

Original papers

HYDRATION OF C_3A IN THE PRESENCE OF ADDITIVES REPLACING THE EFFECTS OF GYPSUM

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The communication presents the results of a complex study of the effects of additives replacing the functions of gypsum, on the hydration of aqueous suspensions of C_3A . The results were utilized to formulate a concept of the hydration of C_3A in the presence of an alkali carbonate and a sulphonated polyphenolate.

INTRODUCTION

Gypsum-free pastes of ground Portland cement clinker tend to harden very rapidly while generating considerable heat of hydration. This effect is eliminated by adding gypsum during the grinding of cement. It is generally acknowledged that the rapid set is due to the aluminate phase and that the gypsum addition retards hydration of C_3A . This retarding effect is caused by the formation of a layer of ettringite, $C_4A_3H_{32}$, on the surface of the clinker particles [1–3]. A number of authors [4, 5] were concerned with the effect of $CaSO_4$ on C_3A and described the basic reaction that allows Portland cement to be utilized on a vast scale.

At present, attention is paid to an inorganic cement based on ground cement clinker, but replacing the function of gypsum by other substances. In these so-called gypsum-free cements, whose properties were described e.g. in [6], gypsum has been replaced by a synergically acting mixture of an alkali metal compound and a sulphonated polyelectrolyte. The cements have the basic feature of being workable at a low water-to-cement ratio. This property gives rise to additional technological advantages, described e.g. in [7].

The present contribution had the aim to establish basic data on the effects of additives substituting the function of gypsum (in the given case Na_2CO_3 , Na_2SiO_3 , and sodium-ferric sulphonated polyphenolate, known under the trade name Kortan FM, or sodium lignosulphonate free of monosaccharides).

EXPERIMENTAL

The C_3A employed in the experiments was prepared synthetically from pure components, and its composition was checked by chemical and X-ray diffraction analyses. The C_3A contained 37.22% Al_2O_3 , 62.05% CaO , 0.67% SiO_2 , 0.05% Fe_2O_3 and

0.2% free CaO . X-ray analysis showed that it contained only traces of $C_{12}A_7$. The specific surface area of the powdered C_3A was about 320 m^2/kg . Before the experiments, the C_3A was ignited at 900°C. Use was further made of sodium-ferric sulphonated polyphenolate (Kortan FM, made by ZAZ Hrádek nad Nisou), sodium lignosulphonate free of monosaccharides (Natroplast, made by JIP Větrní). In addition of Na_2CO_3 , sodium silicate with a Na_2O/SiO_2 ratio of 1.02 was employed. Ground gypsum Harz (98% $CaSO_4 \cdot 2H_2O$) with a specific surface area of 350 m^2/kg was another chemical used.

The powdered C_3A was mixed with water to form suspensions (pastes). The water-to-cement ratio was chosen over the region of satisfactory paste workability in order to make the experimental conditions as close as possible to the water ratio currently used with gypsum-free cements (approx. 0.23–0.28 in the case of pastes).

In preparing the pastes, the additives replacing the function of gypsum were dissolved in the mix water. In a control experiment with C_3A and gypsum, the former was mixed with 5 wt. % of the latter shortly before preparing the paste. The course of hydration of the C_3A pastes over the given time intervals (15 minutes to 7 days) was always stopped by rinsing the paste sample with acetone and drying it for 3 hours in vacuo. The preparations were then kept in a desiccator over $NaOH$.

The samples from the individual time intervals were subjected to thermal analysis, X-ray diffraction analysis and the morphology of the products was studied under a scanning electron microscope.

Within the framework of the present study, the hydration products arising in aqueous suspensions of C_3A , $C_3A + 5\%$ gypsum, $C_3A + 1\%$ or 5% Na_2CO_3 , $C_3A + 0.4\%$ Kortan FM, $C_3A + 1\%$ $Na_2CO_3 + 0.4\%$ Kortan FM (an optimum for the working of gypsum-free cement pastes), $C_3A + 1\%$ $Na_2SiO_3 + 0.4\%$ Kor-

Table I

C₃A + 1% Na₂CO₃ + 0.4% Kortan FM, *w* = 0.30

Time	X-ray analysis	DTA	SEM
15 min	probab. C ₃ AH ₆	probab. C ₃ AH ₆	virtually no hydration products, only traces of cubic phases
60 min to 6 hrs	the same	the same	the same
24 hrs	C ₃ AH ₆	C ₃ AH ₆	hydration products in spots (not layer), both hexagonal and cubic phases present

