

Původní práce

A STUDY OF THE EFFECT OF pH ON THE FORMATION OF CALCIUM HYDROSILICATE COMPONENTS UNDER HYDROTHERMAL CONDITIONS

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The calcium hydrosilicates of the tobermoritic group were prepared by hydrothermal treatment of a mixture of CaO with β -quartz in a aqueous suspension. The crystallization degree of the reaction product was positively affected by addition of SO_4^{2-} and Al^{3+} ions. The pH was adjusted by addition of alkalis and the relationship between pH and the crystallization degree of the calcium hydrosilicate component was determined. Alkalis have been proved to have a negative effect on the formation of crystallically developed phases of the tobermoritic group.

INTRODUCTION

The technology of manufacture of high-pressure cured lime-silicate building materials has till recently been lacking sound foundations of basic research which are indispensable for explaining and preventing the occurrence of anomalous phenomena in technological practice. The present work had the main purpose to investigate closely the effect of alkali sulphates on the formation of the main binding component, 11 Å-tobermorite, in the course of hydrothermal treatment.

Only limited and sporadic data have appeared in literature with respect to the effect of pH on the formation of the main components of the tobermoritic group. When Na_2SO_4 is used as an addition to the mixture of $\text{Ca}(\text{OH})_2$ with β -quartz, it is possible that not only pH but also SO_4^{2-} ions may, under certain conditions, accelerate the transformation of crystallically imperfect hydrosilicate phases to 11 Å-tobermorite [1], [2]. The SO_4^{2-} ions may further be substituted into the phases of the system in question. Whereas substitution of Al^{3+} ions in the lattice of 11 Å-tobermorite has already been well understood [3], [4], [5], it is not the case of the SO_4^{2-} ions. Kalousek [6] and Benton and Kalousek [7] have found that the structure of imperfectly crystallized tobermorite can contain more than 5% SO_3 . According to Diamond [8], SO_4^{2-} ions may also be substituted into the lattice of 11 Å-tobermorite. Šauman and Valtr [9] have proved that the structure of 11 Å-tobermorite can bind at the most 0.5% of SO_4^{2-} ions.

EXPERIMENTAL

The model mixtures were prepared from high-purity Illinois (USA) sand containing 99.73 % SiO_2 , ground in an agate device to pass through sieve No. 230 ASTM; its specific surface corresponded to $3.500 \text{ cm}^2 \text{ g}^{-1}$ (Blaine). The material was characterized as pure β -quartz (low) by X-ray analysis. The other initial components, CaO, was prepared from CaCO_3 A.R. (Merck) by annealing at 1050°C for 4 hours, by grinding in an agate device to pass through No. 230 sieve. All the other reagents were of A.R. purity.

The model suspensions were subjected to hydrothermal treatment in high-pressure cylinders of 45 ml capacity. The vessels containing 30 ml of suspension composed of 1 part solid to 10 parts liquid phase were revolved at a uniform speed of 60 r.p.m. throughout the hydrothermal cycle inside an electric hot-air thermostat. The charge also contained 10 platinum rings made of dia. 1 mm wire.

The pH was measured with type PHM 26 pH-meter by Radiometer, Copenhagen. The instrument was provided with G 202 B and K 401 electrodes from the same manufacturer. The calibration was carried out by means of two buffer solutions, namely S 1001 by Radiometer — pH 6.50 ± 0.02 at 20°C , and with 0.01 M sodium tetraborate — pH 9.225 at 20°C , from the scale of standard buffer solutions of the National Bureau of Standards.

The pH of the reaction mixtures were measured directly in the cylinders, which simultaneously ensured efficient shielding of the electrodes. The specimens being measured were tempered in a water thermostat at 20°C . The solid phase of the suspensions was then dried in flowing N_2 at 105°C for 8 hours and subjected to further analyses.

The microstructural analysis of all the specimens obtained was carried out by the usual methods (X-ray diffractograph by Phillips). On selected samples, the morphology of the binding phases was studied by a Stereoscan 2A scanning electron microscope (Cambridge Scientific Instruments).

