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Synthesis and hardening of fluoralinite cement

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The synthesis of fluoralinite cement and its hydration properties are presented. It was determined that fluoralinite is obtained after 4 hrs of burning at 1100 °C by using an initial composition of 0.89% Al_2O_3, 1.78% MgO, and 0.89% Fe_2O_3 additions. Specimens formed from fluoralinite clinker and ground sand (with a mass ratio of 1:3), hydrothermally cured at 175 °C for 4 hrs, had the highest strength (4.68 MPa). Thus, fluoralinite cement is usable for hydrothermal curing articles. X-Ray analysis showed that after hardening of the mixture of fluoralinite and quartz sand for 28 days in normal conditions, quartz, tobermorite gel, portlandite $Ca(OH)_2$, and CaF_2 prevail in the samples. This mixture hardens in hydrothermal conditions, in calcium hydrosilicate $(0.8–1.5)CaO·SiO_2·(0.5–2.5)H_2O$ (C–S–H (I)) and $Ca(OH)_2$ forms.

Key words: *fluoralinite; mortar; hydration*

1. Introduction

For Portland cement clinker production, 3200 to 3400 kJ/kg of energy is usually needed. It is feasible to diminish energy consumption by adding flux, i.e. additives reducing the temperature of cement formation, into the initial load. Materials containing fluorine compounds may be used as flux [1]. During burning of the mixture of Portland cement raw materials containing fluorine compounds, the following intermediate compounds may be formed: fluorspurite $(2CaO·SiO_2)_2·CaF_2$; fluoralinite $(3CaO·SiO_2)_3·CaF_2$ and fluoralumocalciumsilicate $11CaO·7Al_2O_3·CaF_2$ [2]. Fluorspurite is an analogue of calcium chondrodite $(2CaO·SiO_2)_2·Ca(OH)_2$. This compound is hydraulically inactive and stable up to 1040 °C. At higher temperatures, it decomposes into α'-$2CaO·SiO_2$ and CaF_2 [3].

In the system of $CaO–SiO_2–CaF_2$, $(3CaO·SiO_2)_3·CaF_2$ is richest in calcium. Due to its similarity to chloralinite $(3CaO·SiO_2)_3·CaCl_2$, it has been called fluoralinite. Various difficulties arose in synthesizing pure fluoralinite. Gillioli et al. [4] applied the reagent $CaCO_3$, amorphous SiO_2, and CaF_2 for the synthesis of the pure compound. Insignificant quantities of fluoralinite are formed by heating the initial mixture at

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1200 °C for 24 days. By using an initial mixture of alite $3CaO\cdot SiO_2$ and CaF_2, anhydrous $(3CaO\cdot SiO_2)_3\cdot CaF_2$ was obtained after 2 hrs of exposure at 1130 °C. In both cases, due to the volatility of fluorine, the synthesis was carried out in soldered platinum dishes.

Pure fluoralinite could be synthesized only by applying a special method for preparing the reagents (drying in hot kerosene) [5]. According to the author of [5], pure fluoralinite synthesized with this procedure is stable at temperatures above 1103±3 °C. According to [6], pure fluoralinite is unstable at temperatures lower than 1130 °C and higher than 1175 °C. Cooled slowly, it decomposes into CaO, CaF_2, and $2CaO\cdot SiO_2$. Above 1185 °C, fluoralinite decomposes, forming monoclinic alite – $3CaO\cdot SiO_2$, containing some fluorine ions and CaF_2. An additive of MgO, Al_2O_3, Fe_2O_3 reduces the temperature of formation of fluoralinite to 950–1000 °C [7]. It was synthesized from the mixture of MgO (1%), Al_2O_3 (1%), Fe_2O_3 (1%), and Mn_2O_3 (2%) additives. Akaiwa et al. [8] have noticed that this compound forms in raw materials containing fluorine already at 850 °C. At 1100 °C, fluoralinite containing magnesium, iron and aluminium in the crystal lattice decomposes into CaF_2 and alite $3CaO\cdot SiO_2$.

Therefore, on burning initial mixtures containing fluorine, fluorine-containing intermediate minerals of clinker are formed. The hydration of these minerals has not been investigated properly. After investigating properties of fluorine-containing minerals of clinker and their hydration, an optimal composition of clinker and optimal conditions of its synthesis should be possible to determine. Currently, more attention has been paid to the modification of clinker and its minerals. Cement with a larger amounts of fluorine, iron, sulphur, and chlorine can be produced by burning initial mixtures at reduced temperatures.

