VOL. 14, NO. 14, JULY 2019 ISSN 1819-6608
ARPN Journal of Engineering and Applied Sciences

www.arpnjournals.com

SYNTHESIS AND PROPERTIES OF ALUMINATES CLINKER OF COMPLEX COMPOSITION

Miryuk O. A.
Rudny Industrial Institute Let Oktyabrya Street, Rudny, Kostanay Region, Kazakhstan
E-Mail: psm58@mail.ru

ABSTRACT

The article presents the results of studies on synthesis and hydration of aluminate clinkers and cements containing C_6A_4MS phase. Influence of calcium sulfate and iron oxide additives on thermal transformations during C_6A_4MS synthesis was determined. A method for calculating composition of three-component mixture for, which takes into account MgO and SiO_2 presence in raw materials is proposed. The calculation method makes it possible to optimize phase composition of clinker due to directional choice of the modulus of basicity, silica and magnesia modules. Aluminate clinker was synthesized from raw mixes with different modules values. Dependence of properties of aluminate cements on values of the modules and content of clinker's phases was revealed. Composition of hydrated aluminate cement with the content of C_6A_4MS phase is presented. There was marked strength stability of cement stone of long-lasting hardening.

Keywords: aluminate clinker, calcium magnesium silicoaluminate, clinker formation, cement hydration.

1. INTRODUCTION

Special cements have unique properties and are able to meet the needs of various branches of construction. Of particular practical interest are aluminate cements. High rate of hardening of aluminate cements makes it possible to refuse heat treatment during hardening of concrete [1-3].

Recently, there has been a shortage of alumina-containing raw materials, so the possibility of replacing traditional raw materials with industrial waste is being investigated [4]. To obtain aluminate clinkers raw materials that contain minerals based on silicon, magnesium and iron are used [4-12]. In raw mixtures of complex composition, calcium magnesium silicoaluminate C_6A_4MS is formed, which is also called magnesian pleochroite or Q phase [13-16]. Information about synthesis and properties of C_6A_4MS are few. An understanding of C_6A_4MS effect on the properties of aluminate cements is required.

Objective: to study the processes of synthesis and hardening of aluminate cements containing C_6A_4MS phase.

2. MATERIALS AND METHODS OF INVESTIGATION

For synthesis of the studied phase, a mixture of stoichiometric composition of chemical reagents was used. To obtain clinkers, mixtures of dolomitic limestone, substandard bauxite, and magnetite ore wastes were prepared. Sub-conditioned bauxite contains, %: SiO_2 - 12; Al_2O_3 - 50; Fe_2O_3 - 5; CaO - 1; SO_3 - 4; R_2O - 0.5; others - 2.5; loss on ignition - 25. Chemical composition of magnetite ores waste, %: SiO_2 - 40; Al_2O_3 - 12; Fe_2O_3 - 14; CaO - 13; MgO - 5; S - 7; R_2O - 4; loss on ignition - 5. The samples of raw mix were burned in the temperature range of 1150 -1350 ^{0}C.

Strength properties of cement were determined on samples of size 20x20x20 mm solidified in water.

Phase C_6A_4MS was identified using infrared spectroscopy and microscopy. Composition of clinker and cement stone was analyzed using X - ray phase method. The phase composition of the raw mixture, burnt at temperatures of 800 - 1350 ^{0}C, was determined using general purpose X - ray diffractometer, type DRON - 3M. The diffractometer is equipped with a BSV - 24 type X - ray tube with CuK α - radiation. The diffractograms were processed using difWin program.

3. RESULTS AND DISCUSSIONS

3.1 Synthesis of C_6A_4MS phase

Study of clinker formation in polymineral mixtures is difficult because of variety of processes and compounds. Therefore, a stoichiometric mixture designed for preparation of magnesium calcium silicoaluminate of C_6A_4MS was used for the research. The raw material mixture was prepared from chemically pure reagents of $CaCO_3$ (based on 39.83 % of CaO), Al_2O_3 (48.28 %), SiO_2 (7.12 %), MgO (4.77 %). The raw mix was burned at temperatures of 1150 - 1300 ^{0}C. According to the data of diffractometric analysis, it was established that intensive formation of C_6A_4MS occurs at a temperature of 1250 - 1350 ^{0}C (Figure-1).

