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Effect of Chrysotile Asbestos on Cement Hydration

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Abstract

Hydration of cement in the presence of asbestos was traced by means of hydration heat and adsorption capabilities of asbestos. Asbestos and cement samples were prepared in laboratory in proportions similar to those found in industrial materials. Asbestos was chrysotile by its mineralogical properties, of a short-fibered sort. Hydration heat was determined calorimetrically by means of spherical thermos flasks; adsorption capability of asbestos fibers was determined relative to $Ca(OH)_2$. The hydration process was represented by integral and differential curves, which indicated that hydration heat development was intensified in the presence of asbestos. The results obtained for adsorption have showed that asbestos surface is active, with 10^{18} active sites per cm^2. The isotherms obtained are multistep ones and indicate the formation of two layers of adsorbate. Adsorption capabilities of asbestos intensify cement hydration. © 1997 Elsevier Science Ltd. All rights reserved.

Keywords: Chrysotile asbestos, cement hydration, adsorption capabilities.

INTRODUCTION

Of the different fibers used as an addition to cement, asbestos fibers are still among those most frequently used. They have outstanding properties, such as high elasticity modulus, resistance to high temperatures and chemicals, noncombustibility and stability in the high pH range of the cement paste, as well as a reasonable price. This paper is a contribution to an explanation of the effect of asbestos on cement hydration, which was studied by the measurement of hydration of asbestos–cement and adsorption capabilities of two asbestos samples.

Asbestos surface activity was determined by examining adsorption of $Ca(OH)_2$ to the fibers. Namely, during hydration of clinker materials, hydrated phases are formed of variable composition and $Ca(OH)_2$ content, which can be easily determined quantitatively.

The methodology applied in the present work can be used in the evaluation of other fiber materials that could substitute asbestos regarding their behaviour and influence on the cement hydration process.

EXPERIMENTAL

Samples

Cement: Industrial Portland cement with 20–25% slag PC20T45. Table 1 shows the

Table 1. Chemical composition of PC 20T 45 cement and mineralogical composition of clinker

Chemical composition	*Percentage*	*Mineralogical composition*	*Percentage*
Loss on ignition	1.05	C_3S	
Insoluble	0.45	C_2S	22.0
SiO_2	23.25	C_3A+C_4AF	8.0
Al_2O_3	5.32	CaO	—
Fe_2O_3	2.29		
CaO	59.86		
MgO	2.01		
SO_3	2.40		
Na_2O	0.21		
K_2O	0.71		
CaO (free)	0.35		

Table 2. Chemical composition of asbestos samples

Asbestos sample	*Loss on ignition*	SiO_2	Al_2O_3	Fe_2O_3	*CaO*	*MgO*
AC 6D	12.90	39.01	1.31	5.88	1.60	38.88
AC 7D	12.94	38.88	1.11	5.86	1.27	38.87

chemical composition of cement and mineralogical composition of clinker.

Asbestos: Chrysotile asbestos class 6D and 7D. Table 2 shows the chemical composition of asbestos samples.

XRD and DTA established that asbestos samples belonged to chrysotile asbestos by their mineralogical composition; they were clinochrysotile with 16% orthochrysotile. Brucite and magnesite were identified as non-asbestos components[1].

Table 3 shows the average fiber length as determined by the Bauer McNett classification test, and the specific surface area as determined by the BET method.

Calorimetrical measurements

The cement paste (C) and the asbestos–cement paste (AC) were prepared for calorimetrical measurements with a water–cement (W/C) ratio of 0.476 by mixing cement and asbestos to a ration of 7:1. Hydration heat was determined by the spherical thermos flasks method[2] at 25°C. The data measured were represented by integral curves shown in Figs 1 and 2, and differential curves shown in Figs 3 and 4.

Examination of adsorption of calcium-hydroxide to asbestos

Adsorption of $Ca(OH)_2$ to asbestos samples was examined by measuring the concentration of the $Ca(OH)_2$ solution before and after contact with asbestos. $Ca(OH)_2$ concentration was determined by titration with 0.05 M HCl with methylorange. Experiments were carried out discontinuously, with protection from carbonation.