The aim of this work was to determine conditions of the synthesis of fluoralinite cement and to investigate its properties, such as fluoralinite paste setting and the hydration of mortar formed from mixtures of fluoralinite clinker and ground quartz sand at room temperature and in hydrothermal conditions.

2. Experimental

The materials used in the research were: $CaCO_3$ (POCh S.A., Poland; min. 99% $CaCO_3$; pure p.a.); amorphous $SiO_2\cdot nH_2O$ (loss of mass on ignition 20.4%; Krasny Khimik Sankt Petersburg, Russia; pure); Fe_2O_3 (POCh S.A., Poland; min. 96% Fe_2O_3; pure); $Al(OH)_3$ (Poch S.A., Poland; min. 63–67% Al_2O_3; pure p.a.); $MgCO_3$ (POCh S.A., Poland; min. 24% Mg; pure p.a.); CaF_2 (POCh S.A., Poland; min. 98% CaF_2; pure).

X-ray diffraction analysis was carried out using a DRON-6 diffractometer with Ni-filtered CuK_α radiation. The radiation angle 2Θ was changed in the range 4–60°. Thermographic investigations were carried out by using an STA 409 PC differential scanning calorimeter from Netzsch. The maximum temperature was 1500 °C, and the rate of temperature change was 10 °C/min. IR spectra were recorded with a Perkin

Elmer FT-IR System spectrometer. For the IR analysis, 1 mg of the substance was mixed with 200 mg of KBr and compressed in a forming press under vacuum. Hardening of the samples was carried out in hydrothermal conditions in an autoclave at 175 °C for 4 h. The compression strength was determined by using a model R-05Y4.2 device. The amount of free CaO in the burned samples was determined by the accelerated determination of free CaO.

The chemical content of the initial mixture was chosen (Table 1) according to the theoretical probability of $(3CaO\cdot SiO_2)_3\cdot CaF_2$ formation. The amount of additives (MgO, Al_2O_3 and Fe_2O_3) corresponds to the solubilities of these oxides in the tricalcium silicate lattice.

Table 1. The chemical composition of the initial mixture, wt. %

Oxide	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	F_2
Percentage	63.22	21.99	0.89	0.89	1.78	11.23

The fluoralinite mixture of the initial dry components was thoroughly mixed in a porcelain mill for 1.5 hrs. After milling, the powder was pressed into cylindrical tablets. Then, in an electric stove, part of them were burned at 1050 °C for 1 h, and another part at 1100 °C for 4 h. After burning, the samples were cooled to room temperature, ground and sieved through No. 008 (80 μm) sieve.

3. Results and discussion

Fluoralinite forming conditions. Thermal analysis of the initial fluoralinite mixture has shown (Fig. 1) that a dehydration occurs at 90–100 °C (loss on ignition of the mixture at 90–150 °C was 6%, $\Delta H = 154$ J/g). At 306 °C, a partial dehydration of β-$Al_2O_3\cdot 3H_2O$ (bayerite) occurs and α-AlO(OH) (bemite) is formed ($\Delta H = 95.21$ J/g, the mass loss of the mixture at 280–340 °C was 5.38%), and at 524 °C bemite completely dehydrates ($\Delta H = 32.11$ J/g, the mass loss at 500–550 °C 0.82%). At 800 °C, γ-Al_2O_3 recrystallizes into α-Al_2O_3. The exothermic effect is suppressed, however, by the endothermic dissociation of $CaCO_3$. The decomposition of $CaCO_3$ into CaO and CO_2 starts approximately at 700 °C ($\Delta H = 694.2$ J/g, mass loss of the mixture at 700–880 °C was 21.32%). The process being slow at the beginning, intensifies at 800 °C and at 857.7 °C its rate reaches a maximum. The total mass loss of the mixture at 90–1000 °C is 33.52%.

