

CRYSTALLOCHEMISTRY AND STABILITY OF MONOSULPHOALUMINATE AND ALUMINOFERRITE HYDRATES AND THEIR SOLID SOLUTIONS

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Study of the hydrates $C_3A \cdot C\bar{S} \cdot H_x$, $C_3A \cdot 1/2 C\bar{S} \cdot 1/2 CH \cdot H_x$, $C_3A \cdot CH \cdot H_x$ and $C_3(A, F) \cdot (C\bar{S})_y \cdot (CH)_{1-y} \cdot H_x$ showed that the H_2O content as well as the stability of the hydrates are associated with their laminar structure. According to an accepted model, the compounds consist of cationic, anionic and neutral layers. The Al—Fe substitution in the cationic layer does not affect its thickness, and both the composition and thickness of the anionic layer are variable. Dehydration of each of the hydrates starts in the neutral layer. Under suitable conditions (temperature, relative humidity, reaction time), the dehydration and rehydration processes are reversible, unless the value of x falls below 6, when destruction of the structure occurs. Hydrates with $x = 12$ are stabilized by the presence of alternating cationic and anionic layers. Experimental results have proved that the values of basal diffractions d_{0001} of the hydrates depend on parameters x and y .

INTRODUCTION

The expansion of sulphoaluminate cement pastes on setting and their increasing impermeability during the hardening process are closely associated with the formation of crystalline hydrates by hydration of cement clinker. The way the chemically or physically fixed water is incorporated is therefore of interest not only from the standpoint of structural knowledge, but also from that of the contribution of the hydrates, generally designated the AFm phase, to the physico-chemical properties of the hardened cement-water paste. However, study of the hydration reactions and formation of the hydrates in the system $CaSO_4 - C a (OH)_2 - Al_2O_3 - Fe_2O_3 - H_2O$ is complicated by contamination of the system by ambient CO_2 and by the formation of carbonate phases involving changes in the water content of the hydrates. For example, the $CO_3^{2-} - 2 OH^-$ substitution is in fact nonequivalent by volume and results above all in a change of the lattice parameter c in the hexagonal unit cell of the $C_3A \cdot yCaCO_3 \cdot (1 - y) CH \cdot H_x$ phases, while the change in the a parameter is lower by one order of magnitude. For the sake of comparison, the unit cell of the compound $C_3A \cdot CH \cdot H_{12}$, space group of $R\bar{3}c$ symmetry, has the hexagonal cell parameters $a = 5.73 \text{ \AA}$, $c = 6 \times c' = 47.16 \text{ \AA}$ [$c' = 7.86 \text{ \AA}$ is the reduced value of parameter c representing the thickness of the basic layer oriented perpendicularly to c axis, from which the periodic structure of the substance is created by translation symmetry operation ($c = c'$), or its polytype ($c = nc'$, where n is mostly 3 or 6) by means of partial symmetry operations), whereas the $C_3A \cdot 1/2CH \cdot 1/2CaCO_3 \cdot H_{12}$ phase has the hexagonal cell parameters $a = 5.72 \text{ \AA}$, $c = 49.20 \text{ \AA}$ ($c' = 8.20 \text{ \AA}$) and the $P6_1$ space group symmetry [2].

Use is made of the abbreviated notation of oxides common in cement chemistry: C = CaO, A = Al_2O_3 , F = Fe_2O_3 , S = SO_3 , H = H_2O .

The greatest stability is exhibited by the cationic part of the layer containing the $[\text{Ca}_2\text{M}(\text{OH})_6]^+$ groups, where $M = \text{Al}^{3+}$, Fe^{3+} or $(\text{Al}, \text{Fe})^{3+}$, coordinated by water molecules and producing the stable formation of the type $[\text{Ca}_2\text{M}(\text{OH})_6 \cdot 2 \text{H}_2\text{O}]^+$ Fig. 1 [1, 3–7]. The thickness of the cationic part of the layer is control-

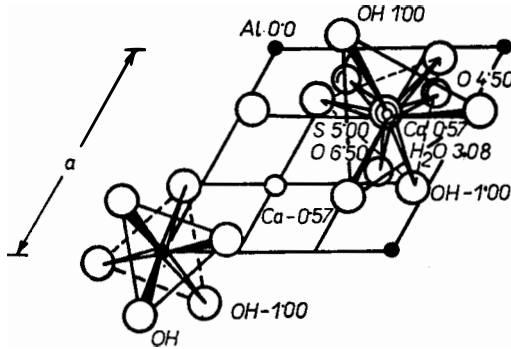


Fig. 1. Scheme of the projection of groups $[\text{Al}(\text{OH})_6]$ and $[\text{Ca}(\text{OH})_6 \cdot \text{H}_2\text{O} \cdot \text{SO}_4]$ into plane (001) with indicated coordinates z (Å) of the atoms.

