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BEHAVIOUR OF $Ca(OH)_2$ IN THE PRESENCE OF THE SET STYRENE-ACRYLATE DISPERSION

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ABSTRACT

The action of the saturated $Ca(OH)_2$ solution on the surface of the set styrene-acrylate dispersion was studied by scanning electron microscope and infrared spectroscopy. The slices of the set dispersion were immersed into the saturated $Ca(OH)_2$ solution. Action in such conditions on and near to the set dispersion surface was investigated in comparison with that in the saturated $Ca(OH)_2$ solution. The obtained results indicate, that first spherical and globular $Ca(OH)_2$ particles arise in the form of long fibres and of cluster habits on the set dispersion surface. $Ca(OH)_2$ is converted continually to the carbonate phase. The carbonate crystallization proceeds first through the aragonite-like and lately through the calcium-like carbonate rise. It is supposed, that air voids formed in the set dispersion surface serve as the CO_2-giving supplies, in which the carbonation proceeds preferentially compared to the $Ca(OH)_2$ solution. *Copyright © 1996 Elsevier Science Ltd*

Introduction

Polymer-modified mortars and concretes have been used as building materials for many years. At present they are drawing more attention as repair materials. Testing methods and quality requirement of concrete-polymer composites have been in progress in Japan, United States of America and United Kingdom of Great Britan [1].

The properties of the polymer-modified mortars are affected by the factors as variations of polymer type, film strength and his formability, as well as the polymer-cement ratio [2]. The addition of the polymer reduces the $Ca(OH)_2$ amount possibly due to adsorption of $Ca(OH)_2$ on the surface of the polymer-film [3]. Various morphological shapes of $Ca(OH)_2$ may create in cement pastes when polymer is present. These changes occur due to the mutual $Ca(OH)_2$ -polymer action. They include mainly rosette-like and long rod shaped particles of the $Ca(OH)_2$ [4, 5]. Hexagonal crystals of the $Ca(OH)_2$ are built up by the individual layers of the plates which are joint together in a parallel fashion. Hydrated calcium silicates (from cement clinker minerals) are very tightly situated around the $Ca(OH)_2$ and exert a pressure on $Ca(OH)_2$ layers with ageing of hydration. Portlandite crystals are pushing together and form a stack of plates [6]. Polymer particles adhere to the surface of the $Ca(OH)_2$ and act as a kind of bond among $Ca(OH)_2$ crystals. The interfacial zone of polymer was reported to be about 15 nm thick [7].

The interaction of the $Ca(OH)_2$ suspension or saturated $Ca(OH)_2$ solution with the polymer dispersion leads to the precipitation and loss of film-forming ability. X-ray powder patterns have shown some changes in the range of 17-23 2θ. An insoluble residue remains when the aged mix of $Ca(OH)_2$ with dispersion was treated with weak hydrochloric acid solution. The residue is believed to be CaO which interacted with polymer and formed some complex compounds. The product is hydrophobic in its character and has increased durability [8]. The cement-polymer interaction is due to the ion bonding causing cross-links which inhibit the film formation property of the polymers. The behaviour of individual Portland cement components with polymers was found to be different when they are present together in cement. The mechanism of this interaction is not clear yet [9].

The interaction of $Ca(OH)_2$ with liquid polymer was studied by many authors [3, 6, 7, 9]. On the contrary it was intended herein to investigate the $Ca(OH)_2$ - polymer behaviour when saturated $Ca(OH)_2$ solution is contacted with the surface of the set polymer. It is supposed that this aspect is a new attempt of the other view into the research of $Ca(OH)_2$ - polymer action. The present article summarizes our results on behaviour of $Ca(OH)_2$ on and near to the set dispersion.

Experimental

Materials. The styrene-acrylate dispersion SOKRAT 2802 A was used in the tests. The dispersion was supplied by Chemical Works Ltd., Sokolov, Czech Republic. Dispersion data are given in Table 1. Calcium oxide was prepared by ignition of $CaCO_3$ (analytical grade) at 1000 °C during 3 hours.

