of the composites.

The available literature does not provide any information on the effect of mica particles on the rheological behaviour of pastes of gypsum-free Portland cement (GPC), the development of the heat of hydration and strengths. The present study is one of the contributions aimed at resolving the subject matter,

Table I

Phase composition of clinker from the Prachovice Cement Works

C_3S	C_2S	C_3A	C_4AF	free CaO
72.1	8.0	8.3	11.0	0.5

Table II

Chemical composition of clinker from the Prachovice Cement Works

SiO_2	CaO	Al_2O_3	Fe_2O_3	MgO	SO_3	Na_2O	K_2O	TiO_2	MnO	free CaO	loss on ignition	insoluble residue
20.53	63.94	5.98	3.27	2.97	0.72	0.16	1.1	0.3	0.09	0.46	0.62	0.05

Table III

Chemical composition, particle size distribution, specific surface and designation of the mica fractions

Oxide	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O
wt. %	49.97	0.53	29.11	1.19	0.87	0.01	2.72	0.11	0.54	10.01
Fraction (μm)		14		56			500 – 1250			
Specific surface (m^2/g)		5.15		0.89			0.42			
Designation		1		2			3			

and deals with cement composites with a matrix of GPC, reinforced with mica particles of various sizes. Part 1 is concerned with the effect of mica particles on the apparent viscosity, the setting time, the development of the heat of hydration and compressive strengths of the cement pastes.

EXPERIMENTAL

For the experiments a Portland clinker from the Prachovice Cement Works, ground with the ABESON-TEA grinding aid to a specific surface of 430 sq.m/kg (Blaine) was used. The chemical and phase composition of the clinker is given in Tables I and II.

Three fractions of muscovite-type mica supplied by the Mědĕnec Works of RD Příbram were tested in composites. The designation of the fractions, their particle size distribution, specific surface (B.E.T.) and chemical composition are listed in Table III.

The control system used in the preparation of composites with the GPC matrix consisted of a combination of 1 wt. % anhydrous soda and 0.4 wt. % of KORTAN-FM, all in terms of the total weight of the composite. KORTAN-FM is the trade name of a sodium-ferric salt of a condensation product of phenol with formaldehyde, the initial raw material being a technical-grade mixture of bivalent phenols. The admixtures were dissolved in water (water-to-cement ratio $w = 0.22$ to 0.24), and the solution then mixed with the mixture of ground clinker and mica flakes.

The setting time and the time course of the hydration reactions were determined by a conduction calorimeter [7].

The apparent viscosity was measured by a rotary viscometer, type RN 211 (FRG).

The compressive strength was determined on a ZD 10/90 tester (FRG) on specimens 2 × 2 × 2 cm in size, after 3, 5 and 24 hours, 7, 28 and 180 days from the preparation. The mean compressive strength was always the average of three test results. For 24 hours after preparation, the specimens were kept in 100% relative humidity, and then immersed in water.

RESULTS AND DISCUSSION

The setting time and the time course of the hydration reactions are listed in tables IV through VI, and plotted in Figs. 1 through 4. The results imply that an addition of the fine mica fraction (< 14 μm) cuts down the setting time of the cement composites. The heat of hydration developed increases with mica additions of up to 6 wt. % and then decreases. Additions of mica with particle sizes less than 56 μm prolonged the setting time and reduced the amount

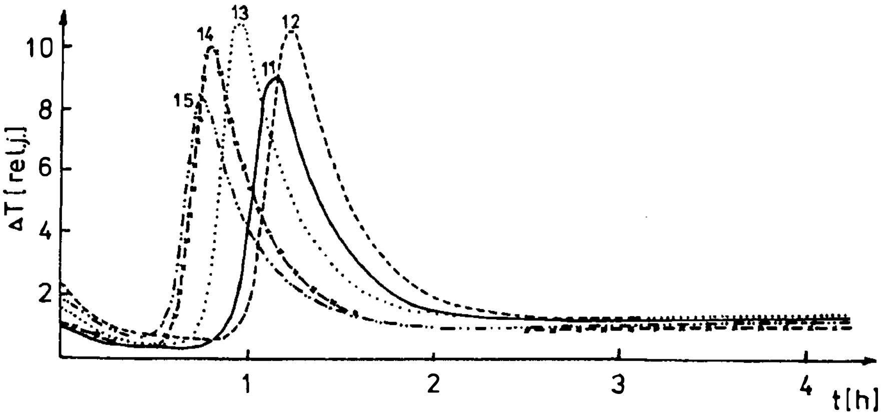

Fig. 1. Time course of the hydration reactions of cement pastes with various contents of mica fraction < 14 μm, w = 0.24. 11 – 0%; 12 – 2%; 13 – 4%; 14 – 6%; 15 – 8%.