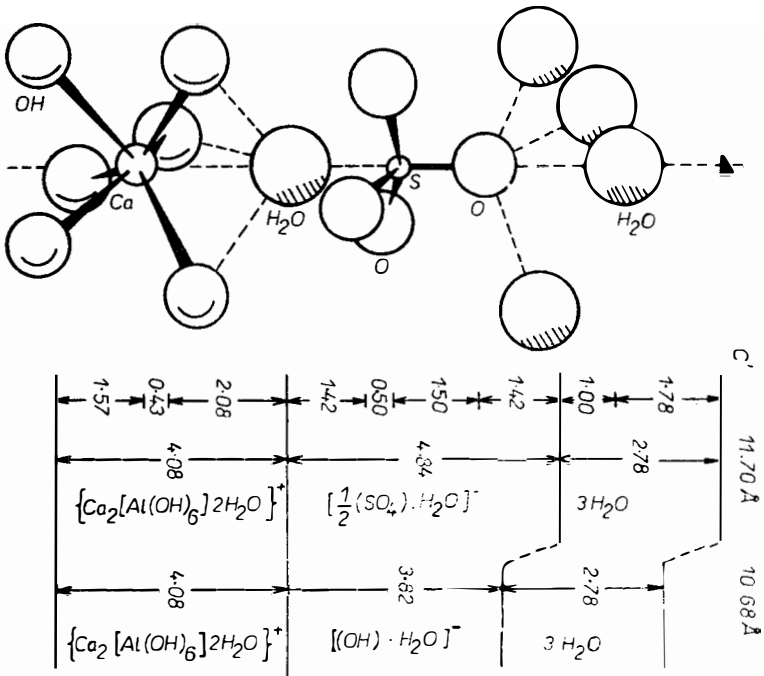


Fig. 2. Structural model of the hydrates $[\text{Ca}_2\text{Al}(\text{OH})_6 \cdot 2 \text{H}_2\text{O}]^+ \left[\frac{1}{2} \text{SO}_4 \cdot \text{H}_2\text{O} \right]^- (3 \text{H}_2\text{O}) - (\text{C}_3\text{A} \cdot \text{CS} \cdot \text{H}_{18})$ and $[\text{Ca}_2\text{Al}(\text{OH})_6 \cdot 2 \text{H}_2\text{O}]^+ [(\text{OH} \cdot \text{H}_2\text{O})]^- (3 \text{H}_2\text{O}) - (\text{C}_3\text{A} \cdot \text{CH} \cdot \text{H}_{18})$. The sections on the reduced ordinate c' ($c' = c/n = d_{0001}$) correlate with the coordinates z of the atoms in Fig. 1.

led by the $[\text{Ca}(\text{OH})_6 \cdot \text{H}_2\text{O}]$ polyhedron with the Ca^{2+} cation and an oxygen atom from water molecule situated on the threefold symmetry axis (Fig. 1). The dimensions and shape of the group $[\text{Ca}(\text{OH})_6 \cdot \text{H}_2\text{O}]$ were determined by X-ray structural analysis [1, 4, 6], (Figs. 1 and 2).

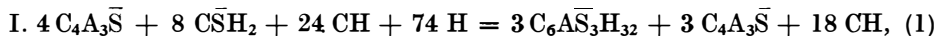
The substitutional changes in the anionic part of the aluminate, sulphoaluminate and AFm phases of the type $\left[\frac{1}{2} y \text{SO}_4^{2-} \cdot (1 - y) \text{OH}^- \cdot \text{H}_2\text{O} \right]$ affect significantly the value of the hexagonal cell parameter c . The AFm phases may also be considered as a solid solution of the end members of the join $\text{C}_3(\text{A}, \text{F}) \cdot \text{CH} \cdot \text{H}_x - \text{C}_3(\text{A}, \text{F}) \cdot \text{CS} \cdot \text{H}_x$ [8], of the type $\text{C}_3(\text{A}, \text{F}) \cdot \text{CS}_y \cdot \text{CH}_{1-y} \cdot \text{H}_x$. Taylor [9] has limited the AFm phases by the value $\text{S}/\text{C} = 1/4$.

Some of the contradicting data in the literature were due, apart from the contamination of hydrates by carbon dioxide, also to the variable amounts of water in the anionic and possibly also the neutral part of the layer containing solely water molecules [10].

The present study had the aim to work out a standard and consistent structural model of the hydrated phases $\text{C}_3\text{A} \cdot \text{CH} \cdot \text{H}_x$, $\text{C}_3\text{A} \cdot \text{CS} \cdot \text{H}_x$, $\text{C}_3\text{A} \cdot 1/2\text{CS} \cdot 1/2\text{CH} \cdot \text{H}_x$ and $\text{C}_3(\text{A}, \text{F}) \cdot \text{CS}_y \cdot \text{CH}_{1-y} \cdot \text{H}_x$ with laminar structure and thus to explain the relative stability of some of the hydrates ($x = 10, 12, 15, 18$) as well as the formation of solid solutions and their effect on the layer thickness.

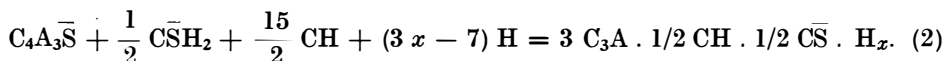
EXPERIMENTAL

The following two-step reaction was used of in the preparation of monosulphoaluminate hydrates having the composition $\text{C}_3\text{A} \cdot \text{CS} \cdot \text{H}_x$:



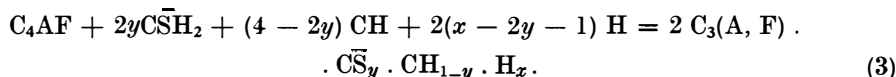
The first stage of the reaction yields ettringite, $\text{C}_6\text{A}\bar{\text{S}}_3\text{H}_{32}$, which in the second stage combines with the unreacted portions of $\text{C}_4\text{A}_3\bar{\text{S}}$ and CH , giving $\text{C}_3\text{A} \cdot \text{CS} \cdot \text{H}_x$. The latter product was isolated from the crystallizing solution after 48 hours by low-temperature filtration or by stirring the crystallization solution with acetone and filtering off the insoluble product which was then dried at a chosen temperature. In the former case, the fine crystals had a higher content of water ($x = 15$), in the latter the hydrates had a variable water content according to the temperature of drying chosen ($x = 10$ or 12).

The solid solution $\text{C}_3\text{A} \cdot 1/2 \text{CH} \cdot 1/2 \text{CS} \cdot \text{H}_x$ was formed by the following reaction:



The rapid course of reaction (2) allows the product to be isolated already after 2 hours of reaction by shaking the crystallization solution with acetone and using vacuum filtration. Solid solutions with a water content of $x = 15.5$ to 16 were isolated.

The solid solution $\text{C}_3(\text{A}, \text{F}) \cdot \text{CS}_y \cdot \text{CH}_{1-y} \cdot \text{H}_x$, AFm phase, is formed by the reaction



The minimum reaction time is 24 hours at room temperature, because during that time the reaction system is contaminated with ettringite. The reactivity of brownmillerite depending on its particle size [11] and the reaction time affect the values of y ; they decrease with reaction time but even extremely long reaction times did not yield a reaction product with $y < 0.3$. The reaction products isolated by vacuum filtration at room temperature or by shaking the crystallization solution with acetone and final drying, had a characteristic water content of $x = 12$.

