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Hydration and structure formation of chloride-activated cement paste

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Abstract. The result of the research is the formulation of chloride-activated high-strength cement paste with accelerated hardening, increased strength, and without heat treatment. The cement paste was activated by introducing a chloride-containing additive into the cement-water system. The additive was synthesized by keeping the cement in a 3 % hydrochloric acid solution, i.e. under conditions of acid corrosion of the binder. The additive is the solid part of the cement-HCl suspension, aged for 24 hours at a ratio of solid and liquid phases of 1:10. The optimized amount of additive is 5 % by weight of dry cement. The effect of the additive on the hardening kinetics, structure, and strength of the activated cement paste was studied. It was established that acid corrosion products of cement have structure-forming activity. A significant increase of the compressive strength of the activated cement paste relative to the control sample was found over the entire hardening interval (1–3–7–28 days). At the daily age of normal hardening, the strength of activated cement paste increased by 165 %. At 28 days of age, the strength increased by 42 %. The X-ray phase and infrared spectral analysis results suggest the following. The acceleration of setting and the increase in the strength of the cement composite is realized due to the intensification of hydration processes and the binding of portlandite, the early formation of structure-forming phases as ettringite and Kuzel salt $\text{Ca}_4\text{Al}_2(\text{OH})_{12}\text{Cl}(\text{SO}_4)_{0.5}\cdot 6\text{H}_2\text{O}$ (analog of Friedel's salt), as well as weakly crystallized calcium hydrosilicates with a tobermorite-like structure.

1. Introduction

Additives affecting the setting and hardening of concrete mixes are widely used [1–5]. Previously, the authors of this article synthesized cement additives in the form of suspensions. Suspensions were obtained as a result of hydration of the same cement in solutions that cause corrosion of cement under conditions of excess liquid phase [6–9]. In such suspensions, hydration of cement occurred simultaneously with its chemical corrosion. It was established that the products of clinker materials' hydration in suspensions, the liquid phase of which are corrosive to cement, have structure-forming properties.

The use of the solid part of suspensions as additives to cement provides an increase in the strength of cement paste. For the synthesis of additives, solutions of aluminum chloride or iron chloride were used. Upon hydrolysis of these salts, a decrease in the pH of the medium occurs. Therefore, hydration in such suspensions proceeded under conditions of acid corrosion of cement [9]. After the introduction of additives in the composition of the cement paste, the compressive strength increased. The increase was 23 % when using additives synthesized with iron chloride and by 30 % when using additives synthesized with aluminum chloride.

Further development of this approach may consist in increasing the aggressiveness of the liquid medium in cement suspensions, namely, during the hydration of cement in a solution of hydrochloric acid HCl. When mixing cement with an HCl solution, neutralization reactions proceed at a very high speed. The suspension is almost instantly saturated with calcium chloride. The presence of calcium chloride in the liquid phase of the suspension significantly affects the phase composition of hydrates formed during the synthesis of additives.

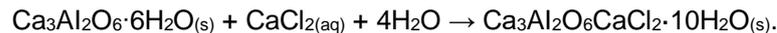
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Calcium chloride is the first documented additive for concrete and belongs to the class of hardening accelerators. An analytical review of the works devoted to the influence of CaCl_2 on the structure and properties of clinker minerals and cement, in general, was published by V.S. Ramachandran et al. [10]. The evolution of the use of calcium chloride since the issuance of a patent for the use of this additive in 1885 until today is widely known in interested scientific and industrial circles. The problem of the use of additives containing chloride ions was discussed, among other things, in [9]. It was noted that the indisputable advantages of such additives are high solubility in water, affordability, low cost, and reliable performance. Chloride additives can be used without restrictions in the production of cellular and lightweight concrete, concrete blocks, road construction elements, and the implementation of small architectural projects.