Preparation of Specimens. The liquid dispersion was left to dry on air for 28 days. The dessicated dispersion was cut to small slices. The saturated $Ca(OH)_2$ solution (SCS) was prepared with water to CaO ratio of 10:1. The experimental arrangement is shown in Fig. 1. A slice of dispersion was immersed into the SCS, which was gently and regularly agitated during the tests. The surface of the dispersion was consequently covered by arising products and studied after 3, 7 and 28 days of the SCS action. Reference sample of SCS prepared in the control test tube without set dispersion was examined, too.

Identification Methods. A JEOL JSM 35 scanning electron microscope (SEM) was used for the investigation of the microstructure of the products formed on and near to the set dispersion surface in comparison with that occured in the control SCS.

Infrared (IR) absorption spectra of the products arising in the control SCS and near to the set dispersion were recorded with PE 983G spectrometer. To examine the 4000-300 cm^{-1} region 0.6 mg of sample was added to about 200 mg of KBr and mixed for 3 min on vibratory grinder. After pressing a pellet with 13 mm diameter was obtained.

TABLE 1

The Certificate of the Styrene-Acrylate Dispersion SOKRAT 2802 A

Technical demands		Values
Total solids	%	48 - 52
pH at 20 °C	-	8 - 10
Viscosity	mPa. s	max. 200
Degree of hydrolysis in alkaline environment	%	max. 10
Of - type index of the dispersion		**Values**
Coagulate	%	max. 0.1
Median of particles size	mm.10^{-3}	0.1 - 0.3
Specific gravity	g.cm^{-3}	1.03
Surface tension	mN.m^{-1}	38 - 41
Of -type index of the film		**Values**
Hardness	%	15 - 24
Adhesive power	g	min. 5
Absorptivity	%	10
MFT	°C	max. 5
Diffusion resistance	-	max. 5000
Ductility	%	700 - 1000
Tensile strength	Mpa	max. 15

Results and Discussion

Microstructure of the Products. The microstructures of the set dispersion surface and of the products formed on and near to the surface of the set dispersion are illustrated in Figs. 2, 3 and 4. Fig. 2 shows the surface of the set dispersion dried for 28 days at 25°C. A large amount of fissures and cracks are evident on the dispersion surface. Dessicated dispersion is characterized by smooth, but rugged and shiny surface. Fig. 3a shows hexagonally shaped laths of $Ca(OH)_2$. On the lower part of the picture spherulites and globulas occur, whereas on the middle part pebbles of hypidiomorphic hexagonal crystals are evident. Figs. 3 b,c,d show that globular $Ca(OH)_2$, arising on the amorphous $Ca(OH)_2$ spherical particles, is being transformed to rhombohedral calcite. In the control SCS and SCS with the slice of set SOKRAT 2802 A dispersion, the content of arised products after three-day hydration is very similar. According to the X-ray diffraction analysis (Fig. 4) $Ca(OH)_2$ occurs prevailingly in tested SPCs whereas the content of the $CaCO_3$ is negligible at that time.

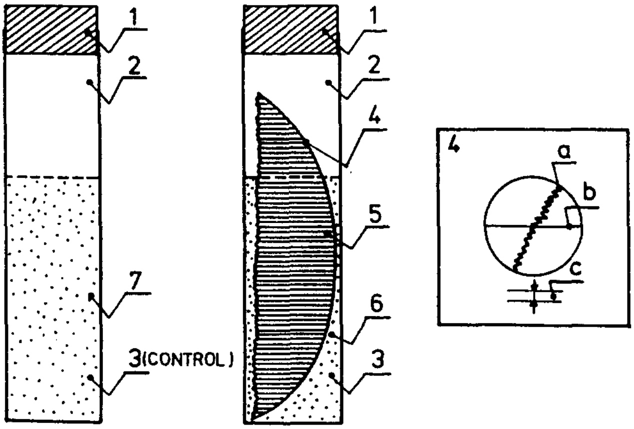


FIG. 1.

