

# SUBSTITUTION OF SULPHATE IONS IN THE HYDROGARNET PHASE

ZDENĚK ŠAUMAN,\* JARMILA ČERNÁ,\* VLADIMÍR LACH,\*\*  
ZDENĚK VALTR \*\*\*

Received 29. 1. 1974

*A 1 : 1 by wt. mixture of mullite ( $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ) with CaO reacts under hydrothermal conditions producing a hydrogarnet phase having the composition  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot 4\text{H}_2\text{O}$ . When a graded amount of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  (15 and 20 % respectively) is added to the starting components before autoclave treatment, the reaction yields hydroxyl-ellestadite  $\text{Ca}_{10}(\text{SiO}_4)_3(\text{SO}_4)_3(\text{OH})_2$  together with "soluble" anhydrite  $\text{CaSO}_4(\text{III})$ .*

*It was shown at the same time that approximately up to 4 %  $\text{SO}_3$  can be substituted in the crystal lattice of the hydrogarnet phase.*

## INTRODUCTION

Hydrothermal processing of mixtures containing cement with admixtures of granulated blast-furnace slag or power station fly ash generally also yields a hydrogarnet phase with the general composition  $\text{C}_3\text{AS}_x\text{H}_{6-2x}$  and  $\text{C}_3\text{A}_{1-y}\text{F}_y\text{S}_x\text{H}_{6-2x}$ . The main aim of the experiments described in this paper was to find to what extent the sulphate ions can be substituted in the hydrogarnet phase (which as a rule is present in cement in the form of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), in the course of the autoclave process. The sulphate ions can also be contained in the hydrogarnet component which is formed in the technological production of cellular concretes based on power station fly ash and granulated blast-furnace slag and lime, since about 3 %  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  is generally added to the raw mix.

The problems involved in substitution of certain ions were studied above all in the case of the main binding component of the autoclaved products—11 Å-tobermorite. Kalousek [1], [2] points out the possibility that the  $\text{SO}_4^{2-}$  ions can replace to a small extent the  $\text{SiO}_4^{4-}$  tetrahedrons, and comes to the conclusion that up to 5 %  $\text{SO}_3$  can enter the lattice of "imperfectly crystalline" tobermorite. Copeland and co-workers [3] show that substitution of sulphate ions in the structure of the hydrosilicate phase of the tobermoritic group takes place in such a way that  $\text{S}^{6+}$  always replaces a  $(\text{Si}^{4+} + 2\text{H}^+)$  group. Benton and Kalousek [4] essentially confirm the possibility of substituting  $\text{SO}_3$  in the lattice of the tobermoritic phase up to 4—5 %. Šauman [5] and in another paper with co-workers [6] proved that the structure of 11 Å-tobermotite could contain up to  $\sim 0.5$  %  $\text{SO}_4^{2-}$ . It was also found [7]—[10] that sulphate ions speed up considerably the kinetics of the hydrotomal reactions between lime and quartz sand or power station fly ash and another siliceous component.

\*) Research Institute of Building Materials, 617 00 Brno 17, Hněvkovského 65.

\*\*\*) Technical University, 662 38 Brno, Gorkého 7.

\*\*\*) Slovak Technical University, Bratislava, Jánská.

The substitution of sulphate ions in the hydrogarnet phase was probably investigated only marginally, since no results pertaining to this complex problem have so far been published in literature.

## EXPERIMENTAL

### Preparation of starting components and the methods employed

The starting component used was mullite ( $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ) which was synthesized from a weighed mix consisting of kaolin (flotated Sedlec kaolin) and corundum ( $\alpha\text{-Al}_2\text{O}_3$ ), to which 1 %  $\text{Na}_2\text{O}$  (as  $\text{NaF}$  was added). From the homogenized mix were pressed specimens in the form of small cylinders which were ignited in a supercatal furnace at  $1,500^\circ\text{C}$  for a period of 5 hours. After grinding and homogenization, the firing was repeated four times and at the same time the composition of the mix was also corrected with respect to the loss of  $\text{SiO}_2$  resulting from its volatilization at the temperature mentioned above.

Calcium oxide was obtained by igniting  $\text{CaCO}_3$  (AR grade) at  $1,050^\circ\text{C}$ , and  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  (AR grade) was employed as the sulphate component.