Chloride ions chemically bind to cement minerals when interacting with the hydroxyl groups of the AFm phases through ion exchange reactions [11–14]. As a result of this interaction, calcium hydrochloroaluminates $\text{CaOAl}_2\text{O}_3\text{CaCl}_2 \cdot 10\text{H}_2\text{O}$ and/or calcium hydrochloroferrites $\text{CaOFe}_2\text{O}_3\text{CaCl}_2 \cdot 10\text{H}_2\text{O}$ are formed [15–17]. The synthesis of hydrochloroaluminates in the presence of calcium chloride during hydration proceeds according to the scheme:



Calcium hydrochloroaluminates and calcium hydrochloroferrites were named Friedel's salts by the name of the scientist who first synthesized calcium hydrochloroaluminate in 1897. The possibility of the formation of analogues of Friedel salts containing not only chloride ions, but also carbonate ions ($\text{AFm}-(\text{CO}_3^{2-}, \text{Cl}^-)$) or sulfate ions ($\text{AFm}-(\text{SO}_4^{2-}, \text{Cl}^-)$) was proved in [18–20]. The crystal structure of the Kuzel's salt $\text{Ca}_4\text{Al}_2(\text{OH})_{12}\text{Cl}(\text{SO}_4)_{0.5} \cdot 6\text{H}_2\text{O}$ was determined by synchrotron powder diffraction [18]. Calcium hydrochlorosulfoaluminate belongs to the Layered Double Hydroxides family [15, 21, 22]. Layered Double Hydroxides is designated by the general formula $[\text{M}^{\text{II}}_{1-x}\text{M}^{\text{III}}_x(\text{OH})_2]^{x+}[\text{A}^{m-}]_{x/m} \cdot n\text{H}_2\text{O}$.

They represent a group of minerals, the structure of which consists of fixed positively charged brucite-like layers formed by ions of multivalent metals and hydroxide ions, the charge of which is balanced by mobile anions located in the interlayer spaces. The layers are formed as a result of the partial replacement of trivalent octahedrally coordinated metal cations with divalent cations. Intercalated molecular water provides the connection of the layers through hydrogen bonds.

In the fixed main layers of Kuzel's salt there are $[\text{Ca}_2\text{Al}(\text{OH})_6]^+$ cations of a fixed composition, between which in the interlayer spaces there are layers of $[\text{Cl}_{0.5}(\text{SO}_4)_{0.5} \cdot 2.5\text{H}_2\text{O}]^-$ anions that can move. In the unmovable basic layers of salts, cations of unchanged composition are fixed, between which moving layers of anions are in the interlayer spaces. Chloride and sulfate ions are arranged in two independent crystallographic regions and can be relatively easily replaced by other anions (for example, $(\text{CO}_3)^{2-}$ and others) without destroying the layered structure of Kuzel's salts.

Studies [13, 14, 23, 24] showed that chlorine ions in hydrated cement chemically bind to hydrated neoplasms of cement, changing their phase composition. Also, it is necessary to take into account the possibility of physical adsorption binding of chlorine ions. Sorption occurs due to the mutual attraction of the Cl^- anions and the hydrated surfaces of the binder minerals due to the van der Waals forces. The reason for this interaction is the dissociation of molecules of hydrated neoplasms of cement, as a result of which hydrates become carriers of surface charges. In [13], the results of a study of the mechanisms of charge formation in cement hydrates and their effect on the adsorption of chloride ions were published. For example, diagrams of the processes of Friedel's salt dissociation and adsorption of chloride ions by cations $[\text{Ca}_2\text{Al}(\text{OH})_6]^+$ are given:



It can be seen from these examples that during adsorption interaction with chlorine anions, the cation charge is compensated (neutralized). Adsorption is described by the Freundlich isotherm, and the results of the adsorption experiment are verified by measuring the ξ -potential [13].

In dissociation of the Kuzel salt, cations of the composition $[\text{Ca}_2\text{Al}(\text{OH})_6]^+$ are also formed. Therefore, the dissociated Kuzel's salt can adsorb chloride ions during the synthesis of the additive in a suspension of cement and HCl, balancing the positive charge.

Molecular dynamics computer simulations are performed to study the structure and dynamical behavior of chloride and associated cations at the interfaces between aqueous solutions and portlandite $\text{Ca}(\text{OH})_2$, Friedel salt $[\text{Ca}_2\text{Al}(\text{OH})_6]\text{Cl} \cdot 2\text{H}_2\text{O}$, tobermorite $\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2$, and ettringite $\text{Ca}_6[\text{Al}(\text{OH})_6]_2[\text{SO}_4]_3 \cdot 26\text{H}_2\text{O}$ [25]. The simulations take into account the flexibility of surface OH-groups and allow for energy and momentum transfer between the solid and solution to effectively simulate the sorption. Studies have shown that the ability to bind Cl^- anions on the surfaces of hydrated neoplasms of cement decreases in subsequence:

Friedel's salt > portlandite > ettringite > tobermorite.

