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IR SPECTROSCOPIC STUDY OF HYDRATION OF CONDENSED SILICA FUME — MODIFIED CEMENT PASTES

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Condensed silica fume, used as concrete and cement additive material, reacts with $Ca(OH)_2$ *liberated in the course of Portland cement hydration, forming supplementary calcium silicate hydrates. Infrared spectroscopy, X-ray diffraction, thermal analysis and scanning electron microscopy were used to study the kinetics of pozzolanic reaction in silica fume-modified cement pastes cured under normal conditions. A characteristic absorption band at* $1120\ cm^{-1}$ *was observed in the IR spectrum of silica fume, which was composed mainly of* SiO_2*.*

Infrared spectroscopy as the only of the methods tested enables to follow the role of silica fume in the process of Portland cement hydration not only through the binding of $Ca(OH)_2$*, but also directly, i.e. from the consumption of silica from added silica fume at some stage of the reaction. A high pozzolanic activity of silica fume from ferrosilicon production was proved by all the methods used.*

INTRODUCTION

The application of infrared (IR) spectroscopy in cement chemistry has increased in recent years. Previous studies [1—3] have shown that IR spectroscopy may be applied in both qualitative and quantitative investigations of clinker minerals as well as of cement composition. Moreover, in many cases IR spectroscopy serves as a useful supplementary method to other methods such as X-ray powder diffraction, thermal analysis, etc.

The fundamental properties of mineral additives like natural pozzolans, slags or fly ash, and their function in the process of Portland cement hydration, have been studied by several authors; a summary is given in [4]. According to Jambor [5, 6], pozzolans react with $Ca(OH)_2$ liberated in the process of Portland cement hydration, forming supplementary hydration products — calcium silicate hydrates. As hydration products differ one from each other in composition and binding properties, the type and pozzolanic activity of the mineral admixture influence markedly the fundamental physico-mechanical properties of hardened cement composites.

Condensed silica fume, a by-product of silicon and ferrosilicon production, is used world-wide as a highly effective pozzolanic admixture in concrete production [7—10]. Having a high silica content (> 90 %) and an extremely small diameter of individual particles (≈ 0.1 μm), silica fume undergoes rapid dissolution in the $Ca(OH)_2$ solution, reaching supersaturation with respect to a new phase in a few minutes. This results in formation of a dense, impermeable structure composed mainly of C—S—H, which has a low C/S ratio [11—13].

X-ray diffraction, thermal analysis and electron microscopy are frequently used to characterize the hydration products in cement pastes. Using these methods, the role of pozzolana in the process of Portland cement hydration can be studied by comparing the amounts of $Ca(OH)_2$ liberated during hydration in pure Portland cement paste with that bound by pozzolana in blended paste of the same water solid ratio [14].

The aim of this paper was to investigate the possibilities of IR spectroscopy in the study of the role of condensed silica fume in the process of Portland cement hydration, and to compare the IR results with the results of other methods.

EXPERIMENTAL

Ordinary Portland cement (OPC) of class PC 400 and condensed silica fume (CSF), a by-product from ferrosilicon production (Oravské ferozliatinárske závody Istebné, Czechoslovakia) were used for preparation of specimens — cubes 20 × ×20×20 mm. The chemical composition of the materials is given in Table I.

Table I
Chemical composition and fundamental physico-chemical properties of materials

Component		Ordinary Portland cement	Condensed silica fume
Chemical composition, wt %.			
SiO_2		19.58	95.57
Al_2O_3		7.58	0.11
Fe_2O_3		3.61	0.20
CaO		61.96	0.56
MgO		1.85	0.91
SO_3		2.13	0.32
Na_2O		0.28	0.12
K_2O		0.91	0.78
Ign. loss		1.01	1.36
Specific surface area, $m^2\ kg^{-1}$	Blaine	336	N
	BET	N	16 600

Mineralogical composition of the cement (Bogue)[3]:
$C_3S = 44.15\,\%$, $C_2S = 22.8\,\%$, $C_3A = 12.02\,\%$, $C_4AF = 11.31\,\%$

The composition of fresh mixtures is presented in Table II. A superplasticizer — sulphonated melamine formaldehyde condensate (0.95 % wt) was used in mixture No. 3 to obtain the same consistency of fresh cement paste as that of mixture No. 2, using a lower water solid ratio $w = 0.24$.