Table II

C₃A + 0.4% Kortan FM, *w* = 0.50

Time	X-ray analysis	DTA	SEM
15 min	C ₃ AH ₆ , C ₂ AH ₈ , C ₄ AH _n diffused peak at 7.6–7.8 Å	C ₃ AH ₆ , C ₄ AH _n	hexagonal phase present, cubic phase less repres., traces of gel-like prod., surface of particles covered with hydration products
1 hr	C ₃ AH ₆	C ₃ AH ₆	cubic and hexagonal phase present, surface of particles covered with a layer of hydration products
2 to 24 hrs	the same	the same	the same

Table III

C₃A + 5% Na₂CO₃, *w* = 0.50

Time	X-ray analysis	DTA	SEM
15 min	C ₃ AH ₆ , traces of C ₄ AČH ₁₁ , C ₄ AH _n	C ₃ AH ₆	plate-shaped hexagonal products cover the entire surface of particles
3 days	C ₃ AH ₆ , C ₄ AH _n , C ₄ AČH ₁₁	C ₃ AH ₆ , C ₄ AH _n , C ₄ AČH ₁₁	the same up to 3 days

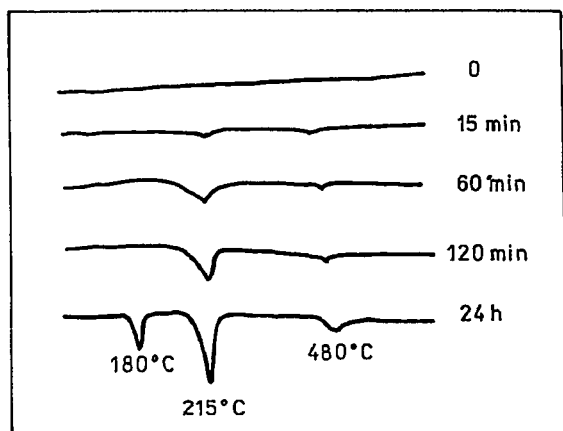


Fig. 2. DTA of products in the mixture $C_3A + 1\% Na_2CO_3 + 0.4\% Kortan FM + H_2O$.

tan FM, $C_3A + 1.3\% Na_2CO_3 + 0.5\% Natroplast$, were examined.

THE RESULTS AND THEIR DISCUSSION

The results obtained from thermal analysis, X-ray diffraction analysis and morphological examination of the products by SEM are listed in the tables for the individual variants of C_3A suspensions. It should be emphasized that the hydration of C_3A has so far been studied at substantially higher water ratios (0.7–10).

The results of a control experiment with hydration of C_3A without any additions at $w = 0.30$ showed, in agreement with the literature, that traces of hexagonal hydrates appeared only at the very beginning of hydration (5 min.). The hydration proceeds only to cubic C_3AH_6 , the hydration degree increasing in terms of time. Hydration of the mixture of $C_3A + 5\%$ gypsum at $w = 0.50$ was also examined. The data obtained are in agreement with published findings [1 through 5], in that formation of ettringite and its gradual conversion to $C_4A\bar{S}H_{12}$ was established. Morphological examination showed that ettringite was formed at the active points of C_3A on the onset of hydration (15 minutes) in the form of separate small crystals. After 1 to 2 hours of hydration, ettringite already covered the entire surface of the C_3A particles (Fig.1).

Table I and Fig. 2 give the results of examination of the system $C_3A + 1\% Na_2CO_3 + 0.4\% Kortan$ at $w = 0.30$. It should be noted that at this water ratio the paste showed a very satisfactory workability. The concentrations of the additives were chosen on the basis of their optimizing for gypsum-free cement pastes [20]. The study of this system shows that the hydration is stopped for a period of about 2 hours, or proceeds at a very low rate. The hydration is distinctly speeded up only after 24 hours.

No explicit and significant evidence of the formation and presence of sulphoaluminate hydrate analogs – carbonate-aluminate hydrates (namely $C_4A\bar{C}H_{11}$) was established. Moreover, during the initial stages, the surface of C_3A was virtually free of any layer of hydration products (cf. Figs. 3 and 4). In this respect, there is a considerable difference compared with the hydration of C_3A in the presence of gypsum, where the ettringite layer forms soon after the hydration has begun. In the subsequent stages of hydration, the system exhibits a suppression of the transition of hexagonal C_3AH_n to cubic C_3AH_6 , where the two products coexist (hydration products after 24 hours).