Comparison of infrared spectrum of C_6A_4MS phase (Figure-2) with the reference spectra of various calcium aluminates reveals similarities of C_6A_4MS and CA structures. This confirms the presence of absorption bands in the area of (650 - 900) cm $^{-1}$, belonging to alumino-oxygen tetrahedral units. A distinctive feature of C_6A_4MS IR spectrum is the band of (1000 - 1040) cm $^{-1}$ - the absorption region for SiO_4 tetrahedral units.

Microscopic examination of clinker in immersion preparations confirmed C_6A_4MS phase presence. Crystal-optic C_6A_4MS characteristics: Ng = 1.673; Np = 1,669. C_6A_4MS phase crystallizes as prismatic C_6A_4MS crystals (Figure-3).

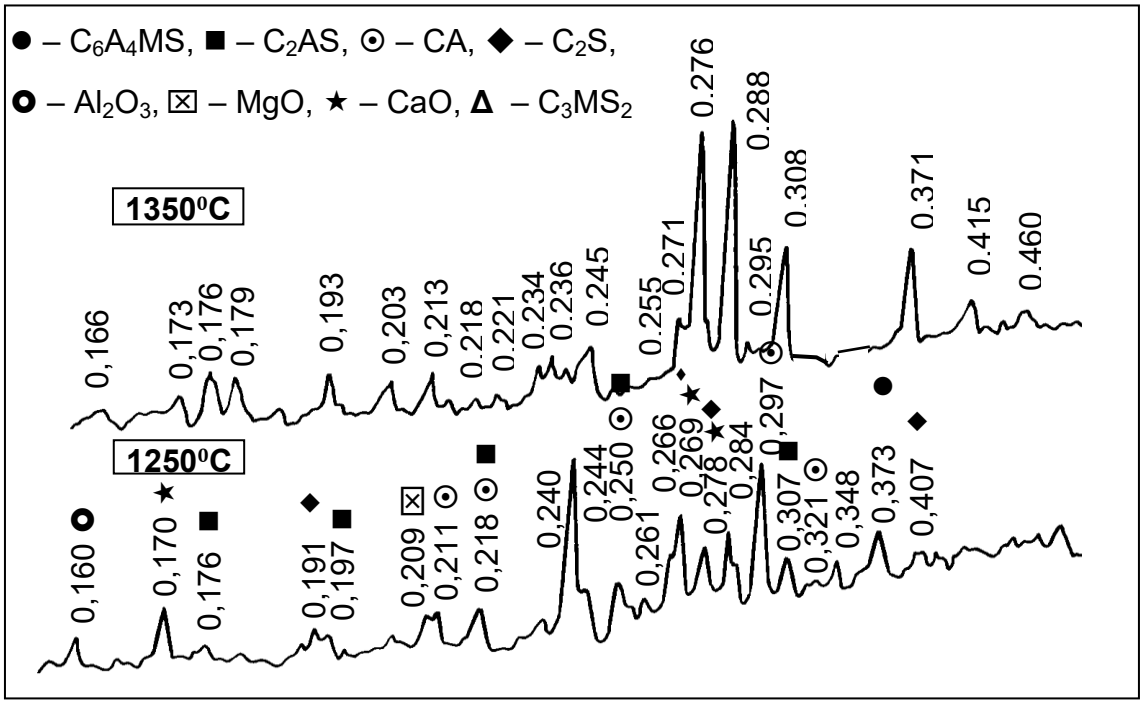

Figure-1. X - ray diffraction patterns of the raw mix burned at different temperatures.