THE RESULTS AND DISCUSSION

The effect of the K^+ and Na^+ alkali ions on the formation of the main binding phases C—S—H gel and 11 Å-tobermorite in the course of hydrothermal treatment of lime-silica mixtures was studied on model suspensions at 175°C using isothermal heating for 5 hours. The solid phase composition was chosen as follows: 80 % wt. quartz + 20 wt. % CaO, which corresponds to the initial molar ratio $\text{CaO}/\text{SiO}_2 = 0.268$. The reaction thus proceeded in a system with a considerable excess of SiO_2 , which, however, corresponds to the composition of technologically processed raw-material mixtures in the production of building materials, where the quartz sand is also a filler. The liquid phase was reboiled distilled water or the same volume of a solution of the respective admixture.

In the case of the plain mixture of quartz with lime, hydrothermal treatment for 5 hours at 175°C does not yield crystalline 11 Å-tobermorite, and the suspension after hydration has pH = 10.50. On gradually adding $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$, the pH value decreases, after an addition of more than 0.5 % $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$ falling below 9.80; this is the point where 11 Å-tobermorite well detectable by X-ray analysis is formed. The values measured are listed in Table I and the X-ray diffraction patterns are shown in Fig. 1.

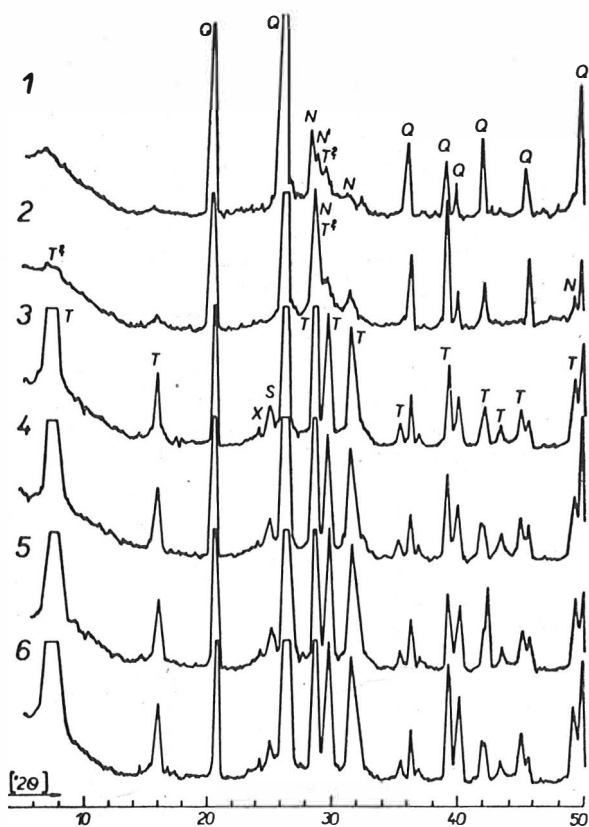


Fig. 1. X-ray diffraction patterns of suspensions containing quartz, CaO and gypsum, 5 hrs/175 °C (Nos. 1-6, Table I); Symbols used: N — “imperfectly crystalline tobermorite”, N' — C—S—H gel, P — CaSO₄ · 1/2H₂O, Q — β-quartz (low), S — CaSO₄ III, T — 11 Å tobermorite, X — xonotlite,

Table I

Suspension of quartz + CaO with an addition of CaSO₄ · 2H₂O, 5 hrs at 175 °C

Mix No.	Quartz (g)	CaO (g)	CaSO ₄ · 2H ₂ O		pH	11 Å — tobermorite
			(mg)	(%)		
1	2.4	0.6	0	0	10.47	—
2	2.4	0.6	15	0.5	10.28	—
3	2.4	0.6	24	0.8	9.76	+
4	2.4	0.6	36	1.2	9.63	+
5	2.4	0.6	48	1.6	9.58	+
6	2.4	0.6	60	2.0	9.53	+

The pattern of mixture [1] exhibits a diffuse reflection at 3.00–3.09 Å, which characterizes the C–S–H gel phase, as well as diffusion lines at about 2.83 Å. In the diffractogram of mix [2] the diffusion character of the lines at 3.08, 2.98 and 2.83 Å is becoming fainter, which indicates to gradual transformation into a more perfectly crystallized phase: C–S–H gel → “imperfectly crystalline tobermorite” → 11 Å-tobermorite. In the diffraction pattern of mix [3] there are all tabellated diffraction lines of 11 Å-tobermorite. The X-ray diffraction patterns of the other three mixes are in principle identical with pattern [3].