To shed some light on the problem, the hydration was studied on a partial system, namely in the suspension of $C_3A + 0.4\% Kortan$ at $w = 0.5$ (the higher water ratio was used owing to a poor workability of the paste). The results listed in Table II and plotted in Fig. 5 show that Kortan alone does not act as a retarding agent in C_3A suspensions. At the onset of hydration, there arise C_4AH_n as well as C_3AH_6 , and further on products of rather gel-like character corresponding to C_2AH_8 by their composition. After one

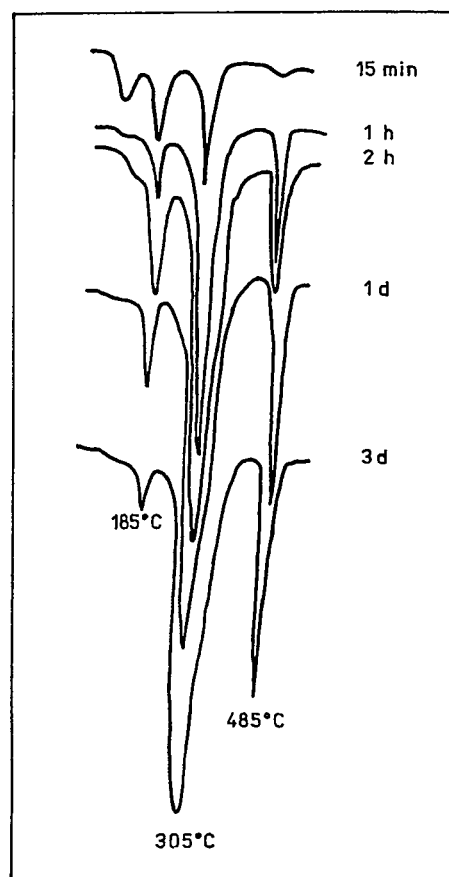


Fig. 5. DTA of hydration products in the mixture $C_3A + 0.4\% Kortan FM + H_2O$.

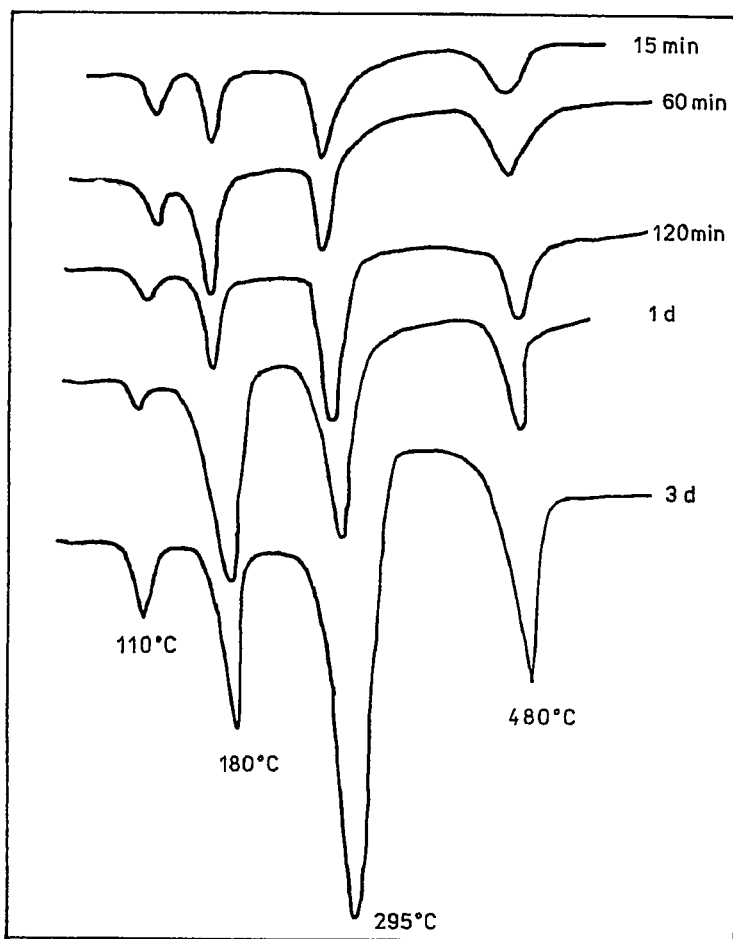


Fig. 7. DTA of hydration products in the mixture $C_3A + 5\% Na_2CO_3 + H_2O$.