The $C_4A_3\bar{S}$ used in reactions (1) and (2) was obtained by heating a homogenized mixture of $CaCO_3$, CSH_2 and AH_3 , all of A. R. purity, at molar ratios 3 : 1 : 3. After decarbonation and heating at 1525 K, the specimens were repeatedly homogenized and heated at 1525 K. The C_4AF employed in reaction (3) was synthesized by heating nitrate-tartrate precursors at 1475 K [11]. The fine fractions of both compounds were obtained by thorough grinding in an agate mortar. They showed a specific surface area of $4050 \text{ cm}^2 \text{ g}^{-1}$ after Blaine. The phase purity was checked by X-ray phase analysis on the Philips 1540 powder diffractometer using $CuK\bar{\alpha}$ or $FeK\bar{\alpha}$ radiation. The $Ca(OH)_2$ was employed in freshly prepared hydrated form after washing with acetone and drying in CO_2 -free atmosphere.

The hydration products were identified by X-ray powder diffraction analysis. The resolution of the basal diffractions is illustrated on the case of hydrates $C_3A \cdot CS \cdot H_{10}(M_{10})$, $C_3A \cdot CS \cdot H_{12}(M_{12})$ and $C_3A \cdot CS \cdot H_{15}(M_{15})$ (Fig. 3).

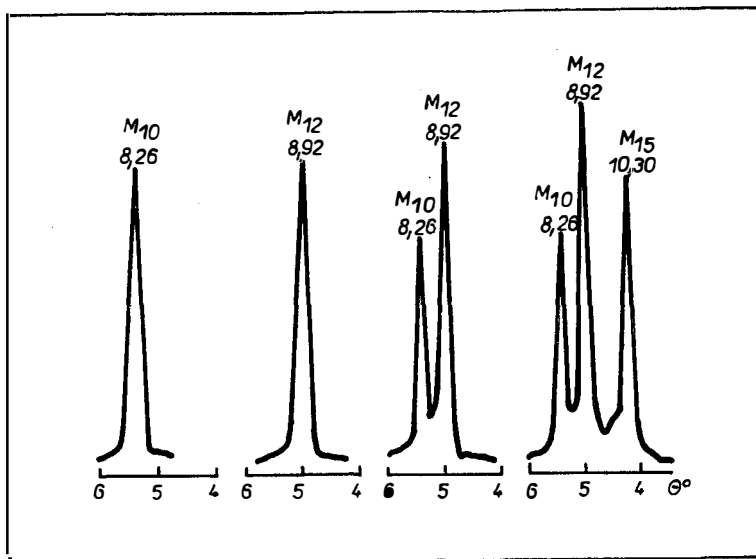


Fig. 3. Positions of basal diffractions (000l) and their interplanar distances d_{000l} (Å) of the hydrates $C_3A \cdot CS \cdot H_{10}$ (M_{10}), $C_3A \cdot CS \cdot H_{12}$ (M_{12}) and $C_3A \cdot CS \cdot H_{15}$ (M_{15}), and their mixtures in X-ray diffraction pattern with the use of $CuK\bar{\alpha}$ radiation.

The content of chemically and physically bound water was determined by thermogravimetric analysis (Derivatograph Q 1500 D) using simultaneous recording of TG, DTG and DTA curves.

RESULTS AND DISCUSSION

The structural model of the laminar hydrates $C_3A \cdot CH \cdot H_x$, $C_3A \cdot \overline{CS} \cdot H_x$, $C_3A \cdot 1/2 CH \cdot 1/2 \overline{CS} \cdot H_x$ and $C_3(A, F) \cdot \overline{CS}_y \cdot CH_{1-y} \cdot H_x$, comprising the cationic, anionic and neutral parts of the layer, was established on the basis of data obtained from X-ray structural analysis [1 through 7] (Table I) and from the dependence of the values of $c'(d_{0001})$ on water content x , as plotted in Fig. 4.

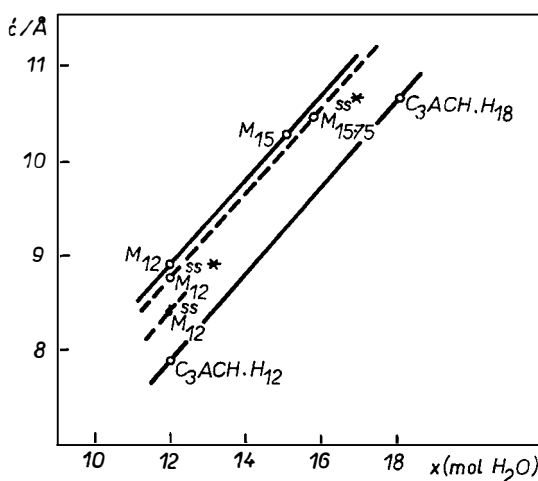


Fig. 4. Relationship of the reduced lattice parameter c' ($c' = c/n = d_{0001}$ Å) of the hydrates $C_3A \cdot \overline{CS} \cdot H_x$ (M_x), $C_3A \cdot CH \cdot H_x$ and $C_3A \cdot 1/2 \overline{CS} \cdot 1/2 CH \cdot H_x$. The symbol M_x^{ss} designates solid solutions composed of layers $\left[\frac{1}{2} SO_4 \cdot H_2O\right]^-$ and $[OH \cdot H_2O]^-$; M_x^{ss*} is the solid solution consisting of layers $\left[\frac{1}{4} SO_4 \cdot \frac{1}{2} OH \cdot H_2O\right]^-$.

In all of the laminar hydrates considered, the cationic part of the layer has the characteristic composition



where M is Fe, Al or (Fe, Al) and a characteristic thickness. The latter was determined by means of position parameters z (in Å) of atoms controlling the thickness (Figs. 1 and 2): $z(OH) = -1.000(5)$ Å; $z(M) = 0$; $z(Ca) = 0.57(1)$ Å; $z(OH)' = 1.000(5)$ Å; $z(H_2O) = 3.08(3)$ Å (Fig. 2). The z parameters and their standard deviations were calculated as selective averages of structural data for the laminar hydrates $C_3A \cdot CH \cdot H_{12}$ [1], $C_3A \cdot \overline{CS} \cdot H_{12}$ [6], $C_3A \cdot CaCl_2 \cdot H_{10}$ [4], $C_3A \cdot CaBr_2 \cdot H_{10}$ [4] and $C_3A \cdot CaI_2 \cdot H_{10}$ [4]. Substitution of Al^{3+} ions by Fe^{3+} ions has a negligible effect on the thickness of the cationic layer as a result of the small difference in the ionic radii ($r_{Fe^{3+}} - r_{Al^{3+}} = 0.11$ Å), which represents 2.7 % of the layer thickness $d_c = 3.08 - (-1.00) = 4.08$ Å.

