Technobius

https://technobius.kz/

Article

Binding properties of synthesized CS glasses activated by alkaline components

Bakhytzhan Sarsenbayev[1], Sultan Auyesbek[1,*], Meiram Begentayev[2],
Nuraly Sarsenbayev[1], Erkin Khaltursunov[3], Gaukhar Sauganova[1]

[1]M. Auezov South Kazakhstan University, Shymkent, Kazakhstan
[2]Kazakh National Research Technical University named after K. Satpayev, Almaty, Kazakhstan
[3]Turin Polytechnic University in Tashkent, Tashkent, Uzbekistan
*Correspondence: sultan_067@mail.ru

Abstract. The paper presents the synthesis and evaluation of hydration and binding properties of individual minerals with glass-like structures in silicate systems, most often found in technogenic materials based on phosphorus and blast furnace slags. This work aims to determine the optimum composition of CS glasses to obtain binders with given properties, the hydration of glasses of different silicate and aluminosilicate compositions in the presence of solutions of soda, sodium hydroxide, and sodium metasilicate was investigated. The results of X-ray phase and differential-thermal analysis, and infrared spectrum are given, and the hydration structure of the calcium oxide-silicon oxide-alkali component system has been studied. The analysis of hydrate neoplasms of the studied binding systems shows that the most optimal conditions for the synthesis of stone strength with stable physical and mechanical properties are created in the presence of gel-like phase reinforced by hydrosilicates and hydroaluminosilicates of alkaline and alkaline-alkaline-earth composition, characterized by fiber-like structure and possessing the ability to epitaxial fusion with each other, as well as gel-like phase, which they reinforce.

Keywords: low basic tobermorite-like hydrosilicates, heat and humidity treatment, alkaline components, differential thermal analysis, slag-alkali binders, hydration.

1. Introduction

The study of properties of individual glasses and minerals included in blast furnaces and phosphorus slags has been studied by many researchers: Lanzhvan S., Keil F., Lapin V.V., Butt Yu.M., and many others. However, the author and his collaborators conducted the most successful research in synthesized glasses and minerals [1], [2].

In [3] the results of studies of the hydraulic activity of one-calcium silicate ($CaOSiO_2$) and gelenite ($2CaOAl_2O_3SiO_2$) were published. Testing of samples of $7 \times 7 \times 7$ cm with and without the addition of activating components was carried out after storage in water for 28 days, steaming according to the regime of 4+8+2 h and autoclave treatment for 4 h at 0.8 MPa. Analyzing the data, it is possible to draw a conclusion that slowly cooled minerals do not possess binding properties. However, at their activation with lime, lime in combination with gypsum and Portland cement clinker the hydraulic activity of CS and C_2AS slightly increases.

Researchers [4] found that the reactivity of glasses mainly depends on the CaO content because calcium depolymerizes the glass structure and increases the reaction rate of glasses. The reactivity of glasses is mainly related to the degree of depolymerization of the glass structure. In this work, eight calcium aluminosilicate glasses have been synthesized, whose compositions reflect the glassy phases of industrial ashes and slags. The selected composition ranges allow the roles of Ca and Al to be distinguished and identified. The effect of Al_2O_3 on the reactivity of the glass is less pronounced and is based on the chemical weakening of the glass structure. However, an increase in

alumina content has a pronounced effect on hydrate phase assembly, bound water content, portlandite consumption, and heat of reaction. The compressive strength of composite cement mortars incorporating synthesized $CaO-Al_2O_3-SiO_2$ glasses was found to depend on both the degree of reaction of the glass and the actual composition of the phases.

In [5] the influence of vanadium oxide on the crystallization of $CaO-Al2O3-SiO2$ (CAS) glass was studied. Specifically, CAS glass-ceramics with deposited hexagonal lamellar particles of metastable $CaAl_2Si_2O_8$ (CASGC-H), which is a layered crystal that was prepared using metallic molybdenum (Mo) particles as a nucleation agent, was investigated. When the parent CAS GC-H glass was crystallized with the addition of vanadium oxide in the range of 0.052-0.21 weight %, the resulting lamellar particles of metastable $CaAl_2Si_2O_8$ showed an increase in aspect ratio from 20 to 15 compared to conventional CAS GC-H.

Furthermore, no crystallization occurred in CAS glass with vanadium oxide in the range of 0.052-0.21 wt% in the absence of metallic Mo particles. At the same time, in CAS glass containing 1.0 wt% vanadium oxide without the addition of Mo metal particles, the precipitation of metastable $CaAl_2Si_2O_8$ was observed. Thus, these results indicated that the aspect ratio of layered crystals in the glass is controlled by the addition of a relatively small amount of vanadium oxide, and a new nucleator was developed for the deposition of metastable $CaAl_2Si_2O_8$ in CAS glass using a relatively high vanadium oxide content.

The authors [6] carried out microstructural control of $CaO-Al_2O_3-SiO_2$ (CAS) glass-ceramics which was achieved by oxidation and mixing with nucleating agents. The CAS glass-ceramics were deposited with hexagonal lamellar particles of metastable layered $CaAl_2Si_2O_8$ (CAS GC-H) crystals, which are usually prepared in a reducing atmosphere forming metallic Mo or W particles as nucleating agents.

The average crystal particle size decreased significantly from 50 to 11 μm when CAS GC-H containing metallic W particles was prepared in an oxidizing atmosphere. Compared with this CAS-GC-H, the crystal particle size increased from 8-20 to 10-30 μm when CAS GC-H was prepared by mixing the glass mass containing metallic Mo and the glass mass containing metallic W particles. These results indicate that the microstructure of CAS GC-H is controlled on a micrometer scale from the parent glass with the same composition by varying the experimental conditions related to the melting state of the glass.