Table IV

$C_3A + 1.3\% Na_2CO_3 + 0.9\% Natroplast, w = 0.30$

Time	X-ray analysis	DTA	SEM
15 min to 2 hrs	C_3AH_6	0	the surface of particles is virtually intact
24 hrs	C_4AH_n, C_3AH_6	C_4AH_n probably C_3AH_6	traces of hexagonal and cubic phases
3 days	C_3AH_6, C_4AH_n $C_4A\bar{C}H_{11}$	C_3AH_6, C_4AH_n	cubic and hexagonal phases numerous

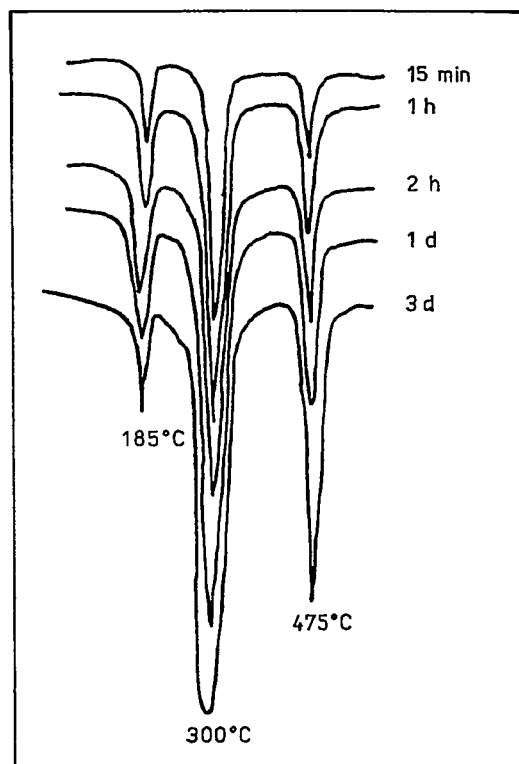


Fig. 6. DTA of hydration products in the mixture $C_3A + 1\% Na_2CO_3 + H_2O$.

hour of hydration, these gel-like products disappear and the hydration degree of C_3A further increases, hexagonal and cubic hydroaluminates co-existing side by side. The results imply that sulphonated polyphenolate does not act as an efficient retarder of the hydration of C_3A .

The results of study of another partial system, namely $C_3A + 1\% Na_2CO_3$ and $5\% Na_2CO_3$, are given in Table III and in Figs. 6 through 8, and indicate that Na_2CO_3 acts as an accelerator of the hydration of C_3A . The presence of carbonate-aluminate hydrates ($C_4A\bar{C}H_{11}$) was established only in the system with the higher Na_2CO_3 concentration (5%), namely in mixture with C_3AH_6 and C_4AH_n , as also found by the authors of [10].

Apart from the basic system using the combination of sulphonated polyphenolate with Na_2CO_3 , also other variants of possible substitutes for gypsum were examined. Table IV and Fig. 9 show the results obtained with the system $C_3A + 1.3\% Na_2CO_3 + 0.9\%$ Natroplast (the concentrations were again the optimized ones for gypsum-free cements). The system likewise performs as a powerful retarder of the hydration of C_3A . After two hours of hydration, virtually no hydration products could be identified; only after 24 hours of hydration, hexagonal C_4AH_n

and cubic C_3AH_6 were identified. After three days, there probably occurs the carbonate-aluminate hydrate $C_4A\bar{C}H_{11}$. Similarly to the system sulphonated polyphenolate + carbonate, the conversion of hexagonal hydroaluminate to the cubic one is blocked and both phases co-exist side by side.

The results for the system $C_3A + 1\% Na_2SiO_3 + 0.4\%$ Kortan FM are given in Table V and in Figs. 10 and 11. The substitution of carbonate by silicate

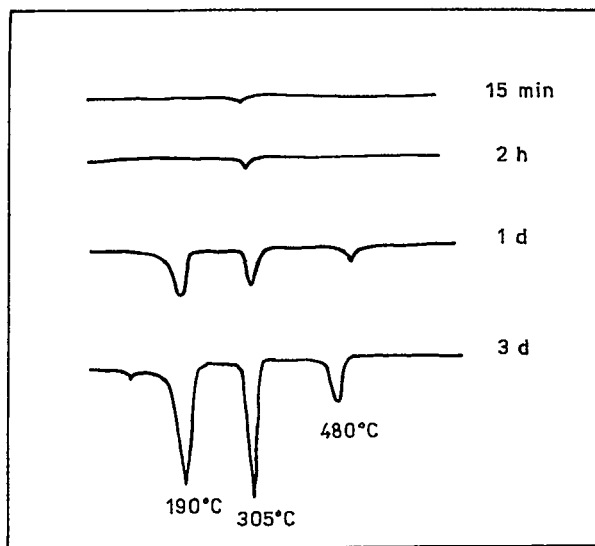


Fig. 9. DTA of products in the mixture $C_3A + 1.3\% Na_2CO_3 + 0.9\%$ sodium lignosulphonate.

