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## Structurization processes of cement composites modified with electrolytic additives

### Процессы структурообразования цементных композитов, модифицированных добавками электролитов

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**Key words:** cement; electrolytic solutions; aluminium and ferric chloride solutions; additives; strength

**Ключевые слова:** цемент; растворы электролитов; хлориды алюминия и железа; добавки; прочность

**Abstract.** There has been research on the impact of  $AlCl_3$  and  $FeCl_3$  solutions on kinetics of cement hardening. The research was carried out in two comparative versions, one of which had the saline solutions introduced into cement as gauge liquid ("water–1% electrolytic solution"), the other had them as additives, synthesized in suspensions "cement – (water–1% electrolytic solution)". It has been stated that the use of  $AlCl_3$  and  $FeCl_3$  solutions as gauge liquids leads to reduction of compression resistance values of modified cement rocks. The value of 28-day hardness, compared to plain cement, is reduced by 18 % in case of cement gauging with  $AlCl_3$  solution, and by 27% in case of binder gauging with  $FeCl_3$  solution. On the contrary, the composites, produced by means of introducing the additives, synthesized within suspensions, into cement paste, have shown a significant boost in 28-day hardness compared to plain sample – by 30 and 23 % accordingly. The analysis of the result studies of the additives by means of XPA and IR-spectral analysis has shown that within the structurization of additives the interrelated changes take place, due to the rapid decrease of portlandite amount and carbonization. The authors suppose the acceleration of setting and the higher strength of cement composite with the introduced additive, synthesized by means of cement exposure to 1 %  $AlCl_3$  solution, to take place due to synergic influence of a number of factors: intensive growth of ettringite crystal seeds and badly crystallized phases of hydrated calcium silicates of tobermorite-like structure; reduction of  $Ca(OH)_2$  in the hard phase of a cement rock; and carbonization effect, which includes the formation of crystal phase for  $Ca_8Al_{12}Fe_2C_{12}(CO_3) \cdot (OH)_2 \cdot 22H_2O$ . The improvement of density properties of a cement composite after introducing the additive, synthesized by means of cement exposure to 1 %  $FeCl_3$  solution, is probably facilitated by gauging of  $Ca(OH)_2$ , or may be explained by "working"  $CaCO_3$  and ettringite microcrystals, catalyzing the intergrowth of composite skeletal frame, or by "working" gelatinous hydrated calcium ferrites and silicates, characterized by a high surface area, which facilitate and boost interphase contacts, increasing the density of cement systems.

**Аннотация.** Изучено влияние добавок электролитов – хлоридов трехвалентных железа и алюминия на кинетику твердения цемента. Исследование проведено в двух сравнительных вариантах, в одном из которых растворы солей вводились в цемент в качестве жидкостей затворения («вода – 1%-й раствор электролита»), в другом – в качестве добавок, синтезированных в составе суспензий «цемент – вода – 1%-й раствор электролита». Установлено, что использование растворов  $AlCl_3$  и  $FeCl_3$  в качестве жидкости затворения приводит к уменьшению значений прочности при сжатии модифицированных цементных камней во всем интервале твердения. Величина 28-ми суточной прочности по сравнению с бездобавочным цементным камнем снижается на 18% в случае затворения цемента раствором хлорида алюминия и на 27% – в случае затворения вяжущего раствором хлорида железа. Композиты, полученные введением в цементное тесто добавок, синтезированных в составе суспензий, напротив, показали значительный прирост 28-ми суточной прочности относительно бездобавочного образца – на 30 и 23%, соответственно. Анализ результатов изучения добавок методами РФА и ИК-спектроскопии показал, что в структурообразовании добавок имеют место взаимозависимые изменения, связанные с резким уменьшением количества портландита и карбонизацией. Авторы предположили, что ускорение