The hydration of pastes water-cured at 20 °C for 3, 28 and 180 days was stopped by drying the samples at 105 °C. The hydrated C_3S pastes were also investigated

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[3] The following symbols universally used for formulating more complex compounds are used in this paper: $C = CaO$, $S = SiO_2$, $A = Al_2O_3$, $F = Fe_2O_3$, $H = H_2O$.

Table II
The composition of fresh mixtures

Mixture	Ordinary Portland cement wt. %	Condensed silica fume wt. %	Water solid ratio w
No. 1	100	—	0.41
No. 2	85	15	0.41
No. 3	85	15	0.24

by IR spectroscopy. Hydration studies, except for electron microscopy, were performed on finely ground powder specimens of pastes.

Infrared absorption spectra were recorded by the Perkin-Elmer spectrophotometer (Model 983-G) in the range 4000 to 400 cm^{-1}, using the KBr pressed-disk technique. X-ray diffractometer Philips PW 1050 and JEOL JSM 35 scanning electron microscope were used for investigation of hydration products. The MOM Budapest thermal analysis system was used to obtain thermograms in the temperature range from room temperature to 1000 °C.

The amount of $Ca(OH)_2$ was determined from TG-curves as the sum of mass weight loss over the temperature range 510—530 °C (endotherm corresponding to dehydration of $Ca(OH)_2$) and beyond 800 °C (endotherm corresponding to decarbonation of $CaCO_3$). The amount of $Ca(OH)_2$ bound by silica fume was determined from the results of thermal analysis by the method which was applied earlier to investigate the influence of fineness and dosage of fly ash on hydration of blended cement pastes [14], using the ratio

$$\text{bound } Ca(OH)_2 = \frac{C_{OPC} \cdot p_{OPC} - C_{CSF}}{C_{OPC} \cdot p_{OPC}} \cdot 100$$

where C_{OPC} is the amount of $Ca(OH)_2$ in pure OPC paste, in % wt; p_{OPC} is the portion of OPC in the blend; C_{CSF} is the amount of $Ca(OH)_2$ in the paste with silica fume addition, in % wt.

RESULTS AND DISCUSSION

Infrared spectra of ordinary Portland cement and condensed silica fume used in the experiments, are shown in Fig. 1.

In the region examined, 4000 to 400 cm^{-1}, there are three types of IR absorption bands of cement to be considered [1, 2]:

i) bands arising from Si—O vibrations of alite at 920 and 520 cm^{-1};

ii) bands attributed to SO_4 stretching vibrations of gypsum at 1460 and 1115 cm^{-1};

iii) bands due to OH vibrations of water at 3437 and 1629 cm^{-1}.

In IR spectrum of silica fume, which is composed mainly of SiO_2 (see Table I), the bands assigned to Si—O vibrations of free SiO_4 at 1120, 800 and 477 cm^{-1} and also the bands of water at 3410 and 1620 cm^{-1} were identified.

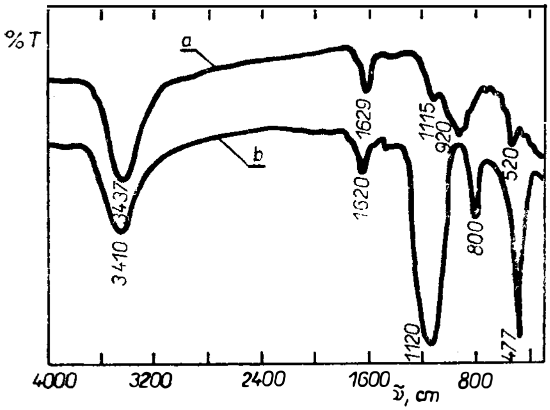

Fig. 1. IR spectra of materials used in the experiments; a) Portland cement, b) condensed silica fume.