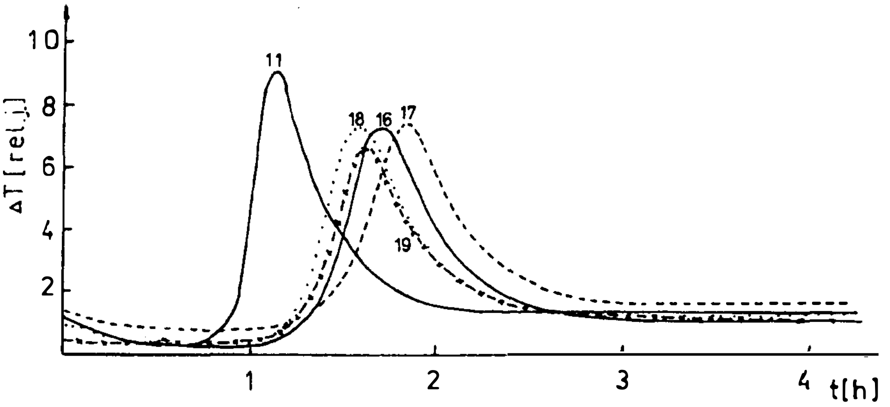

Fig. 2. Time course of the hydration reactions of cement pastes with various contents of mica fraction < 56 μm, w = 0.24. 11 – 0%; 16 – 2%; 17 – 4%; 18 – 6%; 19 – 8%.

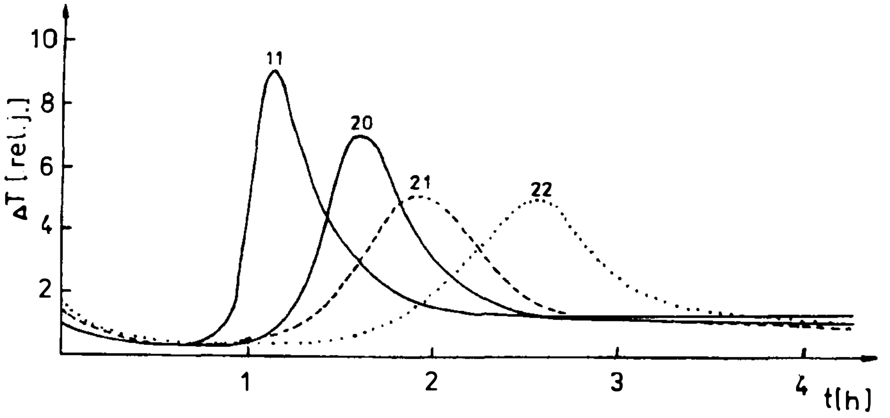

Fig. 3. Time course of the hydration reactions of cement pastes with various contents of mica fraction 500–1250 μm, w = 0.24. 11 – 0%; 20 – 2%; 21 – 4%; 22 – 6%.

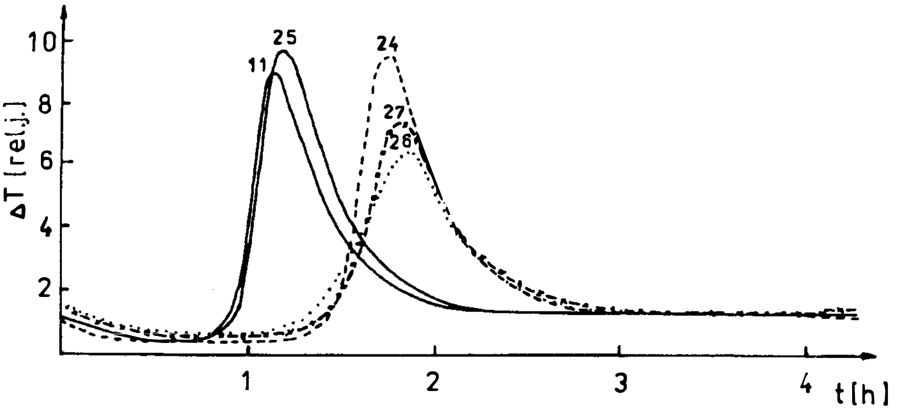

Fig. 4. Time course of the hydration reactions of cement pastes with various contents of mica fraction 500–1250 μm, w = 0.22. 11 – 0%; 24 – 4%; 25 – 6%; 26 – 8%; 27 – 10%.