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схватывания и увеличение прочности цементного композита при введении добавки, синтезированной экспозицией цемента в 1%-м растворе  $AlCl_3$ , реализуется благодаря синергетическому влиянию нескольких факторов: интенсивному росту зародышей кристаллов этtringита – главного армирующего компонента цементной системы и слабо закристаллизованных фаз гидросиликатов кальция тоберморитоподобной структуры, уменьшению количества  $Ca(OH)_2$  в твердой фазе цементного камня и эффекту карбонизации, включая образование кристаллической фазы  $Ca_8Al_{12}Fe_2O_{12}(CO_3) \cdot (OH)_2 \cdot 22H_2O$ . Улучшение прочностных характеристик цементного композита при введении добавки, синтезированной экспозицией цемента в 1%-м растворе  $FeCl_3$ , вероятно происходит благодаря связыванию  $Ca(OH)_2$ , а также может быть объяснено «работой» микрокристаллов этtringита и  $CaCO_3$ , катализирующих прорастание скелетного каркаса композита, а также с «работой» гелеобразных гидроферритов и гидросиликатов кальция, обладающих высокой удельной поверхностью, которые облегчают и улучшают межфазовые контакты, увеличивая плотность цементных систем.

## 1. Introduction

The construction of high-quality and most advanced concretes is one of the main tasks of construction materials engineering. Contemporary construction science employs a wide range of methods [1–12], allowing the targeted exposure of a cement rock (CR) structure, which in a number of ways determines operational parameters of cement concrete and products thereof. The easiest and most efficient means of regulating the gauging properties is the application of additives. Nowadays additives of various purposes are as essential components of a concrete mix, as gauge liquids, aggregate and water. Therefore the approach, devoted to engineering of new, competitive local concrete additives, increasing the strength, corrosive resistance, and providing the durance of concrete, requires special attention.

The analysis of science and research literature has shown, that the concrete technology has a lasting importance of additives, boosting the setting and hardening of concrete – chlorides, carbonates, sulfates, nitrates, silicates, phosphates, and other electrolytic and non-electrolytic solutions and their various combinations. The most common and effective of this far from complete list of chemical additives are still the muriates and their compounds: ultimate advantages of chloride modifiers are their high solubility, reliable performance, availability and low cost.

Experimental research has stated the results of such additives applications to increase at the increase of saline cationic charge: polyvalent cations are by far more effective than the low-valent ones [13–16]. There has also been stated, that the salts of three-valence metals combine the properties of hardening boosters and concrete imporosity boosters (colmatants). The disadvantage of chloride additives is the so-called chloride aggression to the steel fittings. The analytical research of scientific results, presented by foreign and Russian scientists from 1973 to 2004 [17] shows, that the critical concentration of chlorides in concrete is the range of 0.15 % to 3 %, depending on the operational conditions of engineering constructions. According to the standard, effective on the Russian territory (Construction Rules SP 28.13330.2012), as well as the European standard BS EN 206, the maximum allowed amount of chlorides, calculated as ions of  $Cl^-$ , should not exceed 1 % of cement mass in plain concrete, 0.4 % in concrete with prestressed reinforcement, 0.1 % with nonprestressed reinforcement. The corrosion risks may be eliminated by means of simultaneous application of inhibitory agents – nitrates and nitrites of calcium, borates, chromates, katapine [13, 14]. Without any risk chlorides may be applied in aerated concrete technology (cellular and pumice concrete), in construction of concrete slabs, paving elements, construction of outdoor amenities.

The conventional way of applying setting and hardening boosters is their immersion into the gauging liquid. The research [18] has described a scientific approach, according to which the increase of cement rock strength is obtained by means of introducing the additives, synthesized in “cement–water–sugar” suspensions.

The goal of the present study is to examine the influence water solutions of ferric and aluminium chlorides have on structurization processes and compression strength of cement rocks with the application of the given scientific approach. The synthesis of additives has been carried out in “cement-electrolytic solution” suspension. As for the electrolytes, 1 % solutions of  $AlCl_3$  and  $FeCl_3$  have been used. The additives were introduced into “water-cement” system at the stage of cement paste batching. To support the proposed means of introducing the electrolytic solutions into cement systems (CS) scientifically, 1 % solutions of aluminium and ferric chlorides were also used as gauging liquids.