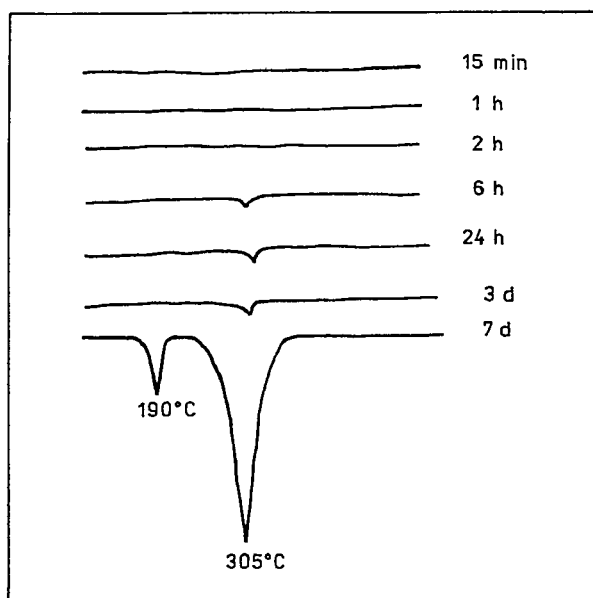


Fig. 10. DTA of products in the mixture $C_3A + 1\% Na_2SiO_3 + 0.4\%$ Kortan FM + H_2O .

Table V

C₃A + 1% Na₂SiO₃ + 0.4% Kortan FM, *w* = 0.30

Time	X-ray analysis	DTA	SEM
15 min	0	0	no traces of hydration products on surface
1 hr	C ₃ AH ₆ , prob. hydrogarnet.	C ₃ AH ₆	indications of cubic phases
7 days	C ₃ AH ₆ , prob. C ₄ A \bar{C} H ₁₁ , no hydrogarnet nor C ₄ AH ₄	C ₃ AH ₆	cubic phase, traces of hexagonal phase

resulted in a strong suppression of initial hydration, where major amounts of hydration products appeared only after 3 to 7 days. In this respect, the system is a still more efficient retarder of the hydration of C₃A than the carbonate + sulphonated polyphenolate one. At the onset of hydration, there appear traces of cubic hydroaluminat C₃AH₆ and hydrogarnet. After 3-7 days, the hydrogarnet disappears and the content of C₆AH₆ increases. Traces of C₄A \bar{C} H₁₁ appear in the course of later stages of hydration as a result of carbonatation. No hexagonal C₄AH_n was found in the products of hydration.

The experimental results obtained demonstrate that an explanation of the effects of the additives replacing gypsum is no simple matter. The retarding effect of the synergic system alkali compound (particularly carbonate) + sulphonated polyelectrolyte should be assessed from the standpoint of the effects of both components. It appears obvious that the separate effects of the additives do not retard the hydration of C₃A; significant retardation is brought about only in the presence of both components.

This conclusion is in agreement with findings described in the literature. Young [11], Chatterji [12] and other authors established repeatedly that the presence of lignosulphonate does not block the hydration of C₃A, and that rather the opposite is the case. Slowing down of the hydration and changes in the morphology of the hydration products of C₃A suspensions resulted from the presence of both gypsum and lignosulphonate.

The other component of the system (alkali carbonate) may form, on the surface of aluminates, compounds analogous to those arising on contact of water with Portland cement. These are analogs of sulphoaluminate complex compounds and carbonate-aluminate hydrates such as C₄A \bar{C} H₁₁. Formation of these compounds was described to result from reactions of C₃A with CaCO₃ or alkali carbonates at higher concentrations [8, 10, 13].

The presence of carbonate-aluminate compounds was not explicitly established in hardened pastes of gypsum-free cements, nor in suspensions of C₃A containing sulphonated polyphenolate or lignine sulphonate and Na₂CO₃, as also pointed out in [9, 14, 15]. However, existence of these compounds is assumed by Brunauer [16], Hanna and Taha [17].