On burning the initial mixture at 1050 °C for 1 h, $CaCO_3$ decomposes into CaO, a part of which reacts with amorphous SiO_2 and forms belite β-$2CaO\cdot SiO_2$ (Fig. 2, curve 1) (CaO = 20.44%). If fluorine compounds are present in the initial mixture, belite forms at lower temperatures than in the batches without fluorine compounds. In accordance with literature data [1, 3], fluorspurite $(2CaO\cdot SiO_2)_2\cdot CaF_2$ may also exist, though it has not been detected under the conditions of our experiments. Increasing the temperature to 1100 °C and prolonging the burning time to 4 h, results in fluoralinite $(3CaO{\cdot}SiO_2)_3{\cdot}CaF_2$ and γ-$2CaO{\cdot}SiO_2$ prevailing in the mixture (Fig. 2, curve 2). Also, intangible quantities of CaF_2 and CaO (CaO = 6.53%) remain. The samples disintegrate on cooling because additives with fluorine compounds promote the polymorphic transition of β-$2CaO{\cdot}SiO_2$ into γ-$2CaO{\cdot}SiO_2$.

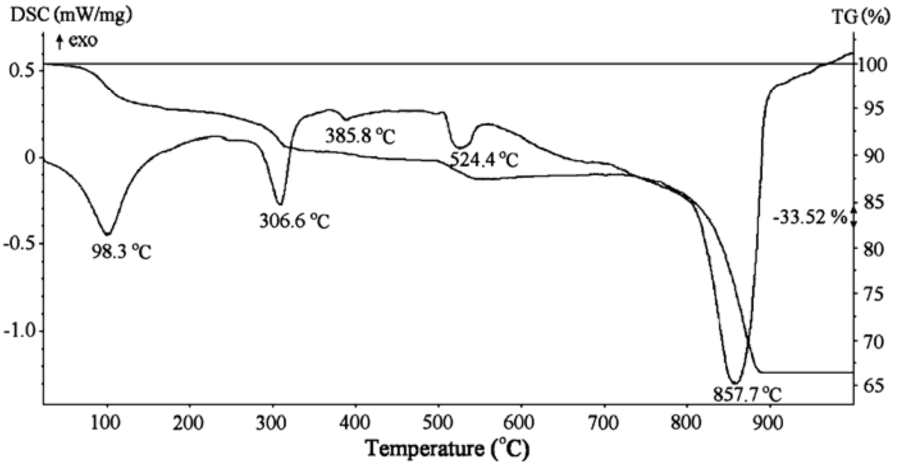

Fig. 1. Thermograms of unburned fluoralinite mixtures

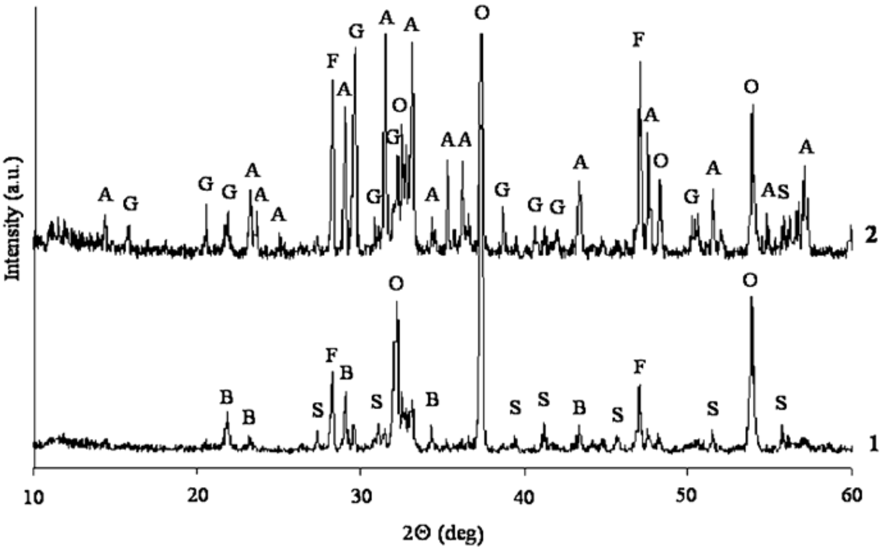

Fig. 2. X-Ray diffraction patterns of fluoralinite mixtures: 1 – burned at 1050 °C for 1 h; 2 – burned at 1100 °C for 4 h; F – CaF_2; O – CaO; B – β-$2CaO{\cdot}SiO_2$; G – γ-$2CaO{\cdot}SiO_2$; A – fluoralinite $(3CaO{\cdot}SiO_2)_3{\cdot}CaF_2$; S – SiO_2

Hydration of fluoralinite mortar. The binding and hardening of cement is the result of interaction between cement powder and water. After mixing Portland cement with water, constituent minerals form various hydrated compounds. The binding properties of fluoralinite clinker have been investigated according to the Portland cement investigation methods [5]. The specific surface area of ground fluoralinite clinker was 460 m^2/kg. Its pastes were prepared using standard water. The consistency and setting time were determined directly using a Vicat apparatus. For fluoralinite clinker paste, the initial set of normal consistency was 9 h, while the final set was 10 h. Compared to the requirements for Portland cement, the initial set of binding was late. Approximately after 10 h from the onset of hydration, a sudden hydration starts and the water in the paste is used to form the new crystals.