According to the author [7], hydration and hardening of unfired slag binders occur through the formation of silicic acid, which further interacts with calcium hydroxide. This physicochemical process results in the formation of calcium hydrosilicates in gel, subcrystalline, and crystalline forms. As they accumulate, these new formations bind together the particles of the hardening system, which, thickening over time, acquires density and strength.

The closest to our ideas about the mechanism of hydration and hardening of slag-alkali binders are the authors of works [8], so further we consider his vision of this mechanism. Processes of hydration of slag-alkali binders develop differently depending on the type of slag and alkaline component of curing systems.

Irrespective of the ways of their development, it is unrealistic to realize hydration only through the dissolution of slag-alkali binder components. In hydration processes occurring in solidifying slag-alkali systems, the formation of hydrogels, rather than the dissolution of silicate components, plays a decisive role.

It follows that the synthesis and evaluation of hydration and binding properties of blast-furnace and phosphorus slag constituents and the development of binding materials on their basis is an urgent problem.

The goal of current research is to investigate and determine the optimum composition of CS glasses for obtaining binders with given properties hydration of glasses of different silicate and aluminosilicate compositions in the presence of solutions of soda, sodium hydroxide, and sodium metasilicate.

2. Methods

Synthesized glasses were obtained by abrupt cooling of melts of the corresponding chemical composition, which were ground in porcelain mills to a specific surface of 350m^2/kg. The materials thus obtained were grouted with solutions of soda, caustic soda, and liquid glass. The test specimens with the size of 1×1×1 cm from a dough of normal density were hardened in natural conditions, in water, and hydrothermal conditions at temperatures of 95 and 175°C under the regime of 1.5+2+4+2 h.

Natural and water-cured specimens were tested after 3, 28, 90, and 360 days, and steamed and autoclaved specimens 24 hours after hydrothermal treatment.

X-ray phase analysis was carried out on a diffractometer URS 50 IM and DRON-3M in the range of angles 2 = 10...+60° at a counter and sample rotation speed of 2° per minute. The decoding of X-ray radiograms was carried out by identification of the obtained data with the characteristics of natural and artificial minerals. DTG, DTA, and TG curves were recorded on a derivatograph of the Paulik R. and Erden L. system of the MOM Budapest company. Spectral analysis was carried out on a Specord-80

3. Results and Discussion

3.1 Calcium oxide-silicon oxide-alkali component system 3CaO ·2SiO$_2$(C$_3$S$_2$)

During the hydration of pure C$_3$S$_2$ in water, the formation of weakly crystallized low basic hydrosilicates like tobermorite 11,3A and insignificant amounts of afvillite is observed.

When gelled with NaOH and Na2SiO3 solutions, the composition of hydration products is represented by afvillite CSH(1), plombierite and sodium-calcium compound NaCa$_2$Si$_3$O$_8$OH$_2$Na$_8$Ca$_8$Si$_5$O$_{26}$H$_{14}$ (d/n = 3.09; 2.26 and 2.01 Å) of cryptocrystalline structure (Figure 1a).

On IR spectrograms the presence of lines at 3340, 1658, 1280, 1100, 883, 673, and 512 cm^{-1} (Figure 1c) is identified with absorption lines characteristic of afvillite, and the formation of low-base hydrate phases is confirmed by the shift of absorption bands at 1000, 1070 cm^{-1} to lower frequencies due to polycondensation of silicon-oxygen groups.