## 2. Methods

In the functioning of a gauge liquid portland cement CEM II / A-Sh 32.5H produced by Topkinsk plant has been used, in correspondence with the Russian State Standard GOST 31108-2003.

Plain Cement Rocks (PCR) and Modified Cement Rocks (MCR):  $MFeCl_3$ ,  $MAiCl_3$ ,  $MFe$  and  $MAI$  have been produced as cubes with the side of 2 cm in regular hardening conditions. The ratio of liquid and solid phases (L/S) was 0.34.

**Table 1. Properties of additives and MCR**

| No. | Additive composition            | Saline solution pH | Additive code | Means of cement modification                       | CR code   |
|-----|---------------------------------|--------------------|---------------|--|-----------|
| 1   | 1% $FeCl_3$ solution            | 2.5                | $FeCl_3$      | Cement + (1% $FeCl_3$ solution, as a gauge liquid) | $MFeCl_3$ |
| 2   | cement + (1% $FeCl_3$ solution) |                    | CFe           | (Cement – $H_2O$ ) + 5% (mass) CFe additive        | MFe       |
| 3   | 1% $AlCl_3$ solution            | 3.8                | $AlCl_3$      | Cement + (1% $AlCl_3$ solution, as a gauge liquid) | $MAiCl_3$ |
| 4   | cement + 1% $AlCl_3$ solution   |                    | CAI           | (Cement – $H_2O$ ) + 5% (mass) CAI additive        | MAI       |
| 5   | cement + $H_2O$ (check)         | –                  | CV            | –  | –         |

MCR production was different by the way of electrolytic introduction into the “cement-water” system. For instance, the rocks  $MFeCl_3$  and  $MAiCl_3$  were produced by means of gauging the plain cement with 1% solutions of  $FeCl_3$  and  $AlCl_3$ , accordingly; for  $MFe$  and  $MAI$  rocks it was the introduction of CFe and CAI additives accordingly into the “water-cement” system; the additives were introduced at the stage of cement paste batching, in amounts of 5% of dry cement mass.

CFe additive was synthesized through the belowmentioned method.

The samples of basic gauge liquid were exposed to 1% ferric chloride with the ratio L/S = 1:5 for 24 hours, having thoroughly mixed the suspension;

After the exposure time was out, the solid part of suspension was separated from the liquid part by means of filtering. To abort the hydration processes the solid residue was processed with acetone and dried in a dessicator over  $CaCl_2$  until reaching a fixed mass;

The additive, prepared in such a manner, was ground in a porcelain mortar until reduced to the size of 008 sieve according to State Standard GOST 6613.

CAI was synthesized by means of exposure of plain cement to 1% aluminium chloride, and then according to steps 1–4.

Ferric and aluminium chlorides were used as hexaqua hydrates  $FeCl_3 \cdot 6H_2O$  (GOST 4147-74) and  $AlCl_3 \cdot 6H_2O$  (GOST 3759-75). While these salts are hygroscopic, before the production of 1% solutions hydrates were brought to fixed mass in a dessicator at the constant temperature  $(110 \pm 5)^\circ C$  (GOST 5382-91).

Test sample CV was synthesized by means of exposing the plain cement to distilled water under the conditions, completely identical to the abovementioned method of additives preparation.

Table 1 presents the means of additives synthesizing and the ways of cement modification with the additives. Table 2 shows the compression strength values (R, MPa) and density changes in MCR (reduction or increase,  $\Delta R$ , %) compared to PCR. Compression strength values of CR aged 1-3-7-28 days were determined based on 6 parallel measurements at every checkpoint. Arithmetical average of strength was calculated from three closest values, providing the margin of error under 4.8%.

Physical and chemical analysis of CFe and CAI additives was carried out in comparison to test sample CV.

Figure 1 and Table 2 present the data on additives and test sample CV examination, obtained by means of IR-spectral analysis. Figure 2 and Table 4 show the results of x-ray phase analysis. IR spectral analysis of the additives were carried out by means of Fourier spectrometer “*Varian Excalibur HE 3600*” at

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the frequency range 400–4000  $\text{cm}^{-1}$ ; for XPA it was X-ray diffraction meter Shimadzu XRD-700 with a copper anode in range of 5–90 deg.