The thickness of the anionic layer, which is characterized by the general composition

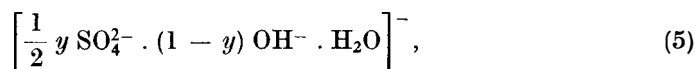


Table I

Crystallographic data of the laminar hydrates $C_3A \cdot CH \cdot H_x$, $C_3A \cdot CS \cdot H_x$, $C_3A \cdot CS_y \cdot CH_{1-y} \cdot H_x$ and $C_3(A, F) \cdot CS_y \cdot CH_{1-y} \cdot H_x$

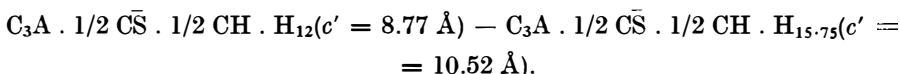
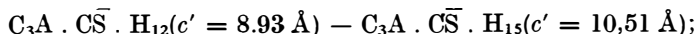
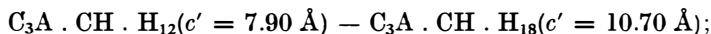
Hydrate Structural formula Space group a_H (Å) c_H (Å) c' (d_{0001}) (Å) (observed value) c' (Å) (calculated value) Literature	$C_3A \cdot CH \cdot H_{10}$ $[Ca_2Al(OH)_6 \cdot 2 H_2O]^+$ $[OH \cdot \square]^-$ 7.40 14,15	$C_3A \cdot CH \cdot H_{18}$ $[Ca_2Al(OH)_6 \cdot 2 H_2O]^+$ $[OH \cdot H_2O]^- (3 H_2O)$ 10.70 10.68 14—17
Hydrate Structural formula Space group a_H (Å) c_H (Å) c' (d_{0001}) (Å) (observed value) c' (Å) (calculated value) Literature	$C_3A \cdot CH \cdot H_{12}$ $[Ca_2Al(OH)_6 \cdot 2 H_2O]^+$ $[OH \cdot H_2O]^-$ R3c 5.73 47.16 7.86—7.92 7.90 1,3	$C_3A \cdot CS \cdot H_8$ $[Ca_2Al(OH)_6 \cdot H_2O]^+$ $[OH \cdot \square]^-$ 8.05 18—20
Hydrate Structural formula Space group a_H (Å) c_H (Å) c' (Å) (observed value) c' (Å) (calculated value) Literature	$C_3A \cdot CS \cdot H_{10}$ $[Ca_2Al(OH)_6 \cdot 2 H_2O]^+$ $[\frac{1}{2} SO_4 \cdot \square]^-$ 8.26 3, 13, 18—20, present study	$C_3A \cdot CS \cdot H_{15}$ $[Ca_2Al(OH)_6 \cdot 2 H_2O]^+$ $[\frac{1}{2} SO_4 \cdot H_2O]^- (\frac{3}{2} H_2O)$ 10.30 10.31 3, 21, present study
Hydrate Structural formula Space group a_H (Å) c_H (Å) c' (Å) (observed value) c' (Å) (calculated value) Literature	$C_3A \cdot CS \cdot H_{12}$ $[Ca_2Al(OH)_6 \cdot 2 H_2O]^+$ $[\frac{1}{2} SO_4 \cdot H_2O]^-$ R3 5.76 26.74 8.92—8.93 8.92 3, 6, 14, 18, 19, 21, the present study	$C_3A \cdot 1/2 CS \cdot 1/2 CH \cdot H_{12}$ $[Ca_2Al(OH)_6 \cdot 2 H_2O]^+$ $[\frac{1}{4} SO_4 \cdot \frac{1}{2} OH \cdot H_2O]^-$ 8.77 8.77 12, 13

Hydrate Structural formula	$C_3A \cdot 1/2 \bar{CS} \cdot 1/2 CH \cdot H_{15.75}$ $[Ca_2Al(OH)_6 \cdot 2 H_2O]^+$ $\left[\frac{1}{4} SO_4 \cdot \frac{1}{2} OH \cdot H_2O \right]^-$ $\left(\frac{15}{8} H_2O \right)$	$C_3(A,F) \cdot \bar{CS}_{0.6} \cdot CH_{0.4} \cdot H_{12}$ $[Ca_2Al(OH)_6 \cdot 2 H_2O]^+$ $[0.3 SO_4 \cdot 0.4 OH \cdot H_2O]^-$
Space group		
a_H (Å)		
c_H (Å)		
c' (Å)	10.52	8.50
(observed value)		
c' (Å)	10.52	8.52
(calculated value)		
Literature	the present study	the present study
Hydrate Structural formula	$C_3(A,F) \cdot \bar{CS}_{0.8} CH_{0.2} \cdot H_{12}$ $[Ca_2Al(OH)_6 \cdot 2 H_2O]^+$ $[0.4 S\bullet_4 \cdot 0.2 OH \cdot H_2O]^-$	$C_3(A,F) \cdot \bar{CS}_{0.4} \cdot CH_{0.6} \cdot H_{12}$ $[Ca_2Al(OH)_6 \cdot 2 H_2O]^+$ $[0.2 SO_4 \cdot 0.6 OH \cdot H_2O]^-$
Space group		
a_H (Å)		
c_H (Å)		
c' (Å)	8.70	8.30
(observed value)		
c' (Å)	8.72	8.31
(calculated value)		
Literature	the present study	the present study

The symbol \square represents the vacant position of H_2O molecule after dehydration.

depends on its stoichiometry, i.e. on parameter y . The calcium aluminate hydrates $C_3A \cdot CH \cdot H_x$ are characterized by $y = 0$, the calcium sulphoaluminate hydrates $C_3A \cdot \bar{CS} \cdot H_x$ by the value $y = 1$ and the solid solutions $C_3(A, F) \cdot \bar{CS}_y \cdot CH_{1-y} \cdot H_x$ can exhibit y values over the interval $0 < y < 1$. The value of $c'(d_{0001})$ depends linearly on y only when layers of $\left[\frac{1}{2} SO_4^{2-} \cdot H_2O \right]$ alternate with layers of $[OH^- \cdot H_2O]$ in the solid solution considered, and when no $SO_4^{2-} \leftrightarrow 2 OH^-$ substitution takes place within the framework of one layer. In such a case, the thickness of anionic layer d_a is affected preferentially by the dimensions of the SO_4^{2-} anion and the dependence of c' on y could not be linear. The problem will be discussed in another part of the study.