IR spectra of pure OPC pastes

Infrared spectra of hydrated cement pastes are given in Fig. 2. The main differences between the IR spectra of hydrated OPC pastes and the IR spectrum of cement (Fig. 1) are as follows:

i) Si—O absorption band at 970 $\mathrm{cm^{-1}}$, due to calcium silicate hydrate;

ii) OH absorption band at 3638 $\mathrm{cm^{-1}}$ assigned to OH stretching vibrations of calcium hydroxide liberated during cement hydration;

iii) doublet at 1480 and 1420 $\mathrm{cm^{-1}}$, attributed to CO_3 vibrations in $CaCO_3$.

The intensity of absorption bands of hydration products ($Ca(OH)_2$, C—S—H) increase and those of the constituent mineral phases in Portland cement decrease

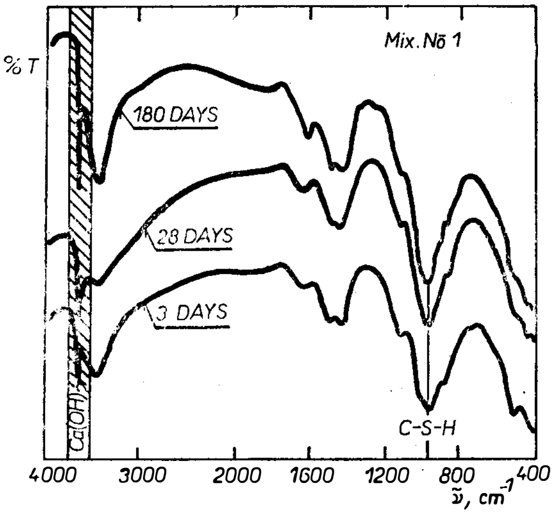

Fig. 2. IR spectra of pure OPC paste (w = 0.41).

when the stage of progressive hydration has passed (Fig. 2). IR absorption bands of the main hydration products observed in IR spectra of OPC pastes in Fig. 2 are similar to those of hydrated C_3S pastes (Fig. 3).

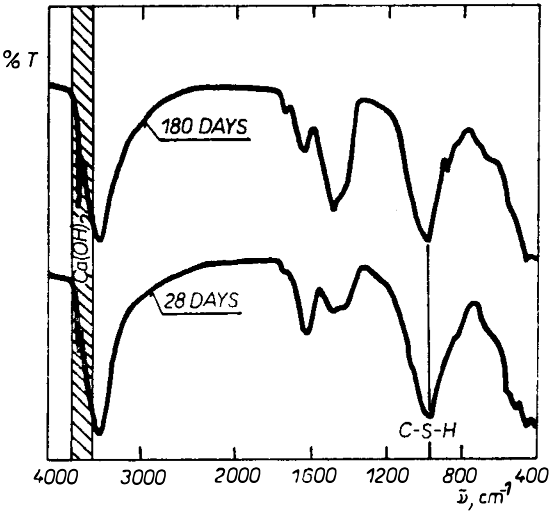

Fig. 3. IR spectra of hydrated C_3S.

IR spectra of blended pastes

IR spectra of blended pastes, i.e. the pastes with partial cement replacement by silica fume, are given in Figs. 4 and 5.

The main bands of hydration products, $Ca(OH)_2$ at 3638 cm^{-1} and C—S—H at 970 cm^{-1}, identified in IR spectra of blended pastes, are similar to those of OPC

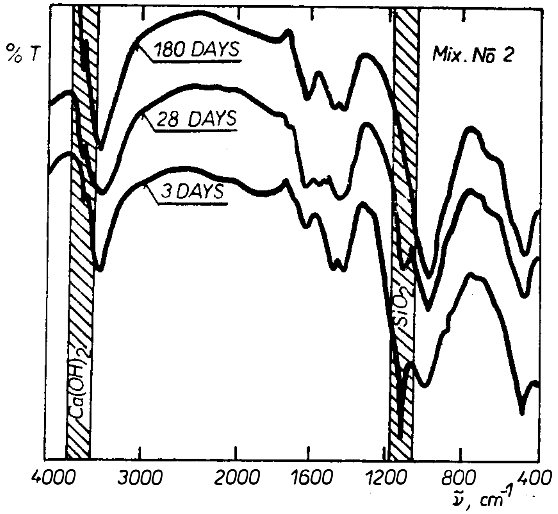

Fig. 4. IR spectra of cement paste with silica fume addition ($w = 0.41$).