of heat generated by hydration. The same applies to the 500–1250 μm mica fraction.

The dependence of apparent viscosity on the mica addition is plotted in Figs. 5 and 6. In the case of the coarsest fraction (i.e. 500–1250 μm), increasing additions of mica are responsible for a considerable decrease of apparent viscosity. This allows pastes with a lower water-to-cement ration to be prepared, compared to mica-free pastes. On the other hand, the finest mica fractions bring about a sharp increase in apparent viscosity, so that this was no longer measurable for contents of 4 wt. % to 8 wt. % at the given receipt. The materials were difficult to work, almost of no practical use. The apparent viscosity increased with increasing doses of mica with particle sizes of up to 56 μm (4–8 wt. %).

The development of compressive strength is listed in Tables IV through VI. One can see that in most cases the addition of mica leads to decreased strength (compared to mica-free control specimens), the largest decrease being due to mica particle sizes of 500 to 1250 μm. This is in agreement with the findings by Beaudoin [4] and Mikhail [8] for composites with mica and glass reinforcement respectively.

The main cause of the different effects of the three mica fractions tested on the cement pastes, is obvi-

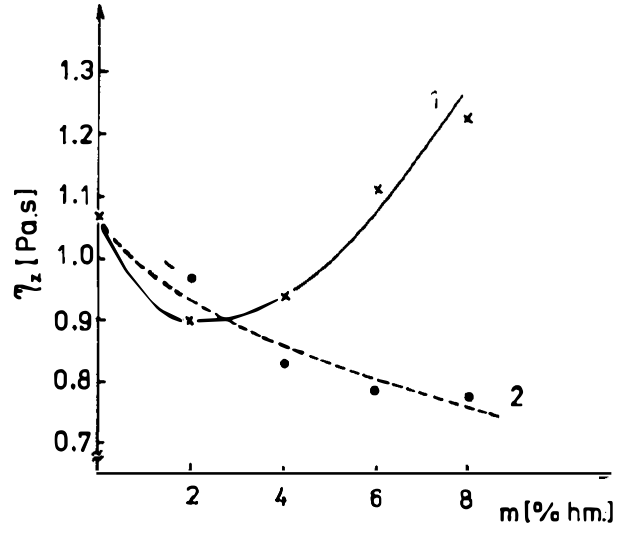

Fig. 5. Apparent viscosity of cement pastes vs. the content of mica fraction < 56 μm and 500–1250 μm, w = 0.24. 1 – mica fraction 56 μm; 2 – mica fraction 500–1250 μm.

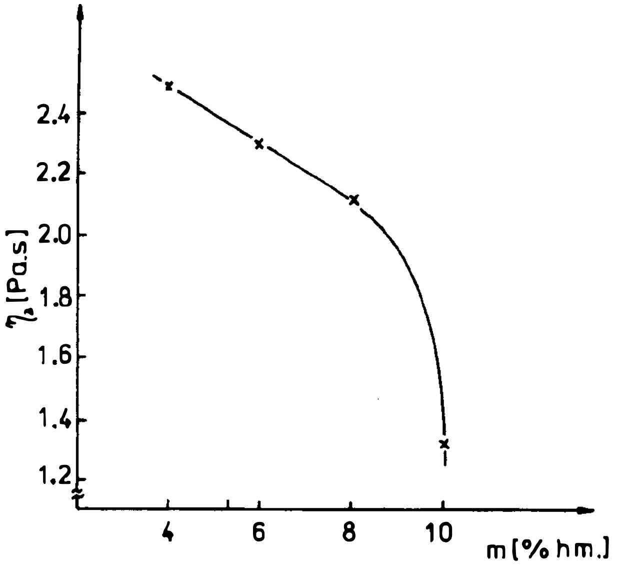

Fig. 6. Apparent viscosity of cement pastes vs. the content of mica fraction 500–1250 μm, w = 0.22.