The neutral layer consists of H_2O molecules only. Its thickness is given by the comparison of the $c'(d_{0001})$ values for the pairs of hydrates having identical composition of the cationic and anionic parts of the layer and differing only in water H_x in the neutral layer. Such pairs can be selected by means of the data in Table I:



These pairs determine thickness d_n of the neutral layer, reduced to a content of 6 H₂O, at 2.80 Å, 2.76 Å and 2.80 Å respectively, with the mean value of 2.78 Å.

The thickness of the neutral layer, d_n , of an arbitrary hydrate H_x , where x lies within the interval $12 < x < 18$, can be calculated (on the condition of a linear dependence of layer thickness d_n on x) by means of the equation

$$d_n = \frac{x - 12}{6} \cdot 2.78 \text{ \AA}. \quad (6)$$

Thickness d_a of the anionic layer can be established by means of experimental values of c' and the known water content x , as well as the known thickness of the cationic layer, $d_c = 4.08 \text{ \AA}$:

$$d_a = c' - d_c - d_n = \left(c' - 4.08 - \frac{x - 12}{6} \cdot 2.78 \right) \text{ \AA}. \quad (7)$$

Such data are available for the hydrates C₃A · CH · H₁₂ and C₃A · CH · H₁₈ for which the following anionic layer thickness d_a was established by means of equation (7), the known values of c' and x (Table I): 3.82 Å and 3.84 Å respectively, the mean value being $d_a = 3.83 \text{ \AA}$. Similarly, the values of $d_a = 4.85 \text{ \AA}$ and 4.83 Å with a mean of 4.84 Å were determined for the hydrates C₃A · CS · H₁₂ and C₃A · CS · H₁₈.

In the case of sulphoaluminate-ferrite solid solutions C₃(A, F) · CS_{*y*} · CH_{1-*y*} · H₁₂ the layer thickness c' was found to depend linearly on the y value (Fig. 5). The layer thickness c' can be determined from the equation

$$c' = [7.90 + (8.93 - 7.90) y] = [7.90 + 1.03y] \text{ \AA}, \quad (8)$$

where the coefficient 1.03 is formally equal to the difference of c' values of the end members of the solid solution series C₃(A, F) · CS_{*y*} · CH_{1-*y*} · H₁₂, i.e. C₃A · CS · H₁₂ and C₃A · CH · H₁₂. The regression line in Fig. 5 has a slope of 1.01(2).

Equation (8), which represents the linear dependence of c' on y , holds only when the structure of monosulphate-aluminate or aluminoferrite hydrate consists of alternate layers of the type $\left[\frac{1}{2} \text{SO}_4 \cdot \text{H}_2\text{O} \right]^-$ and $[\text{OH} \cdot \text{H}_2\text{O}]^-$ in a ratio conforming to the given stoichiometry. However, if the SO₄²⁻ - 2 OH⁻ substitution takes place within each layer, the dependence of c' on y will no longer be linear, as the size of the larger SO₄²⁻ anion present in the anionic layer will be mainly responsible for the layer thickness c' at a given value of x . The values $c' = 8.30 - 8.50 \text{ \AA}$ were found for the hydrate C₃A · 1/2 CS · 1/2 CH · H₁₂ [12]. The value of $c' = 8.415 \text{ \AA}$, calculated for composition $y = 1/2$ by means of equation (8), lies within the interval of experimental values. The value $c' = 8.77 \text{ \AA}$ was declared as a standard one for the hydrate C₃A · 1/2 CS · 1/2 CH · H₁₂ [13] and, in agreement with our model, represents a structure with anionic layers of $[1/4 \text{SO}_4^{2-} \cdot 1/2 \text{OH}^- \cdot \text{H}_2\text{O}]$ with substituted SO₄²⁻ and OH⁻ ions in each anionic layer and a dominating effect of sulphate anions on the layer dimensions. Point S in Fig. 5 represents the deviation from linearity $c' = f(y)$ in the series of solid solutions for the hydrate C₃A · 1/2 CS · 1/2 CH · H₁₂.

Dehydration of aluminate and sulphoaluminate hydrates starts in the neutral layer. After its dehydration, the water content in the anionic layer decreases and the x value varies over the range of $10 < x < 12$. Vacancies are formed in the anionic layer whose thickness is reduced. The C₃A · CH · H₁₂ hydrate, for example,

has the reduced value of $c' = 7.90 \text{ \AA}$ and the anionic layer thickness $d_a = 3.83 \text{ \AA}$, whereas the $C_3A \cdot CH \cdot H_{10}$ hydrate has the layer thickness $c' = 7.40 \text{ \AA}$ and the anionic layer thickness $d_a = 3.32 \text{ \AA}$ (Table I). Similarly, with hydrate $C_3A \cdot CS \cdot H_{10}$, the values $c' = 8.26 \text{ \AA}$ and $d_a = 4.16 \text{ \AA}$ decrease as compared to the hydrate $C_3A \cdot CS \cdot H_{12}$ for which the values $c' = 8.93 \text{ \AA}$ and $d_a = 4.84 \text{ \AA}$ were determined (Table I).