pastes in Fig. 2. Lower amounts of $Ca(OH)_2$, especially in the paste with silica fume and superplasticizer, were found in IR spectra of silica fume-modified cement pastes in Figs. 4 and 5. Additionally, a strong decrease in intensity of the SiO_2 band at 1120 cm^{-1} was observed in blended pastes as hydration proceeded. Carbonates (absorption band at 1480 cm^{-1}), formed by carbonation of pastes by atmospheric carbon dioxide, appeared in the IR spectrum of paste with silica fume and superplasticizer (Fig. 5).

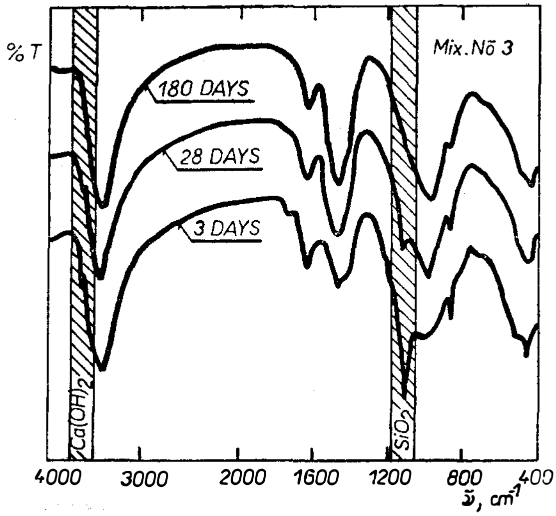

Fig. 5. IR spectra of cement paste with silica fume and superplasticizer (w = 0.24).

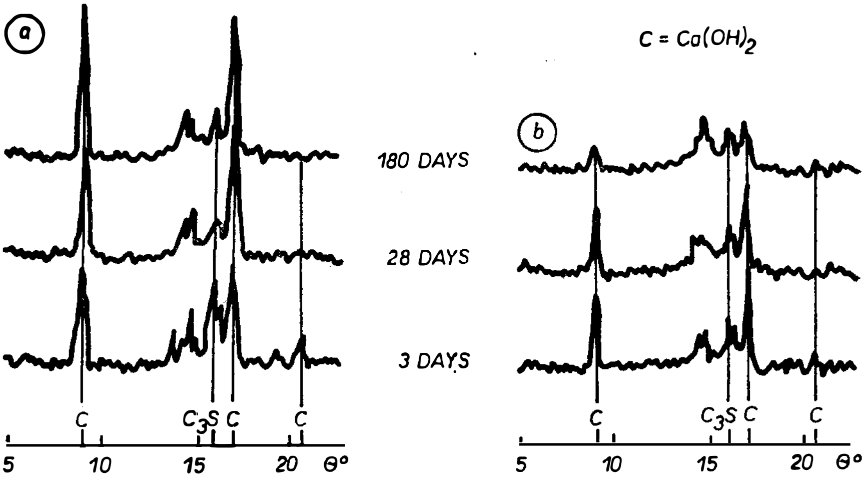

Fig. 6. The X-ray diffraction patterns of pastes; a) pure OPC paste, b) paste with silica fume addition (w = 0.41).