The gradual crystallization development of 11 Å-tobermorite can also be observed on the scanning electron micrographs. The study was concerned with specimens of three hydrothermally treated mixtures, the composition of which is listed under the numerals [1], [2] and [3] in Table I.

The morphology of the quartz-lime mixture after high-pressure curing is illustrated by Fig. 2, showing well discernible quartz grains the surface of which is coated with a gel layer. When 0.5 % CaSO₄ · 2H₂O was added (Figs. 3 and 4), the surface of quartz grains is still more disturbed and in the gel layer there begin to appear islets of leafy

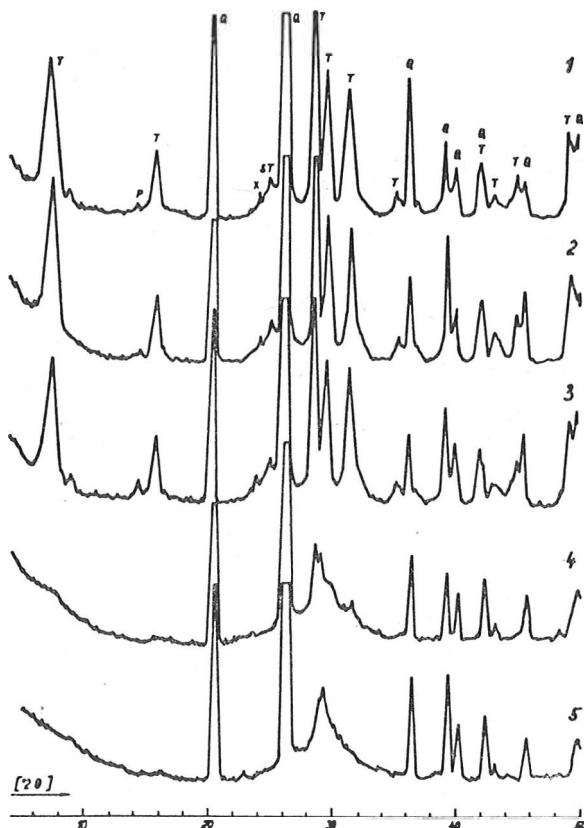


Fig. 6. X-ray diffraction patterns of suspensions containing quartz, CaO and Al₂(SO₄)₃ with an addition of NaOH, 5 hrs/175 °C (Nos. 1–5 Table I). For the list of symbols, refer to Fig. 1.