The dough of the mortar is formed from the mixture of the fluoralinite clinker and ground quartz sand (with the specific surface area S = 352 m^2/kg), in various ratios: 1:1 (mix 1), 1:2 (mix 2), and 1:3 (mix 3). The ratio of water to solid substances, V/K, was 0.5. The fresh dough of the mixture was moulded in 2 cm steel cubes. Part of them were cured in 90% relative humidity (RH) at 20 ºC for 24 h, then specimens were remoulded and cured under tap water for 3, 7, 14, and 28 days at 20 ºC, and finally broken. Another part of them was processed for 4 h at 175 °C in hydrothermal conditions, i.e. under saturated water vapour. After exposure, their compression strengths were determined. Six samples were measured for each test, and the mean values were considered.

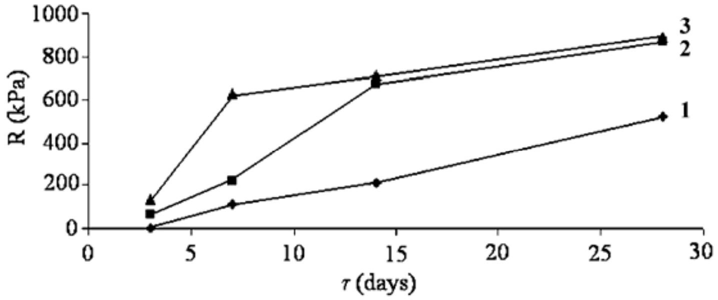

Fig. 3. Compression strength of fluoralinite mortar during hardening in normal conditions with ratios of fluoralinite mix to quartz sand: 1 – 1:1; 2 – 1:2; 3 – 1:3

It was determined that the strengths of all specimens increased, but the rate of strength increase was not constant (Fig. 3). At the initial stage of the experiment (until 7 days), the specimen strength increases depending on the amount of quartz sand. The samples having been formed from the mixture of fluoralinite and quartz sand with the ratio of 1:3 (mix 3) developed a compression strength of about 650 kPa, while the smallest strength was obtained for the specimen with the least amount of sand (the strength of mix 1 was approximately 110 kPa). After 14 days, the compression strengths of mixtures 2 and 3 reached approximately 710 kPa, and slightly increased further after 28 days by reaching ca. 880 kPa. The strength of the specimens of mixtures in which the fluoralinite cement and quartz sand ratio is 1:1 (mix 1)grew slower and after 28 days of hardening reached only 500 kPa. From the obtained results, a positive influence of sand additive on sample strength is evident.

For the 1:1 ratio of fluoralinite to sand, it was determined that the compression strength was 1.34 MPa after hardening at 175 °C (τ_{iso} = 4 h) in saturated water vapour. In normal conditions, the largest compression strength of approximately 520 kPa was recorded after 28 days. By increasing the quantity of sand in the mixture to the ratio of 1:2, the compression strength of autoclave products was increased to 2.31 MPa. The most significant compression strength, 4.68 MPa, was attained for the optimal ratio of 1:3 (Fig. 4).