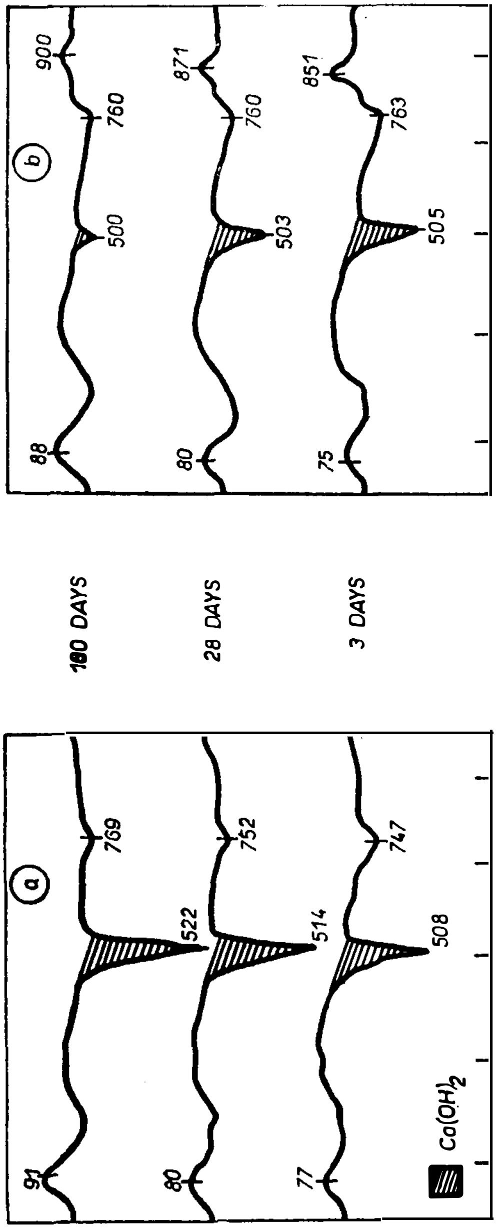

Fig. 7. Differential thermal analysis curves of pastes; a) pure OPC paste, b) paste with silica fume addition (w = 0.41).

The results of X-ray powder diffraction of the pastes are given in Fig. 6. Though a part of portlandite in the pastes may be formed in the amorphous state, from the intentensity of X-ray diffraction peak corresponding to $Ca(OH)_2$ one can distinguish a markedly lower amount of $Ca(OH)_2$ in pastes with silica fume addition (Fig. 6b) compared to pure OPC pastes at the same time of hydration (Fig. 6a).

The differences in the amounts of $Ca(OH)_2$ in pastes with and without silica fume addition are also evident from the DTA curves of pastes given in Fig. 7 and from the amounts of $Ca(OH)_2$ in the pastes and the amounts of $Ca(OH)_2$ bound by silica fume, which are given in Table III.

Table III

The amounts of $Ca(OH)_2$ in cement pastes

Composition of paste			Hydration time days	Amount of $Ca(OH)_2$ wt. %	Bound $Ca(OH)_2$ %
Portland cement wt. %	Condensed silica fume wt. %	Water solid ratio *w*			
100	—	0.41	3 28 180	16.5 20.8 22.7	—
85	15		3 28 180	9.9 8.4 6.8	29 52 65
100	—	0.24	3 28 180	8.9 12.3 14.7	—
85	15(+)		3 28 180	4.5 3.8 2.2	40 64 82

(+) with superplasticizer

The results of X-ray diffraction and thermal analysis are in good agreement with the character of hydration products observed in the pastes after 3 and 28 days of hydration (Figs 8, 9): portlandite was the dominant hydration product in the OPC paste, while lack of $Ca(OH)_2$ and densification of the structure composed mainly of C—S—H was characteristic of paste modified with silica fume.

Supplementary calcium silicate hydrates formed in the pores of the paste with silica fume addition were observed (Figs 8b, 9b).

The changes in $Ca(OH)_2$ content, identified by X-ray diffraction, thermal analysis and scanning electron microscopy, are in good agreement with the results obtained by IR spectroscopy (Figs. 2, 4, 5).

A remarkable increase in the amount of bound $Ca(OH)_2$, caused by better re-dispersion of CSF in the pastes is observed when condensed silica fume has been combined with superplasticizer (Figs, 4, 5, Table III).

In addition, comparing the changes in the intensity of the IR absorption band at 1120 cm^{-1}, IR spectroscopy enables the consumption of silica fume in the hydration process to be studied. The results obtained correlate well also with the changes of total porosity, pore-size distribution and altogether help to explain the differences in physicomechanical properties of cement pastes and mortars with and without silica fume addition [15, 16].

All the methods confirmed a high pozzolanic activity of condensed silica fume from ferrosilicon production which was used in the experiments.