a) X-ray images

b) Thermograms
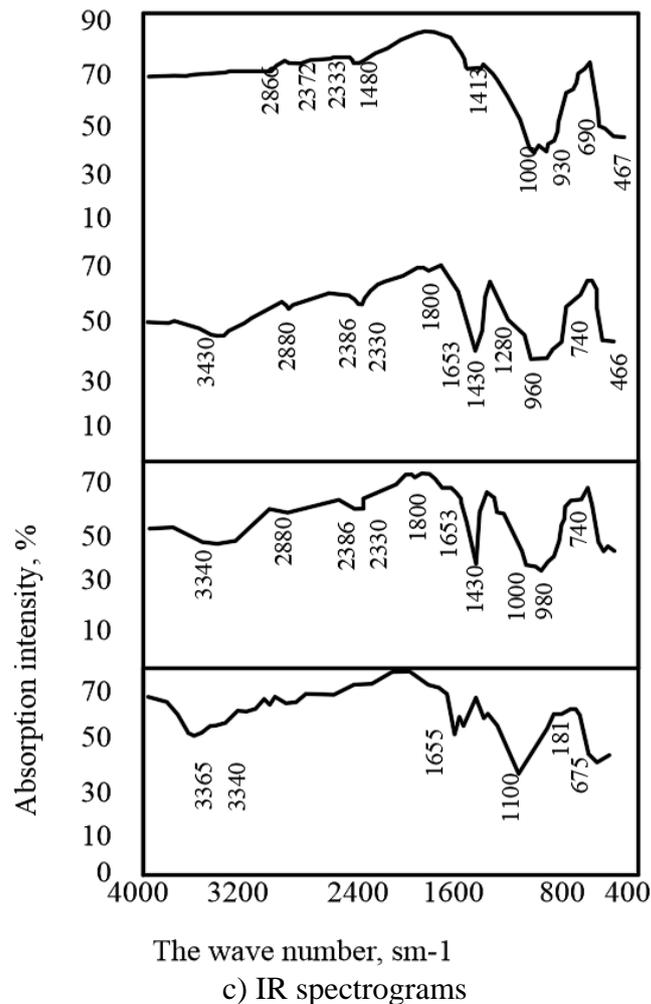
The wave number, sm-1

c) IR spectrograms
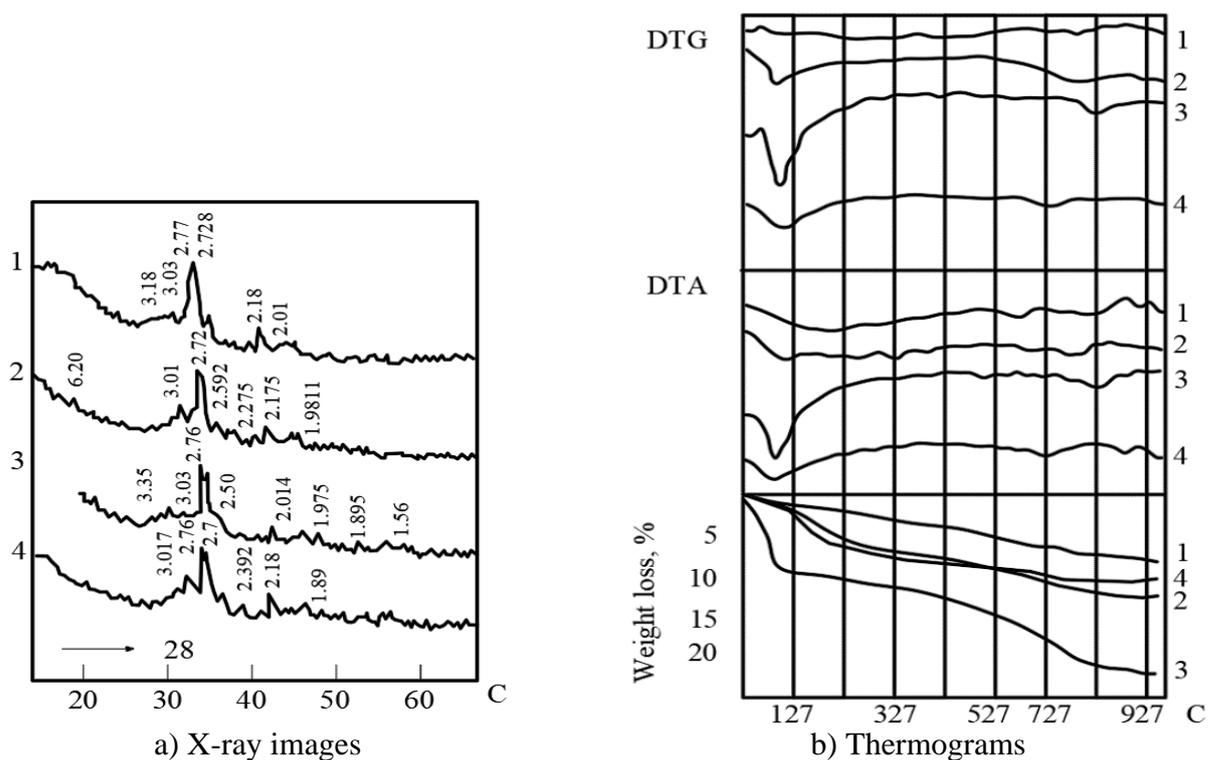
Figure 1 – Results of the analysis of a stone based on a glass-like analog of C_3S_2

On DTA according to Figure 1(b), the presence of endothermic effects at 240, 320, 520, and 800 °C is due to stepwise dehydration, and endothermic effects at 100, 130 °C and exo-effect at 850 °C tobermorite dehydration and α-CS crystallization. The phase composition of the firing products of the composition based on C3S2 and NaOH according to Figure 2.2 is represented by β-C2S and $Na_2O·CaO·SiO_2$, and the composition based on C_3S_2, $Na_2O·SiO_3$-β-CS, C_3S_2 and an insignificant amount of α - CS (Figure 2).

Comparison of phase compositions of hydration and dehydration products of glass-like C_3S_2 hydrated with NaOH and Na_2SiO_3 solutions shows that in the first case, more intensive destruction of glassy substance and formation of more mixed sodium-calcium compounds are observed, while at the hydration of C_3S_2 in the presence of Na_2SiO_3 afvillite and low-basic tobermorite-like hydrosilicates with inclusions of alkali ions are formed.

After heat and humidity treatment, the phase composition of hydration products of glass-like C_3S_2 in the presence of NaOH and Na_2SiO_3 along with compounds formed during curing under normal conditions in accordance with Figure 3 includes low-basic hydrosilicates of scautite type (d/n=3.03; 2,78; 2,39 and 2,29 Å), and transformations of calcium hydrosilicates within isomorphous phases (CSH(I)→scoutite) almost does not affect physical and mechanical properties of dispersed structures, as the new phase forms good contacts of aggregation with the disappearing one.

On the DTA curve according to Figure 1b the formation of $C_3S_2H_3$ is confirmed by the presence of endo-effect at 360...400 °C and exo-effect at 780 °C, the shift of which in the low-temperature region is due to the presence of Na^+ ions, and the synthesis of tobermorite-like calcium

hydrosilicates by the presence of endo-effects at 90...220 °C, 300...340 °C and exo-effect at 900 °C, associated with the crystallization of β - C_3S.

The formation of sodium-calcium compounds during hydration of C_3S_2 with NaOH solution under conditions of heat and humidity treatment is confirmed by the presence of endo effects at 540-550-600 ºC on the DTA curve.

At mixing of glass-like C_3S_2 with NaCO3 solution in the composition of hydration products (after the heat and humidity treatment) in addition to compounds formed at hydration in the presence of NaOH - a phase of pyrsonite type $Na_2Ca(CO_3)_2·25H_2O$ was identified, the formation of which is confirmed by the presence of endothermic effect at 760 ºC on the DTA-curve in accordance with Figure 3b.

3.2 The system of CaO-SiO2(CS)

During hydration of the glass-like analog under normal conditions, the degree of hydrolytic degradation is insignificant.