In [13], data are also given on the ability of portlandite to participate in adsorption interactions with a chloride ion. The authors of [24] believe that under certain conditions there is a likelihood of interactions of this kind between ettringite and Cl^- . However, most scientists agree that the participation of these phases in the process of physical binding of chlorine ions is unlikely, very insignificant.

It is generally accepted [13, 26, 27] that among all hydration products present in ordinary Portland cement, only two are almost completely responsible for the ability to interact with chloride ions: CSH gel and AFm phases (for example, monosulfate hydrate). In this case, the CSH gel has a dominant value in the process of physical bonding of chlorine ions, due to the high value of the specific surface and the mass content of this phase in the composition of hydrated cement.

Despite a detailed analysis of the structure-forming effects of the cement hydration process, the available publications do not contain detailed information on cement hydration in solutions containing hydrochloric acid, as well as on the use of products of such hydration as an additive to cement.

The study is aimed at obtaining the formulation of chloride-activated cement paste with the increased strength and accelerated hardening, without heat treatment.

2. Methods

The additive and cement paste are made from Portland cement of class CEM II / A-Sh 32.5H manufactured by Topkinsky Cement LLC (Topki, Kemerovo Region, Russia). Cement met the requirements of the Russian State Standard GOST 31108-2003 "General structural. Portland clinker cements. Specifications". Table 1 shows the synthesis conditions of the additive and the control specimen.

Table 1. The synthesis conditions of the additive, control sample and activated cement paste.

The specimen	The composition of the additive	The ratio of the components of the additive	The composition of the cement paste
The additive, the modified cement paste	Cement and 3 % HCl solution	1:10	Cement, the additive 5 % by weight, water with a W / C ratio of 0.34
Reference specimen	Cement and water	1:10	Cement, water with a W / C ratio of 0.34

The synthesis of additives and chloride-activated cement paste was carried out as follows.

1. To prepare a 3 % HCl solution, hydrochloric acid was used according to the Russian State Standard GOST 3118 Reagents. Hydrochloric acid. Specifications ($\rho = 1.13 \text{ g/cm}^3$) and distilled water according to the Russian State Standard GOST 6709 Distilled water. Specifications.

2. Cement was kept in a 3 % HCl solution at a solid to liquid ratio of 1:10 for 24 hours after thoroughly mixing this suspension.

3. After 24 hours, the solid part of the suspension was separated from the liquid by filtration. To stop the hydration processes, the solid residue was treated with acetone and dried in a desiccator over calcium chloride CaCl_2 to constant weight.

4. The dry solid residue was crushed before passing through a 0.08 mm square opening sieve according to Russian State Standard GOST 6613-86 "Square meshed woven wire cloths. Specifications". The crushed residue was used as an additive in cement.

5. The additive was used in amounts of 2 %, 5 % and 10 % by weight of dry cement.

6. The prepared additive was mixed with cement and shut with water at a W/C ratio of 0.34. specimens in the form of cubes with a 2 cm edge were made of non-admixture cement paste and modified cement paste. specimen s solidified under normal conditions. After reaching the 28-day maturity of the specimens, their compressive strength was measured. The compressive strength of cement paste at the age of 1, 3, 7, and 28 days was determined based on six measurements for each age. The arithmetic average value of strength was calculated based on the 3 closest values. This provided an error of no more than 4.1 %.

7. The specimens destroyed during the test were crushed before passing through a 0.08 mm square opening sieve according to the Russian State Standard GOST 6613-86 "Square meshed woven wire cloths. Specifications" and were dried in a desiccator over calcium chloride CaCl_2 to constant weight.

The structure of the additive, control specimen, non-additive cement paste, and modified cement paste was studied by X-ray diffraction (XRD) and infrared spectroscopy. The X-ray diffraction meter Shimadzu

XRD-700 with a copper anode in range of 5–90 deg and the Fourier spectrometer "Varian Excalibur HE 3600" at the frequency range 400–4000 cm^{-1} was used.