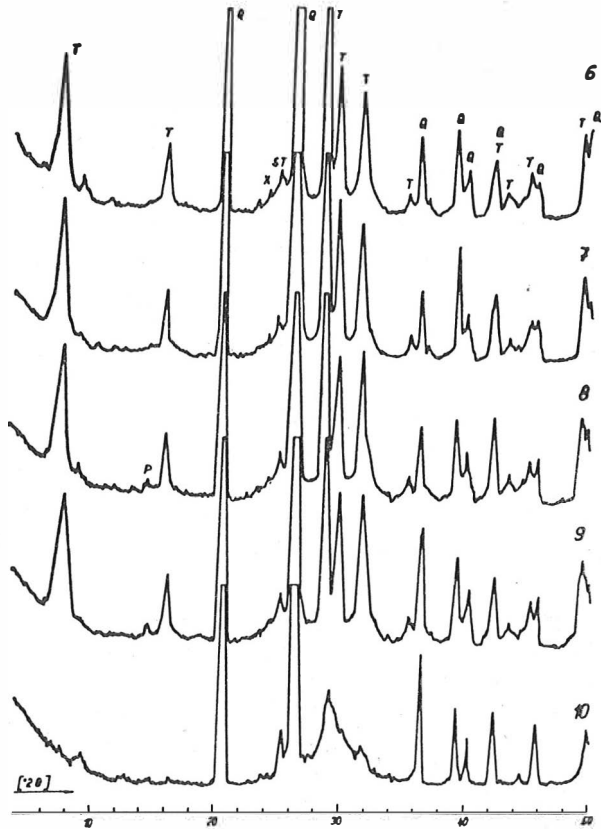


Fig. 7. X-ray diffraction patterns of suspensions containing quartz, CaO and $\text{Al}_2(\text{SO}_4)_3$ with the addition of Na_2SO_4 , 5 hrs/175 °C (Nos. 6—10. Table II). For the list of symbols, refer to Fig. 1.

formations characterizing 11 Å-tobermorite. On the next micrograph (Fig. 5) of a specimen of hydrated quartz-lime suspension containing 0.8% $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, one can observe the typical leaf or plate-shaped crystals of 11 Å-tobermorite covering the surface of all the quartz grains.

An analogous situation was observed with suspensions of quartz-lime- $\text{Al}_2(\text{SO}_4)_3$ mixtures after adding stepped up amounts of NaOH and Na_2SO_4 . The results of the measurements are listed in Table II. The X-ray patterns of the two series are shown in Figs. 6 and 7. Aluminium sulphate was added to the basic quartz-lime mixture because the Al^{3+} ions very strongly promote formation of 11 Å-tobermorite. However, as indicated by the further measurements, a high content of alkalis in the reaction system may paralyse even this very positive effect.

Mixtures [1] to [3] exhibit very intensive lines corresponding to 11 Å-tobermorite. The diffraction patterns [4] and [5] show a somewhat diffuse character of the line 3.04 Å, characterizing the C—S—H gel phase; the diffraction at 11.3 Å is no more discernible. The X-ray diffraction patterns of mixtures [6] to [9] are essentially identical, showing a very strong diffraction of 11 Å-tobermorite, whereas the pattern

Table II

Suspension of quartz with CaO and $\text{Al}_2(\text{SO}_4)_3$ with an addition of NaOH, Na_2SO_4 — 5 hrs/175 °C

Mix No.	Quartz (g)	CaO (g)	$\text{Al}_2(\text{SO}_4)_3$ (mmole)	NaX* (mmole)	pH	11 Å — tobermorite
1	2.4	0.6	0.125	0	9.26	+
2	2.4	0.6	0.125	0.25	9.32	+
3	2.4	0.6	0.125	0.375	9.39	+
4	2.4	0.6	0.125	0.75	10.64	—
5	2.4	0.6	0.125	1.5	11.14	—
6	2.4	0.6	0.125	0	9.33	+
7	2.4	0.6	0.125	0.125	9.32	+
8	2.4	0.6	0.125	0.187	9.33	+
9	2.4	0.6	0.125	0.375	9.46	+
10	2.4	0.6	0.125	0.75	10.29	—

*) NaX = NaOH (1—5); = Na_2SO_4 (6—10)

of mixture [10] is already characterized by a very diffuse reflection at 3.04 Å, corresponding to C—S—H gel, and by a low-intensity diffraction at 2.82 Å, while the basal reflection of tobermorite at 11.3 Å is missing.

The Table II indicates that when the pH of suspension after concluded hydrothermal treatment exceeds the value $\text{pH} = 10$, 11 Å-tobermorite cannot be safely proved in the reaction mixture. This finding provided the reason for controlling the pH with a buffer solution.

Adjustment of pH with a buffer solution introduced before the reaction would obviously be impossible owing to the reactions between the buffer and calcium hydroxide, although the buffer alone would not be changed by the hydrothermal conditions.