After heat and humidity treatment the composition of hydrate neoplasms is represented by $C_3S_2H_3$ and partially crystallized tobermorite-to-like calcium hydrosilicates, the formation of which is confirmed by the presence on the DTA-curve of endothermic effects at 240 .... 260, 320, 470 ºC (dehydration of $C_3S_2H_3$), endo effect at 240 ºC and exo effect at 880...960 ºC (dehydration of low-base calcium hydrosilicates).
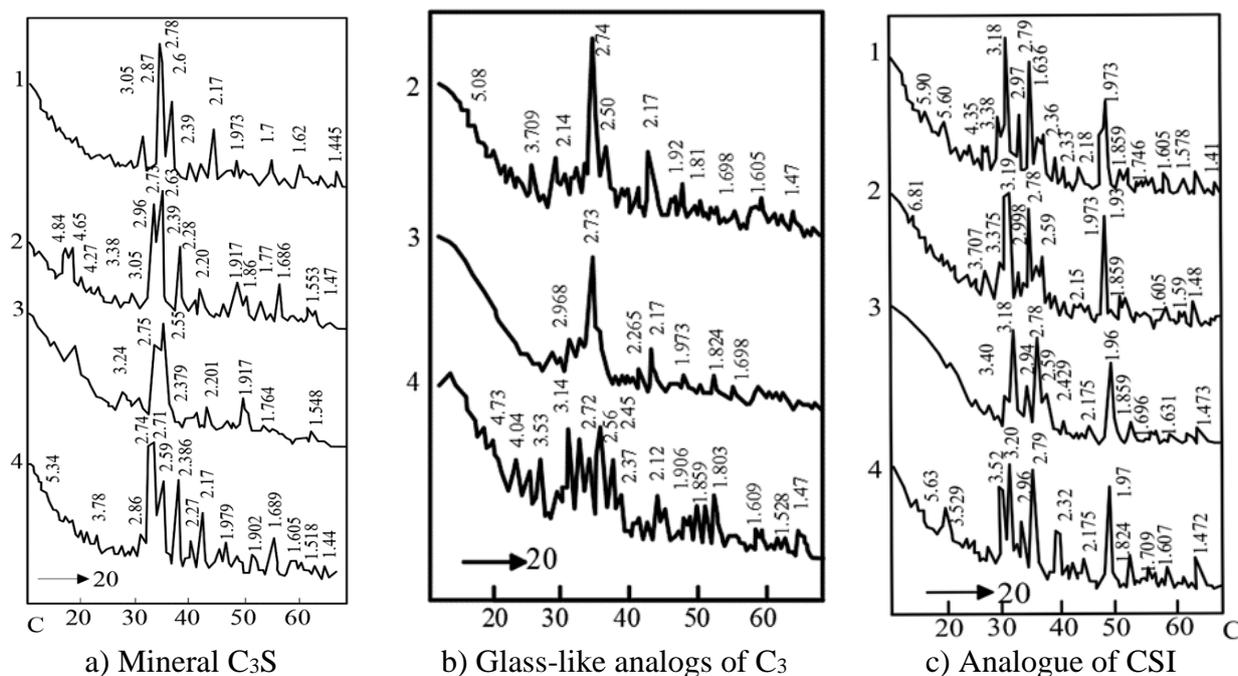

Figure 2 – X-ray images of a stone dehydrated at N = 1000 °C: 1 – water; 2 – solution NaOH; 3 – solution Na_2CO_3; 4 – solution Na_2SiO_3

a) Mineral C_3S b) Glass-like analogs of C_3 c) Analogue of CSI

During hydration of the glass-like analog of CS in the presence of NaOH, the phase composition of neoplasms after 28 days of hardening in accordance with Figure 4a is represented by low-base phases of the cryptocrystalline structure: gyrolite (d/n = 3.36; 3.15; 3.02; 2.52; 2.45; 2.25 Å) and pectolite.

On the DTA curve, in accordance with Figure 4 (b), the appearance of endothermic effects at 140...180 ° C, 500...780 °C, and the exo-effect at 820 °C is due to dehydration of gyrolite, and the exo-effect at 860...880 °C is due to dehydration of CSH(I) and crystallization of β-CS. The displacement of the exo-effect to the region of elevated temperatures is explained by the high content of calcium in the composition of the hydrosilicate phases.

The shaft of the eco effect to the region of elevated temperature is explained by the high content of calcium in the composition of the hydrosilicate phases.

After heat and moisture treatment at T=100 °C, the presence of C6S6H (d/n) carbonatite was noted in the phase composition of hydration products along with CSH(I) and tobermorite = 3.23; 3.0; 2.83; 2.72; 2.51 and 2.04 Å) (Figure 3d).

The formation of low-basic tobermorite-like phases is confirmed by the presence on the DTA curve of endothermic effects at 90 ...120 °C, 300...340 °C, and an exo-effect at 900°C, and xonotlite by the appearance of endoeffects at 800 ...880 °C.

During hydration of glassy CS in the presence of Na_2CO_3, regardless of the hardening conditions, in accordance with Figure 4a, the composition of the neoplasms is represented by CSH(I), gyrolite, pectolite and $NaCa(CO_3)_2 \cdot 2H_2O$ (d/n = 4.92; 3.16; 2.88; 2.65; 2.57; 2.5; 2.02; 1.89; 1.82 Å).

The DTA curve in accordance with Figure 4b shows weak endothermic effects at 740, 820, and 960 °C, corresponding to the dehydration of $CaCO_3$.

During the hydration of glass-like CS in the presence of Na_2SiO_3, the composition of the hardening products is represented by compounds of cryptocrystalline structure: CSH(I), gyrolite, pectolite, and tobermorite. On the IR spectrogram, the presence of law-o basic calcium hydrosilicate is confirmed by the presence of absorption bands at 3365, 1635, 1173, 1075, 997, 897, and 524 cm^{-1} (Figure 4).