Our results indicate that the delay in the onset of hydration of C₃A in the presence of sulphonated polyelectrolyte and alkali carbonate can be explained by the concept of adsorption of the sulphonated electrolyte on the surface of C₃A and/or on the products of its hydration. As shown by a number of other studies, adsorption of lignine sulphonate is most extensive on the products of hydration of clinker minerals, namely C₄AH_n or C-S-H [18, 19]. A layer of hydration products of submicron thickness may form on the surface of C₃A at the beginning of hydration (C₄AH_n pervaded with CaCO₃, or directly C₄A \bar{C} H₁₁) with a strongly adsorbed sulphonated electrolyte. However, we have not been able to prove the existence of this layer by the methods available.

The explanation of the delay of the onset of hydration by chemical reaction on the surface of C₃A is supported also by other experimental data. When the carbonate was replaced with silicate in the synergic system [1], the hydration products were found to contain hydrogarnets, which may also take part in the initial stages of hydration in retarding the beginning of hydration of C₃A. The possibility of formation of carbonate-aluminate complexes as a cause of retarding hydration is likewise supported by the results reported in [20] of studying the system ground clinker - lignosulphonate - NaOH where it was just the absence of carbonate which brought about a quick set.

Another possible variant of the explanation of the mechanism involved in retarding the set, is the effect of the solution of alkali carbonate + sulphonated electrolyte on the pH of the suspension. As shown

by our results [20], the mixtures act as a buffer over a comparatively wide concentration range, namely in the strongly alkaline region. It is possible that the solution of the substances affects the concentration of Ca²⁺ ions during hydration of the clinker minerals. In the suspensions of gypsum-free cements, a decrease of the content of Ca(OH)₂ was actually established at the beginning of hydration [9, 15].

The data obtained show that to explain fully the mechanism involved in retarding the hydration of C₃A or ground clinker in the absence of gypsum, further physicochemical study has to be made, aimed above all at the adsorption of surface-active substances on the surface of clay minerals or clinker particles, in particular in the presence of inorganic salts.

CONCLUSION

The complex study of the system C₃A + sulphonated electrolyte + alkali salt allowed the following conclusions to be formulated:

1. Sulphonated polyelectrolyte (lignosulphonate, sulphonated polyphenolate) + alkali carbonate or silicate act synergically as an agent retarding the beginning of hydration of C₃A suspensions. Sulphonated polyphenolate or alkali carbonate (silicate) alone do not function as retarders of C₃A hydration.
2. In the beginning of hydration of the system C₃A + lignosulphonate or sulphonated polyphenolate + Na₂CO₃, the presence of carbonate-aluminate hydrates (as analogs of sulphoaluminate hydrates in the reaction of C₃A with gypsum and water) was not safely established. During the first stages of hydration of this system, small amounts of cubic hydroaluminates are formed, and in the further stages co-exist with hexagonal hydroaluminates.
3. During hydration in the system C₃A + sulphonated polyphenolate + silicate, no hydroaluminates are formed in the initial stages which produce a hydrogarnet phase.
4. Delay of the onset of hydration of C₃A (and thus also hydration of gypsum-free cements) in the presence of a sulphonated polyelectrolyte and an alkali compound has not yet been explicitly explained. The retardation is probably not only due to the formation of a layer of hydrates on the surface of C₃A, and adsorption phenomena on the surface of particles should also be considered. One also cannot rule out formation of a thin layer of hydration products (hydroaluminates, C₄A·CH₁₁) which inhibits further hydration. Existence of such a layer could not yet be proved.

The present paper should be regarded as an introduction into the study of the complex mechanism

of the effects of additives replacing the functions of gypsum in suspensions of clinker minerals or ground clinker. The basic data obtained so far should be supplemented by those provided by other methods (e.g. ESCA, or examination of adsorption phenomena on the surface of clinker minerals) in the following stages of research.

Acknowledgement

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HYDRATACE C_3A ZA PŘÍTOMNOSTI PŘÍŠAD NAHRAZUJÍCÍCH PŮSOBENÍ SÁDROVCE