A test arrangement for examining the SCS action on and near to the set dispersion surface. 1 = tube closure, 2 = air over the solution, 3 = saturated $Ca(OH)_2$ solution (SCS), 4 = slice of set SOKRAT 2802 A dispersion, 4a = slice cutt, 4b= diameter, d = 20 mm, 4c= thickness, t = 3 mm, 5 = products on the set dispersion studied by SEM, 6 = products near to the set dispersion studied by SEM and IR spectroscopy, 7 = products in the control SCS studied by SEM and IRS.

Fig. 5a shows massive idiomorphic hexagonal $Ca(OH)_2$. Similar shape and habit of the products arising on (Fig. 5a) and near (Fig. 5 b,c) to the set dispersion was observed. Hexagonal crystals typical for $Ca(OH)_2$ were identified in Fig. 5d, which presents the products formed in control SCS.

Kinetics of the Products Development. Clusters of gel-like spherical particles of $Ca(OH)_2$ around extremely long, fibril products of calcite occur on the surface of the set dispersion, and emerge from the bottom of the dispersion slice (Fig. 3a). Clody arrangement of anhedral

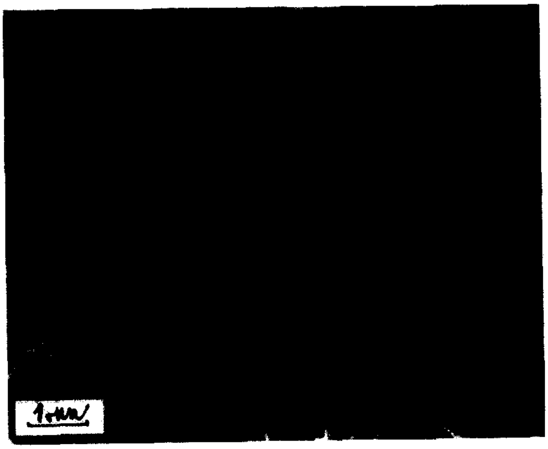


FIG. 2.
SEM (microphotograph) of the set dispersion surface.