On the DTA curve, in accordance with Figure 4b, the main endothermic effect of tobermorite dehydration at 128 °C is shifted toward low temperatures due to the introduction of Na^+ ions into its composition.

The thermogravimetric curve has no sharp fractures, and mass loss is observed in the temperature range of 20...800 ^{0} C. In the composition of the dehydration products at a temperature of 1000 ^{0} C, the predominance of β-CS was noted and with an insignificant content in accordance with Figure 4b. During the heat and moisture treatment of CS, closed with a solution of Na_2SiO_3, a clearer crystallization of low-base hydrosilicate phases is observed.
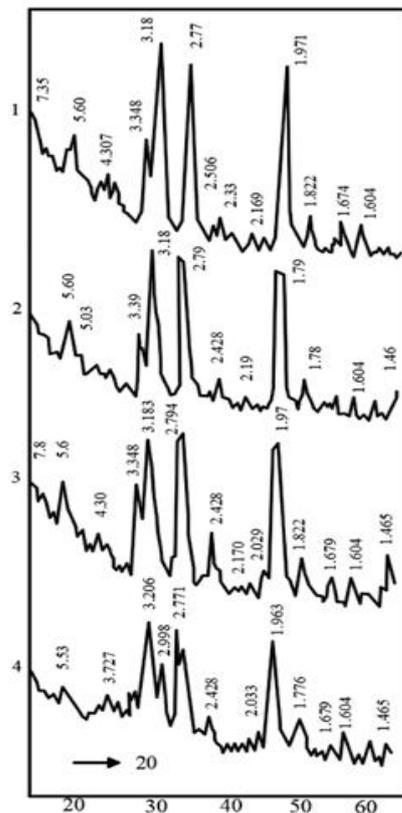
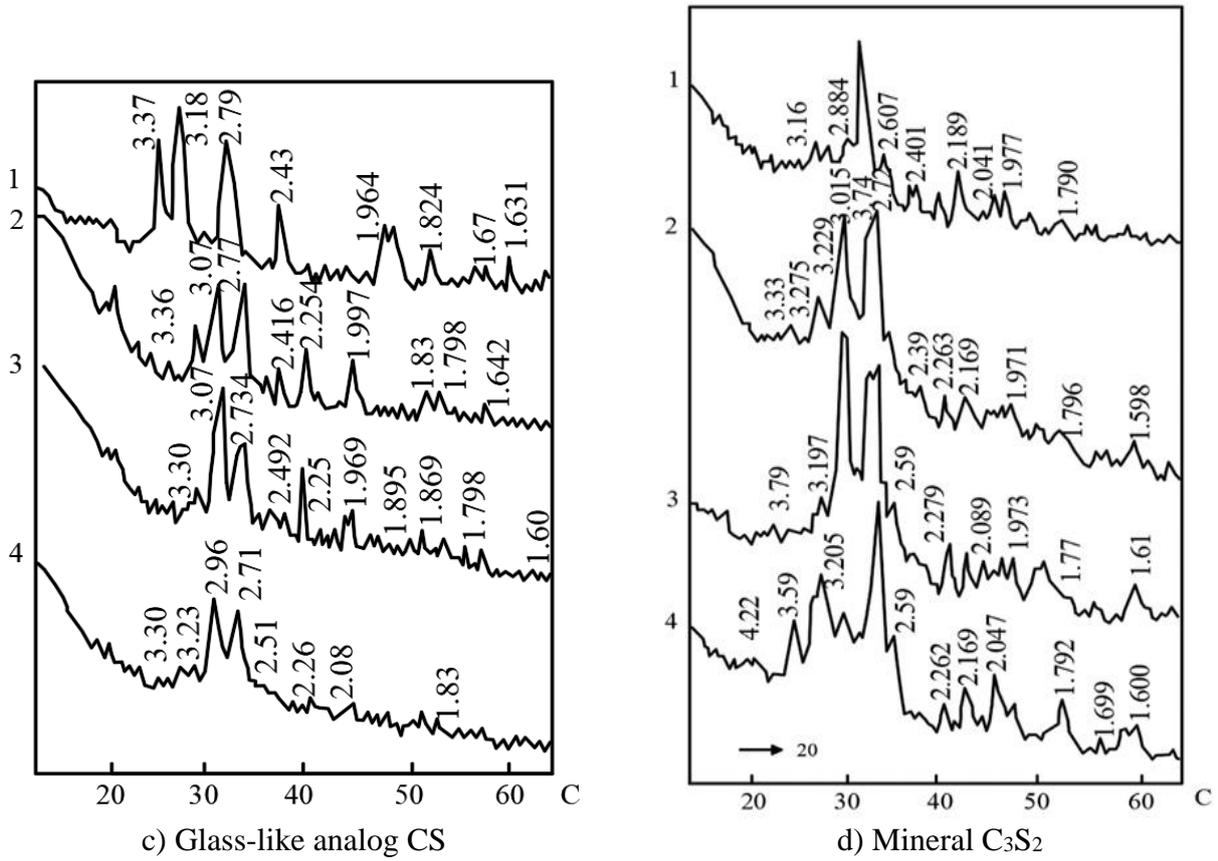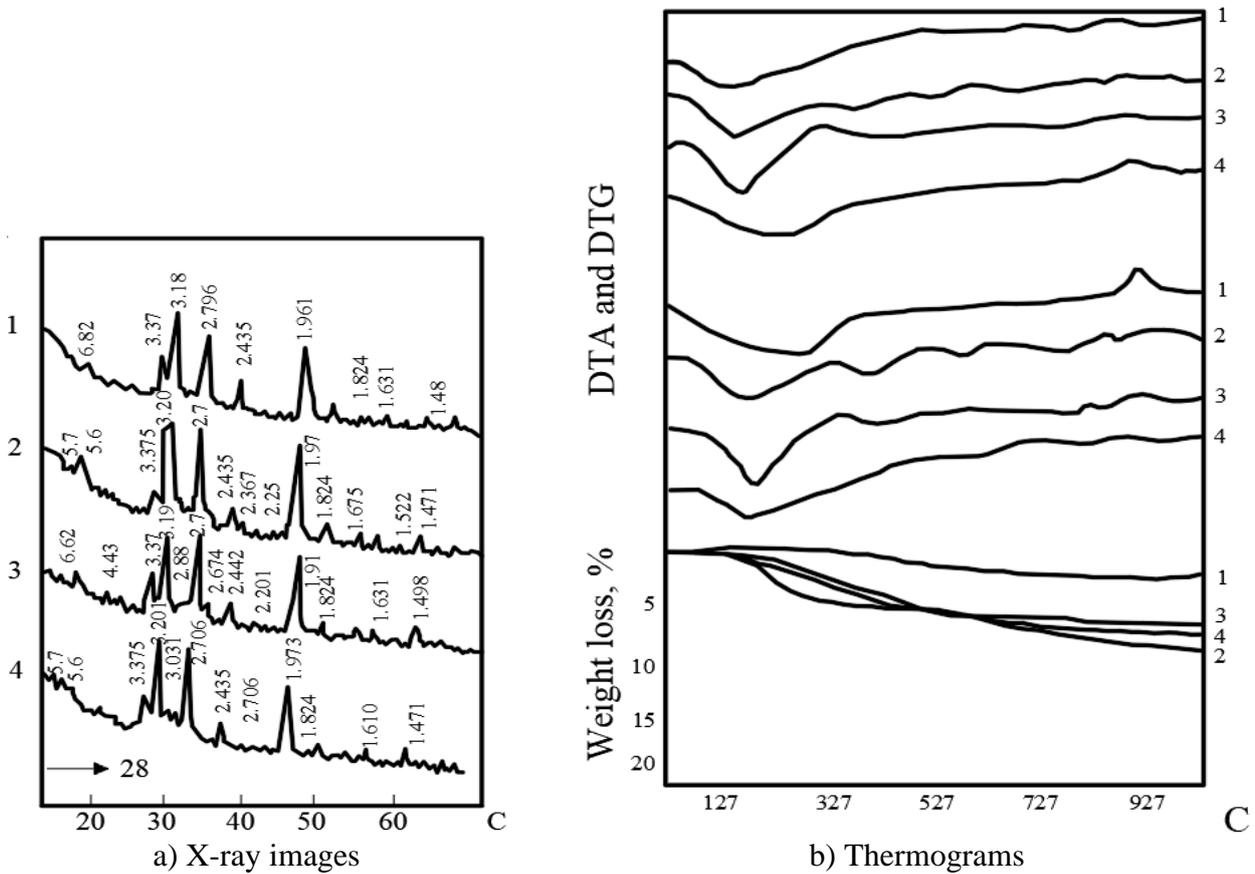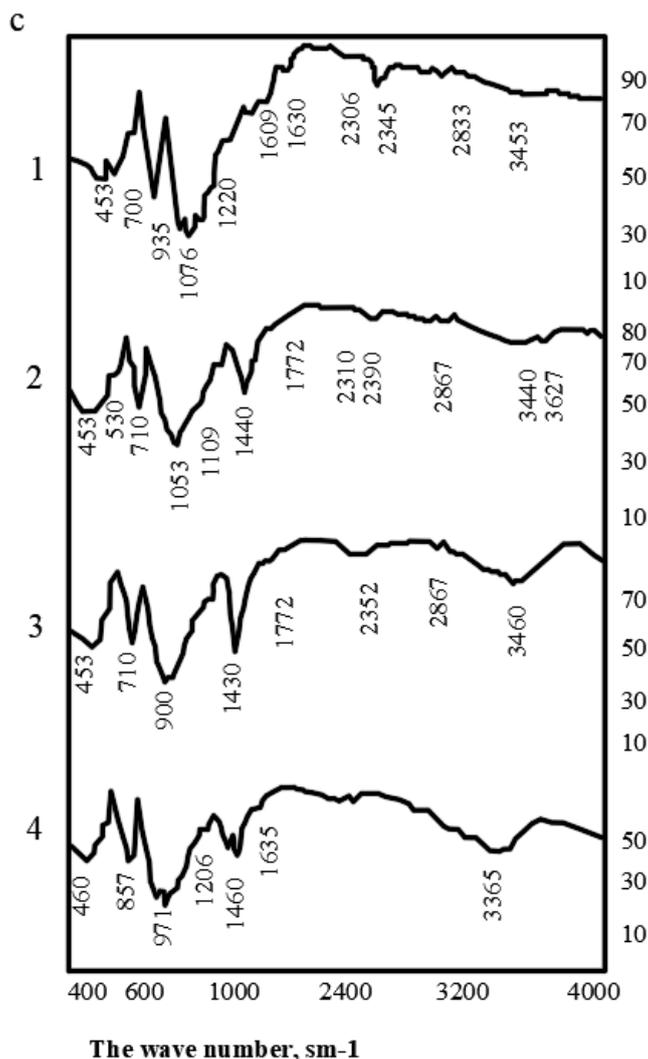a) Mineral CS   b) Mineral C_3S_2

c) Glass-like analog CS
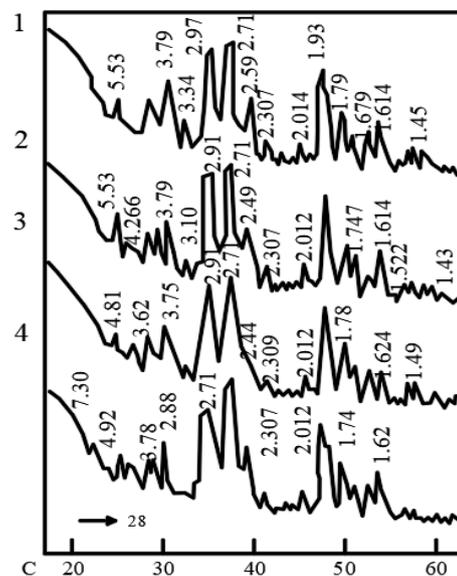
d) Mineral C_3S_2