The main physical methods used were X-ray diffraction (X-ray diffractograph "Mikro 111", with goniometer and proportional counter and direct recording on paper), radiation  $\text{CuK}_\alpha$ , and infrared spectral analysis (Infracord 337 of Messrs. Perkin-Elmer with the range  $2.5\text{--}25\ \mu\text{m}$ ).

Differential thermal and gravimetric analyses (Derivatograph of Hungarian manufacture) and the scanning electron microscope (Stereoscan, Cambridge Scientific Instruments, Cambridge, England) were also employed.

Table I

Composition of mixture for hydrothermal processing

Series "A"

| Mixture designation | $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ [g] | CaO [g] | $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ [%] | $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ [g] | CaO [g] | $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ [%] | Mixture designation [%] |
|---------------------|--|---------|---|--|---------|---|-------------------------|
| 1                   | 1.50   | 1.50    | 0   | 1.00   | 1.20    | 0   | I                       |
| 2                   | 1.50   | 1.50    | 3   | 1.00   | 1.20    | 3   | II                      |
| 3                   | 1.50   | 1.50    | 5   | 1.00   | 1.20    | 5   | III                     |
| 4                   | 1.50   | 1.50    | 10  | 1.00   | 1.20    | 10  | IV                      |
| 5                   | 1.50   | 1.50    | 15  | 1.00   | 1.20    | 15  | V                       |
| 6                   | 1.50   | 1.50    | 20  | 1.00   | 1.20    | 20  | VI                      |
| 7                   | 1.50   | 1.50    | 30  | 1.00   | 1.20    | 30  | VII                     |
| 8                   | 1.50   | 1.50    | 50  | 1.00   | 1.20    | 50  | VIII                    |

Two series of mixes in the weight ratios 1 : 1 and 1.0 : 1.2 (higher CaO content) were prepared from mullite and CaO. To both series of starting components was added  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  in amounts of up to 50 %, as can be seen from Table I. After homogenization a certain quantity of distilled water ( $\sim 30\%$ ) was added and the specimens in the form of moistened mixes as microcubes

were hydrothermally processed in small pressure vessels at 175 °C; a 16 hour isothermal holding period was used.

ANALYSIS OF RESULTS

The evaluation of X-ray diffraction analysis of selected mixtures of series "A" is depicted in Fig. 1.

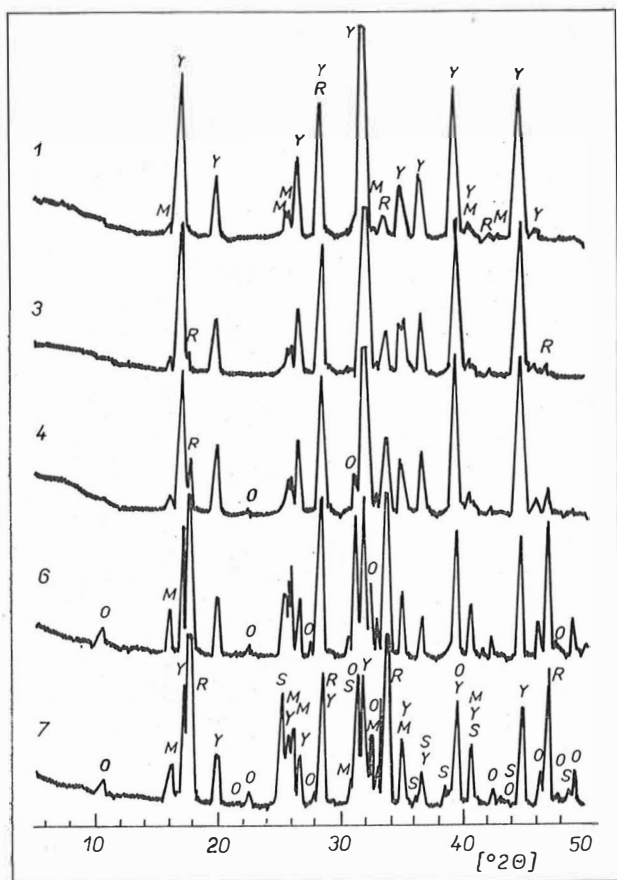


Fig. 1. X-ray diffraction diagrams of series "A" mixtures  $3Al_2O_3 \cdot 2SiO_2 : CaO = 1 : 1$  with a graded admixture of  $CaSO_4 \cdot 2H_2O$ ; 175 °C/16 hours. 1 — 0 %  $CaSO_4 \cdot 2H_2O$ , 3 — 5 %  $CaSO_4 \cdot 2H_2O$ , 4 — 10 %  $CaSO_4 \cdot 2H_2O$ , 6 — 20 %  $CaSO_4 \cdot 2H_2O$ , 7 — 30 %  $CaSO_4 \cdot 2H_2O$ . Symbols employed: M — mullite; O — hydroxyllestadite; R — calcium hydroxide; S — soluble anhydrite; Y — hydrogranet phase.