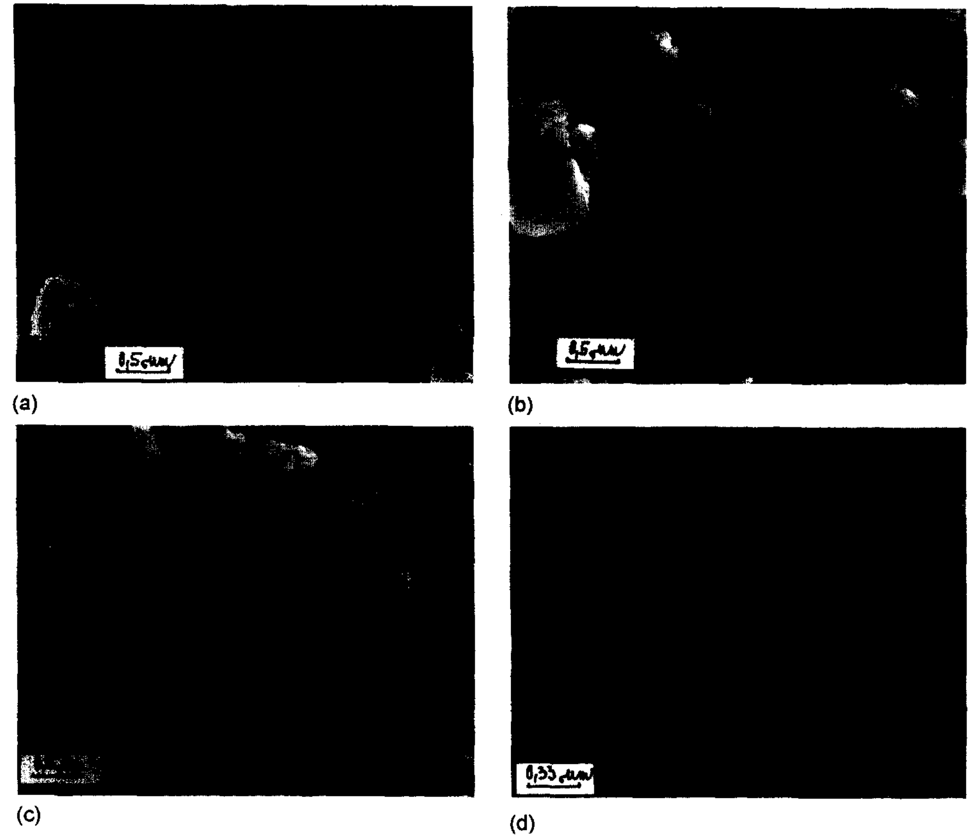


FIG. 3.

SEM of the products on the set dispersion surface (a) after 3 days and (b, c, d) after 7 days of the SCS action.

grains of the carbonate products grow up on the surface of the set dispersion and on long fibres (Fig. 3 b,c,d). Clusters consist of chain-linked layered flat and coin-like particles. Spots of the fibres rise and globulas represent probably the origin cracks or fissures on the dispersion surface. The SCS flows into these open sites and thus the supposition for next arising and further development of the products by crystallization are accomplished. Developed idiomorphic products are supposed to be the result of the action of SCS with the solid portion of the dispersion (Fig. 3). As the action of SCS proceeds the volume share of the carbonate phase is increased and the surface of the set dispersion is completly covered by the carbonate products (Fig. 5a).

Kinetics of carbonates crystallization may be interpreted as follows: the globular shape of $Ca(OH)_2$ particles appears distinctly after 3 days of the SCS action. After seven days rhombohedral crystallites of carbonates stringly arranged and randomly connected to distinct chains appear on the set dispersion surface. The content of the carbonate products continually increases up to 28 days of the SCS action and the microstructure is densified.

The interaction of liquid polymer with hydrated cement particles was explained by Y.Ohama according to the three-step simplified model of the structure formation process including the formation of a comatrix phase in which the hydrated cement phase and poly-