Figure 3 – Radiographs of a stone: 1-with water; solutions: 2 - NaOH; 3 - Na_2CO_3; 4 - Na_2SiO_3
(heat and moisture treatment at N = 95 ± 5 °C according to the regime 3+6+3+2)

a) X-ray images

b) Thermograms

c) IR spectrograms
Figure 4 – Results of the analysis of a stone based on a glass-like analog of CS closed
with 1 – water; 2 – solution NaOH; 3 – solution Na_2CO_3; 4 – solution Na_2SiO_3 (28 days
of storage in water)

Thus, the reduced strength and water resistance of an artificial stone based on glass-like CS, compared with the strength of a stone based on glass-like C_3S_2, are due to the phase composition of hydration products represented by girolite, CSH(I) and pectolite, which do not possess crystallochemical affinity and belong to various categories of compounds.

According to the data of physico-mechanical tests given in Table 1, binders based on glass-like C_3S_2 hydrated with Na_2SiO_3 solution are characterized by the greatest hydraulic activity. The high strength (55...113 MPa) and its constant growth over time are due to the formation of epitaxially fused compounds in the hydration products: afvillite (monoclinic) and tobermorite-like hydrosilicates (orthorhombic) syngony.

Consequently, the most optimal conditions for the synthesis of strength artificial stone in the Na_2O-CaO-SiO_2-H_2O system are created by hydration of binders of the glass-like analogue C_3S_2 with the formation of artificial stone, characterized by high rates of strength gain in the early stages of hardening and strength up to 125 MPa during long-term storage. This is due to the peculiarities of the structure of glassy calcium silicate, as well as the phase composition of hydration products: the ratio of gel-like and crystalline phases and the ability of hydrate compounds to form strong epitaxial accretions.
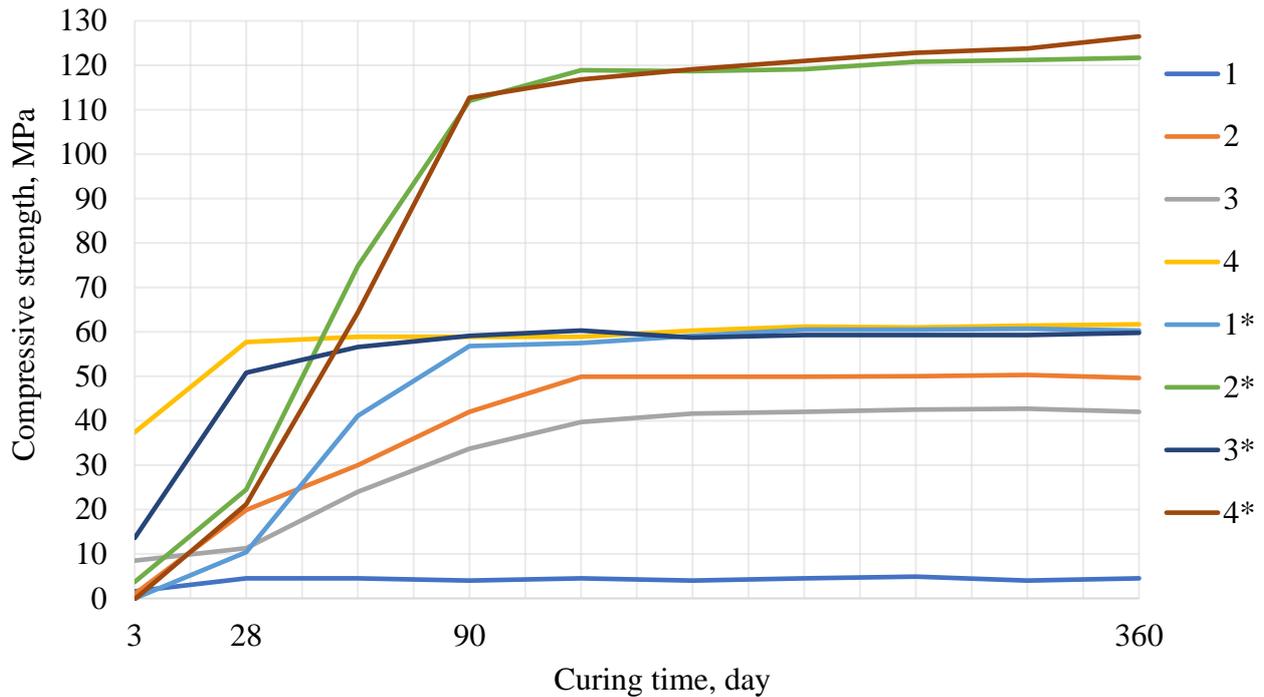
Figure 5 – Dependence of the strength of the binder based on C_3S_2 on the curing time with alkaline component: 1 – NaOH; 2 – Na_2CO_3; 3 – Na_2SiO_3; 4 – H_2O (*after aqueous storage)

Table 1 – Results of physical and mechanical tests of artificial stone based on hydrated glasses

