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STUDY OF BROWNMILLERITE PREPARED AT 1200 °C

II. Reactivity with Water

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(Dedicated to the memory of the late Ing. Ján Petrovič, CSc.)

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X-ray diffraction methods and thermal analysis were used to determine the changes in phase composition of the systems C_4AF—H*) *and* C_4AF—$C\bar{S}H_2$—H *in the course of hydration of brownmillerite* (C_4AF) *synthesized by solid state reactions. The reactivity of substance in question was assessed on the basis of the time dependence of relative representation of the individual phases determined semiquantitatively from the diffractometric data.*

Reactions of C_4AF *with water give rise to a* Fe*-substituted hydrogarnet phase,* $C_3(A.\ F)H_6$, *while the so-called* AFm *phase is formed in the presence of* $C\bar{S}H_2$. *Under identical reaction conditions, the relative contents of* C_4AF *found are lower than the values reported for* C_4AF *synthesized from melt. The increase in the rate of the heterogeneous reactions is ascribed to the effect of the amorphous component and to that of the small crystals of* C_4AF *present after the synthesis in solid state on increasing the density of reaction centres at the brownmillerite-water boundary.*

INTRODUCTION

Reactions of the ferritic phase with water in pastes of cement clinkers produce the following Fe-substituted phases: ettringite (the AFt phase), monosulphate aluminate hydrate (the AFm phase) and hydrogarnet $C_3(A,\ F)H_6$ [2, 3]. The literature cited deals with the technological consequences of the formation of these phases in the process of the cement pastes hardening.

The main ferritic phase in cement clinker, brownmillerite, has been described in the literature in detail including its reactivity with water [4—15]. The composition of the hydration products is affected by the reaction conditions [4—8, 13—15], as well as by the properties which C_4AF has acquired in the course of its synthesis [1, 9, 10, 18]. Studies [4—8, 13—15] describe findings on the reactivity of melt-synthesized C_4AF with water. The reactions of C_4AF alone with water yield at first a hexagonal phase, $C_4(A,\ F)H_{13}$ and eventually hydrogarnet, $C_3(A,\ F)H_6$. The AFt and AFm phases being formed in the presence of $C\bar{S}H_2$ exhibit variable compositions and properties.

The aim of the present study was to get more information on the relation between the conditions of the synthesis and the properties of brownmillerite. The factors influencing the reactivity of C_4AF synthesized in solid state were determined, together with the composition of the products of its reactions with water. The results were compared with the reactivity of C_4AF synthesized from melt.

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*) Cement chemistry notation used: C—CaO, A—Al_2O_3, F—Fe_2O_3, $\bar{S}$—SO_3, H—H_2O.

EXPERIMENTAL

The solid state synthesis of brownmillerite at 1200 °C was described in Part I [1], the crystallographic data are given in [18]. The reactivity with water was studied on C_4AF prepared at 1200 °C, either via a nitrate-tartrate precursor or directly from a mixture of oxides. After firing at the given temperature the substances were separated into fractions by sieving: $\Phi\ (C_4AF)/\mu m$ 0—25, 25—40, 40—60, 60—90. Use was also made of $C\overline{S}H_2$ of AR grade, acetone of AR grade and distilled water.

The classified grain size fractions of brownmillerite and their mixtures with $C\overline{S}H_2$ were reacted with water under the following conditions: $20 \leqq \vartheta/°C \leqq 180$, $1 \leqq t/h \leqq 30 \times 24, 0 \leqq \frac{n(C\overline{S}H_2)}{n(C_4AF)} \leqq 4, \quad 0.5 \leqq \frac{n(\text{liquidus})}{n(\text{solidus})} \leqq 10$. The reactions were interrupted by washing with acetone and subsequent drying at 60 °C. The phase composition of the solid reaction products was determined from the results of X-ray semiquantitative analysis and using thermal analysis as a supplementary method.