In the recorded X-ray diffraction diagram the sample without gypsum exhibited intensive diffractions of the hydrogranet phase with the approximate composition  $3CaO \cdot Al_2O_3 \cdot SiO_2 \cdot 4H_2O : 5.03, 2.78 \text{ \AA}$ , and others; furthermore there were substantially less intensive reflections of  $3Al_2O_3 \cdot 2SiO_2 :$

2.55; 3.41 Å and  $\text{Ca}(\text{OH})_2$  : 2.63 and 4.90 Å. In the case of lower gypsum additions (mixes [2] and [3]), no essential differences in the X-ray diffraction diagrams were noted. In mixture [4] it was possible to identify the diffractions of hydroxyl-ellestadite  $[\text{Ca}_{10}(\text{SiO}_4)_3(\text{SO}_4)_3(\text{OH})_2]$  of a low intensity, in the X-ray

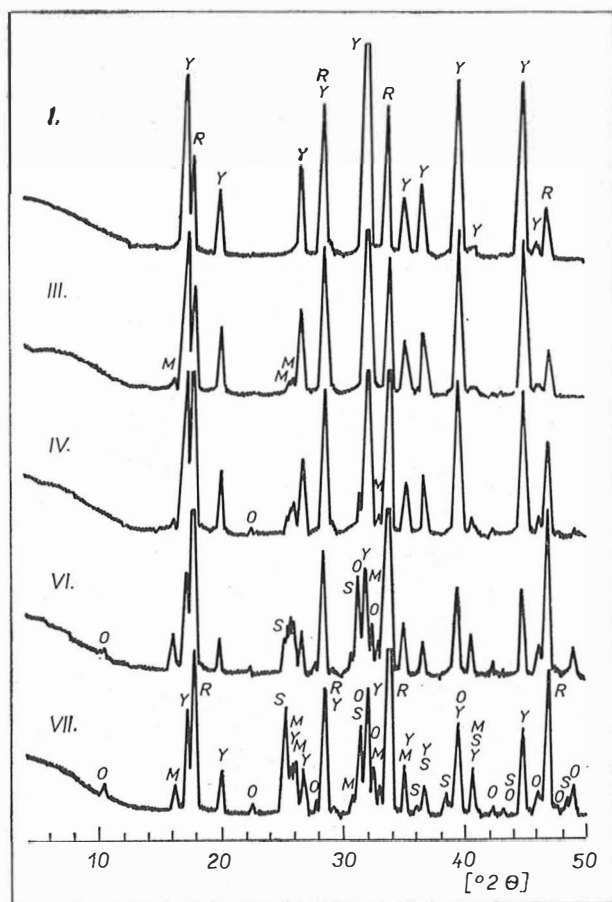


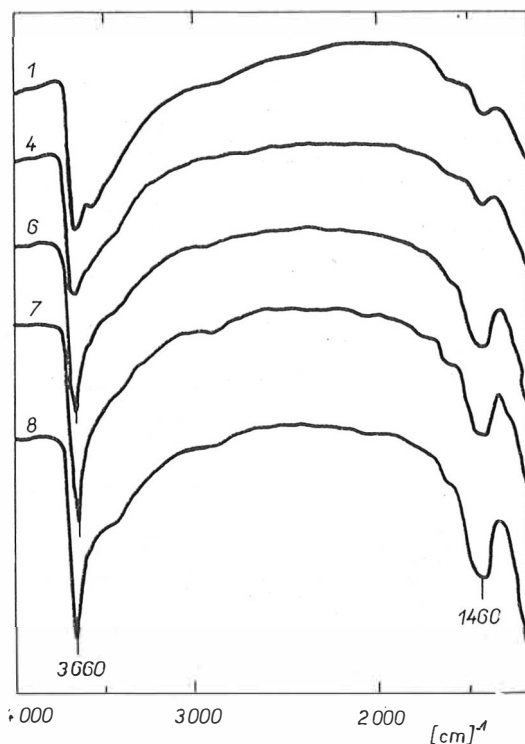
Fig. 2. X-ray diffraction diagrams of series "B" mixtures. 175 °C/16 hours. I — 0 %  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , III — 5 %  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , IV — 10 %  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , VI — 20 %  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , VII — 30 %  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ .

diagram of sample [5] they were still more intensive. Mixtures [6], [7] and [8] are characterized by hydroxyl-ellestadite diffractions of approximately identical intensity; in the last two samples [7] and [8] there additionally appeared lines belonging to "soluble" anhydrite —  $\text{CaSO}_4(\text{III})$  : 3.50 and 2.85 Å. The intensity of the hydrogarnet phase diffractions decreases with increasing concentration of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , whereas the intensity of the  $\text{Ca}(\text{OH})_2$  lines is higher.

The X-ray diffraction diagrams of series "B" mixtures are presented in Fig. 2. The X-ray diagram of the mixture without gypsum is characterized by very intensive lines of the hydrogarnet phase; the sample contains no mullite, but a significantly larger quantity of unreacted calcium hydroxide in comparison with the identical mixture in series "A".

The X-ray diffraction diagram of mixture (II) differs only slightly from the previous one; in the X-ray diagram of mix (III) there appear the mullite lines (2.55, 3.41 and 3.45 Å) of a minute intensity, in sample (IV) also those of hydroxyllestadite (2.28, 2.84 and 3.46 Å). In comparison with the previous one, sample (V) is characterized by increased contents of both  $\text{Ca}(\text{OH})_2$  and hydroxyllestadite and by a reduced content of the hydrogarnet phase.

Very small amounts of  $\text{CaSO}_4(\text{III})$  have also been determined.



*Fig. 3. Infrared spectra of selected series "A" samples. 175 °C/16 hours. Range 4,000 — 1,200  $\text{cm}^{-1}$ .*

With mixtures (VI), (VII) and (VIII) there are no substantial differences in the hydroxyllestadite content: in comparison with series "A" the amount of  $\text{CaSO}_4(\text{III})$  is somewhat higher. The intensity of  $\text{Ca}(\text{OH})_2$  diffractions is increased in proportion to the amount of the sulphate added.

The infrared absorption spectra were scanned in the range 4,000—1,200 and 1,300—400  $\text{cm}^{-1}$ . The spectra for series "A" mixtures are shown in Fig. 3 in the

range 4,000—1,200  $\text{cm}^{-1}$  and in Fig. 4 in the range 1,300—400  $\text{cm}^{-1}$ . In this series sample [1] appeared as a pure hydrogarnet phase with a low  $\text{Ca}(\text{OH})_2$  absorption at 3,660 and 1,460  $\text{cm}^{-1}$ . These absorption bands significantly increased for the higher concentrations with the increasing content of  $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$  added. In sample [3] the absorption band at 1 140  $\text{cm}^{-1}$  begins to manifest itself as a common one for mullite, hydroxyllestadite and anhydrite.