CONCLUSIONS

The results of the present examination lead to the following conclusions:

- IR spectroscopy was found to be a useful tool for studying the changes in the changes in the formation of hydration products ($Ca(OH)_2$, C—S—H) of cement pastes cured at normal conditions. A good correlation was found when comparing the results of IR spectroscopic study of cement pastes with the results of X-ray powder diffraction, thermal analysis and scanning electron microscopy;
- a characteristic absorption band at 1 120 cmI^1 was observed in the IR spectrum of condensed silica fume, composed mainly of amorphous SiO_2. Infrared spectroscopy as the only method used in this study, enables to follow the role of condensed silica fume in the process of Portland cement hydration not only through the binding of $Ca(OH)_2$, but also directly from the consumption of SiO_2 at various stages of the reaction;
- a high pozzolanic activity of condensed silica fume was proved by all the methods used.

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SLEDOVANIE HYDRATÁCIE CEMENTOVÝCH KAŠÍ S PRÍMESOU KREMIČITÉHO ÚLETU METÓDOU IČ-SPEKTROSKOPIE

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Kremičitý úlet, používaný ako aktívna puzolánová prímes do betónu, ovplyvňuje proces hydratácie cementu a vytváranie fázového zloženia zatvrdnutej cementovej kaše. K sledovaniu vplyvu kremičitého úletu z výroby ferosilícia na proces hydratácie cementu bola popri bežne používaných metódach rtg-fázovej difrakčnej analýzy, vážkovej termickej analýzy a riadkovacej elektrónovej mikroskópie použitá takisto infračervená spektroskopia. Kremičitý úlet, ktorého hlavnou zložkou je oxid kremičitý prítomný v amorfnom stave, vykazuje v oblasti vlnočtov od 4000 do 400 cm^{-1} v IČ-spektre intenzívny absorpčný pás pri vlnočte 1120 cm^{-1}. To umožňuje sledovať zmeny vo vytváraní fázového zloženia zmesných cementových kaší nielen podľa zmien v obsahu $Ca(OH)_2$, podobne ako pri vyššie uvedených metódach výskumu, ale takisto priamym sledovaním, založeným na zisťovaní zmien spotrebovaného SiO_2 v priebehu reakcie.

Výsledky sledovania priebehu hydratácie cementu za prítomnosti kremičitého úletu sú v dobrej zhode s výsledkami vyššie uvedených experimentálnych metód a prispievajú k bližšiemu posúdeniu zmien vo vytváraní fázového zloženia a s tým súvisiacimi zmenami v tvorbe pórovej štruktúry a výsledných fyzikálno-mechanických vlastností cementových kompozitov. Všetky použité metódy výskumu potvrdili poznatky o vysokej puzolánovej aktivite kremičitého úletu z výroby ferosilícia.

Obr. 1. IČ spektrá použitých materiálov; a) portlandský cement, b) kremičitý úlet.

Obr. 2. IČ spektrá cementovej kaše bez prímesi kremičitého úletu (w = 0,41).

Obr. 3. IČ spektrá hydratovaného C_3S.

Obr. 4. IČ spektrá cementovej kaše s prímesou kremičitého úletu (w = 0,41).

Obr. 5. IČ spektrá cementovej kaše s prímesou kremičitého úletu a superplastifikátorom (w = 0,24).

Obr. 6. Difraktogramy cementových kaší; a) bez prímesi, b) s prímesou kremičitého úletu (w = 0,41).

Obr. 7. Diferenčné termogramy cementových kaší; a) bez prímesi, b) s prímesou kremičitého úletu (w = 0,41).

Obr. 8. Snímky lomovej plochy cementových kaší po 3 dňoch tvrdnutia vo vode riadkovacím elektrónovým mikroskopom; a) kaša bez prímesi, b) kaša s prímesou kremičitého úletu (w = 0,41).

Obr. 9. Snímky lomovej plochy cementových kaší po 28 dňoch tvrdnutia vo vode riadkovacím elektrónovým mikroskopom; a) kaša bez prímesi, b) kaša s prímesou kremičitého úletu (w = 0,41).