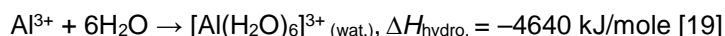
**Table 2. Compression strength  $R$ , (MPa) and density increase (reduction) values  $\Delta R$  (%) of MCR compared to PCR**

| No. | CR                 | Period of hardening, days |                |      |                |      |                |      |                |
|-----|--------------------|---------------------------|----------------|------|----------------|------|----------------|------|----------------|
|     |                    | 1                         |                | 3    |                | 7    |                | 28   |                |
|     |                    | $R$                       | $\Delta R, \%$ | $R$  | $\Delta R, \%$ | $R$  | $\Delta R, \%$ | $R$  | $\Delta R, \%$ |
| 1   | PCR                | 4.1                       | –              | 31.2 | –              | 37.3 | –              | 43.2 | –              |
| 2   | MFeCl <sub>3</sub> | 2.7                       | –33            | 24.2 | –22            | 24.4 | –34            | 31.4 | –27            |
| 3   | MFe                | 5.0                       | +25            | 40.3 | +29            | 43.4 | +16            | 53.4 | +23            |
| 4   | MAiCl <sub>3</sub> | 3.4                       | –16            | 35.0 | +13            | 34.4 | –7             | 35.3 | –18            |
| 5   | MAi                | 5.1                       | +25            | 41.2 | +32            | 44.3 | +19            | 56.4 | +30            |

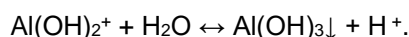
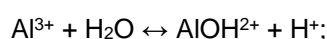
### 3. Results and Discussion

Results presented in table 2 prove that the application of 1 % ferric and aluminium chloride solutions as gauge liquids provide the reduction of compression strength of cement rocks MAiCl<sub>3</sub> and MFeCl<sub>3</sub> at the whole period of hardening. In addition to that the value of 28-day strength compared to PCR is reduced by 18 % for the MAiCl<sub>3</sub> rock, produced by means of adding aluminium chloride into cement, and by 27 % for MFeCl<sub>3</sub> rock, produced by mixing the gauge liquid with ferric chloride. MAi and MFe rocks, produced by introducing into “cement-water” system the additives, synthesized in suspensions “cement – 1 % saline solution (AlCl<sub>3</sub> or FeCl<sub>3</sub>)”, on the contrary, have shown a significant increase in strength compared to PCR – by 30 % and 23 % accordingly.

The process of three-valence metal saline solutions interacting with cement is rather complex and has a number of common things and differences, depending on the character of saline cation. Thus, due to the heavy charge and a small diameter (for Al<sup>3+</sup> – 0.057 nm, for Fe<sup>3+</sup> – 0.067 nm), cations of these metals in water solutions are highly hydrated. In acidic conditions aquatic complexes of ferric and aluminium ions are coordinated to six ligands – water molecules. Through the example of Al<sup>3+</sup> cation it reads as following:

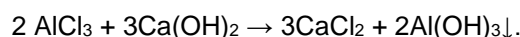


Aquatic complex of aluminium hexahydrate easily enters hydrolysis reaction, which undergoes with co-production of various products in acidic and alkaline conditions, provided by amphoteric character of aluminium. If, for the sake of simplification, water molecules included into complex salts, produced during the hydrolysis, are left out, and hydronium ion H<sub>3</sub>O<sup>+</sup> is supplemented with hydrogen ion H<sup>+</sup> among the reaction products, that will be read as follows:



The ratio of hydrolysis products depends on pH value. Aquatic complex [Al(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup> is stable at pH ranging from 0 to 4, then its amount in hydrolysis products is reducing, and at pH = 6 aluminium hexahydrate is not registered; AlOH<sup>2+</sup> appears at pH = 3, its value peaks at pH = 5, and at pH = 6.5 divalent cation disappears; Al(OH)<sub>2</sub><sup>+</sup> is produced at pH = 4, its maximum amount is registered at pH = 6, while at pH = 7.5 it is already nonexistent; Al(OH)<sub>3</sub> appears at pH = 4.5, peaks at pH = 7.5, reaching pH = 11 aluminium hydroxide is not registered [20].