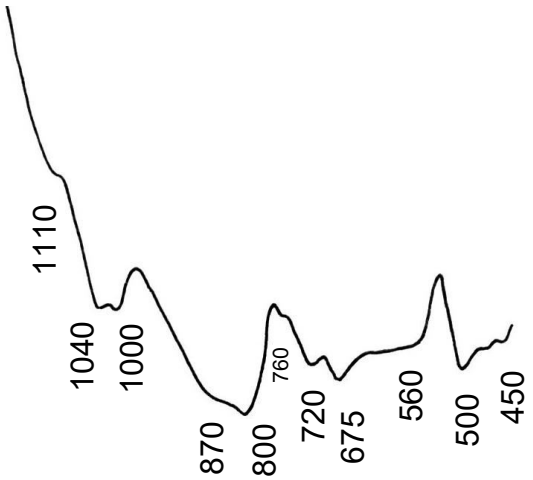

Figure-2. Infra-red spectrum C_6A_4MS.

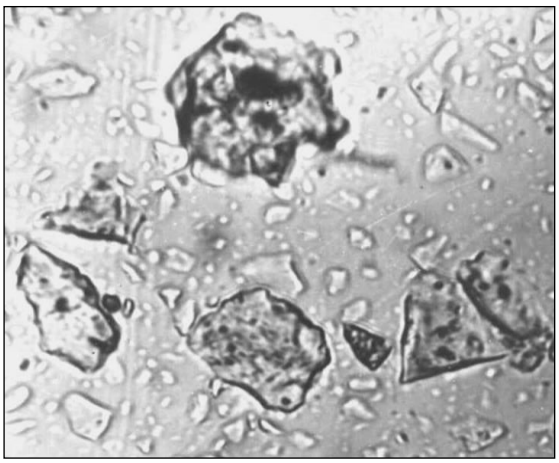

Figure-3. Crystals C_6A_4MS (x 500).

3.2 Effect of additives on C_6A_4MS phase formation

Formation of C_6A_4MS in the presence of calcium sulfate, which is introduced for modified aluminate clinkers [17-20], was studied. $CaSO_4$ was added to stoichiometric mixture designed for synthesis of C_6A_4MS in the amount of 5 wt. % over 100 % (Figure-4). When $CaSO_4$ is added to the mixture, part of calcium aluminates is converted to calcium sulfoaluminate $3(CA)CaSO_4$. The amount of gehlenite C_2AS decreases as a result of the following reaction:

$$3C_2AS + 3C + CaSO_4 \rightarrow 3(CA)CaSO_4 + 3C_2S. \quad (1)$$

A significant proportion of dicalcium silicate C_2S is converted to calcium silicosulfate $2(C_2S)CaSO_4$ and does not participate in C_6A_4MS formation.

Therefore, coexistence of $3(CA)CaSO_4$ and C_6A_4MS is possible in aluminate clinkers with initial and predominant formation of calcium sulfoaluminate.

In alumina-containing raw materials combinations of impurities of silicon, magnesium and iron are not uncommon. The effect of Fe_2O_3 on C_6A_4MS formation phase was studied. Phase changes were revealed during burning of the raw mix, calculated to produce C_6A_4MS, with addition of 10 wt. % of Fe_2O_3 in excess of 100% (Figure-5).

With introduction of Fe_2O_3, intermediate phases CF, C_2F, C_2MF are formed by reducing the amount of calcium aluminates; C_6A_4MS synthesis is intensified, including with participation of C_2MF, C_6A_2F:

$$4CA + C_2S + C_2MF \rightarrow C_6A_4MS + C_2F, \quad (2)$$

$$C_2MF + 3A + 3C + C_2AS \rightarrow C_6A_4MS + CF, \quad (3)$$

$$C_6A_2F + CA + C_2AS + M \rightarrow C_6A_4MS + C_2F + C. \quad (4)$$

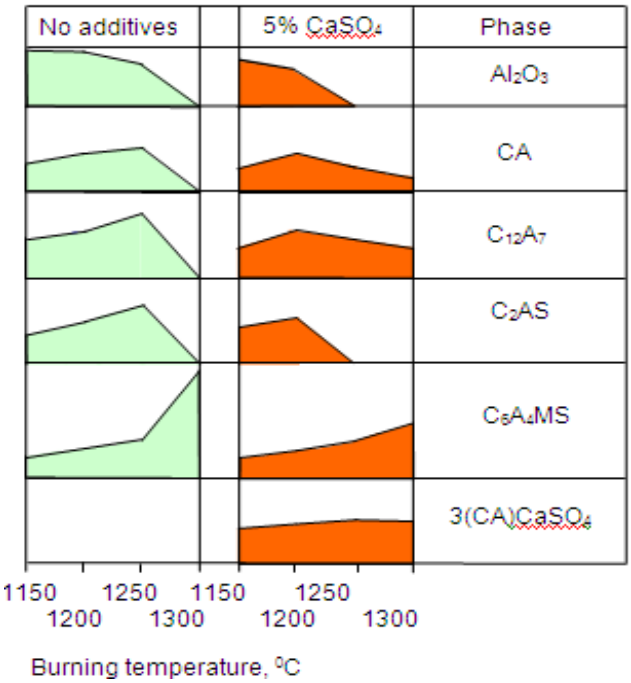

Figure-4. Effect of $CaSO_4$ on phase transformations in C_6A_4MS synthesis.

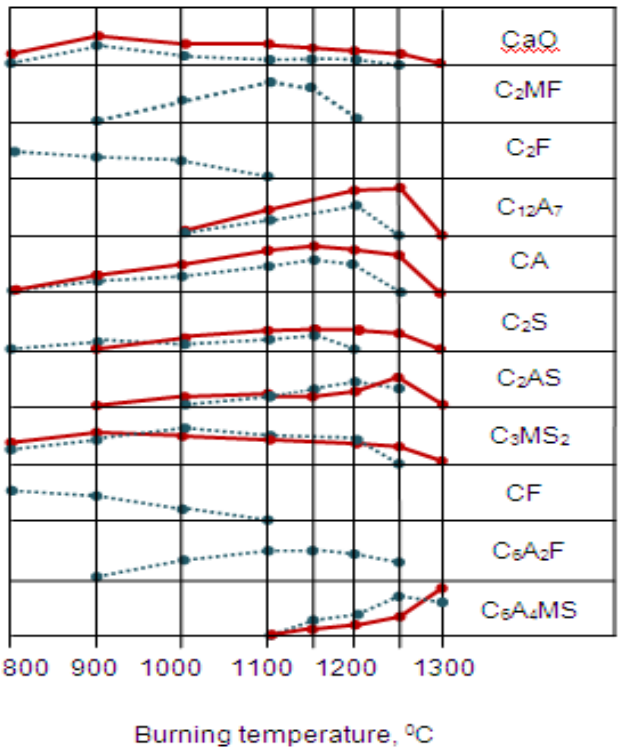

Figure-5. Fe_2O_3 influence on phase formation during synthesis of C_6A_4MS.

The content of C_6A_4MS in iron-containing clinker is reduced by almost 20 %. Along with the C_6A_4MS phase, C_6A_2F, C_2AS, which are not involved in synthesis of C_6A_4MS is present in the calcined mixture. Clinker formation in the iron-containing mixture is completed at 1250 - 1280 ^{0}C, with increase in temperature the clinker melts. Melting of clinker is accompanied by decay of C_6A_4MS with release of CA.

3.3 Method of calculating the composition of raw mixes for aluminate clinkers

Lime stones and bauxites with different content of SiO_2 and MgO, waste products of magnetite ores were used for clinkers synthesis with the content of C_6A_4MS phase.

A method for calculating the composition of raw mixes for aluminate clinkers production using modules a, n, and m has been developed.