ИССЛЕДОВАНИЕ ГИДРАТАЦИИ ЦЕМЕНТНЫХ ТЕСТ С ДОБАВКОЙ СИЛИКАТНОГО УНОСА С ПОМОЩЬЮ МЕТОДА ИК-СПЕКТРОСКОПИИ

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Силикатный унос, используемый в качестве активной пузолановой добавки в бетон, оказывает влияние на процесс гидратации цемента и на образование фазового состава застывающего цементного теста. Для исследования влияния силикатного уноса из производства ферросилиция на процесс гидратации цемента пользовались кроме обычно применяемых методов ртг-фазового дифракционного анализа, весового термического анализа и сканирующей электронной микроскопии также инфракрасной спектроскопией. Силикатный унос, основным компонентом которого является оксид четырехвалентного кремния, находящийся в аморфном состоянии, выделяется в области волнового числа в пределях от 4000 до 400 $см^{-1}$ в инфракрасном спектре интенсивной абсорбционной полосой при волновом числе 1120 $см^{-1}$. Таким образом можно исследовать изменения в образовании фазового состава смешанных цементных тест не только на основании изменения содержания $Ca(OH)_2$, как это было при сверх приводимых методах исследования, но и на основании прямого исследования, основывающегося на установлении изменений расходовавшегося SiO_2 во время хода реакции.

Результаты исследования хода гидратации цемента в присутствии силикатного уноса находятся в хорошем согласии с результатами приводимых экспериментальных методов и помагают более подробному исследованию изменений в образовании фазового состава и связанных с ним изменений в образования пористой структуры и окончательных физико-механических свойств цементных композитов. Все используемые методы исследования подтвердили полученные данные относительно высокой пузолановой активности силикатного уноса из производства ферросилиция.

Рис. 1. ИК спектры используемых материалов: a) портландский цемент, b) силикатный унос.

Рис. 2. ИК спектры цементного теста без добавки силикатного уноса (w = 0,41).

Рис. 3. ИК спектры гидратированного C_3S.

Рис. 4. ИК спектры цементного теста с добавкой силикатного уноса (w = 0,41).

Рис. 5. ИК спектры цементного теста с добавкой силикатного уноса и суперпластификатором (w = 0,24).

Рис. 6. Дифракционная картина цементных тест: a) без добавки, b) с добавкой силикатного уноса (w = 0,41).

Рис. 7. Разностные термограммы цементных тест; a) без добавки, b) с добавкой силикатного уноса (w = 0,41).

Рис. 8. Съемки поверхности излома цементных тест после 3 суток застывания в воду, полученные посредством сканирующего электронного микроскопа; a) тесто без добавки, b) тесто с добавкой силикатного унюса (w = 0,41).

Рис. 9. Съемки поверхности излома цементных тест после 28 суток застывания в воду, полученные посредством сканирующего электронного микроскопа; a) тесто без добавки, b) тесто с добавкой силикатного уноса (w = 0,41).