The X-ray powder diffraction patterns were step-scanned on a HZG_84A diffractometer with $FeK_{\bar{\alpha}}$ ($\lambda = 0.193\,73$ nm) or $CuK_{\bar{\alpha}}$ radiation ($\lambda = 0.154\,1$ nm) in steps of 0.05 deg θ or 0.025 deg θ with 20 s per step. The patterns were processed by the ADR 2 systems of programs [16] providing the values of interplanar distances d(obs) and their relative intensities $I(r) = I/I_0$. The d(obs) values were assigned to the reference values d_{hkl}(ref) of the individual phases under the condition

$$\Delta d_{hkl} = |\, d(\text{obs}) — d_{hkl}(\text{ref}) \,| \leqq 0.002 \text{ nm}. \tag{1}$$

The relative contents of the phases in the reaction stages investigated were determined according to the relative changes in the intensities of diffractions, a selection of which is given in Table I. The ratios of the relative intensities of these diffractions in the individual reaction stages to the relative intensities of the diffractions of the pure phase were determined:

$$Y(p, i) = \frac{I(r, p, d_{pi}, t)}{I(r, p, d_{pi})}, \tag{2}$$

where $I(r, p, d_{pi}, t)$ is the relative intensity of the i-th diffraction of phase p at time t of the reaction,

$I(r, p, d_{pi})$ is the relative intensity of the i-th diffraction of pure phase p.

Table I

Diffractions of detected phases p and changes in their relative intensities from which the values of $Y(p, i)$ and $\bar{Y}(p)$ were determined

p	Phase	p	i	d_{pi}/nm	hkl	$I(r, p, d_{pi})$	$I(r, p, d_{pi}, t)$
1	C_4AF	1	1	0.367	130,040	0.20	0.20—0
		1	2	0.279	200	0.35	0.35—0
		1	3	0.266	141	1.0	1.0 —0
2	$C_4(A, F)H_{13}$	2	1	0.792	001	1.0	0 —0.42
		2	2	0.287	112	0.40	0 —0.17
3	$C_3(A, F)H_6$	3	1	0.336	321	0.40	0 —0.40
		3	2	0.282	420	0.80	0 —0.80
		3	3	0.231	521	1.0	0 —1.0

The content of each of the phases p is characterized by the arithmetic mean in the individual reaction stages (t = const):

$$\bar{Y}(p) = \frac{\sum\limits_{i=1}^{n} Y(p, i)}{n}, \tag{3}$$

where p is constant,
n is the number of selected i-th diffractions of phase p (cf. Table I).

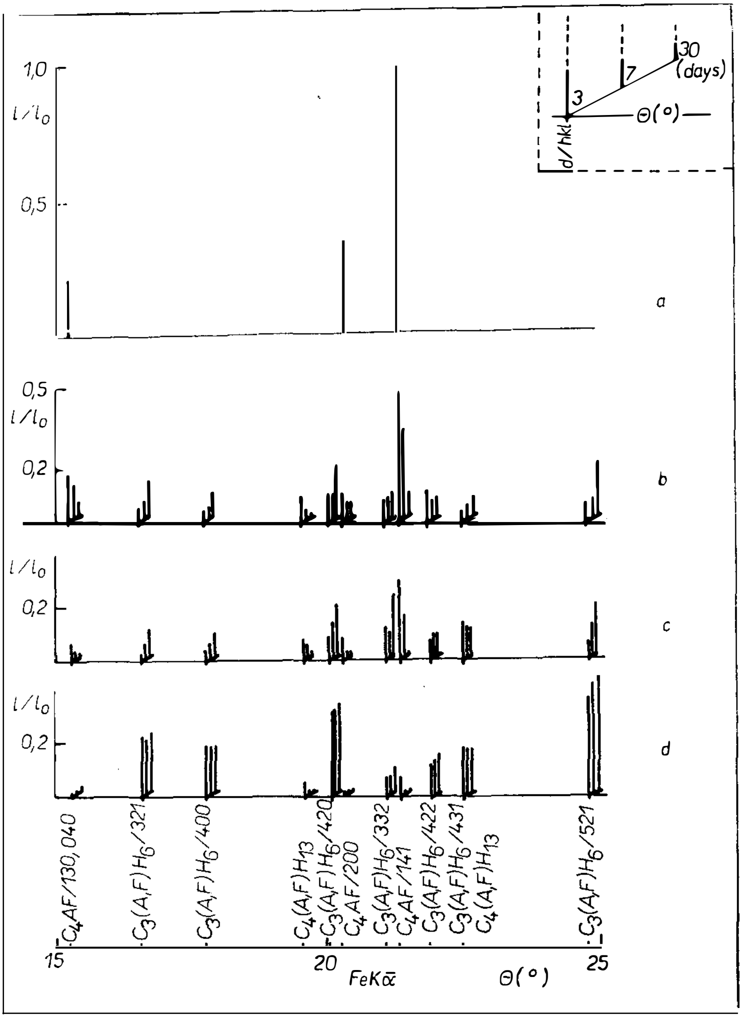

Fig. 1. Line transcription of parts of X-ray powder diffraction patterns of C_4AF *(a) and of the reaction products of grain size fractions of* C_4AF *with* H *at 20 °C (b—d) after 3, 7 and 30 days of duration;*
b: 90 ≧ Φ(C_4AF)/μm ≧ 60, c: 60 ≧ Φ(C_4AF)/μm ≧ 40, d: 40 ≧ Φ(C_4AF)/μm > 0.