The modulus of basicity expresses the degree of saturation of alumina with calcium oxide and characterizes the ratio of CaO: Al_2O_3:

$$a = \frac{C - 1.87S - 1.05F - 0.70SO_3}{0.55A}, \quad (5)$$

where C, S, F, SO_4, A – content of oxides in the raw mix or clinker, %;

1.87 - is the ratio of CaO mass to the mass of SiO_2 in C_2S;

1.05 - is the ratio of CaO mass to the mass of Fe_3O_3 in C_3F;

0.70 - is the ratio of CaO mass to the mass of SO_4 in $CaSO_4$;

0.55 - is the ratio of CaO mass to the mass of Al_2O_3 in CA.

For values of a ≥ 1 in the clinker, formation of inert C_2AS is excluded.

The silica module n expresses proportion of SiO_2 bound in C_6A_4MS, and the ratio between aluminate and silicate phases of the clinker as follows:

$$n = \frac{0.147A}{S}, \quad (6)$$

where 0.147 - is the ratio of SiO_2 to Al_2O_3 mass in C_6A_4MS.

The magnesia modulus m characterizes the ratio of MgO required for binding

Al_2O_3 in C_6A_4MS, to the total concentration of MgO:

$$m = \frac{0.099A}{M}, \quad (7)$$

where 0.099 - is the ratio of MgO mass to the mass of Al_2O_3 in C_6A_4MS.

To minimize the content of C_2S and limit of free MgO proportion in the clinker, it is advisable to increase the values of the modules: n ≥ 0.5; m ≥ 0.5.

Raw mixes were burnt at a temperature of 1300 - 1320 ^{0}C until complete binding of calcium oxide. Analysis of diffractograms shown in Figure-6 indicates a complex composition of clinkers. In the highly basic clinker 1C,

along with 3(CA) $CaSO_4$ and C_3A is present. Increase in silica in the mixture for clinker 2C causes the appearance of C_2S belite. In the low-base clinker 3C, C_2AS gehlenite dominates, it contains C_2S belit and small amounts of 3(CA) $CaSO_4$ and C_3A are preserved. Synthesis of clinkers with a given content of magnesium silicoaluminate calcium indicates the validity of calculations of raw mix composition, made by the proposed method.

The phase composition of clinkers affects hardening of cements (Table-1). Cements 2C and 3C contain silica phases and harden slowly. Cement 3C includes gehlenite and is characterized by low strength during all test periods.

Table-1. Properties of cements based on raw mixes of different composition.

Aluminate clincer	Raw mixture modules			Compression resistance, MPa, at the age of, 24-hour day	
	a	n	m	3	28
1C	1.25	1.35	1.10	78	80
2C	1.20	0.65	0.70	68	89
3C	0.65	0.70	1.10	21	27
Portland cement				73	79

Aluminate clinkers were synthesized, differing in the value of silica module (Table 2). Raw mixes were burned at temperatures of 1300 - 1370 ^{0}C.

Strength properties of cements depend on the content of aluminate phases and achieve the highest performance under increased values of silica module ($n \geq 1$). Presence of calcium monoaluminate in K - 1.5 clinker provides accelerated hardening in the early period. Total MgO content in clinkers of K – 1.5; K - 1.0 and K - 0.5 exceeds the recommended limit and, accordingly, is equal to, wt.%: 5.1; 5.4; 6.1. However, the main part of magnesium oxide is bound in calcium magnesium silicoaluminate. Periclase concentration is low (Table-2) and does not cause destructive changes in the cement stone during hardening.