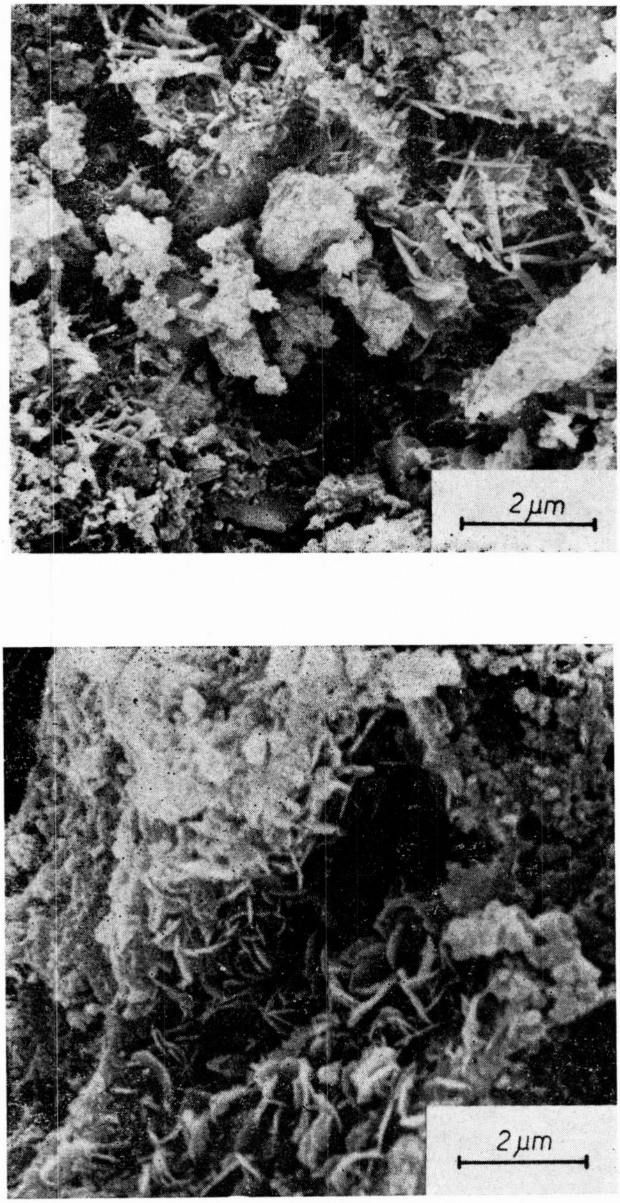

Fig. 8. SE micrographs of pastes after 3 days of hydration; a) pure OPC paste, b) paste with silica fume addition ($w = 0.41$).

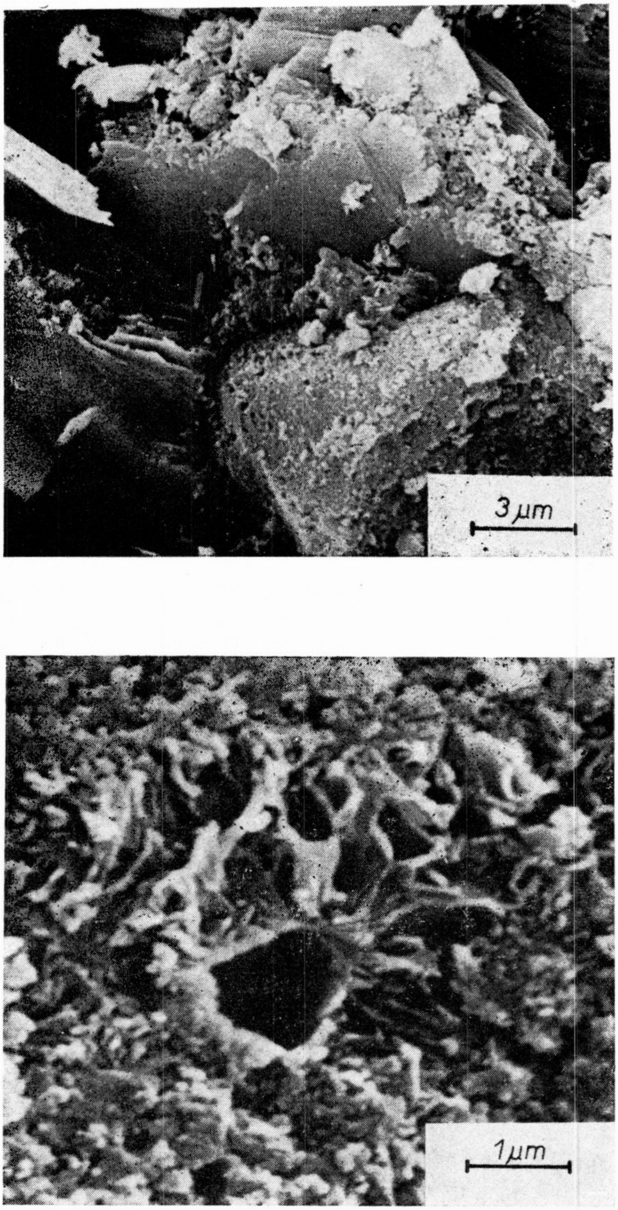

Fig. 9. SE micrographs of pastes after 28 days of hydration; *a) pure OPC paste, b) paste with silica fume addition ($w = 0.41$).*