The values of $\bar{Y}(p)$ represent the relative content of each phase p in the system in the course of the reactions studied ($0 \leq t/h \leq 24 \times 30$) and are regarded as a measure of reactivity of C_4AF with water. The results are expressed as a plot of $\bar{Y}(p)$ for $p = C_4AF$, $C_4(A, F)H_{13}$ and $C_3(A, F)H_6$ vs duration of the reaction and the particle size of the initial substance (Fig. 4). These results and the data from [5], processed in the same way, were used to compare the reactivity of C_4AF synthesized in solid state with that synthesized from melt. The findings on the phase composition of the respective reaction products were supplemented by the results of thermal analysis (Derivatograph Q 1500 D) and by the comparison with thermoanalytical data on the phases determined by X-ray phase analysis and those on hydrated aluminium and ferric oxides [5, 7, 8, 18].

RESULTS AND DISCUSSION

Brownmillerite synthesized in solid state at 1200 °C and reacted with water at room temperature (Fig. 1) forms a metastable hexagonal phase, $C_4(A, F)H_{13}$ and finally a hydrogarnet, $C_3(A, F)H_6$. C_4AF synthesized from melt behaves similarly

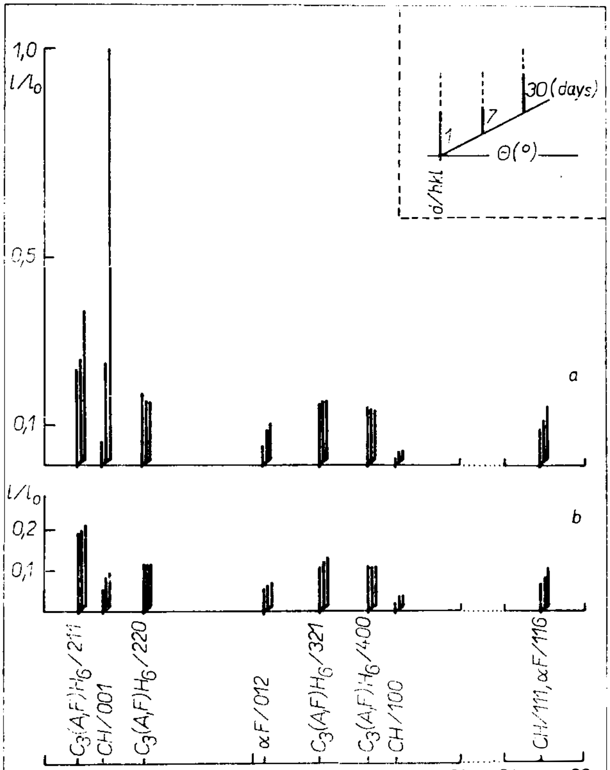

Fig. 2. Line transcription of parts of X-ray powder diffraction patterns of the reaction products of reaction of C_4AF *and* H *at 180 °C (a) and at 90 °C (b) after 1, 7 and 30 days of duration.*

[4—8, 15]. Reaction temperatures of 80 °C and higher cause the partial decomposition of the hydrogarnet producing αF and CH [4, 7, 15], the degree of decomposition in the given system depends on the temperature and the duration of reaction (Fig. 2).

The presence of $C\bar{S}H_2$ in the reaction system changes distinctly the phase composition of the reaction products. The formation of the AFt phase, $C_6(A, F)\bar{S}_3H_{32}$ [13] in studied system depends on the ratio $n(C\bar{S}H_2)/n(C_4AF)$ and the duration of the reaction (Table II). The X-ray powder difraction patterns of products isolated after 30 days of reaction at room temperature (Fig. 3) reveal the typical diffractions of the AFm phase, which forms limited solid solutions in the series $C_4(A, F)H_{13}$—$C_4(A, F)\bar{S}H_{12}$ [2, 3, 6, 7].