Contacting cement, hydrolysis of aluminium chloride is boosted, while pore liquid ions OH<sup>–</sup> gauge nascent ions H<sup>+</sup> (or, more precisely, hydronium ions H<sub>3</sub>O<sup>+</sup>), emitting water (neutralization reaction). Simultaneous ion-exchange reaction of AlCl<sub>3</sub> with Ca(OH)<sub>2</sub> is also possible:



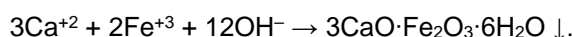
While alkaline properties of liquid phase of cement are quickly restored to regular values (pH ≈ 12 [13, 15, 16]), residual aluminium hydroxide, produced by means of hydrolysis and ion-exchange reactions, transforms into soluble aluminate-ion [Al(OH)<sub>4</sub>]<sup>–</sup>:



According to [19, 20]  $\text{Al(OH)}_3$  starts the transformation into  $[\text{Al(OH)}_4]^-$  at  $\text{pH} = 7.5$  already, while the maximum amounts of aluminate-ion are registered having reached  $\text{pH} = 11$  and higher.

Ferric hexahydrate  $[\text{Fe(H}_2\text{O)}_6]^{3+}$  is also susceptible to hydrolysis and may partake in the neutralization reaction while contacting cement. The authors [21] remark the difficulties in studying hydrolysis products of  $\text{FeCl}_3$ , different from  $\text{AlCl}_3$ , due to the rapid speed of hydrolysis reactions and  $\text{Fe(OH)}_3$  setting. Theoretically it is also possible to have an ion-exchange reaction between calcium hydroxide and ferric chloride solution ( $2\text{FeCl}_3 + 3\text{Ca(OH)}_2 = 2\text{Fe(OH)}_3\downarrow + 3\text{CaCl}_2$ ). However, low solubility product of ferric hydroxide ( $\text{SP}_{\text{Fe(OH)}_3} = 3.8 \cdot 10^{-38}$ ) facilitates its settling since the first contact of saline solution with the gauge liquid, before the reactions in question. It has been stated in [22] that  $\text{Fe(OH)}_3$  from 1 %  $\text{FeCl}_3$  solution settles at  $\text{pH} \approx 2.5$  already, its maximum amount is registered at  $\text{pH} = 4-5$  (according to data of [23] – within the range of  $\text{pH} = 4.5-5.5$ ). With the increase of  $\text{pH}$  in  $\text{FeCl}_3$  solutions the existence of a polycation has been proved, with the compound  $[\text{Fe}_{24}\text{O}_{12}(\text{OH})_{32}]^{+16}$ , which environment is similar to the structure of crystalline ferric oxyhydroxide  $\beta\text{-FeOOH}$  [21].

Having recovered the regular  $\text{pH}$  values of cement porous liquid,  $\text{Al}^{+3}$  and  $\text{Fe}^{+3}$  cations, bearing amphoteric properties, are included into the corresponding oxygen-containing anions. Moreover, while aluminium cation at  $\text{pH} = 11$  completely enters a soluble aluminate, ferric cation transforms into calcium hydroferrite (CHF) of low solubility [13]:



Settling CHF has a gelatinous structure and may clog CR pores.

The differences in additives structurization are reflected in the results, obtained by means of IR spectral analysis and XPA. Thus, IR-spectre of CAI additive is different from test sample CV spectre by the significant increase of absorption in every area, characteristic for cement systems (Figure 1).