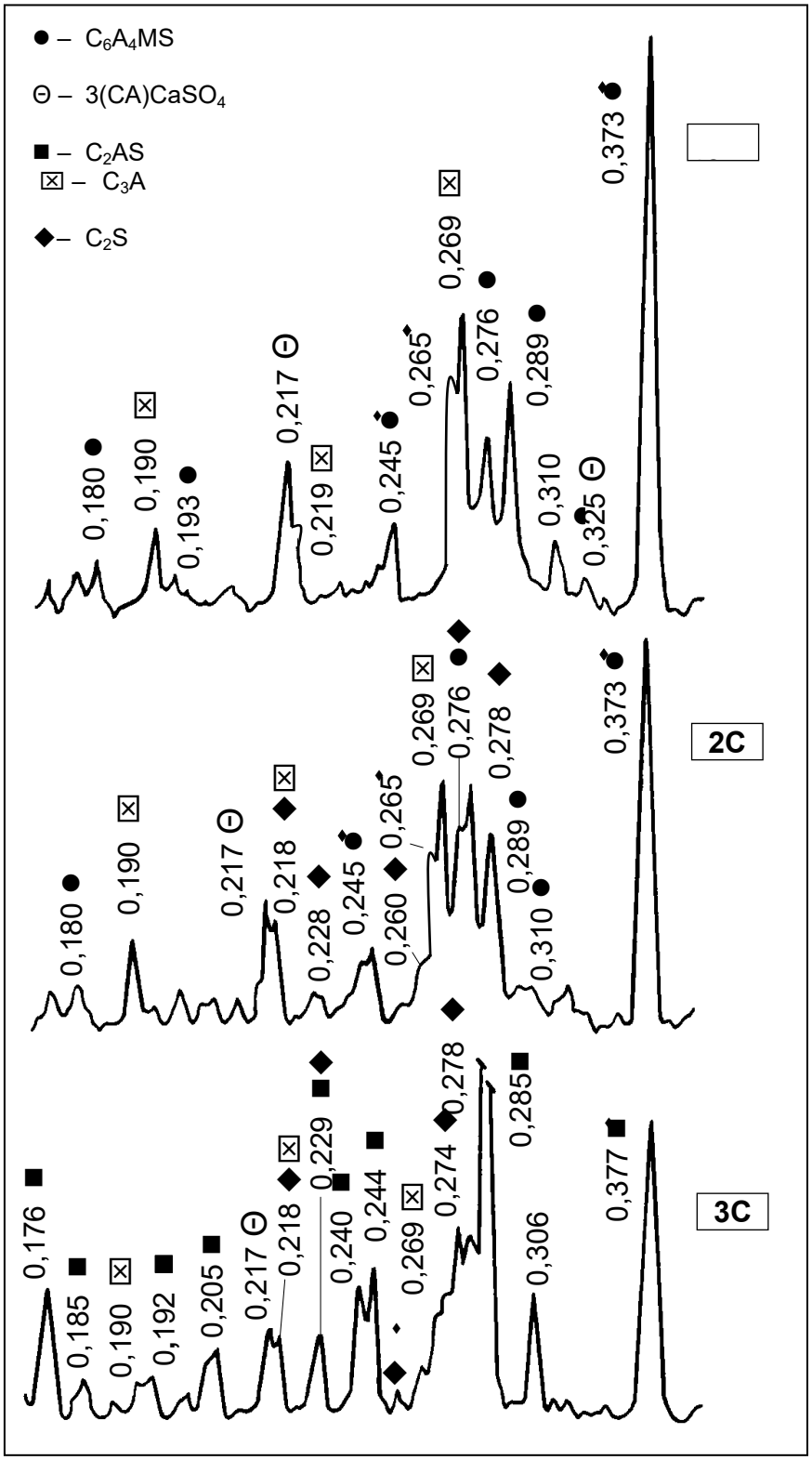

Figure-6. X-ray of aluminate clinkers of different composition.

Table-2. Effect of phase composition on the properties of aluminate clinkers.