Table II

Formation of the AFt and AFm phases in the system C_4AF—$C\bar{S}H_2$—H at 20 °C

$n(C\bar{S}H_2)/n(C_4AF)$		4		4/3		Notice	
t/*h*		24	30 × 24	24	30 × 24		
AFt phase		+	+	+	—	+ phase present — phase absent	
AFm phase		—	+	+	+		
Analytical diffractions: *d*/nm	AFt — $C_6(A, F)\bar{S}_3H_{32}$ [13]	0.973	0.561	0.498	0.348	0.256	0.221
	AFm [6, 7]	0.830		0.287	0.273	0.244	0.233
	$C_4(A, F)H_{13}$ [6, 8]	0.792		0.287		0.245	0.224
	$C_4(A, F)\bar{S}H_{12}$ [7]	0.890		0.297	0.277	0.242	0.235

The A—F and $\bar{S}$—H substitutions affect the values of interplanar distances [6, 7, 13] as well as the thermoanalytical properties [6, 7] in a way that has not so far been defined, and this renders exact identification of the AFt and AFm phases difficult. However, these phases are said to play a significant role in the development of technologic properties of cement clinker pastes, particularly at an elevated content of the ferritic phase [2, 3].

Apart from confirming the findings described above, the thermal analysis proved the presence of amorphous hydrated oxides of aluminium and iron. The results indicate that the reactivity of brownmillerite with water is affected by the reaction temperature, the duration of the reaction and by the presence of $C\bar{S}H_2$. The effect of particle size on the rate of the reaction of brownmillerite with water is discussed below. The reactivity of C_4AF synthesized in solid state is compared to that of C_4AF synthesized in melt on the basis of changes in relative representations of the individual phases in the course of reactions of respective grain size fractions and by means of the values determined according to [5] (Fig. 4).

The size of the C_4AF particles and the ratio $n(C\bar{S}H_2)/n(C_4AF)$ influence the degree to which C_4AF has reacted and the formation of the hydrogarnet phase and of the AFm phase (Figs. 1 and 3, Table II). The results shown in Fig. 4 indicate that the

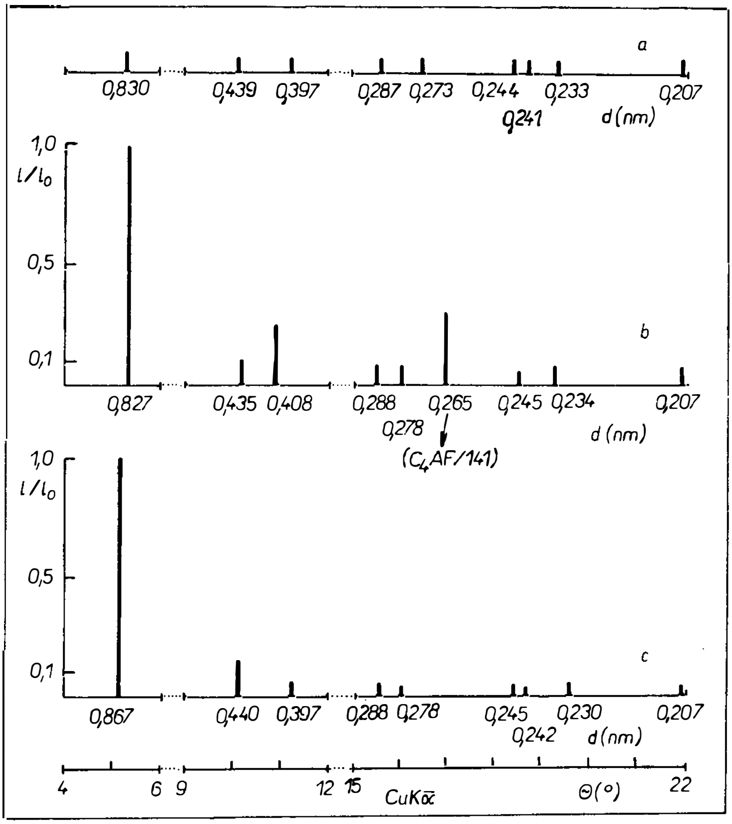

Fig. 3. Line transcription of parts of X-ray powder diffraction patterns of the AFm *phase according to* [6] (*a*) *and of the reaction products of* C_4AF *with* $C\bar{S}H_2$ *and* H *at 20 °C after 24 hours* (*b*) *and 30 days* (*c*) *of duration;*

b: $90 \geqq \Phi(C_4AF)/\mu m \geqq 60$, $n(C\bar{S}H_2)/n(C_4AF) = 4/3$, $t/h = 24$,

c: $40 \geqq \Phi(C_4AF)/\mu m > 0$, $n(C\bar{S}H_2)/n(C_4AF) = 4/3$, $t/h = 24 \times 30$.

