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INVESTIGATION OF THE INTERACTION OF SILICON-ORGANIC COMPOUNDS AND $Ca(OH)_2$*

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The new phases produced in the interaction of chloro-silane distillation residues and $Ca(OH)_2$ are different in the case of alkyl and aryl silane derivatives. X-ray phase analysis results about the composition of the new phases are strongly supported by the IR spectra, too.

Introduction

One of the ways to improve the corrosion resistance of cement-based building materials is to decrease the $Ca(OH)_2$ content of the starting materials. In this case the microstructure of cement stone will change. As an inexpensive hydrophobizing agent the by-product of chloro-silane manufacturing can be applied, namely the distillation residue, which contains chloro-silanes, alkyl-chloro-disiloxanes, bis-silyl-alkylates and $C_6 - C_9$ hydrocarbons. The active chlorine content of the mixture was 48%, which was reduced to 6–7% by hydrolysis or alkoxylation (i.e. treatment with i-propyl alcohol).

The modelling of the optimal hydrophobization circumstances of these cement mixtures was carried out with $Ca(OH)_2$. A $Ca(OH)_2 - H_2O$ suspension with a mass ratio of 2 : 1 was treated with hydrophobizing agents, then after 24 hours the phase composition of the powdered samples was studied based on X-ray phase diagrams and IR spectra.

For the treatment of samples as hydrophobizing agent the residue of the distillation of methyl- (MK), methyl-vinyl- (MVK) and phenyl- (FK) chloro-silane production as well as W-290 (Wacker Chemie, West-Germany) were used. The last product is a polysiloxane oligomer with long alkyl chain and it was used as a solution in an organic solvent.

From the IR spectrum of the model compound $Ca(OH)_2$ (Fig. 1) it can be seen that it was transformed into the carbonate on contacting with air (bands at 1450, 875, 420 cm^{-1}).

The X-ray diffractograms of the $Ca(OH)_2$ sample hydrophobized using MK and MVK (Fig. 2) do not prove the incorporation of Si-O group into the sample. However, the wide band appearing in the IR spectrum refers to the presence of Si-O-Si or Si-O-C bonds. After extraction of samples with hexane the intensity of the wide band characteristic of the stretching vibration of siloxanes decreases and the wide band splits into several peaks (in the range of 1130–1010 cm^{-1}), which means non-reacting low molecular weight siloxanes can be removed

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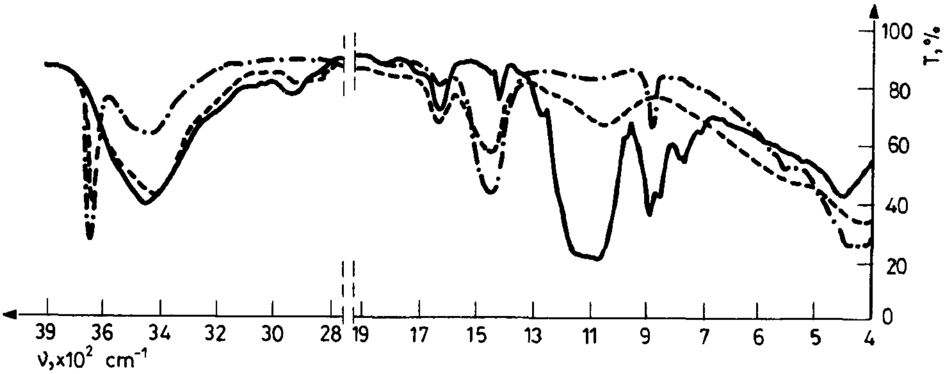

Fig. 1. IR spectra: 1, MVK (——); 2, $Ca(OH)_2$ (–.–.–); 3, Hydrophobized $Ca(OH)_2$ (----)

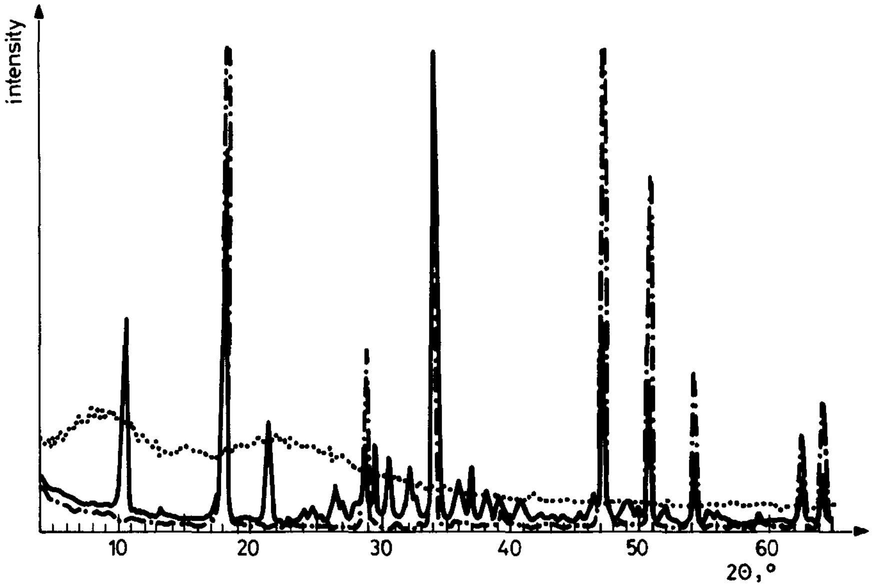

Fig. 2. X-ray diffractograms: 1, MVK (----); 2, $Ca(OH)_2$ (–.–.–); 3, Hydrophobized $Ca(OH)_2$ (——)

from the sample. The bands at 3600–3100 and 1700–1600 cm^{-1} belong to the bound water. The amount of this bound water does not decrease on drying at 180 ^{0}C to constant weight.