Table 3. Average fiber length and BET specific surface area for asbestos samples

Asbestos sample	*Average length (mm)*	*Specific surface (m^2/g)*
AC 6D	0.73	25.2
AC 7D	0.65	23.4

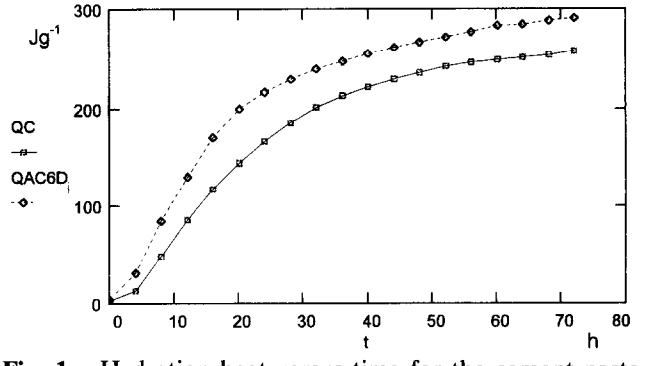

Fig. 1. Hydration heat versus time for the cement paste (C) and asbestos–cement paste AC 6D.

First, it was necessary to determine the time needed to reach the equilibrium adsorption: 1 g of sample, which had been dried for 3 h at 105°C, was placed into 200 ml of saturated $Ca(OH)_2$ solution in a closed PE flask. The suspension was kept in a thermostat at a

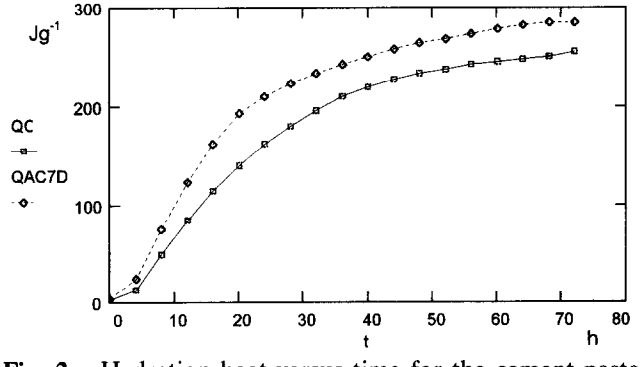

Fig. 2. Hydration heat versus time for the cement paste (C) and asbestos–cement paste AC 7D.

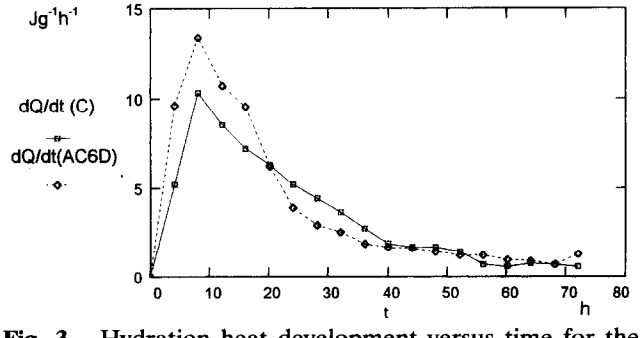

Fig. 3. Hydration heat development versus time for the cement paste (C) and asbestos–cement paste AC 6D.

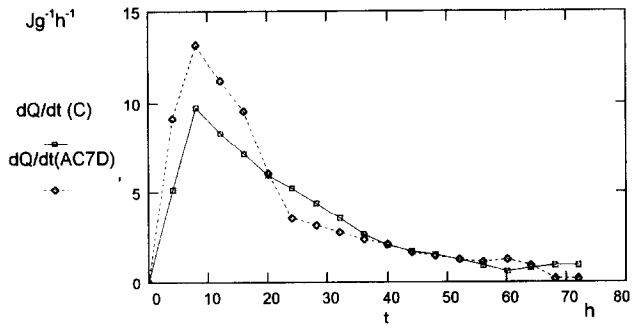

Fig. 4. Hydration heat development versus time for the cement paste (C) and asbestos–cement paste AC 7D.