The possibility was further considered of transforming the already formed C—S—H gel to crystalline 11 Å-tobermorite by a new hydrothermal reaction in a medium having a pH value favourable for its formation. However, no crystalline phase was created, even though the pH after the new hydrothermal reaction had the desirable value. This passivity of the C—S—H gel cannot be influenced by additional introduction of gypsum, nor by a new hydrothermal reaction, in spite of the fact that the pH value has again decreased.

CONCLUSION

Hydrothermal treatment of the mixture consisting of 80 parts quartz and 20 parts CaO at 175 °C for 5 hours in aqueous suspension and in a medium having pH 10.5 yielded a component of essentially gel-type character (C—S—H gel) exhibiting diffraction at 3.04 Å or other phases, which have been called "imperfectly crystalline tobermorite", showing the characteristic diffraction line at 3.08 Å. Stepped-up additions of SO_4^{2-} or Al^{3+} ions to the basic mixture resulted in a gradual increase

of the crystallization degree of the final hydrosilicate phase, and after concluded hydrothermal treatment the pH of the medium was about 9.8 or lower, which is favourable for the formation of 11 Å-tobermorite. The morphology of the transformation of gel-type components into a perfectly crystalline phase has been explicitly proved by scanning electron micrographs.

The raising of pH of the reaction medium by alkalies has strongly paralyzed the positive effect of sulphate and aluminium ions, and no crystalline components of the tobermoritic group were formed in the medium having pH 10.3 and higher.

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STUDIUM VLIVU pH PROSTŘEDÍ NA VZNIK VÁPENATÝCH HYDROSILIKÁTOVÝCH SLOŽEK ZA HYDROTERMÁLNÍCH PODMÍNEK

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Hydrotermálním zpracováním směsi sestávající z 80 d. křemene + 20 d. CaO při 175 °C po dobu 5 h v podobě vodné suspenze byla v prostředí o hodnotě pH 10,5 získána složka v podstatě gelovitého charakteru (C—S—H gel), vykazující difrakci ~ 3,04 Å nebo další fáze, kterou jsme označili „nedokonale krystalický tobermorit“ s charakteristickou difrakční linií ~ 3,08 Å. Při odstupňovaném přidavku SO₄²⁻ nebo Al³⁺-iontů k základní směsi bylo zjištěno postupné zvyšování stupně krystalizace vzniklé hydrosilikátové fáze a prostředí po ukončené hydrotermální reakci vykazovalo hodnotu pH ~ 9,8 resp. nižší, vhodné ke vzniku 11 Å-tobermoritu. Morfologie přechodu gelovitých složek na dokonale krystalickou fázi byla názorně prokázána snímky z elektronového rastrovacího mikroskopu.

Zvýšením pH reakčního prostředí alkáliemi byl silně paralyzován pozitivní vliv síranových a hlinitých iontů a v prostředí o hodnotě pH 10,3 a vyšší nevznikly krystalické složky tobermoritické skupiny.

Obr. 1. Rentgenové difrakční záznamy suspenzí křemene s CaO a sádrovcem, 5 h/175 °C (č. 1—6 tab. I). Užití symboly: N — „nedokonale krystalický tobermorit“; N' — C—S—H gel; P — CaSO₄ · 1/2 H₂O; Q — β-křemen (nízký); S — CaSO₄III; T — 11 Å-tobermorit; X — wonolít

Obr. 2. Stereoelektronogram suspenze křemen + CaO, 5 h/175 °C.

Obr. 3. Stereoelektronogram suspenze křemen + CaO + 0,5% CaSO₄ · 2 H₂O, 5 h/175 °C.

Obr. 4. Stereoelektronogram suspenze křemen + CaO + 0,5% CaSO₄ · 2 H₂O, 5 h/175 °C.

Obr. 5. Stereoelektronogram suspenze křemen + CaO + 0,8% CaSO₄ · 2 H₂O, 5 h/175 °C.

Obr. 6. Rentgenové difrakční záznamy suspenzí křemene s CaO + Al₂(SO₄)₃ s přidávkem NaOH, 5 h/175 °C (č. 1—5 tab. II). Užití symboly viz obr. 1.