particle size is one of the factors influencing the reactivity of C_4AF (cf. Fig. 4a—c) and that C_4AF prepared in solid state is more reactive with respect to water (Fig. 4, curves) than C_4AF synthesized from melt (points 1^5, 3^5 in Fig. 4).

The results obtained are in agreement with the general relationship also verified in the chemistry of cement [11, 12], namely that the occurence of defects and the density of reaction centres increase with decreasing of the particle size, with the direct consequence on the increase of the reaction rates of heterogeneous reactions taking place at the solid-liquid boundary. The latter also explains the higher reactivity of C_4AF being studied, which contains a significant portion of the so-called amorphous component and small crystallites [1, 18].

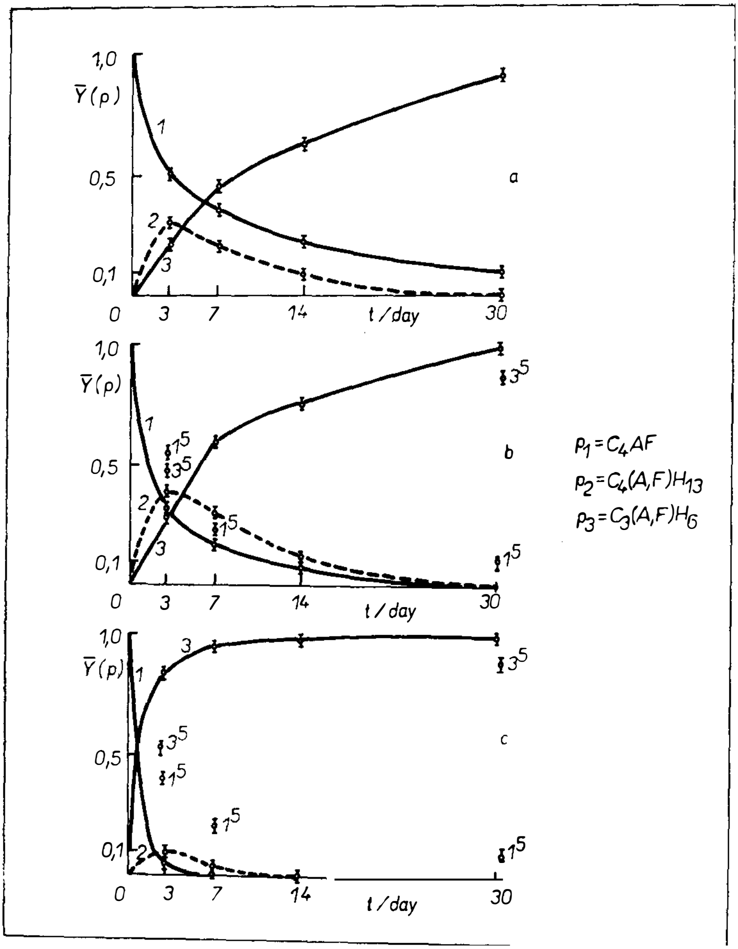

Fig. 4. Relationships $\bar{Y}$ *(p) for p =* C_4AF *(curves 1), p =* $C_4(A, F)H_{13}$ *(curves 2) and p =* $C_3(AF)H_6$ *(curves 3) in the course of reactions of* C_4AF *grain size fractions with* H *at 20 °C;*
a: 90 ≧ $\Phi(C_4A, F)/\mu m$ *≧ 60, b: 60 ≧* $\Phi(C_4AF)/\mu m$ *≧ 40, c: 40 ≧* $\Phi(C_4AF)/\mu m$ *> 0.*
1^5, 3^5 *are the values of Y (p) determined from [5] for* C_4AF *synthesized in melt* (1^5) *and the final product of its reaction with* H *at 20 °C —* $C_3(A, F)H_6$ (3^5).