Table IV

The setting time and compressive strengths of the cement pastes. Prachovice clinker, 0.04 wt. % of grinding aid, $S = 430$ m^2/kg (Blaine), mica fraction 1, $w = 0.24$

Sample no.	m (wt. %)	Setting time (min.)	Compressive strengths (MPa)					
			3h	5h	24h	7 days	28 days	180 days
11	0	57	5.9	16.8	53.5	71.5	101.5	109.5
12	2	53	6.4	18.0	51.3	70.5	93.5	99.0
13	4	47	5.8	17.0	47.5	65.0	88.0	96.6
14	6	37	5.4	16.0	43.0	67.0	68.5	93.5
15	8	38	5.4	16.0	49.0	59.5	75.5	78.5

m – mica additon

Table V

The setting time and compressive strengths of the cement pastes. Prachovice clinker, 0.04 wt. % grinding aid, $S = 430$ m^2/kg (Blaine), mica-fraction 2, $w = 0.24$

Sample no.	m (wt. %)	Setting time (min.)	Compressive strengths (MPa)					
			3h	5h	24h	7 days	28 days	180 days
16	2	84	4.5	15.0	58.5	76.5	91.3	102.5
17	4	88	4.1	13.0	56.5	69.5	78.5	96.0
18	6	96	4.1	8.1	51.0	73.0	82.0	105.0
19	8	94	3.6	9.0	49.5	70.0	76.5	90.0

m – mica additon

ously related to their different specific surfaces and thus also different amounts of the aqueous solutions of additives adsorbed on their surface. The finest fraction with the largest surface area (5.15 sq.m/g) reduces significantly the proportion of the free aqeous solution in the cement paste, and this results in an increase in apparent viscosity, accelerated setting and speeding up of hydration heat liberation. On the contrary, the coarsest fraction of the mica particles (0.42 sq.m/g) bounds only a small proportion of the dissolved admixtures, which necessarily leads to lower apparent viscosity in view of the decreasing cement content, as well as to a delayed setting time and retarded development of the heat of hydration.

CONCLUSION

The following conclusions can be drawn from the present study of composites prepared with a matrix based on gypsum-free Portland cement and mica reinforcement of various particle fractions:

1. a) Addition of mica with particles up to 14 μm in size shortens the setting time and causes a sharp increase in apparent viscosity. Amounts exceeding 2 wt. % yielded badly workable pastes of almost no practical use.
   b) Mica of up to 56 μm particle size retards the setting time of the GPC pastes. The apparent viscosity of cement pastes increases on

Table VI

The setting time and compressive strengths of the cement pastes. Prachovice clinker, 0.04 wt. % of grinding aid, $S = 430\ \mathrm{m^2/kg}$ (Blaine), mica-fraction 3, $w = 0.22$ and 0.24

Sample no.	m (wt. %)	w	Setting time (min.)	Compressive strengths (MPa)					
				3h	5h	24h	7 days	28 days	180 days
20	2	0.24	79	5.0	13.5	47.5	72.5	86.0	84.0
21	4	0.24	85	3.5	8.1	50.5	62.5	63.5	82.5
22	6	0.24	111	3.3	6.8	49.0	56.0	64.0	73.0
23	8	0.24	102	3.1	6.5	46.5	57.0	54.0	71.5
24	4	0.22	90	5.5	18.0	52.0	66.0	69.0	79.0
25	6	0.22	92	4.4	18.0	57.0	68.5	75.0	77.5
26	8	0.22	91	4.2	13.0	50.5	60.5	64.0	74.0
27	10	0.22	91	4.0	9.0	45.0	47.5	58.0	60.0

m – mica additon

exceeding the 2 wt. % mica content, as compared to mica-free controls.

c) Mica fraction 500–1250 μm retards the setting time of GPC pastes and reduces their apparent viscosity. In this way it was possible to prepare composites with a very low water-to-cement ratio ($w = 0.22$), and thus to mildly improve the early compressive strengths (within 5 hours of preparing the paste).

d) The different effects of the mica fractions employed on the properties of the composites are obviously due to their different specific surfaces and thus to the different amounts of adsorbed aqueous solution of admixtures on their surfaces.