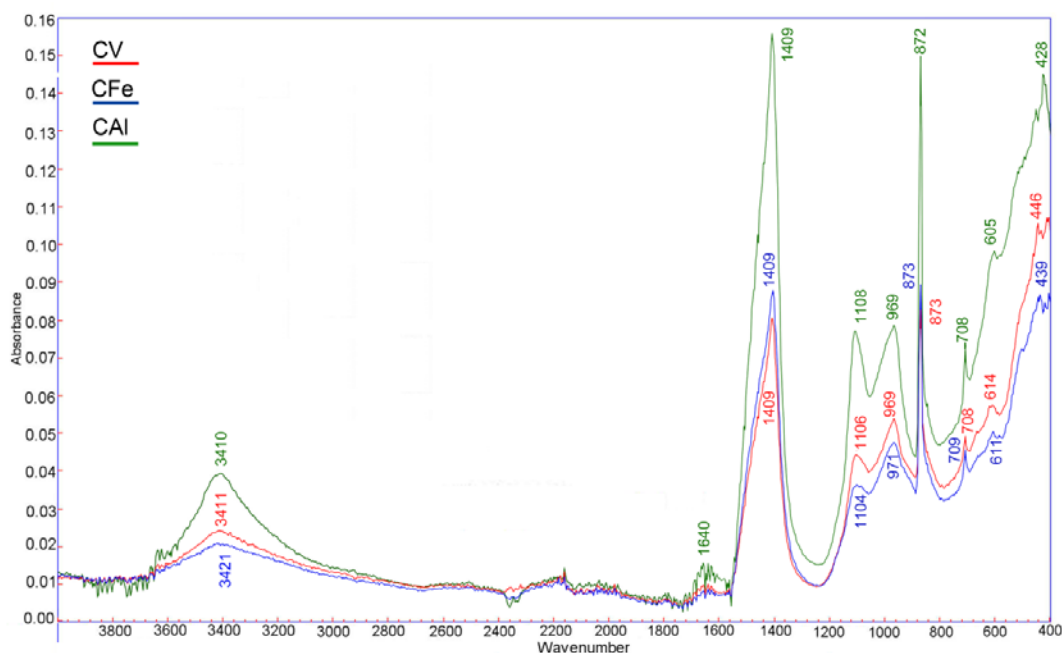


Figure 1. IR-spectres of CAI and CFe additives and test sample CV

Increase of peak height with the maximum of  $3410 \text{ cm}^{-1}$  indicates a more intensive formation of hydrated calcium sulfoaluminates (HCSA), hydrated calcium sulfates (HCS) and other hydrated phases, which have crystallization water in their molecules, appearing at the reaction of gauge liquid with aluminium chloride solution. Ettringite is also registered in the existence of adsorption bands in spectral areas of  $1000-1100 \text{ cm}^{-1}$  and  $400-600 \text{ cm}^{-1}$  [24, 25]. Spectral lines intensity in all the abovementioned intervals compared to the test sample CV is significantly increased (table 3). According to X-ray microanalysis high fuzziness of absorption profile  $400-600 \text{ cm}^{-1}$  proves the irregular structure of octahedral  $\text{Al-O}_6$  groups [25], determined by the high amount of aluminium ions in ettringite crystals. The differences, found in oscillation spectre, are corresponding to the XPA data (Figure 2, table 4) – the height of HCSA reflexes in CAI additive

compared to CV is raised by 40–54 % (the measurements were carried out on  $2\theta$  with reflection angles:  $9.016^\circ$ ,  $15.530^\circ$ ,  $19.988^\circ$  and  $22.962^\circ$ ).