CONCLUSION

1. C_4AF synthesized in solid state at 1200 °C combines with water producing the same hydrated phases as C_4AF synthesized from melt. The presence of $C\bar{S}H_2$ in the reaction system is responsible for the formation of AFt and AFm phases which are technologically significant.

2. C_4AF synthesized in solid state is more reactive than C_4AF synthesized from melt. The higher reactivity is associated with the content of an amorphous compo-

nent and of small crystallites in C_4AF after its solid state synthesis and with their effect on the number of defects in the substance and on the density of reaction centres at the brownmillerite-water boundary.

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ŠTÚDIUM BROWNMILLERITU PRIPRAVENÉHO PRI 1200 °C.

II. REAKTIVITA S VODOU

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Syntézu brownmilleritu reakciami v tuhej fáze pri 1200 °C sme popísali v časti I. Časť II sa zaoberá reaktivitou tejto látky s vodou a porovnáva ju s údajmi publikovanými pre C_4AF syntetizovaný v tavenine; ako miera reaktivity sa použili časové závislosti relatívneho zastúpenia fáz C_4AF, $C_4(A, F)H_{13}$ a $C_3(A, F)H_6$ v reakčných sústavách.

Výsledky rtg. semikvantitatívnej analýzy a termickej analýzy potvrdzujú v širokom intervale teplôt, trvania reakcií, ako aj prídavkov $C\bar{S}H_2$ vznik známych hydratovaných fáz: $C_4(A, F)H_{13}$, $C_3(A, F)H_6$, fáza AFt, fáza AFm (obr. 1—3). Účinok veľkosti častíc C_4AF na rýchlosť reakcie brownmilleritu s vodou (obr. 4) je v súhlase so všeobecne platnou závislosťou, podľa ktorej so zmenšovaním rozmerov častíc stúpa defektnosť, zvyšuje sa hustota reakčných centier a teda aj rýchlosť heterogénnych reakcií. C_4AF syntetizovaný v tuhej fáze je voči vode reaktívnejší (krivky na obr. 4) ako C_4AF syntetizovaný v tavenine (body 1^5, 3^5 na obr. 4). Vyššia reaktivita študovaného C_4AF je, v zmysle vplyvu veľkosti častíc, podmienená malými kryštalitmi, ktorých vznik je preferovaný počas syntézy C_4AF v tuhej fáze.

Obr. 1. Čiarový prepis častí práškových rtg. difrakčných záznamov C_4AF (*a*) *a produktov reakcií vysitovaných frakcií* C_4AF *s* H *pri 20 °C po 3, 7 a 30 dňoch trvania reakcie* (*b—d*); *b*: $90 \geqq \Phi(C_4AF)/\mu m \geqq 60$, *c*: $60 \geqq \Phi(C_4AF)/\mu m \geqq 40$, *d*: $40 \geqq \Phi(C_4AF)/\mu m > 0$.

Obr. 2. Čiarový prepis častí práškových rtg. difrakčných záznamov produktov reakcii C_4AF *s* H *pri 180 °C (a) a 90 °C (b) po 1, 7 a 30 dňoch trvania reakcie.*

Obr. 3. Čiarový prepis častí práškových rtg. difrakčných záznamov fázy AFm *podľa [6] (a) a produktov reakcii* C_4AF *s* $C\bar{S}H_2$ *a* H *pri 20 °C po 24 hodinách (b) a 30 dňoch (c) trvania reakcie.* b: $90 \geqq \Phi\ (C_4AF)/\mu m \geqq 60$, $n(CSH_2)/n(C_4AF = 4/3$, $t/h = 24$; c: $40 \geqq \Phi\ (C_4AF)/\mu m > 0$, $n(CSH_2)/n(C_4AF) = 4/3$, $t/h = 30 \times 24$.

Obr. 4. Závislosti $\bar{Y}$ *(p) pre* $p = C_4AF$ *(krivky 1),* $p = C_4(A, F)H_{13}$ *(krivky 2) a* $p = C_3(A, F)H_6$ *(krivky 3) v priebehu reakcii vysitovanýchfrakcii* C_4AF *s* H *pri 20 °C; a:* $90 \geqq \Phi(C_4AF)/\mu m \geqq 60$. *b:* $60 \geqq \Phi(C_4AF)/\mu m \geqq 40$, *c:* $40 \geqq \Phi(C_4AF)/\mu m > 0$. 1^5, 3^5 *— hodnoty* $\bar{Y}$ *(p) určené z výsledkov [5] pre* C_4AF *syntetizovaný v tavenine* (1^5) *a finálny produkt jeho reakcie s* H *pri 20 °C —* $C_3(A, F)H_6$ (3^5).