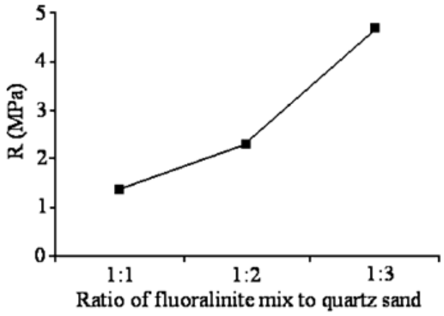

Fig. 4. Compression strength of fluoralinite mortar hardened at 175 °C for 4 h

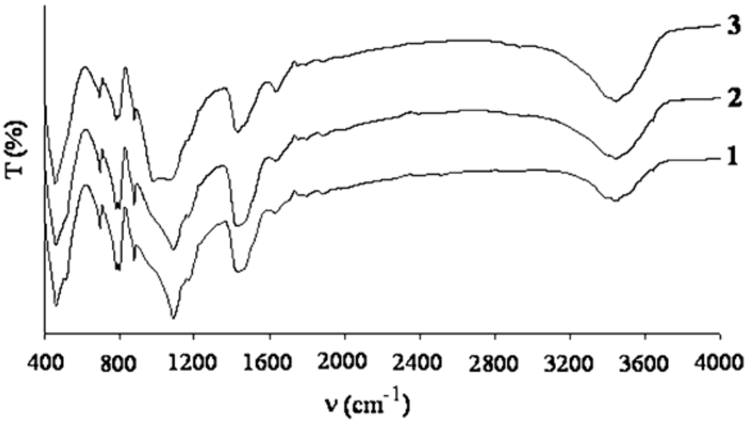

Fig. 5. IR spectra of the mortar dough of mixture 1: 1 – after 3 days of hydration; 2 – after 28 days of hydration, 3 – cured at 175 °C for 4 h

When investigating the differences in the structures of crystal materials, valuable information can be derived from infrared (IR) spectra. The IR spectra (Fig. 5) of mixture 1 are nearly identical. The most important difference appears in the spectra of the samples processed hydrothermally at 175 °C for 4 h (Fig. 5, curve 3) differ most considerably. The distinct band of selective absorption in the frequency range 1250–830 cm^{-1} indicates valence vibrations of Si–O and Al–O bonds. The band at 450 cm^{-1} is typical of the active inner vibrations in the SiO_4^{4-} tetrahedron. Moving on from the island, group, and ring silicates to chain, layer, and network ones (quartz), the IR absorption band in the range 1250–830 cm^{-1} shifts to higher frequencies). In all samples the ν_1 vibrations of CO_3^{2-} are dominant for the 875 cm^{-1} frequencies, and ν_2 (CO_3^{2-}) prevail in the range 1400–1500 cm^{-1}.

A typical double band of the Si–O–Si bond is seen in the range 770–790 cm^{-1} of the IR spectrum. On the basis of IR spectra, water forms are ascertained. Absorption bands at 1650 cm^{-1} indicate deformation vibrations of simple water molecules, and broader absorption bands in the range 2800–3700 cm^{-1} imply vibrations of OH^- groups.

In the IR spectra of mixture 2, the same changes occur as for mixture 1, only the vibrations of CO_3^{2-} are different. Also, during the hardening of the sample in normal conditions, there is no absorption band at 1650 cm^{-1}, typical of deformation vibrations of simple water molecules. It appeared, however, in samples cured at 175 °C for 4 h. Since water present in the mixture is not bound by hydrogen bonds, a narrow absorption band at 3700 cm^{-1} exists, which corresponds to the vibrations of isolated OH^- groups.

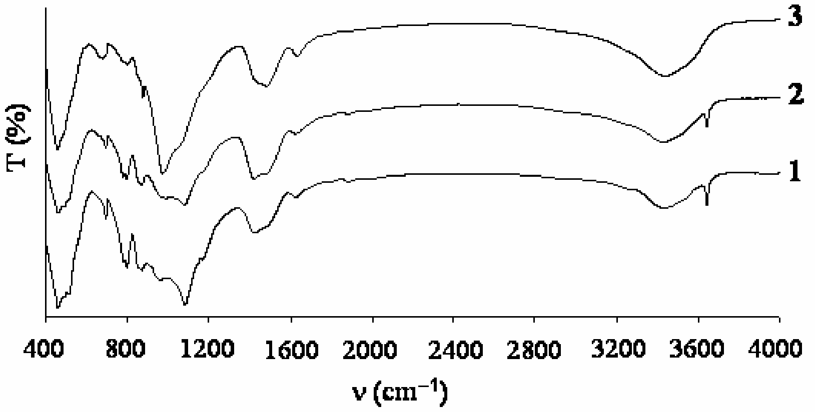

Fig. 6. IR spectra of the mortar dough of mixture 3: 1 – after 3 days of hydration; 2 – after 28 days of hydration, 3 – cured at 175 °C for 4 h

By analysing the IR spectra (Fig. 6) of mixture 3, it has been established that the spectra of silicon-oxygen compounds are typical and consist of two distinct selective absorption bands: in the range 1250–830 cm^{-1} (valence Si–O bonds and Al–O vibrations) and in the range 590–500 cm^{-1} (deformation vibrations of Si–O bonds).