Characteristics	Aluminate clinker		
	K - 1.5	**K - 1.0**	**K-0.5**
Basicity module, a	1.0	1.0	1.0
Silica module, n	1.5	1.0	0.5
Magnesian module, m	0.9	0.8	0.6
Phase content, %:			
– C_6A_4MS	67	84	58
– $3(CA)CaSO_4$	7	8	11
– C_4AF	5	6	10
– CA	20	no	no
– C_2S	no	no	17
– MgO (periclase)	0.6	1.3	3.4
Compression resistance, MPa			
– 24-hour day	57	51	39
– 7 twenty-hour days	83	79	67
– 28 twenty-hour days	105	115	94

The proposed method of calculating the composition of three-component mixtures is focused on formation of C_6A_4MS phase in the clinker. Formation of magnesium silicoaluminate is not the main goal, but serves as a way to maximize conversion of inert compounds into the active phase. In addition, each 1 % of MgO is able to bind 1.49 % of SiO_2 and convert 6.77 % of inert gehlenite into the active phase of C_6A_4MS. On the other hand, 0.5% of MgO is involved in the formation of every 10% of magnesium calcium silicoaluminate. This allows you to increase the level of permissible total MgO content in the clinker.

3.4 Hydration of cement with a high content of C_6A_4MS phase

The processes of hydration and hardening of cement with a high content of C_6A_4MS were investigated. Cement was obtained from clinker with modules: a = 1.1; n = 0.98; m = 1.01 (Table-3). Phase composition of clinker, wt. % is: C_6A_4MS - 55; C_3A - 12; $C_{12}A_7$ - 11; 3(CA) $CaSO_4$ - 15; C_4AF - 7.

Cement is characterized by moderate setting speed, intensive hardening in the first three days, stable development of strength and maintaining of high strength values while long-range hardening (Table-3).

Table-3. Basic characteristics of cement.

Standard consistency, %	Setting time, h-min		Compression resistance, MPa, at the age of, 24-hour day					
	start	**finish**	**1**	**3**	**7**	**14**	**28**	**3600**
27.7	1 - 55	2 - 50	41	70	72	87	99	70

The nature of cement hardening reflects characteristics of C_6A_4MS hydration phase. Analysis of diffractograms of cement in the early periods of hydration (Figure-7) indicates the initial formation of C_4AH_{13} (d = 0.804 nm), CAH_{10}subsequent formation (d = 1.43; 0.716 nm) and C_2AH_8 (d = 1.08 nm). On the radiograph of a stone at the age of 1 day, reflections of ettringite are noted (d = 0.98; 0.49 nm), formed during hydration of calcium sulfoaluminate.

Stable increase in cement stone strength during long-term hardening is associated with increased stability of hexagonal calcium hydroaluminates, low rate of their recrystallization. CAH_{10} (d = 1.43; 0.720; 0.375; 0.255 nm) was found in cement hardened for 10 years; its content exceeds the amount of C_3AH_6 (d = 0.514; 0.336; 0.278; 0.228; 0.202 nm) and AH_3 (d = 0.482; 0.440; 0.240 nm).