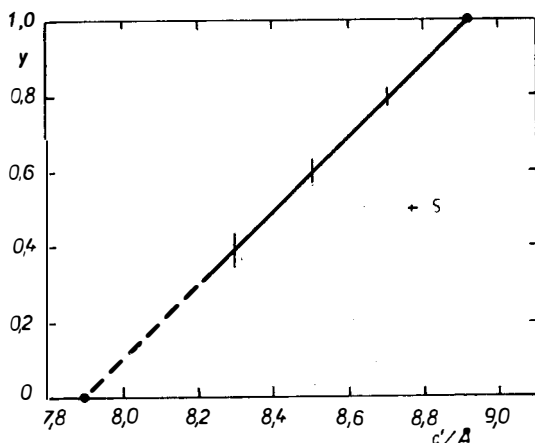


Fig. 5. Relationship between reduced lattice parameter c' ($c' = c/n = d_{0001} \text{ \AA}$) and y for the hydrates $C_3(A, F) \cdot CS_y \cdot CH_{1-y} \cdot H_{12}$. The stoichiometry of the hydrates (fractions of CaO , Fe_2O_3 , SO_3 oxides) was determined on the ARL SEMQ instrument with the Keveex 7000 adapter for EDS electron microanalysis (at the Central Institute of Inorganic Chemistry of the Academy of Sciences of GDR in Berlin). The standard deviations of the y values are represented by the length of abscissae in the corresponding positions. Point S belongs to solid solution $C_3A \cdot 1/2 CS \cdot 1/2 CH \cdot H_{12}$ composed of $[1/4 SO_4 \cdot 1/2 OH \cdot H_2O]^-$ layers. The points close to the regression line represent solid solutions composed of $[OH \cdot H_2O]^-$ and $[1/2 SO_4 \cdot H_2O]$ layers.

The cationic part of the layer is dehydrated only after the complete dehydration of the neutral and anionic parts of the layer ($6 < x < 10$); however, the water content must not decrease below $x = 6$. In that case the structure would disintegrate and the reversible hydration and rehydration processes, otherwise taking place at suitable temperatures and partial water vapour pressure, would no longer be possible.

References

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KRYŠTALOCHEMIA A STABILITA MONOSULFÁTOALUMINÁTOVÝCH A ALUMINÁTOFERITICKÝCH HYDRÁTOV A ICH TUHÝCH ROZTOKOV

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1. Vrstvenaté hydráty $C_3A \cdot \bar{C}\bar{S}_y \cdot CH_{1-y} \cdot H_x$, resp. $C_3(A, F) \cdot \bar{C}\bar{S}_y \cdot CH_{1-y} \cdot H_x$ ($0 \leq y \leq 1$) sú zložené z kationovej $[Ca_2Al(OH)_6 \cdot 2 H_2O]^+$, aniónovej $\left[\frac{1}{4} y SO_4^{2-} \cdot \frac{1}{2} (1-y) OH^- \cdot H_2O \right]^-$ a neutrálnej $[3 H_2O]$ vrstvy, ktoré sú vzájomne rovnobežné a orientované kolmo k osi c . Redukovaná hrúbka celej vrstvy $c' = c/n$ (n je celé číslo), resp. d_{0001} , je v uvažovanom štruktúrnom modeli aditívnou funkciou hrúbky kationovej, d_c , aniónovej, d_i a neutrálnej, d_n , vrstvy, tzn. $c' = d_c + d_i + d_n$. Hrúbka kationovej vrstvy zostáva konštantná vo všetkých uvažovaných hydrátoch ($d_c = 4,08 \text{ \AA}$). Hrúbka aniónovej vrstvy je lineárnou funkciou koeficientu y : $d_a = (3,83 + 1,01y) \text{ \AA}$ pre $x \geq 12$, ale len v prípade, keď sa v štruktúre striedajú vrstvy typu $[OH^- \cdot H_2O]$ s vrstvami typu $\left[\frac{1}{2} SO_4 \cdot H_2O \right]^-$. V prípade, keď sa striedajú vrstvy $\left[\frac{1}{4} y SO_4 \cdot \frac{1}{2} (1-y) OH^- \cdot H_2O \right]^-$, závislosť d_a na y nie je lineárna.

2. Tuhé roztoky $C_3(A, F) \cdot \bar{C}\bar{S}_y \cdot CH_{1-y} \cdot H_x$ majú tendenciu vytvárať štruktúry, v ktorých sa striedajú aniónové vrstvy $[OH^- \cdot H_2O]^-$ s vrstvami $\left[\frac{1}{2} SO_4 \cdot H_2O \right]^-$, kým tuhé roztoky $C_3A \cdot \bar{C}\bar{S}_y \cdot CH_{1-y} \cdot H_x$ prednostne vytvárajú aniónové vrstvy, v ktorých sú zastúpené súčasne SO_4^{2-} a OH^- ióny.

3. Dehydratácia vrstvenatých hydrátov $C_3A \cdot \bar{C}\bar{S}_y \cdot CH_{1-y} \cdot H_{18}$, resp. $C_3(A, F) \cdot \bar{C}\bar{S}_y \cdot CH_{1-y} \cdot H_{18}$ začína v neutrálnej vrstve (minimálny obsah vody $12 H_2O$), pokračuje dehydratáciou aniónovej vrstvy (minimálny obsah vody $10 H_2O$) a ako posledná dehydratuje kationová vrstva, pre ktorú nesmie klesnúť hodnota x pod hranicu 6, aby nenastala deštrukcia štruktúry. V intervale hodnôt $6 < x \leq 18$ je možná za vhodných teplotných podmienok a parciálneho tlaku pár H_2O reverzibilná hydratácia a dehydratácia vrstvenatej fázy. V intervale $10 \leq x < 12$ dochádza k úniku molekúl vody z aniónovej vrstvy, v intervale $6 \leq x < 10$ z kationovej vrstvy, čo spôsobuje ich kontrakciu.

Obr. 1. Schéma projekcie skupín $[Al(OH)_6]$ a $[Ca(OH)_6 \cdot H_2O \cdot SO_4]$ do roviny (001) s vyznačenými súradnicami z (Å) atómov.

Obr. 2. Štruktúrny model hydrátov $[Ca_2Al(OH)_6 \cdot 2 H_2O]^+ \left[\frac{1}{2} SO_4 \cdot H_2O \right]^- (3 H_2O) - (C_3A \cdot \bar{C}\bar{S} \cdot H_{18})$ a $[Ca_2Al(OH)_6 \cdot 2 H_2O]^+ [OH^- \cdot H_2O]^- (3 H_2O) - (C_3A \cdot CH \cdot H_{18})$. Úseky na redukovanej osi c' ($c' = c/n = d_{0001}$) korelujú so súradnicami z atómov na obr. 1.