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V bezsádrovcových portlandských cementech je nahrazen sádrovec synergicky působící směsí alkalické sloučeniny (uhlíčitán, křemičitan) a sulfonovaného polyelektrolytu (ligninsulfonan, sulfonovaný polyfenolát). Komplexní studium (DTA, RTG, SEM) systému C_3A + sulfonovaný polyelektrolyt + alkalická sůl bylo zaměřeno na objasnění mechanismu retardace hydratace C_3A . Výsledky ukázaly, že roztoky sulfonovaného polyelektrolytu (ligninsulfonan, sulfonovaný polyfenolát) + alkalický uhlíčitán resp. křemičitan působí synergicky a silně oddalují počátek hydratace C_3A . Na počátku hydratace systému C_3A + ligninsulfonan, sulfonovaný polyfenolát + Na_2CO_3 nebyla jasně prokázána přítomnost karbonátoaluminátových hydrátů jako analogů sulfátoaluminátových produktů při reakci C_3A se sádrovcem. Na počátku hydratace tohoto systému vznikají v malé míře hexagonální hydroalumináty, které jsou v dalším období v koexistenci s hexagonálními hydroalumináty. Při hydrataci v systému C_3A + sulfonovaný polyfenolát + křemičitan sodný nedochází na počátku hydratace ke vzniku hydroaluminátů a vzniká hydrogranátová fáze.

Oddálení počátku hydratace C_3A (a tím hydratace bezsádrovcových cementů) není pravděpodobně dáno jedno-

značně vznikem hydrátů na povrchu C_3A , jak je tomu i v případě portlandských (sádrovcových) cementů. Nelze vyloučit vznik velmi tenké vrstvy hydratačních produktů (hydroaluminátů či $C_4A\dot{C}H_{11}$) na povrchu C_3A se silně adsorbovaným sulfonovaným polyelektrolytem, která zabraňuje další hydrataci C_3A . Existenci takové vrstvy se zatím nepodařilo prokázat.

Obr. 1. Hydratační produkty ve směsi C_3A + 5% sádrovce + H_2O , 2 hodiny hydratace.

Obr. 2. DTA produktů ve směsi C_3A + 1% Na_2CO_3 + 0.4% Kortan FM + H_2O .

Obr. 3. Hydratační produkty ve směsi C_3A + 1% Na_2CO_3 + 0.4% Kortan FM + H_2O , 1 hodina hydratace.

Obr. 4. Hydratační produkty ve směsi C_3A + 1% Na_2CO_3 + 0.4% Kortan FM + H_2O , 24 hodin hydratace.

Obr. 5. DTA produktů ve směsi C_3A + 0.4% Kortan FM + H_2O .

Obr. 6. DTA produktů ve směsi C_3A + 1% Na_2CO_3 + H_2O .

Obr. 7. DTA produktů ve směsi C_3A + 5% Na_2CO_3 + H_2O .

Obr. 8. Hydratační produkty ve směsi C_3A + 5% Na_2CO_3 + H_2O , 15 minut hydratace.

Obr. 9. DTA produktů ve směsi C_3A + 1.3% Na_2CO_3 + 0.9% ligninsulfonan sodný.

Obr. 10. DTA produktů ve směsi C_3A + 1% Na_2CO_3 + 0.4% Kortan FM + H_2O .

Obr. 11. Hydratační produkty ve směsi C_3A + 1% Na_2SiO_3 + 0.4% Kortan FM + H_2O , 24 hodin hydratace.

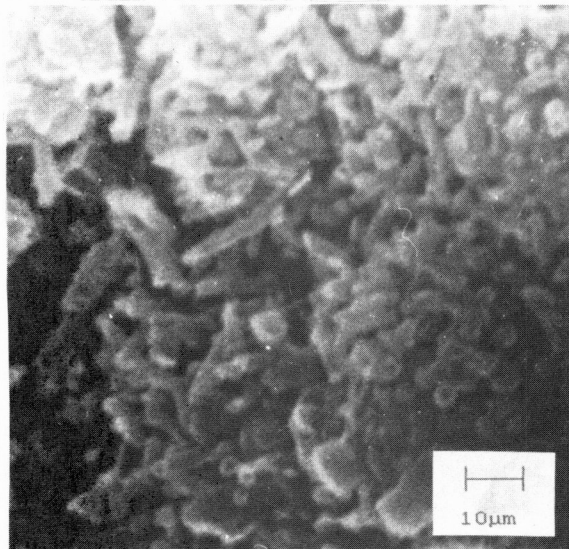


Fig. 1. Hydration products in the mixture C_3A + 5% gypsum + H_2O , 2 hours of hydration.