temperature of 20°C. At specified time intervals, the clear part was separated by decanting, and the concentration of $Ca(OH)_2$ in the residue was determined. The quantity of $Ca(OH)_2$ adsorbed was calculated according to the expression

$$n_a = ((c_o - c_{eq})V)/G, \quad (1)$$

where: n_a = quantity of $Ca(OH)_2$ adsorbed (mmol/g); C_o = initial $Ca(OH)_2$ concentration (mmol/dm^3); C_{eq} = equilibrium $Ca(OH)_2$ concentration (mmol/dm^3); V = volume of the solution (dm^3); and G = mass of the adsorbent (g). It took 2 days to reach equilibrium adsorption. In order to obtain adsorption isotherms, a series of $Ca(OH)_2$ solutions was prepared; their concentrations ranged from approximately 2.2 to 22 mmol/dm^3. Fibers were placed in contact with the solution for a period of 2 days. Immediately before and after the contact, the $Ca(OH)_2$ concentration in the solution was determined, and the quantity of $Ca(OH)_2$ adsorbed was calculated according to eqn (1). The experimental conditions were the same as for the determination of time needed to reach equilibrium adsorption.

Figures 5 and 6 show adsorption isotherms of quantity of n_a adsorbed relative to equilibrium concentration C_{eq}.

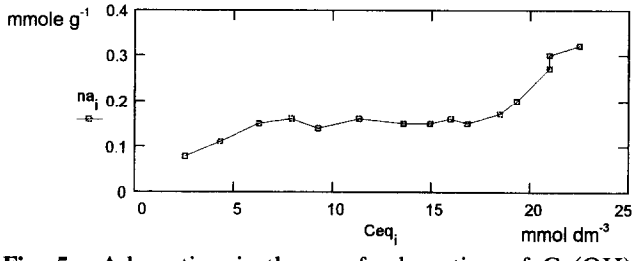

Fig. 5. Adsorption isotherm of adsorption of $Ca(OH)_2$ to asbestos AC 6D sample.

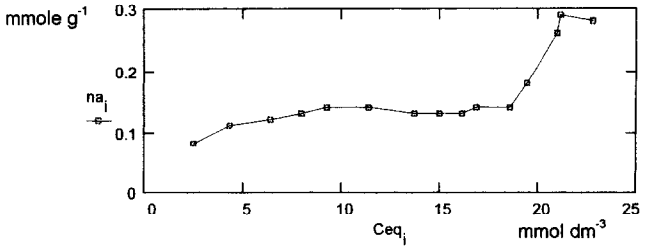

Fig. 6. Adsorption isotherm of adsorption of $Ca(OH)_2$ to asbestos AC 7D sample.

DISCUSSION

Reactions of clinker minerals with water are exothermic so that the process of cement hydration can be traced by determination of hydration heat. As seen from Figs 1–4, the curves of hydration heat and heat development rate relative to time have a characteristic flow that indicates several stages of cement hydration. A rapid increase in the rate of heat liberation, which marks the stage of accelerated hydration, reaches its maximum after 8 h of hydration for cement samples and for asbestos–cement samples. A comparison of results obtained for heat in cement samples with those obtained for asbestos–cement ones has indicated that the values obtained for asbestos–cement are higher. In the presence of asbestos, a higher total quantity of heat is developed, and the value of dQ/dt is higher. The kinetic curves obtained confirm the results of previous examinations[3,4], which state that hydration reaction is intensified in the presence of asbestos.

Examination of the adsorption of $Ca(OH)_2$ to asbestos can provide an insight into asbestos activity during hydration. Chrysotile asbestos has a high specific surface that is the cause of its powerful adsorption capabilities. Examinations of adsorption of different materials to asbestos fibers have established[5,6] that adsorption is especially high in hydroxides of alkaline-earth metals. It was then established that, depending on the sort and degree of disintegration, 1 g of chrysotile adsorbs 0.29–1.66 mmol of $Ca(OH)_2$, which is comparable to absorption capabilities of active carbon of 0.52 mmol/g. Results obtained for the adsorption of $Ca(OH)_2$ to AC 6D and AC 7D asbestos samples are in agreement with these data and amount to 0.311 and 0.284 mmol/g at saturated concentration of $Ca(OH)_2$.