2. In most cases, the addition of mica resulted in a decrease of compressive strengths, compared to mica-free controls.
3. The amount of liberated heat of hydration decreases with increasing mica content in the composite.
4. To be able to evaluate the composites in question in a complex way, one should also know their other physical and chemical properties such as apparent density, flexural strength, Young's modulus of elasticity and resistance to aggressive chemical media. Determination of these parameters will be the subject of a continuing study.

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VLIV SLÍDOVÝCH ČÁSTIC NA VLASTNOSTI KOMPOZITŮ S MATRICÍ Z BEZSÁDROVCOVÝCH PORTLANDSKÝCH CEMENTŮ

1. část

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Byla připraveny kompozity s matricí z bezsádrovcového portlandského cementu, jež obsahovaly 2–10% hm. podílu slídy s různou velikostí částic. Účinek slídy byl diskutován z hlediska zdánlivé viskozity cementových kaší, časového průběhu hydratačních reakcí, vývoje hydratačního tepla a pevností v tlaku. Ze studia kompozitů vyplývají tyto poznatky:

1. a) Přídavek slídy o velikosti částic pod 14 μm způsobuje zkrácení počátku tuhnutí bezsádrovcového portlandského cementu a strmý nárůst zdánlivé viskozity. Při dávkách nad 2% hm. slídy byly připraveny obtížně zpracovatelné směsi, pro praxi téměř nepoužitelné.
   b) Slída o velikosti částic pod 56 μm prodlužuje počátek tuhnutí bezsádrovcového portlandského cementu. Zdánlivá viskozita cementových kaší, vůči standardu bez slídy, po překročení 2% hm. obsahu slídy vzrůstá.
   c) Frakce slídy o velikosti částic 500–1250 μm prodlužuje počátek tuhnutí bezsádrovcového portlandského cementu a snižuje zdánlivou viskozitu cementových kaší. To umožnilo připravit kompozity s nízkým vodním součinitelem ($w = 0.22$), čímž se o málo zlepšily krátkodobé pevnosti v tlaku (za 5 hodin od rozmíchání směsi).
   d) Odlišné působení použitých frakcí slídy v kompozitech je zřejmě způsobeno jejich rozdílným měrným povrchem a tím i rozdílným množstvím adsorpčně vázaného množství vodného roztoku přísad na jejich povrchu.
2. Ve většině případů došlo za přítomnosti slídy k poklesu pevností v tlaku oproti standardu bez slídy.
3. Množství vybaveného hydratačního tepla klesá s rostoucím obsahem slídy v kompozitu.
4. Pro komplexní hodnocení sledovaných kompozitů je nutné znát jejich další fyzikální a chemické vlastnosti charakterizované objemovou hmotností, pevností v tahu za ohybu, Youngovým modulem pružnosti a odolností proti účinkům agresivního prostředí. Zjišťování těchto parametrů je předmětem pokračujícího studia.

Obr. 1. Časový průběh hydratačních reakcí cementových kaší s různým množstvím slídy frakce < 14 μm, w = 0,24. 11 - 0%; 12 - 2%; 13 - 4%; 14 - 6%; 15 - 8%.

Obr. 2. Časový průběh hydratačních reakcí cementových kaší s různým množstvím slídy frakce < 56 μm, w = 0,24. 11 - 0%; 16 - 2%; 17 - 4%; 18 - 6%; 19 - 8%.

Obr. 3. Časový průběh hydratačních reakcí cementových kaší s různým množstvím slídy frakce 500–1250 μm, w = 0,24. 11 - 0%; 20 - 2%; 21 - 4%; 22 - 6%.

Obr. 4. Časový průběh hydratačních reakcí cementových kaší s různým množstvím slídy frakce 500–1250 μm, w = 0,22. 11 - 0%; 24 - 4%; 25 - 6%; 26 - 8%; 27 - 10%.

Obr. 5. Závislost zdánlivé viskozity cementových kaší na množství slídy frakce < 56 μm a 500–1250 μm, w = 0,24. 1 - slída frakce 56 μm; 2 - slída frakce 500–1250 μm.

Obr. 6. Závislost zdánlivé viskozity cementových kaší na množství slídy frakce 500–1250 μm, w = 0,22.