Obr. 3. Polohy bazálnych difrakcií (0001) a ich medzivrstvinné vzdialenosti d_{0001} (Å) hydrátov $C_3A \cdot \bar{C}\bar{S} \cdot H_{10}$ (M_{10}), $C_3A \cdot \bar{C}\bar{S} \cdot H_{12}$ (M_{12}) a $C_3A \cdot \bar{C}\bar{S} \cdot H_{15}$ (M_{15}) a ich zmesi v rtg. difrakčnom zázname s použitím žiarenia $CuK\alpha$.

Obr. 4. Závislosť hodnôt redukovaného mriežkového parametra c' ($c' = c/n = d_{0001}$ Å) hydrátov $C_3A \cdot \bar{C}\bar{S} \cdot H_x$ (M_x), $C_3A \cdot CH \cdot H_x$ a $C_3A \cdot \bar{C}\bar{S} \cdot 1/2 CH \cdot H_x$. Symbolom M_x^* sú označené

tuhé roztoky zložené z vrstiev $\left[\frac{1}{2} \text{SO}_4 \cdot \text{H}_2\text{O}\right]^-$ a $[\text{OH} \cdot \text{H}_2\text{O}]^-$; M_x^{**} je tuhý roztok zložený z vrstiev $\left[\frac{1}{4} \text{SO}_4 \cdot \frac{1}{2} \text{OH} \cdot \text{H}_2\text{O}\right]^-$.

Obr. 5. Závislosť hodnôt redukovaného mriežkového parametra c' ($c' = c/n = d_{0001}$ Å) na y u hydrátov $\text{C}_3(\text{A}, \text{F}) \cdot \text{CS}_y \cdot \text{CH}_{1-y} \cdot \text{H}_{12}$. Stechiometria hydrátov (zastúpenie oxidov CaO , Fe_2O_3 , SO_3) sa stanovila na prístroji ARL SEMQ s nadstavbou Keveex 7000 pre EDS elektrónovú mikroanalýzu na Centrálnom ústave anorganickej chémie AV NDR v Berlíne. Standardné odchýlkky hodnôt y sú reprezentované dĺžkou čiar v zodpovedajúcich polohách. Bod S patrí tuhému roztoku $\text{C}_3\text{A} \cdot 1/2 \text{CS} \cdot 1/2 \text{CH} \cdot \text{H}_{12}$ zloženému z vrstiev $[1/4 \text{SO}_4 \cdot 1/2 \text{OH} \cdot \text{H}_2\text{O}]^-$. Body pozdĺž regresnej priamky reprezentujú tuhé roztoky zložené z vrstiev $[\text{OH} \cdot \text{H}_2\text{O}]^-$ a $(1/2 \text{SO}_4 \cdot \text{H}_2\text{O})^-$.

КРИСТАЛЛОХИМИЯ И СТАБИЛЬНОСТЬ,
МОНОСУЛЬФАТА АЛЮМИНАТНЫХ И АЛЮМИНАТОФЕРРИТНЫХ
ГИДРАТОВ И ИХ ТВЕРДЫХ РАСТВОРОВ

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1. Слоистые гидраты $\text{C}_3\text{A} \cdot \text{CS}_y \cdot \text{CH}_{1-y} \cdot \text{H}_x$, или $\text{C}_3(\text{A}, \text{F}) \cdot \text{CS}_y \cdot \text{CH}_{1-y} \cdot \text{H}_x$ ($0 \leq y \leq 1$) состоят из катонного $[\text{Ca}_2\text{Al}(\text{OH})_6 \cdot 2 \text{H}_2\text{O}]^+$, анионного $\left[\frac{1}{4} y \text{SO}_4^{2-} \cdot \frac{1}{2} (1-y) \bullet \text{H}^- \cdot \text{H}_2\text{O}\right]^-$ и нейтрального $[3 \text{H}_2\text{O}]$ слоев, которые взаимно параллельны и ориентированы перпендикулярно к оси c . Восстановленная толщина всего слоя $c' = c/n$ (n — целое число), или d_{0001} , является в рассматриваемой структурной модели аддитивной функцией толщины катонного, d_c , анионного, d_a и нейтрального, d_n слоев, т. е. $c' = d_c + d_a + d_n$. Толщина катонного слоя остается постоянной во всех рассматриваемых гидратах ($d_c = 4,08$ Å). Толщина анионного слоя является линейной функцией коэффициента y : $d_a = (3,83 + 1,01y)$ Å для $x > 12$, но только в случае, когда в структуре чередуются слои типа $[\text{OH} \cdot \text{H}_2\text{O}]^-$ со слоями типа $\left[\frac{1}{2} \text{SO}_4 \cdot \text{H}_2\text{O}\right]^-$. В случае, когда чередуются слои $\left[\frac{1}{4} y \text{SO}_4 \cdot \frac{1}{2} (1-y) \bullet \text{H}^- \cdot \text{H}_2\text{O}\right]^-$, зависимость d_a от y не является линейной.

2. Твердые растворы $\text{C}_3(\text{A}, \text{F}) \cdot \text{CS}_y \cdot \text{CH}_{1-y} \cdot \text{H}_x$ стремятся образовать структуры, в которых чередуются анионные слои $[\text{OH} \cdot \text{H}_2\text{O}]^-$ с слоями $\left[\frac{1}{2} \text{SO}_4 \cdot \text{H}_2\text{O}\right]^-$, в результате чего возникают твердые растворы $\text{C}_3\text{A} \cdot \text{CS}_y \cdot \text{CH}_{1-y} \cdot \text{H}_x$ преимущественно образуют анионные слои, в которых имеются одновременно как SO_4^{2-} , так и OH^- ионы.

3. Дегидратирование слоистых гидратов $\text{C}_3\text{A} \cdot \text{CS}_y \cdot \text{CH}_{1-y} \cdot \text{H}_{18}$, или $\text{C}_3(\text{A}, \text{F}) \cdot \text{CS}_y \cdot \text{CH}_{1-y} \cdot \text{H}_{18}$ начинается в нейтральном слое (минимальное содержание воды $12 \text{H}_2\text{O}$), продолжается дегидратированием анионного слоя (минимальное содержание воды $10 \text{H}_2\text{O}$) и последним дегидратацией подвергается катонный слой, в котором не допустимо понижение величины x ниже 6, чтобы не наступила деструкция структуры. В интервале величин $6 < x \leq 18$ возможна при пригодных условиях температуры и парциального давления паров H_2O обратимая гидратация и дегидратация слоистой фазы. В интервале $10 \leq x < 12$ происходит удаление молекул воды из анионного слоя, в результате чего наступает уменьшение объема.