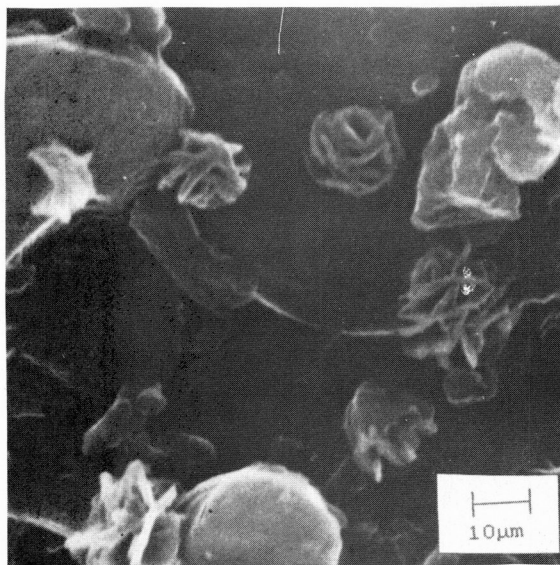


Fig. 3. Hydration products in the mixture C_3A + 1% Na_2CO_3 + 0.4% Kortan FM + H_2O , 1 hour of hydration.

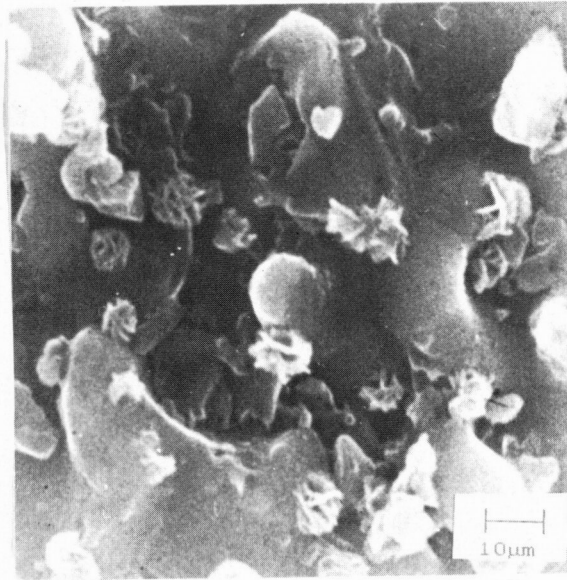


Fig. 4. Hydration products in the mixture $C_3A + 1\% Na_2CO_3 + 0.4\% Kortan FM + H_2O$, 24 hours of hydration.

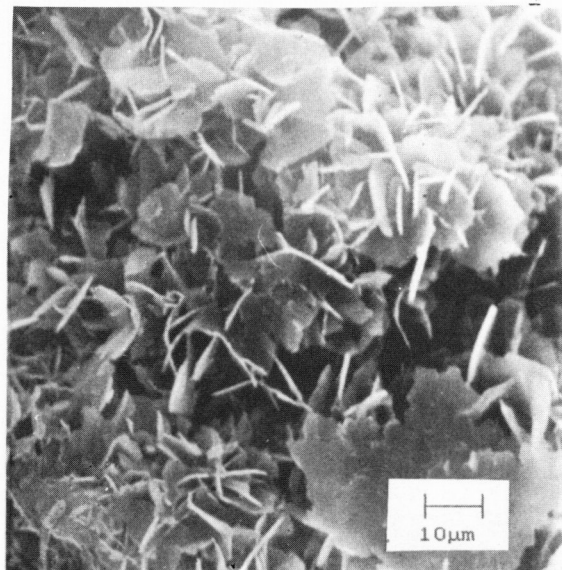


Fig. 8. Hydration products in the mixture $C_3A + 5\% Na_2CO_3 + H_2O$, 15 minutes of hydration.

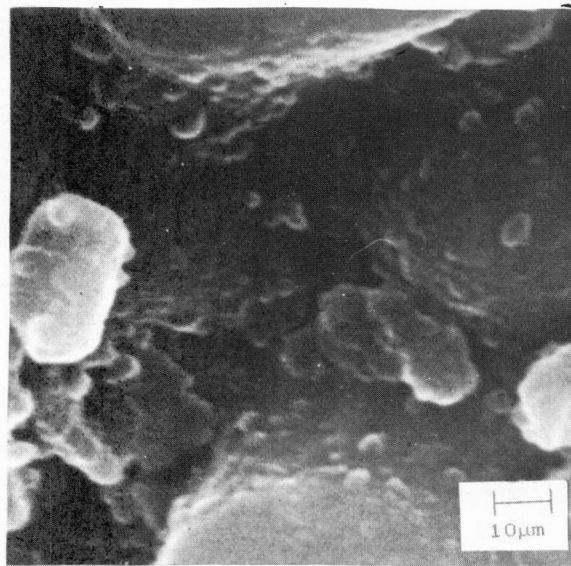


Fig. 11. Hydration products in the mixture $C_3A + 1\%$ $Na_2SiO_3 + 0.4\%$ Kortan FM + H_2O , 24 hours of hydration.