3. Results and Discussion

3.1. The age-strength relation of cement paste at different percentages of additives

Table 2 shows the compressive strength of chloride-activated cement pastes depending on the amount of additive. It is seen that a stable result of an increase in strength during the entire hardening period is provided by an additive introduced in an amount of 5 % by weight. Therefore, an additive in the amount of 5 wt.% Was used to activate the cement paste. After hardening within 24 hours, the strength of such a cement paste increased by 165 % compared with non-additive samples; at the age of 28 days, the increase in strength was 42 %.

Table 2. The effect of the amount of additive on the strength of cement pastes.

Cement age, days	Additive by dry cement mass, %			
	0%	2%	5%	10%
	The compressive strength of cement paste, mPa			
1	4.3	1.6	11.4	1
3	31	20	42.9	7
7	37	32	52.3	16
28	43.5	52	61.8	32

3.2. The X-ray phase analysis and infrared spectra of the additive and the control specimen

Holding the cement in the HCl solution changes the result of the hydration process. X-ray diffraction revealed qualitative and quantitative differences in the phase composition of the synthesized additive as compared to the control specimen (pure cement and water). From Fig. 1 it can be seen that in the structure of the additive the following changes take place in comparison with the control specimen:

- a significant decrease in the intensity of reflections of silicate phases – alite and belite;
- lack of reflections of portlandite and ettringite;
- formation of the Kuzel salt $\text{Ca}_4\text{Al}_2(\text{OH})_{12}\text{Cl}(\text{SO}_4)_{0.5} \cdot 6\text{H}_2\text{O}$.

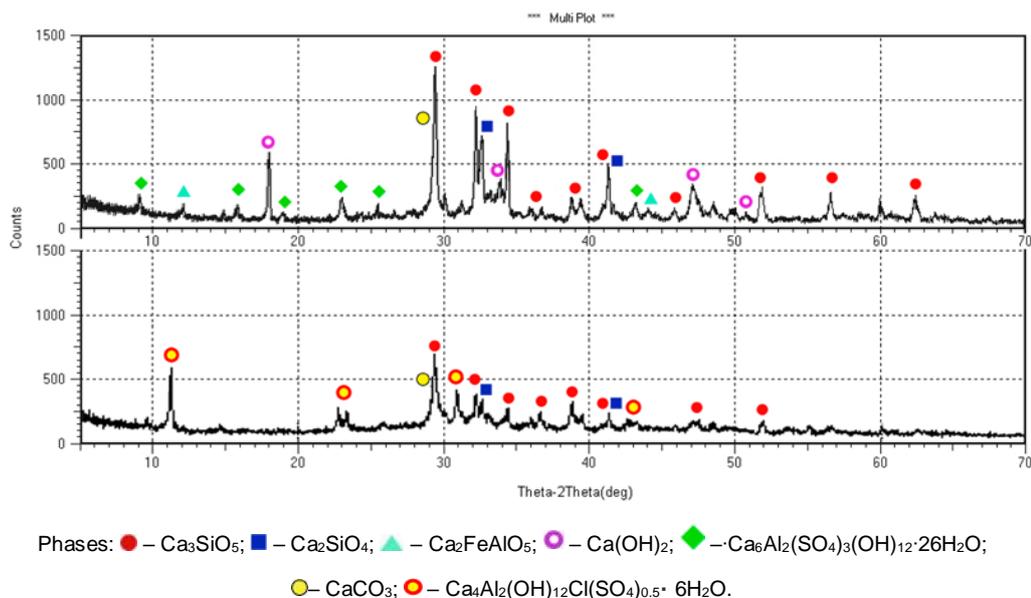
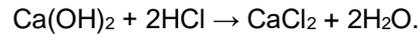


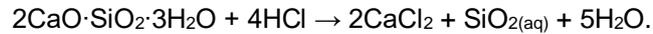
Figure 1. The XRD graphs of the additive (lower curve) and the control specimen (upper curve).

The noted features of phase formation occurring in the cement – HCl slurry suspension are explainable. Thus, a sharp decrease in the reflections of silicate phases in the X-ray phase analysis curves of the additive indicates an acceleration of the binder hydration in the presence of hydrochloric acid.