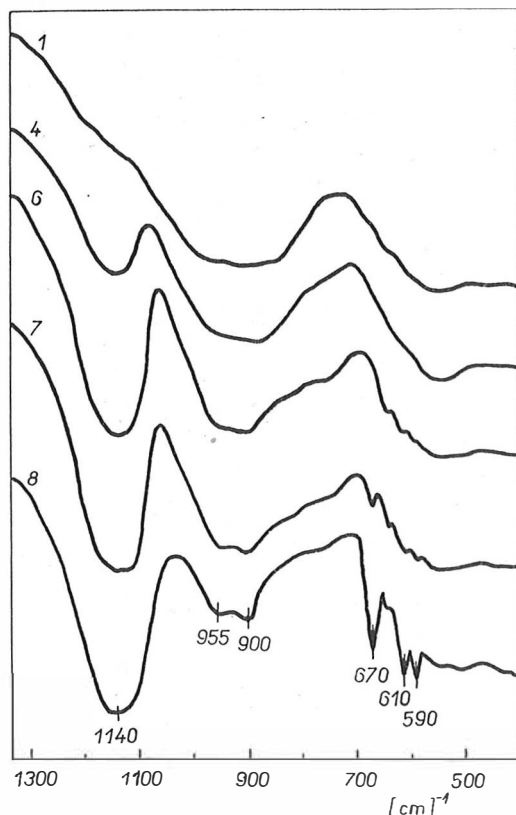


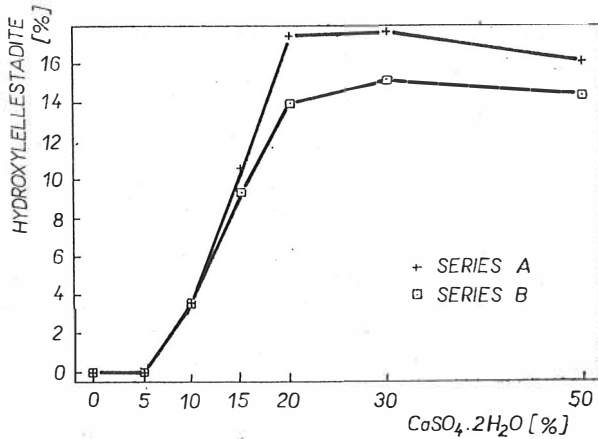
Fig. 4. Infrared spectra of selected series "A" samples 175 °C/16 hours.  
Range 1,300 — 400  $\text{cm}^{-1}$ .

With a fall-off of the hydrogarnet component at higher concentrations of  $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$  added, there begins to take shape the hydroxyllestadite absorption at 955 and 900  $\text{cm}^{-1}$  and furthermore the absorptions 670, 610 and 590  $\text{cm}^{-1}$  which are common for hydroxyllestadite and anhydrite that are increased in proportion with the growing concentration of the dihydrate added.

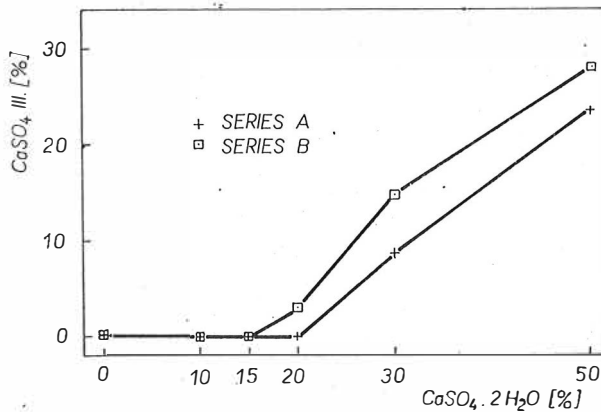
The spectra of series "B" samples are similar to those of series "A". Sample (I) again appears as a pure hydrogarnet phase with an admixture of  $\text{Ca}(\text{OH})_2$  — the absorptions (3,660 and 1,450  $\text{cm}^{-1}$ ) are more intensive than in series "A" and gradually increase with growing concentration of the  $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$  added.

In comparison with series "A" the intensity of the absorption bands for hydroxyllelladite and anhydrite is smaller.

In view of the results obtained by the previous methods it was essential to carry out a quantitative X-ray determination of hydroxyllelladite and "soluble" anhydrite in the autoclaved mixtures. The results of the hydroxyllelladite content determinations are graphically plotted in Fig. 5 and for  $\text{CaSO}_4(\text{III})$  in Fig. 6.



*Fig. 5. Hydroxyllelladite content vs. amount of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  added.*



*Fig. 6.  $\text{CaSO}_4(\text{III})$  content vs. amount of added  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ .*

From these determinations it follows that the hydroxyllelladite content in the mixtures of the two series up to 5%  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  is practically zero, whereupon with an addition of the sulphate component it rapidly increases, from 20—30% it is almost constant and afterwards it drops very gently.

The  $\text{CaSO}_4(\text{III})$  content increases in proportion to the amount of gypsum added (from 20 and 15%, respectively, of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ); the higher an-

hydrite content was noted in the samples of series "B, conversely" to the case of hydroxylellestadite.

The results of the determinations were converted to SO<sub>3</sub> contents listed in Tables II and III.

Table II

| Amount of CaSO <sub>4</sub> · 2 H <sub>2</sub> O added | SO <sub>3</sub> content on the basis of hydroxylellestadite content |            |            |
|--|---|------------|------------|
|  | [%]   | Series "A" | Series "B" |
| 10   |   | 0.84       | 0.87       |
| 15   |   | 2.55       | 2.26       |
| 20   |   | 4.18       | 3.58       |
| 30   |   | 4.25       | 3.49       |
| 50   |   | 3.89       | 3.49       |