Glass composition	Hardener	Compressive strength, MPa									
		After natural storage for a day				After water storage for a day				After heat and humidity treatment at a temperature of, °C	
		3	28	90	360	3	28	90	360	95	175
CS	H_2O	7.4	13.2	31.5	34.0	P	P	P	P	5.8	22.0
	NaOH	10.7	13.5	32.3	37.0	15.0	16.6	16.0	28.0	15.0	36.5
	Na_2CO_3	2.5	5.8	34.9	36.0	2.5	19.9	30.0	33.7	26.5	34.9
	Na_2SiO_3	23.2	34.8	69.7	72.0	33.0	35.7	45.0	69.0	50.0	66.0
C_3S_2	H_2O	1.0	1.5	3.3	5.8	2.5	15.0	59.4	63.0	1.5	30.0
	NaOH	5.0	20.0	43.0	48.0	12.5	49.5	57.0	62.0	20.0	35.0
	Na_2CO_3	8.0	12.5	35.0	42.0	5.0	21.5	113.2	121.0	35.0	55.0
	$Na_2O·SiO_3$	37.5	57.5	59.4	63.0	33.0	55.0	113.5	125.0	62.5	71.0

Note: P is the soaking of the samples

4. Conclusions

1. The phase composition of hydration products plays a leading role in the formation of the structure of artificial stone of alkaline-alkaline-earth composition and determines its physical and mechanical properties. The analysis of the hydrate formation of the studied binder in the CS system shows that the most optimal conditions for the synthesis of stone strength with stable physical and mechanical properties are created when the hydration products contain a gel-like phase reinforced with hydrosilicates and hydroaluminosilicates of alkaline and alkaline-alkaline earth composition, characterized by a fibrous structure and having the ability to epitaxial fusion with each other, as well as the gel-like phase that they reinforce.

2. In the "calcium oxide – silicon oxide – alkaline component" system, high–strength stone (28 days – 53-58 MPa, 1 year – 125 MPa) is synthesized based on calcium silicates $1.5 \leq C/S \leq 2$

and the phase composition of hydration products is represented by low-basic hydrosilicates of the amitobermorite group, afvillite and alkaline-alkaline-earth hydrosilicates various degrees of crystallization ($NaCO_2$ SiO_3O_8OH; $Na_2Ca_8Si_5O_{26}H_{14}$).

References
[1] P. P. Budnikov and V. L. Pankratov, "Hydraulic activity of monocalcium silicate and helenite," in *Chemistry and technology of silicates*, Kiev: Naukova dumka, 1964, pp. 375–382.

[2] P. P. Budnikov, B. C. Gorshkov, and T. A. Khmelevskaya, "Assessment of the astringent properties of slags according to their chemical and mineralogical composition," in *Chemistry and technology of silicates*, Kiev: Naukova dumka, 1964, pp. 446–457.

[3] P. P. Budnikov and B. C. Gorshkov, "Investigation of hydrated synthetic minerals of alumina slags," in *Chemistry and technology of silicates*, Kiev: Naukova dumka, 1964, pp. 437–445.

[4] S. Kucharczyk *et al.*, "Structure and reactivity of synthetic CaO-Al2O3-SiO2 glasses," *Cem Concr Res*, vol. 120, pp. 77–91, Jun. 2019, doi: 10.1016/j.cemconres.2019.03.004.

[5] S. Machida, K. Katsumata, K. Maeda, and A. Yasumori, "Effect of Vanadium Oxide on the Crystallization of CaO–Al 2 O 3 –SiO 2 Glass," *ACS Omega*, vol. 8, no. 9, pp. 8766–8772, Mar. 2023, doi: 10.1021/acsomega.2c08246.

[6] S. Machida, K. Maeda, K. Katsumata, and A. Yasumori, "Microstructural Control of CaO–Al 2 O 3 –SiO 2 Glass Ceramics by Oxidation and Mixing with Nucleation Agents," *ACS Omega*, vol. 7, no. 37, pp. 33266–33272, Sep. 2022, doi: 10.1021/acsomega.2c03799.

[7] M. M. Sychev, *Hardening of binders*. L: Stroyizdat, 1974.

[8] B. K. Sarsenbayev, Z. A. Estemesov, J. T. Aimenov, N. B. Sarsenbayev, and A. J. Aimenov, *Slag-alkali binding concretes*. Shymkent, 2016.

Information about authors:
Bakhytzhan Sarsenbayev – M. Auezov South Kazakhstan University, Shymkent, Kazakhstan, stroitelstvo_uku@mail.ru

Sultan Auyesbek – M. Auezov South Kazakhstan University, Shymkent, Kazakhstan, sultan_067@mail.ru

Meiram Begentayev – Kazakh National Research Technical University named after K. Satpayev, Almaty, Kazakhstan, m.begentayev@satbayev.university

Nuraly Sarsenbayev – M. Auezov, South Kazakhstan University, Shymkent, Kazakhstan, nurali777_@mail.ru

Erkin Khaltursunov – Turin Polytechnic University in Tashkent, Tashkent, Uzbekistan, e.khaltursunov@polito.uz

Gaukhar Sauganova – M. Auezov, South Kazakhstan University, Shymkent, Kazakhstan, saughanova@mail.ru

Author Contributions:
Bakhytzhan Sarsenbayev – concept, editing, drafting.
Sultan Auyesbek – data collection, testing, modeling.
Meiram Begentayev – editing the article and raising funds.
Nuraly Sarsenbayev – methodology, resources, analysis.
Erkin Khaltursunov – analysis, interpretation, modeling.
Gaukhar Sauganova – visualization, interpretation, methodology.

Conflict of Interest: The authors declare no conflict of interest.

Use of Artificial Intelligence (AI): The authors declare that AI was not used.