Table 4. Ratio of quantity of $Ca(OH)_2$ adsorbed at the second plateau to that adsorbed at the first plateau

Asbestos sample	n_{a1} *(mmol/g)*	n_{a2} *(mmol/g)*	n_{a1}/n_{a2}
AC 6D	0.155	0.311	2.006
AC 7D	0.135	0.284	2.102

Adsorption isotherms shown in Figs 3 and 4 are multistep ones; their shape is characteristic of the formation of multimolecular layers of adsorbate[7,8]. The quantity of $Ca(OH)_2$ adsorbed increases with the increase in concentration, and is then constant for a certain period. The linear part, the plateau, represents the end of formation of the first monomolecular layer. When the concentration of the $Ca(OH)_2$ solution approaches saturation, adsorption increases again and reaches its maximum. This value is roughly doubled, which indicates that the second layer is formed, as shown in Table 4, where n_{a1} and n_{a2} denote the quantity of $Ca(OH)_2$ adsorbed at the first and the second plateau respectively.

From the values obtained for n_{a1}, the number of adsorbed Ca^{2+} ions per surface unit was calculated according to:

$$number\ of\ adsorbed\ Ca^{2+}-ions\ m^2 = (n_{a1}N)/S, \tag{2}$$

where: n_{a1} = number of moles of $Ca(OH)_2$ adsorbed in formation the monomolecular layer (mol/g); N = Avogadro number; and S = BET specific surface (m^2/g). Table 5 shows the number of Ca^{2+} ions adsorbed to the asbestos samples examined.

The values obtained for the number of adsorbed Ca^{2+} ions agree with the results of measurement of the number of active sites obtained by Bonneau *et al.*[9]. In their experiments of adsorption with agents for determination of the character and number of active sites on the surface of chrysotile, they have proved that the lateral surface of the fibers has distinct electrondonor properties, and density of active sites ranging from 10^{17} to $10^{18}/m^2$. To understand the formation of base sites, one should know the structure of chrysotile: chrysotile fibers of the formula $Mg_3Si_2O_5(OH)_4$ represent a series of parallel coils of philosilicate leaves of the kaolinite type, consisting of a layer of SiO_4 tetrahedrons with $MgO_2(OH)_4$ octahedrons lying on their outer sides. Due to partial dissolution of the octahedral layer, Mg^{2+} ions migrate, cationic vacancies are formed, and an excess negative charge appears on the surface of hydroxide groups, so that the lateral surface of the fibers attracts positive ions from the solution.

Table 5. Number of Ca^{2+} ions adsorbed per asbestos surface unit

Asbestos sample	*Number of* Ca^{2+} *ads./*m^2
AC 6D	3.70×10^{18}
AC 7D	3.47×10^{18}

The effect of asbestos on cement hydration is thus explained by adsorption of Ca^{2+} ions from the liquid phase. As asbestos is a very powerful adsorbant, the reactions that take place in its presence will be intensified. Because of that, the concentration of Ca^{2+} ions in the solution will decrease, and the balance will shift in the direction of hydration process development.

The results thus obtained for hydration heat in cement containing asbestos of different adsorption capabilities have indicated that the maximum quantity of $Ca(OH)_2$ adsorbed (na_{max}) corresponds to the maximum heat release rate (dQ/dt_{max})[4]. The measurements have therefore led to the conclusion about the compatibility of the two different methods of examination of the effect of asbestos (and other fibers as well) on cement hydration. The maximum values for adsorption and heat release rate were:

$$\frac{n_{a\,max}\ (mmol/g)}{AC\ 6D\ 0.311 > AC\ 7D\ 0.284}$$

$$\frac{dQ/dt_{max}}{AC\ 6D\ 13.452 > AC\ 7D\ 13.233}.$$

As the differences in physical properties (the particle size distribution) and impurities present were not evident in the samples analyzed, they were observed when comparing the differential curves of hydration heat. Finally, a number of examinations have led to the conclusion that development of the hydration heat in individual stages of this process corresponds to the explanation of the adsorption isotherm curves,

indicating the effect of asbestos fibers on cement hydration.

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