Table III

| Amount of CaSO <sub>4</sub> · 2 H <sub>2</sub> O added | SO <sub>3</sub> content on the basis of anhydrite content |            |            |
|--|---|------------|------------|
|  | [%]   | Series "A" | Series "B" |
| 10   |   | —          | —          |
| 15   |   | —          | —          |
| 20   |   | —          | 1.76       |
| 30   |   | 5.06       | 8.82       |
| 50   |   | 13.76      | 16.46      |

Table IV

SO<sub>3</sub> content in autoclaved mixtures

| Sample | SO <sub>3</sub> [%] in hydroxylellestadite and anhydrite |                     |            |            |            |            |
|--------|--|---------------------|------------|------------|------------|------------|
|        | Amount of CaSO <sub>4</sub> · 2 H <sub>2</sub> O added   | SO <sub>3</sub> [%] | Series "A" | Difference | Series "B" | Difference |
|        | 10   | 4.65                | 0.84       | 3.81       | 0.87       | 3.78       |
|        | 15   | 6.97                | 2.55       | 4.42       | 2.26       | 4.71       |
|        | 20   | 9.30                | 4.18       | 5.12       | 5.34       | 3.96       |
|        | 30   | 13.95               | 9.31       | 4.64       | 12.31      | 1.64       |
|        | 50   | 23.25               | 17.65      | 5.60       | 19.95      | 3.30       |



In Table IV is presented the amount of the added sulphate component before hydrothermal processing and the  $\text{SO}_3$  content calculated on the basis of the amounts of  $\text{Ca}_{10}(\text{SiO}_4)_3(\text{SO}_4)_3(\text{OH})_2$  and  $\text{CaSO}_4(\text{III})$  which were formed in the course of the reaction. The simultaneously presented difference between these values represents the assumed  $\text{SO}_3$  content in the crystal lattice of the hydrogarnet component. In the case of series A samples, the average value of substituted  $\text{SO}_3$  is 4.72 % and in series B it is 3.48 %.

It can thus be assumed that despite a certain lack of accuracy in the quantitative X-ray determinations, about 4 %  $\text{SO}_3$  can be bound in the crystal lattice of the hydrogarnet component. As can be seen from the scanning electron micrographs, there can be observed no substantial differences in the morphology of particles of the pure hydrogarnet component (Fig. 7) and the phase which contains about 4 %  $\text{SO}_3$  (Fig. 8).

### CONCLUSION

The problem of the possible substitution of sulphate ions in the crystal lattice of the hydrogarnet phase with the probable composition  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot 4\text{H}_2\text{O}$  was studied on two series of samples having different  $\text{CaO} : 3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$  weight ratios, to which a graded amount of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  (3–50 %) was added. After hydrothermal processing (175 °C/16 hours) it was found that the content of hydroxyllestadite— $\text{Ca}_{10}(\text{SiO}_4)_3(\text{SO}_4)_3(\text{OH})_2$ —was higher in series “A” mixtures which were characterized by the same CaO to mullite weight ratio, whereas in series “B” samples (higher CaO content) the amount of the “soluble” anhydrite— $\text{CaSO}_4(\text{III})$ —was conversely higher. It was proved that already at a concentration of 10 %  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , hydroxyllestadite was formed in the mixtures of both series, whereas the formation of ‘soluble’ anhydrite was observed in series “B” samples after having added 20 %  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  and in the series “A” after the addition of 30 %  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ .

It was found by means of quantitative X-ray analysis that up to about 4 %  $\text{SO}_3$  can be substituted in the lattice of the hydrogarnet phase.

### References

- [1] Kalousek G. L.: *Mat. Res. Std.* 5, 592 (1965).
- [2] Kalousek G. L.: Private communication.
- [3] Copeland L. E., Bodor E., Chang T. N., Weise C. H.: *J. PCA Res. Dev. Lab.* 9, 61 (1967).
- [4] Benton E. J., Kalousek G. L.: *Cer. Bull.* 48, 586 (1969).
- [5] Šauman Z.: Research Report of Research Institute of Building Materials, Brno (Brno 1972).
- [6] Šauman Z., Valtr Z.: Substitution of Sulphate Ions in the Crystal Lattice of 11 Å-Tobermorite. VI-th Inter. Symp. Chem. Cements, Moskva 1974.
- [7] Šauman Z.: *Proceed. Third Intern. Symp. Autocl. Calc. Silic. Build. Prod.*, Paper No. 2.4. Utrecht 1973.
- [8] Šauman Z.: *Proceed. Sec. Intern. Symp. Sci. Res. Silic. Chem.* I, 25, Brno 1972.
- [9] Šauman Z.: *Stavivo* 51, 4 (1973).
- [10] Šauman Z.: *Silikattechnik* 24, 272 (1973).