Obr. 7. Rentgenové difrakční záznamy suspenzí křemene s CaO + Al₂(SO₄)₃ s přidávkem Na₂SO₄, 5 h/175 °C č. 6—10 tab. II). Užití symboly viz obr. 1.

ИЗУЧЕНИЕ ВЛИЯНИЯ pH СРЕДЫ НА ОБРАЗОВАНИЕ
СОСТАВЛЯЮЩИХ КАЛЬЦИЙГИДРОСИЛИКАТОВ
В ГИДРОТЕРМАЛЬНЫХ УСЛОВИЯХ

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При помощи гидротермальной обработки смеси, состоящей из 80 частей кварца + 20 частей CaO при 175 °C в течение 5 часов в виде водной суспензии была в среде величины pH 10,5 получена составляющая в сущности гелеобразного характера (С—S—H гель) показывающая дифракцию ~ 3,04 Å или другая фаза, которая была нами обозначена „несовершенный кристаллический тоберморит“ с характеристической линией дифракции ~ 3,08 Å.

При ступенчатом добавлении SO_4^{2-} или Al^{3+} -ионов к основной смеси было определено постепенное повышение степени кристаллизации образовавшейся фазы гидросиликата и среда после законченной гидротермальной реакции показывала величину pH ~ 9,8 или ниже, удобную для образования 11 Å — тоберморита. Морфология перехода гелеобразных составляющих в совершенно кристаллическую фазу была наглядно обоснована при помощи снимков из электронного сканирующего микроскопа. Повышением pH реакционной среды при помощи щелочей было сильно подавлено положительное влияние сульфатных и глинистых ионов; в среде величины pH 10,3 и выше не были образованы кристаллические составляющие тоберморитической группы.

Рис. 1. Рентгеновские дифракционные записи взвесей кварца с CaO и гипсом, 5 ч/175 °C (№ 1—6 табл. I); N — несовершенно кристаллический тоберморит, N' — С—S—H гель, P — $CaSO_4 \cdot 1/2 H_2O$, Q — β -кварц (низкий), S — $CaSO_4$ III, T — 11 Å-тоберморит, X — ксонолит.

Рис. 2. Стереозлектронограмма взвеси кварц + CaO, 5 ч/175 °C.

Рис. 3. Стереозлектронограмма взвеси кварц + CaO + 0,5 % $CaSO_4 \cdot 2 H_2O$, 5 ч/175 °C.

Рис. 4. Стереозлектронограмма взвеси кварц + CaO + 0,5 % $CaSO_4 \cdot 2 H_2O$, 5 ч/175 °C.

Рис. 5. Стереозлектронограмма взвеси кварц + CaO + 0,8 % $CaSO_4 \cdot 2 H_2O$, 5 ч/175 °C.

Рис. 6. Рентгеновские дифракционные записи взвесей кварца с CaO + $Al_2(SO_4)_3$ с добавкой NaOH, 5 ч/175 °C (№ 1—5 табл. II). Обозначения см. рис. 1.

Рис. 7. Рентгеновские дифракционные записи взвесей кварца с CaO + $Al_2(SO_4)_3$ с добавкой Na_2SO_4 , 5 ч/175 °C (№ 6—10 табл. II). Обозначения см. рис. 1.

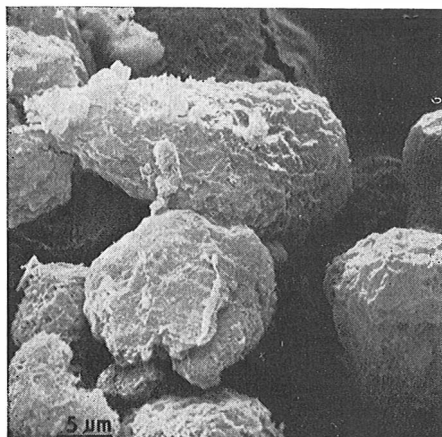


Fig. 2. S.E.M. of quartz-CaO suspension, 5 hrs/175 °C.