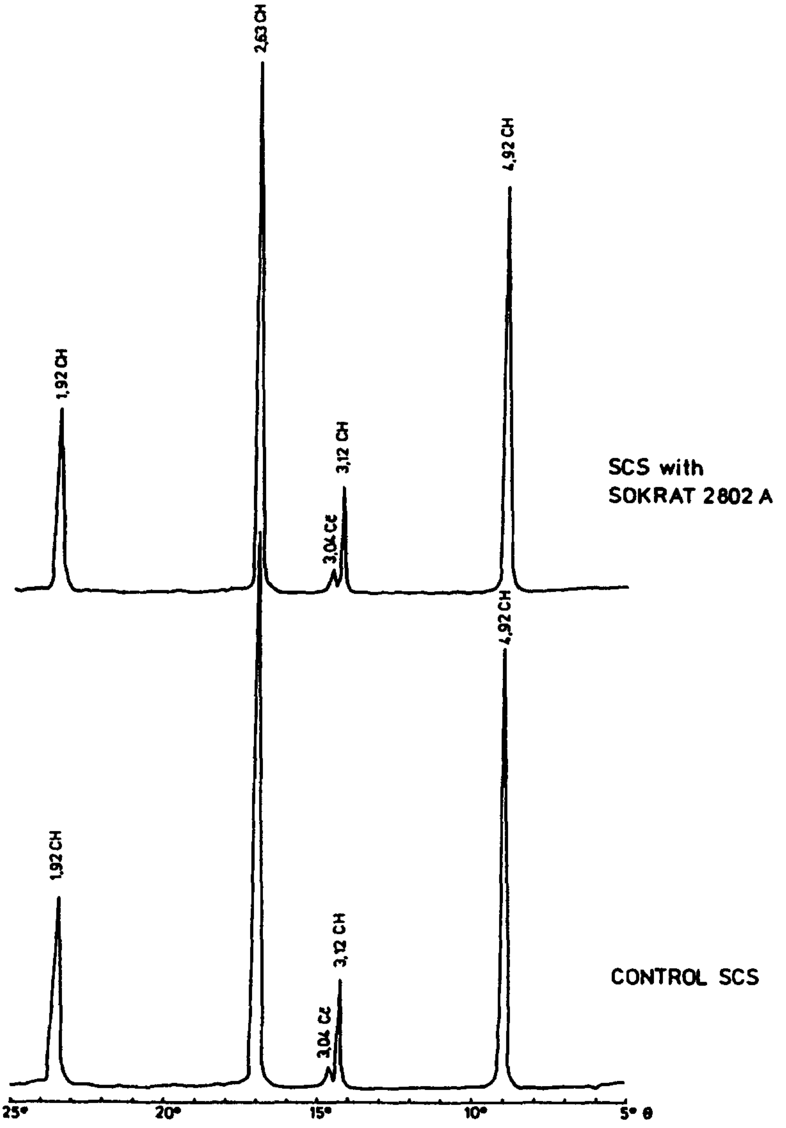
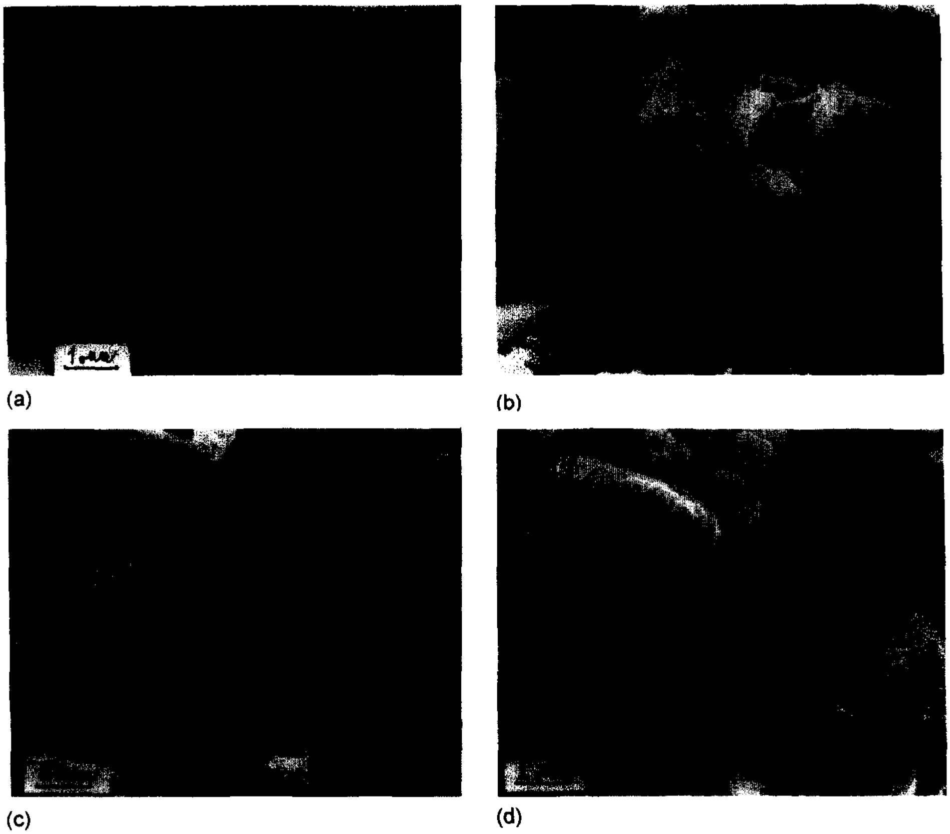


FIG. 4.
X-ray diffraction patterns of the control SCS and SCS with SOKRAT 2802 A after 3 day of action.

mer phase interpenetrated into each other. The cement hydrates are enveloped with polymer films or membranes with ageing of the hydration course [10].