The absence of portlandite in the composition of the additive is due to the occurrence of neutralization reactions between clinker cement minerals of an alkaline nature and hydrochloric acid. In this case, the least chemically resistant to acid is precisely Portlandite, since Portlandite begins to decompose even at pH = 12.5 [28]:



Calcium hydrosilicates interact with acid by the reaction:



X-ray phase analysis data are consistent with the results obtained by infrared spectroscopy (Fig. 2). An increase in the height of absorption bands with maxima of 3410 (+71 %) and 1640 cm^{-1} (+200 %) indicates an intensification of the formation of compounds containing chemically bound water. A signal amplification with a maximum of 969 cm^{-1} (+136 %) indicates an increase in the rate of accumulation of weakly crystallized tobermorite-like hydrosilicates in the additive.

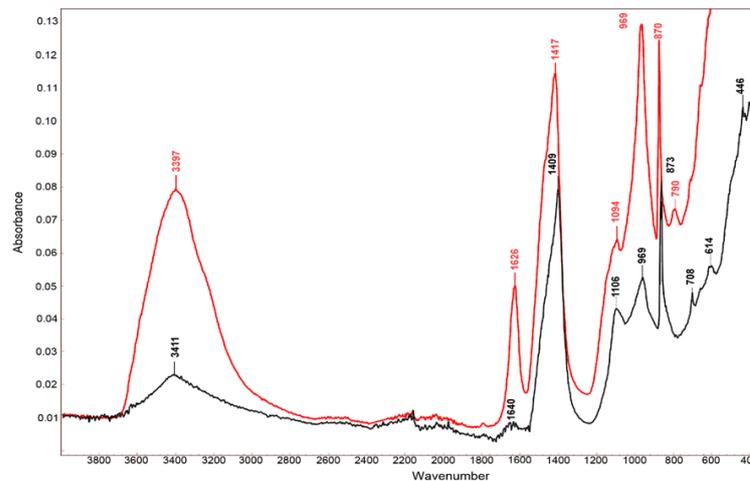


Figure 2. Infrared spectra of the additive (red) and the control specimen (black).

3.3. The X-ray phase analysis and infrared spectra of the modified cement paste and non-additive cement paste

The X-ray phase analysis of the additive shows that the presence of calcium chloride in the liquid phase of the suspension affects the process of cement hydration. The presence of calcium chloride causes the synthesis of Kuzel salt. Also, ettringite does not form during the 24-hour preparation procedure. The authors [23, 29–32] also showed the possibility of phase transformations:



in cement pastes with the participation of chlorine ions in hydration processes. However, the X-ray diffraction pattern of the chloride-containing additive contains reflections of both Kuzel salt and ettringite. In this case, the height of the reflections of calcium hydrosulfoaluminate recorded in the diffraction patterns for the 28-day non-additive cement paste and the modified cement paste is the same. This means that the introduction of the additive does not create competitive conditions for the formation and growth of AFt and AFm phases. Kuzel salt microcrystals germinating in a hydrating cement paste (mainly in the pores) do not create any chemical or physical, including steric, obstacles for the development of ettringite and other structure-forming phases. On the contrary, the formation of a crystalline framework with the introduction of additives is significantly accelerated. This is evidenced by the high daily strength of the modified cement paste (Table 2). The hardening of the modified cement paste is also facilitated by the binding of portlandite. The binding of portlandite in a chloride-containing cement paste is seen in the decrease in Ca(OH)_2 reflections by 7–9 % compared to a non-additive cement paste (Fig. 3). In the infrared spectrum of the modified cement paste, the height of the absorption band with a maximum of 951 cm^{-1} was increased by 22 % (Fig. 4). This indirectly confirms the increase in the number of tobermorite-like hydrosilicates, which are the main carriers of the strength of cement paste.