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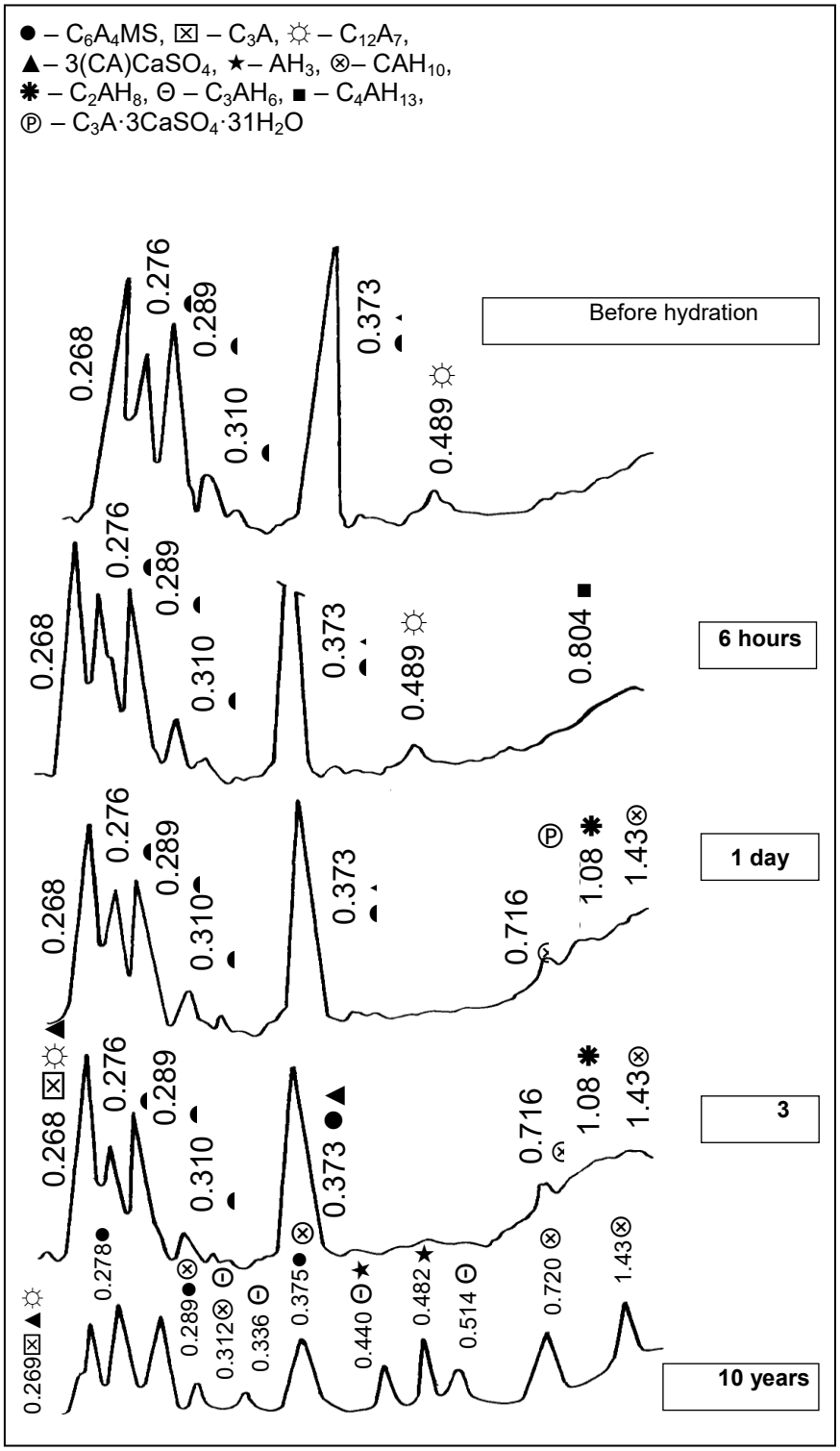

Figure-7. X-ray of hydrated cement.

Duration of hexagonal calcium hydroaluminates existence is achieved by stabilizing effect of hydrated magnesium-containing and silicon-containing ions formed during hydrolysis of initial C_6A_4MS phase and incorporated into the matrix structure.

4. CONCLUSIONS

Calcium magnesium silicoaluminate C_6A_4MS is a preferred magnesium-containing and silica-containing phase of aluminate clinkers. When C_6A_4MS is formed, mutual «neutralization» of SiO_2 and MgO impurities undesirable for aluminate clinkers occurs. Formation of C_6A_4MS is accompanied by minimization or exclusion of

C_2AS, C_2S and MgO phases, characterized by low hydration activity.

The combined presence of C_6A_4MS and 3(CA) $CaSO_4$ in aluminate clinkers was established during initial and predominant formation of calcium sulfoaluminate. Formation of C_6A_4MS is promoted by increased concentration of Fe_2O_3.

High hydraulic activity of cements containing calcium magnesium silicoaluminate indicates reasonability of C_6A_4MS phase presence in the aluminate clinker.

The developed method for calculating of mixtures' composition makes it possible to optimize phase composition of aluminate clinker using the specified values of basicity modulus of (a > 1), silica module (n > 0.5) and magnesian module (m > 0.5). Possibility of directed influence on the formation and properties of aluminate clinkers contributes to expansion of raw materials resources for cement production.

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