ИССЛЕДОВАНИЕ БРОВНМИЛЛЕРИТА, ПРИГОТОВЛЕННОГО ПРИ ТЕМПЕРАТУРЕ 1200 °С

II. ВЗАИМОДЕЙСТВИЕ С ВОДОЙ

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Первая часть была посвящена синтезу бровнмиллерита, реагирующего в твердой фазе при температуре 1 200 °С. Во второй части рассматривается взаимодействие данного вещества с водой в сопоставлении с данными, опубликованными относительно C_4AF синтетизированного в расплаве; в качестве степени реактивности использовали временные зависимости относительного содержания фаз C_4AF, $C_4(A, F)H_{13}$ и $C_3(A, F)H_6$ в реакционных системах.

Результаты рентгеновского полуколичественного анализа и термического анализа подтверждают в широком интервале температур, длительности реакций, включая Добавки $C\bar{S}H_2$ образование известных гидратированных фаз: $C_4(A, F)H_{13}$, $C_3(A, F)H_6$, фазы AFt, фазы AFm (рис. 1—3). Действие размера частиц C_4AF на скорость взаимодействия бровнмиллерита с водой (рис. 4) находится в согласии с общедействующей зависимостью, согласно которой уменьшением размеров частиц растет дефектность, повышается плотность реакционных центров, а следовательно скорость гетерогенных реакций. C_4AF, синтезированный в твердой фазе, является относительно воды более реактивным (кривые на рис. 4) по сравнению с C_4AF, синтезированным в расплаве (точки 1^5, 3^5 на рис. 4). Более высокая реактивность исследуемого C_4AF, в значении влияния размера частиц, обусловлена аморфным компонентом и небольшими кристаллами, образующимися преимущественно во время синтеза C_4AF в тревдой фазе.

Рис. 1. Линейная перезапись частей порошковых рентгеновских дифракционных записей C_4AF *(a) и продуктов реакций просеиванных фракций* C_4AF *с* H *при температуре 20 °С после 3, 7 и 30 суток длительности реакций (b — d); b:* $90 \geqq \Phi(C_4AF)/\mu м \geqq 60$, *c:* $60 \geqq \Phi(C_4AF)/\mu м \geqq 40$, *d:* $40 \geqq (C_4AF)/\mu м > 0$.

Рис. 2. Линейная перезапись частей порошковых рентгеновских дифракционных записей продуктов реакций C_4AF *с* H *при температуре 180 °С (a) и 90 °С (b) после 1, 7 и 30 суток длительности реакции.*

Рис. 3. Линейная перезапись частей порошковых рентгеновских дифракционных записей AFm *согласно [6] (a) и продуктов реакций* C_4AF *с* $C\bar{S}H_2$ *и* H *при температуре 20 °С после суток (b) и 30 суток (c) длительности реакции; b:* $90 > \Phi(C_4AF)/\mu м \geqq 60$, $n(CSH_2)/n(C_4AF) = 4/3$, $t/h = 24$; *c:* $40 \geqq \Phi(C_4AF)/\mu м \geqq 0$, $n(C\bar{S}H_2)/n(C_4AF) = 4/3$, $t/h = 30 \times 24$.

Рис. 4. Зависимости $\bar{Y}(p)$ *для* $p = C_4AF$ *(кривые 1),* $p = C_4(AF)H_{13}$ *(кривые 2) и* $p = C_3(A, F)H_6$ *(кривые 3) в ходе реакций просеиванных фракций* C_4AF *с* H *при температуре 20 °С; a:* $90 \geqq \Phi(C_4AF)/\mu м \geqq 60$, *b:* $60 \geqq \Phi(C_4AF)/\mu м \geqq 40$, *c:* $40 \geqq \Phi(C_4AF)/\mu м > 0$. 1^5, 3^5 *— величины* $\bar{Y}(p)$, *полученные из результатов [5] для* C_4AF *синтезированного в расплаве* (1^5) *и окончательный продукт его реакции с* H *при температуре 20 °С —* $C_3(A, F)H_6$ (3^5).