On the contrary it is reported here, that $Ca(OH)_2$ and carbonate particles arised fluently on the set dispersion surface creating thus a close-packed dense layer of the products.

Identification of the Products. Infrared spectra of the products arising in the control SCS after 3 days and the IR spectra of the SCS products arising near to the set dispersion after 3, 7 and 28-days are shown in Fig. 6. No absorption bands assigned to styrene-acrylate (SOKRAT) were found in the IR spectra of the samples taken near to the set dispersion (Fig.



(a) (b) (c) (d)

FIG. 5.

SEM of the products after 28 days of the SCS action on the set dispersion surface (a), near to the set dispersion (b, c) and in the control SCS (d).

6 b,c,d). It proves that only SCS products were studied by IR spectroscopy. The IR spectra of these products are very similar and show all bands reported for portlandite [10]. Sharp and intensive band at 3635 cm^{-1} assigned to OH stretching vibrations indicates the presence of $Ca(OH)_2$ A broad band near 3420 cm^{-1} and the weaker band near 1630 cm^{-1} are attributed to the OH vibrations of molecular water [11]. The absorption bands near 1440 cm^{-1} and 874 cm^{-1} assigned to the stretching and bending vibrations of $(CO_3)^{2-}$ anion reflect the presence of carbonate phase in the sample.

Prevailingly amorphous character of the carbonate phase is supposed to be present in the 3 day SCS products, as no diffraction lines due to carbonate phase were found by XRD. In the area between 1100-1000 cm^{-1} weak overlapped bands are present in the IR spectra of all samples studied. Though the absorption in this region was reported for $Ca(OH)_2$ [10] the assignment of the bands is not clear, yet. The strong absorption bands near 386 and 314 cm^{-1} are due to Ca-O vibration coupled with OH bending vibration.

The most pronounced changes observed in IR spectra (Fig. 6) are the changes in the shape and the intensity of the carbonate band near 1440 cm^{-1}. The control SCS shows a broad band with two inflexions at 1458 and 1425 cm^{-1} (Fig. 6a). At least two absorption bands due to different carbonate phases are supposed to be overlapped in this region. The absorption at 1458 cm^{-1} was assigned to carbonates with aragonite structure and the absorption at 1425