SUBSTITUCE SÍRANOVÝCH IONTŮ V HYDROGRANÁTOVÉ FÁZI

Zdeněk Šauman,\*) Jarmila Černá,\*) Vladimír Lach,\*\*) Zdeněk Valtr\*\*\*)

K studiu substituce síranových iontů v krystalové mřížce hydrogranátové fáze pravděpodobného složení  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot 4\text{H}_2\text{O}$  byly připraveny dvě série vzorků na základě dvou různých váhových poměrů  $\text{CaO} : 3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ , k nimž bylo přidáno odstupňované množství  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  (3 — 50 %). Po hydrotermálním zpracování (175 °C/16 h) bylo zjištěno, že obsah hydroxyllestaditu —  $\text{Ca}_{10}(\text{SiO}_4)_3(\text{SO}_4)_3(\text{OH})_2$  je vyšší ve směsích série "A", vyznačující se stejným váhovým poměrem  $\text{CaO}$  a mullitu, kdežto ve vzorcích série "B" (vyšší obsah  $\text{CaO}$ ) je nopak vyšší množství vzniklého „rozpuštěného“ anhydritu —  $\text{CaSO}_4(\text{III})$ . Bylo prokázáno, že již při koncentraci 10 %  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  dochází u obou sérií ke tvorbě hydroxyllestaditu, kdežto vznik „rozpuštěného“ anhydritu byl pozorován ve směsích série "B" po přidání 20 %  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  a u série "A" po přidavku 30 %  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ . Použitím kvantitativní rentgenometrické metody bylo zjištěno, že v mřížce hydrogranátové fáze může být substituováno až kolem 4 %  $\text{SO}_3$ .

Obr. 1. Rentgenové difrakční záznamy směsí série "A"  $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 : \text{CaO} = 1 : 1$  s odstupňovaným přidavkem  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ; 175 °C/16 h.

1 — 0 %  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , 3 — 5 %  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , 4 — 10 %  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ .

6 — 20 %  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , 7 — 30 %  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ .

Použité symboly: M — mullit, O — hydroxyllestadit, R — hydroxid vápenatý, S — rozpustný anhydrit, Y — hydrogranátová fáze.

Obr. 2. Rentgenové difrakční záznamy směsí série "B". 175 °C/1h.

I — 0 %  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , III — 5 %  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , IV — 10 ± %  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ,

VI — 20 %  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , VII — 30 %  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ .

Obr. 3. Infračervená spektra vybraných vzorků série „A“. 175 °C/16 h. Rozsah 4000—1200  $\text{cm}^{-1}$ .

Obr. 4. Infračervená spektra vybraných vzorků série "A". 175 °C/16 h. Rozsah 1300—400  $\text{cm}^{-1}$ .

Obr. 5. Závislost obsahu hydroxyllestaditu na množství přidávaného  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ .

Obr. 6. Závislost obsahu  $\text{CaSO}_4(\text{III})$  na množství přidávaného  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ .

Obr. 7. SEM vzorku hydrogranátové fáze (směs 1).

Obr. 8. SEM vzorku hydrogranátové fáze subst. (směs 5).

ЗАМЕЩЕНИЕ СЕРНОКИСЛЫХ ИОНОВ В ГИДРОГРАНАТОВОЙ ФАЗЕ

Зденек Шауман\*), Ярмила Черна,\*) Владимир Лач,\*\*) Зденек Валтр\*\*\*)

Для исследования замещения сернокислых ионов в кристаллической решетке гидрогранатовой фазы с предполагаемым составом  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot 4\text{H}_2\text{O}$  приготовили две серии образцов, полученных на основании двух разных весовых отношений  $\text{CaO} : 3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ , к которым добавляли дозированное количество  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  (3—50 %). На основании гидротермической обработки (175 °C/16 часов) было установлено, что содержание гидроксиллестадита —  $\text{Ca}_{10}(\text{SiO}_4)_3(\text{SO}_4)_3(\text{OH})_2$  больше в смеси серии "A", отличающиеся одинаковым весовым отношением  $\text{CaO}$  и мullита, в то время как в образцах серии "B" (большее с рдержание  $\text{CaO}$ ) имеется наоборот большее количество образовавшегося „растворимого“ ангидрита —  $\text{CaSO}_4(\text{III})$ . Было доказано, что уже при концентрации 10 %  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  образуется в обеих сериях

\*) Výzkumný ústav stavebních hmot, Brno.