Рис. 1. Схема проекции групп $[\text{Al}(\text{OH})_6]$ и $[\text{Ca}(\text{OH})_6 \cdot \text{H}_2\text{O} \cdot \text{SO}_4]$ в плоскость (001) с обозначенными координатами z (Å) атомов.

Рис. 2. Структурная модель гидратов $[\text{Ca}_2\text{Al}(\text{OH})_6 \cdot 2 \text{H}_2\text{O}]^+ \left[\frac{1}{2} \text{SO}_4 \cdot \text{H}_2\text{O}\right]^- (3 \text{H}_2\text{O})$ ($\text{C}_3\text{A} \cdot \text{CS} \cdot \text{H}_{18}$) и $[\text{Ca}_2\text{Al}(\text{OH})_6 \cdot 2 \text{H}_2\text{O}]^+ [\text{OH} \cdot \text{H}_2\text{O}]^- (3 \text{H}_2\text{O}) (\text{C}_3\text{A} \cdot \text{CH} \cdot \text{H}_{18})$. Отрезки на редуцированной оси c' ($c' = c/n = d_{0001}$) коррелируют с координатами z атомов на рис. 1.

Рис. 3. Положения основных диффракций (000l) и их межплоскостные расстояния d_{000l} (Å) гидратов $C_3A \cdot CS \cdot H_{10}$ (M_{10}), $C_3A \cdot CS \cdot H_{12}$ (M_{12}) и $C_3A \cdot CS \cdot H_{15}$ (M_{15}) и их смесей в диффрактограмме с применением излучения $CuK\alpha$.

Рис. 4. Зависимость величин редуцированного параметра решетки c' ($c' = c/n = d_{0001}$) гидратов $C_3A \cdot CS \cdot H_x$ (M_x), $C_3A \cdot CH \cdot H_x$ и $C_3A \cdot 1/2 CS \cdot 1/2 CH \cdot H_x$. Через символ M_x^{ss} обозначены твердые растворы, состоящие из слоев $\left[\frac{1}{2} SO_4 \cdot H_2O \right]^-$ и $[OH \cdot H_2O]^-$, M_x^{ss} — твердый раствор, состоящий из слоев $\left[\frac{1}{4} SO_4 \cdot \frac{1}{2} OH \cdot H_2O \right]^-$.

Рис. 5. Зависимость величин редуцированного параметра решетки c' ($c' = c/n = d_{0001}$ Å) от y у гидратов $C_3(A, F) \cdot CS_y \cdot CH_{1-y} \cdot H_{12}$. Стехиометрия гидратов (замещение оксидов CaO, Fe_2O_3 , SO_3) установили посредством прибора ARL SEMQ с добавкой Kevex 7000 для EDS электронного микроанализа в Центральном институте неорганической химии АН ГДР в Берлине. Стандартные отклонения величин y представляет длина линий в соответствующих положениях. Точка S отвечает твердому раствору $C_3A \cdot 1/2 CS \cdot 1/2 CH \cdot H_{12}$, состоящему из слоев $[1/4 SO_4 \cdot 1/2 OH \cdot H_2O]^-$. Точки вдоль регрессионной прямой отвечают твердым растворам, состоящим из слоев $[OH \cdot H_2O]^-$ и $[1/2 SO_4 \cdot H_2O]^-$.

NOVÝ DRUH TEPELNE IZOLAČNÉHO MATERIÁLU z keramických vláken, ktorý môže byť nanášaný striekaním na oceľový, alebo keramický podklad, uviedla firma Carborundum Resistant Material pod názvom „Sprayfrax“. Práca s ním je 4 krát rýchlejšia, ako inštalovanie ukotvených modulov z keramického vlákna. Izolácia je určená na opravy pecí, pevných vozov, ako protipožiarna ochrana zásobníkov v chemickom priemysle a pod. Vyrábajú sa dva druhy pre teploty do 1100 °C a 1400 °C. Materiál je odolný proti väčšine chemikálií, okrem HF, H_3PO_4 a konc. alkáliam.

Interceram, č. 1, 1988

Palčo

TRENDY V OBLASTI PROGRESÍVNÍ KERAMIKY V USA. Podle studie firmy JACA Corp. americké firmy vyrábějící progresivní keramiku více než zdvojnásobí prodej do r. 1990. Odbyt progresivní keramiky v r. 1985 činil 2,5 mld \$, během tří let se má zvýšit na 5,6 mld \$.

JACA ve studii uvádí řadu trendů pozorovaných v oblasti progresivní keramiky:

- více amerických i cizích firem vstupuje na americký trh, soustřeďují se na keramické díly a prášky;
- zvyšuje se aktivita firem v nejrůznějších akvizicích, joint — venture a licencích;
- rozšiřuje se používání progresivní keramiky v komerčních a vojenských leteckých a kosmických dopravních prostředcích včetně pokračujícího vývoje levných dílů pro automobilové motory;
- konstrukční a oteřuvzdorná keramika nahrazuje tradiční kovové součástky.

Industrial Ceramics 8, 1988, č. 1, 35

Doušková

NOVÝ SUPRAVODIČ, dosahující nulové elektrické vodivosti při 323 K, vyvinula Electro-technical Laboratory of Agency of Industrial Science and Technology. Výrobní metoda zahrnuje opakované předslinování a slinování surovin na bázi oxidů Yr, Ba a Cu včetně blíže nespécifikované sloučeniny.

Ind. Cer., 8, 1988, č. 1, s. 29

Fryntová

SUPRAVODIVOST PŘI TEPLOTĚ MÍSTNOSTI (27 °C) byla dosažena u sloučenin na bázi Yt, Ba, Cu a O, vyvinutých společností Sumimoto Electric Industries. Meissnerův jev byl pozorován při teplotě 273 K. Prozatím je vyráběno 5 typů testovaných supravodičů s průměrem 7 mm a tloušťkou 5 mm. Vzorky se vyznačují nízkou hustotou proudu — 50 mA/cm² při 237 K.

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Fryntová