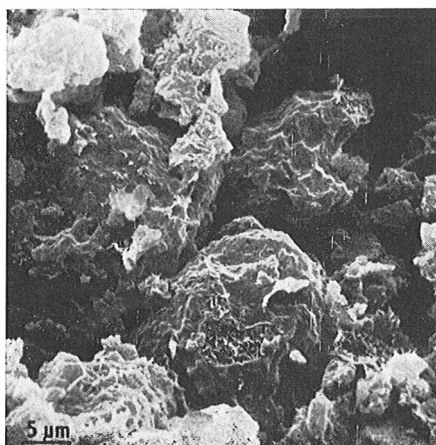


Fig. 3. S.E.M. of suspension containing quartz + CaO + 0.5% CaSO₄ · 2 H₂O, 5 hrs/175 °C.

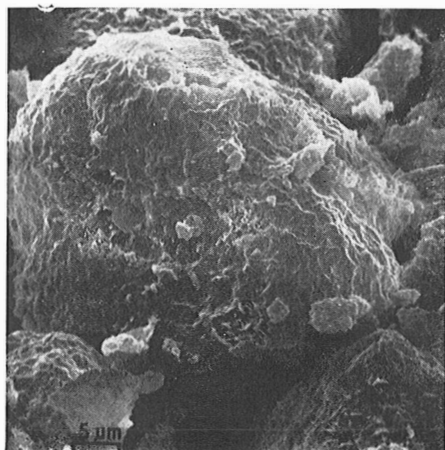


Fig. 4. S.E.M. of suspension containing quartz + CaO + 0,5% CaSO₄ · 2 H₂O, 5 hrs/175 °C.

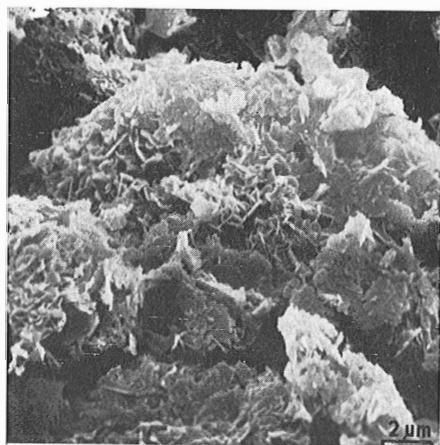


Fig. 5. S.E.M. of suspension containing quartz + CaO + 0,8% CaSO₄ · 2 H₂O, 5 hrs/175 °C.

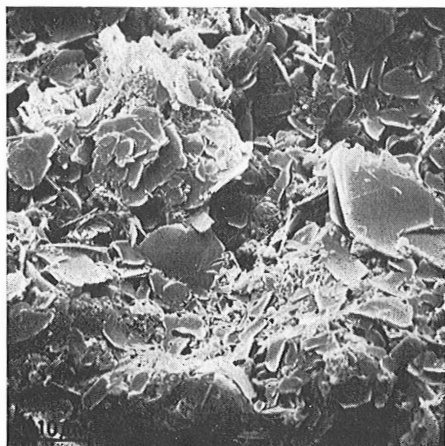


Fig. 8. S.E.M. of the mixture $C_3A + CaCO_3$ (1 : 1) — 2 hrs/181 °C.

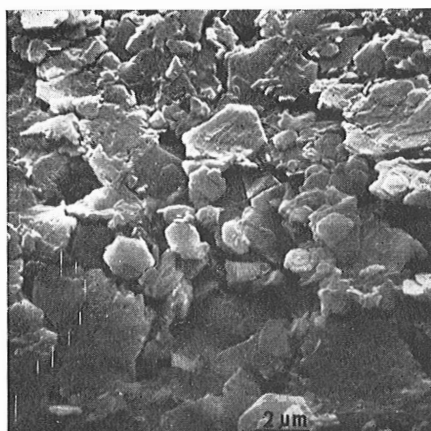


Fig. 9. S. E. M. of the mixture $C_3A + CaCO_3$ (1 : 1) — 168 hrs/25 °C.