In the IR spectrum of MVK the stretching frequency of the Si-H bond can be observed at 2258 cm^{-1}. This band cannot be found in the spectrum of the hydrophobized product because the Si-H bond is hydrolysed in alkaline medium.

On the basis of X-ray diffractograms it has been found that $Ca(OH)_2$ reacts with the residue of distillation only in the presence of water. In the X-ray diffractogram of MK there is a wide band in the range of 2θ 8–12^{0} (d/n = 0.73–1.25 nm; 0.81–0.821 nm) and a diffuse band can be observed between 2Θ 19–28°. The X-ray diffractograms of MVK, of $Ca(OH)_2$ and of the product of interaction can be seen in Fig. 2. The more combined hydrocarbon group bonded to silicon reduces the regularity of the hydrolysed particles. The calcite bands in the X-ray diffractogram prove the particular transformation of $Ca(OH)_2$ into $CaCO_3$.

In the course of the reaction the amount of $Ca(OH)_2$ decreases. This process is indicated by the IR spectra, but even better by X-ray diffractograms by a decrease in the intensity of the $Ca(OH)_2$ bands (in this respect first of all the d/n = 0.3097–0.3112; 0.1793–0.1798 and 0.1684–0.1687 nm bands are characteristic). The d/n values of the new crystalline phase occurring on hydrophobization are summarized in Table I.

Table I

Relative peak intensities of $Ca(OH)_2$ hydrophobized with MVK or MK

N°	$\frac{d}{n}$, nm	Relative intensity	N°	$\frac{d}{n}$, nm	Relative intensity	N°	$\frac{d}{n}$, nm	Relative intensity
1	0.8328	10	8	0.2926	4	15	0.1952	3
2	0.6605	1	9	0.2771	3	16a	0.1876	1
3	0.4161	5	10	0.2426	3	16b	0.1857	1
4	0.3688	1	11	0.2362	1	17	0.1845	1
5	0.3597	1	12	0.2218	2	18	0.1757	1
6	0.3376	2	13	0.2058	1	19	0.1651	1
7	0.3301	1	14	0.1997	1	20	0.1526	0.5

16a. only for MVK; 16b. only for MK

The data of the X-ray diffractograms of the new phase do not agree with those found in the literature [1–4]. The intense bands observed at d/n = 0.8328 and 0.4161 nm characterise the natural calcium-alumina-silicates ($CaO.Al_2O_3.7SiO_2.1,7H_2O$ and $CaO.Al_2O_3.4SiO_2.6H_2O$), alkali- and alkaline earth metal silicates, as well as calcium-chloro-hydrosulphato-aluminate ($3CaO.Al_2O_3.CaSO_4$, $CaCl_2.12H_2O$). At the same time the band at d/n = 0.832 nm can be found in the X-ray diffractogram of $Ca(CH_3COO)Cl.5H_2O$. The starting components do not contain any alumina and alkali metal, thus organic acids with short chain are formed in the presence of HCl arising from the reaction of the distillation residue and due to the large specific surface area. Hence, the crystalline phase may contain calcium-alkylate-chloride, too. In the differential IR spectrum of the new phase weak bands can be observed at 645, 615 and 465 cm^{-1} (the deformation frequencies of carboxylate ion), but the stretching frequency of carboxylate ion cannot be identified unambiguously.

On the basis of IR spectra it can be stated that during the hydrophobization with FK siloxane chains are built into the product (in the range of the stretching frequencies of Si-O-Si group two peaks occur). In the X-ray diffractograms there are bands characteristic of the new phase, which have not yet been identified, at d/n = 0.8349; 0.5315; 0.2757; 0.2371; 0.1878 and 0.1637 nm.

Hydrophobization made with W-290 (not containing chlorine) yields a product containing a high amount of polysiloxanes with long carbon chain. This material contains the minimum quantity of OH groups (only one sharp band can be observed at 3635 cm^{-1} in the IR spectrum and only weak bands at d/n = 0.2453 and 0.1637 in the X-ray diffractograms). In this case the siloxane oligomer chain is bonded at the surface and in the pores of material, so it prevents water uptake.

Experimental

The X-ray diffractograms were taken by an X-ray diffractometer type JDX-IOPA applying a copper anticathode and nickel filter in the range of 4–65°. The rotation speed of the goniometer was 0.04 °/ms.

The IR spectra were taken by an IR spectrometer model UR–20 in KBr pellets.

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