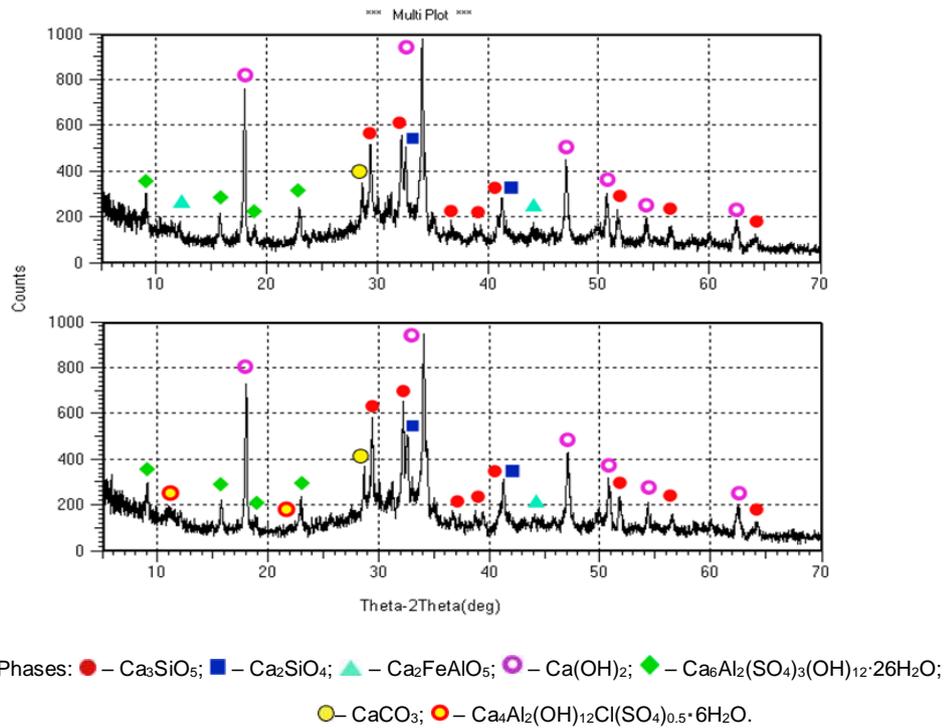


Figure 3. The XRD graphs of the modified cement paste (lower curve) and non-additive cement paste (upper curve).

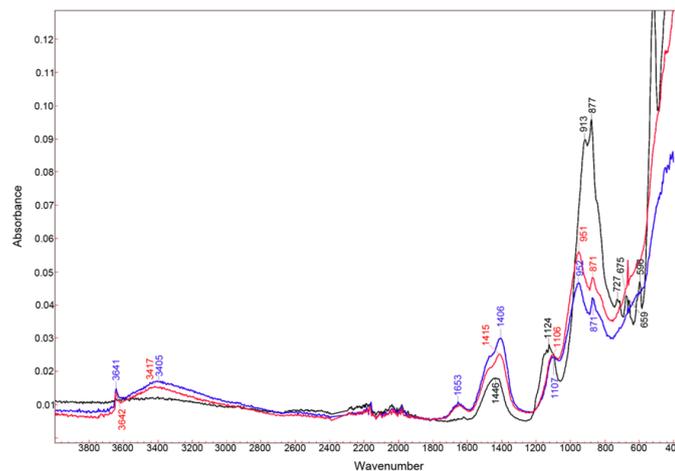


Figure 4. Infrared spectra of the initial cement (black), non-additive cement paste (blue), modified cement paste (red). The cement pastes' age is 28 days.

An increase in the intensity of reflexes of silicate phases (29 , 32 , 41.5° on a 2θ scale) in the structure of chloride-activated cement paste by 8–12 % compared with non-additive cement paste indicates a more complete hydration of the chloride-activated cement paste when reaching 28 days age. This can be explained by the fact that the reflections of the phases of highly basic hydrosilicates (CSH II) are superimposed on the reflections of silicate phases. Therefore, the reflex height of these phases is summed. [33].

4. Conclusions

The studies and the interpretation of the results proposed in the article allow to draw the following conclusions:

1. The additive synthesized by keeping cement in a 3 % HCl solution at a solid to liquid ratio of 1:10 for 24 hours, i.e. under conditions of acid corrosion of cement, it has structure-forming properties. The use of the additive significantly accelerates the setting and increases the strength of the cement paste. In the daily age of normal hardening, the strength of the cement paste increases by 165 %, in the 28-day age increases by 42 %.

2. The results of studying the structure of modified cement paste by XRD and IR methods suggest that the acceleration of setting and increase in strength characteristics are caused by the intensification of hydration processes and the binding of portlandite, the early formation of structure-forming phases of ettringite and Kuzel salt $\text{Ca}_4\text{Al}_2(\text{OH})_{12}\text{Cl}(\text{SO}_4)_{0.5}\cdot 6\text{H}_2\text{O}$, as well as the early formation of weakly crystallized calcium hydrosilicates of a tobermorite-like structure.

3. The proposed chloride-activated cement paste formulation after final refinement can be recommended for concrete building mixtures with accelerated hardening, increased strength, and without heat treatment.

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