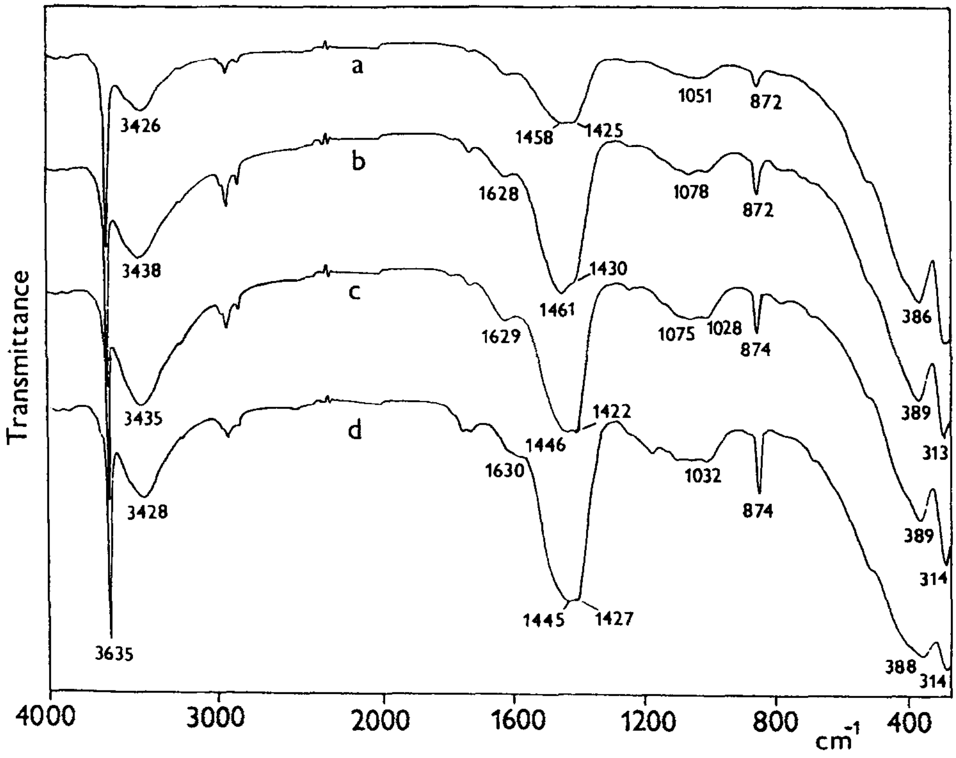


FIG. 6.
Infrared spectra of the products in the control SCS after 3 days (a), the products arising near to the set dispersion surface after 3 (b), 7 (c) and 28 (d) days of the SCS action.

cm^{-1} to carbonates with calcite structure [11]. The polymorphous modifications of carbonates are transformed with the time of the SCS action near the set dispersion (Figs. 6 b,c,d). The absorption band at 1461 cm^{-1} with shoulder near 1430 cm^{-1} in the IR spectrum of 3-day SCS (Fig. 6 b) shows aragonite-like carbonate to be present as main carbonate phase. Seven and 28-day action gives slightly resolved doublet at 1446 and 1422 cm^{-1} and at 1445 and 1427 cm^{-1}, respectively. The observed shift of the carbonate band to the lower wavenumbers (1458 and 1461 vs. 1446 and 1445 cm^{-1}) reveals that calcite-like carbonate is forming as dominant carbonate phase after 7 and 28 days of action.

The intensity of the carbonate band reflects the amount of carbonate phase present in the sample. Comparison of the intensities of the band near 1440 cm^{-1} for control SCS and SCS near the set dispersion at the same time (3 days) shows higher carbonation of SCS in the presence of suspension (Figs. 6 a,b). The similar intensity of the above mentioned band for 3- and 7-day action of the SCS near the set dispersion indicates similar carbonate content present in the samples (Figs. 6 b,c). The most intensive carbonate band observed for 28-day action reveals the highest amount of the carbonates. Corresponding with intensity changes in the band near 1440 cm^{-1} are the changes in the band of carbonate at 874 cm^{-1}. The increase in the intensity for 3, 7 and 28 day action of SCS near dispersion compared to 3 day action of control SCS reflects the increase in carbonate content in the samples (Fig. 6).

Conclusions

1. The smooth dispersion surface is covered by long fibres and gel-like clusters of the products when the set dispersion slice are immersed into the SCS. It is believed, that the spots of the fibres and clusters rise follow the direction of the original cracks and fissures on the set dispersion surface and act as a crystallization centres for preferential growth of the products.

2. Both $Ca(OH)_2$ and carbonates were identified in the SCS contacted with the set dispersion. The products development is characterized by the rise of the spherical and globular $Ca(OH)_2$ particles which are then converted to the rhombohedral crystallites of carbonates stringly arranged and randomly connected into the distinct chains.

3. The indentification study of the products shows that aragonite-like carbonates are present as the main carbonate phase after 3-day action of the SCS near to the set dispersion surface. Calcite-like carbonates are forming as the dominant carbonate phase after 7 days. The significant increase in the carbonate content near to the set dispersion surface compared to that in the control SCS was found for the same time of the action. The set dispersion surface is the promoter of the carbonate phase crystallization possibly due to the numerous air-voids arrested in the set dispersion surface, acting as CO_2-giving supplies. These conclusions are valid under the experimental conditions used.

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