Absorption bands at 1650 cm^{-1} represent deformations of simple water molecules. The absence of an absorption band at 3700 cm^{-1} indicates that there are no isolated OH groups in mixture 3.

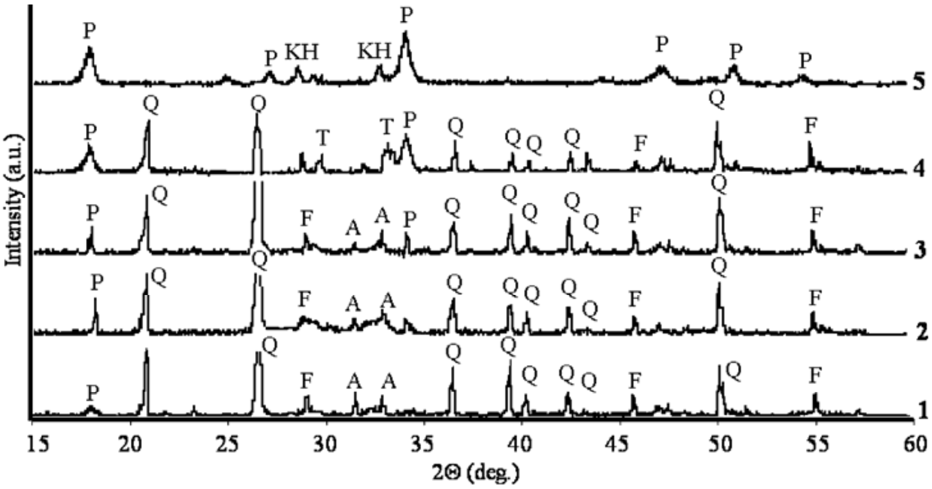

Fig. 7. X-Ray diffraction patterns of the hydration of mixture 3: 1 – after 3 days of hydration; 2 – after 7 days of hydration, 3 – after 14 days of hydration; 4 – after 28 days of hydration; 5 – cured at 175 °C for 4 h. F – CaF_2; P – $Ca(OH)_2$; A – fluoralinite $(3CaO{\cdot}SiO_2)_3{\cdot}CaF_2$, KH – C-S-H(I) calcium silicates hydrate; Q – SiO_2 (quartz); T – tobermorite gel

Based on the X-ray analysis of mixture 3 mortar (Fig. 7), it was established that after 3 days of hydration, quartz, $Ca(OH)_2$, and CaF_2 prevail in the specimen. They remain stable after 28 days of hydration at normal conditions. During the primary stages of hardening, until 14 days of hydration, fluoralinite $(3CaO{\cdot}SiO_2)_3{\cdot}CaF_2$ was still detected. After 28 days of hydration at normal conditions, it was no longer found and new hydration products, namely tobermorite gel and portlandite $Ca(OH)_2$, were formed.

During the hardening of the fluoralinite mortar in hydrothermal conditions (in an autoclave), portlandite $Ca(OH)_2$ forms and, together with the calcium oxide present in the clinker, reacts with quartz. Consequently, low base calcium hydrosilicate C–Si–H (I) is formed. After hydrothermal processing, spectral features of neither quartz nor fluoralinite are recorded.

The X-ray diffraction patterns of the hydration products of mixtures 1 and 2 are similar.

4. Conclusion

The mixture of Al_2O_3 (0.89%), Fe_2O_3 (0.89%), MgO (1.78%), and CaF_2 (11.23%) additives in cement batch burned at 1100 °C for 4 h gives fluoralinite. At 1050 °C, attempts of synthesizing fluoralinite were unsuccessful.

In the conditions of our experiments, samples formed from fluoralinite clinker and quartz sand (1:3), autoclaved at 175 °C for 4 h, have the largest strength (4.68 MPa). Thus, fluoralinite clinker is appropriate for being used in autoclave products.

X-Ray analyses have shown that when the mixture of fluoralinite and quartz sand is hardened for 28 days in normal conditions, quartz, tobermorite gel, portlandite $Ca(OH)_2$, and CaF_2 prevail in the samples. When the fluoralinite mortar is hardened in hydrothermal conditions (in an autoclave), portlandite $Ca(OH)_2$ and low base calcium hydrosilicates C-S-H (I) are formed.

Bonds between Si–O, Al–O, Si–O–Si, OH^-, and CO_3^{2-} prevail in the obtained samples of fluoralinite mortar.

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