\*\*\*) Vysoké učení technické, Brno.

\*\*\*) Slovenská vysoká škola technická, Bratislava.

\*) Научно-исследовательский институт строительных материалов, Brno.

\*\*\*) Политехнический институт, Brno.

\*\*\*) Словацкий политехнический институт, Братислава.

### Substitution of Sulphate Ions...

гидроксилеллестадит, в то время как образование „растворимого“ ангидрита заметили в смесях серии „Б“ после добавки 20 %  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  и у серии „А“ после добавки 30 %  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ . С помощью количественного рентгенометрического метода установили, что в решетке гидрогранатовой фазы может замещаться приблизительно до 4 %  $\text{SO}_3$ .

Рис. 1. Рентгеновская дифракционная запись смесей серии „А“  $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 : \text{CaO} = 1 : 1$  с дозированной добавкой  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ; температура 175 °С, выдержка 16 часов.

1—0 %  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , 3—5 %  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , 4—10 %  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , 6—20 %  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , 7—30 %  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ . М — муллит, О — гидроксилеллестадит, R — гидрат окиси кальция, S — растворенный ангидрит, У — гидрогранатовая фаза.

Рис. 2. Рентгеновская дифракционная запись смесей серии „Б“, температура 175 °С выдержка 16 часов. I — 0 %  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , III — 5 %  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , IV — 10 %  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , VI — 20 %  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , VII — 30 %  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ .

Рис. 3. Инфракрасные спектры подобранных образцов серии „А“, температура 175 °С, выдержка 16 часов, диапазон 4,000—1,200  $\text{cm}^{-1}$ .

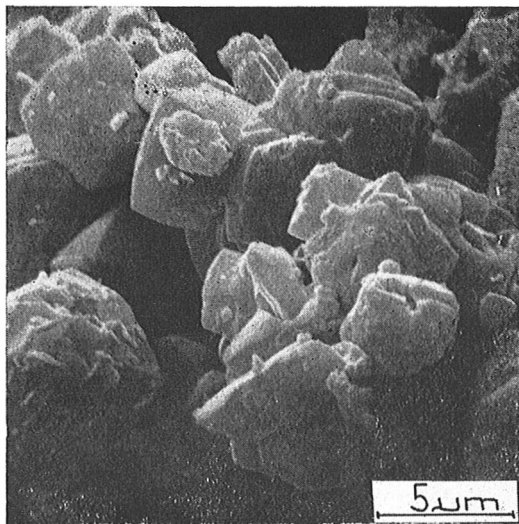
Рис. 4. Инфракрасные спектры подобранных проб серии „А“, температура 175 °С, выдержка 16 часов, диапазон 1,300—400  $\text{cm}^{-1}$ .

Рис. 5. Зависимость сожержания гидроксилеллестадита от количества добавляемого  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ .

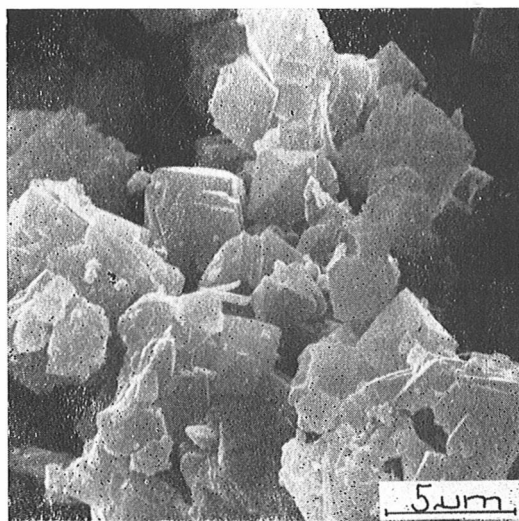
Рис. 6. Зависимость сожержания  $\text{CaSO}_4$  (III) от количества добавляемого  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ .

Рис. 7. SEM образца гидрогранатовой фазы (смесь 1).

Рис. 8. SEM образца гидрогранатовой фазы замещ. (смесь 5).



*Fig. 7. SEM of hydrogarnet phase sample (mixture No. 1).*



*Fig. 8. SEM of substituted hydrogarnet phase sample (mixture No. 5).*