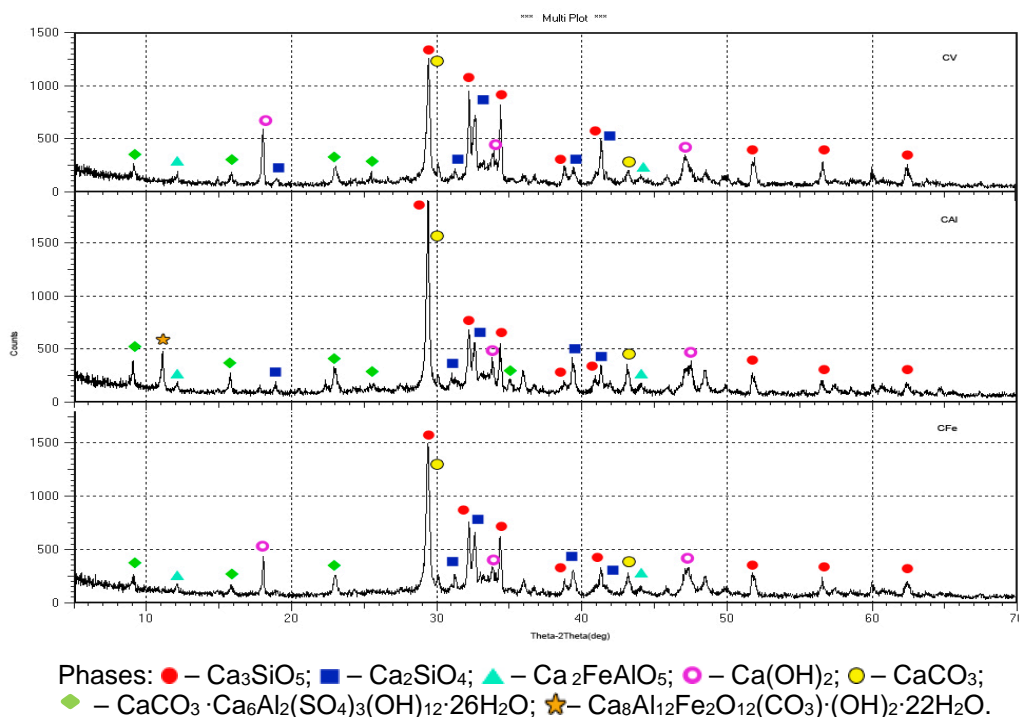
There has also been registered the increase in analytical signal, responsible for the formation of low-crystallized phases of HCS of tobermorite-like structure ( $969\text{ cm}^{-1}$ ). In IR records of CAI this signal is increased by 51 % compared to CV. It is difficult to determine HCS by means of XPA, while the reflections of these phases are overridden by the reflexes of other plain and hydrated crystalline phases of the gauge liquid.

**Table 3. IR-analysis results for MAI and MFe additives, and test sample CV**

| Adsorption band, $\text{cm}^{-1}$ | Assignment  | $I_{\text{additives}} / I_{\text{CV}} \cdot 100\%$ |                |
|-----------------------------------|---|--|----------------|
|                                   |   | MAI  | MFe            |
| 3640                              | Stretching vibrations $(\text{OH})^-$   | present  | absent         |
| 3410                              | Stretching and deformational vibrations of $\text{H}_2\text{O}$ in crystallohydrates                                    | +60  | Under CV level |
| 1650                              | Characteristic adsorption region of $\text{H}_2\text{O}$  | +50  | CV level       |
| 1409                              | $\text{CaCO}_3$   | +90  | +9             |
| 872                               | Symmetrical stretching vibrations $(\text{CO}_3)^{2-}$  | +83  | +10            |
| 1108                              | Coupled vibrations S–O of $(\text{SO}_4)^{2-}$ compounded in ettringite and stretching vibrations of $(\text{AlO}_4)^-$ | +77  | Under CV level |
| 969                               | Asymmetric vibrations of bridge bonds of Si–O–Si and symmetric and asymmetric vibrations of end bonds of Si–O           | +51  |                |
| 614                               | $(600\text{--}700\text{ cm}^{-1})$ – deformational vibrations of $(\text{AlO}_4)^-$                                     | +69  |                |
| 605                               |   | +45  |                |
| 428                               |   | +34  |                |

Figure 1 and the data of Table 3 show that cement exposure in  $\text{AlCl}_3$  solution (CAI additive) facilitates the rapid boost in gauge structure carbonization: the intensity of absorption bands of  $1409$  and  $872\text{ cm}^{-1}$  compared to test sample CV, produced by cement exposure to distilled water, is increased by 90 % and 83 % correspondingly. X-ray evidence also registers the increase of reflection height, corresponding to  $\text{CaCO}_3$  (Figure 2).

It is known, that out of cement hydrated phases the most susceptible to carbonization is  $\text{Ca}(\text{OH})_2$ . Thermodynamic calculations [26] have shown the reaction between  $\text{Ca}(\text{OH})_2$  and  $\text{CO}_2$  with its transformation into  $\text{CaCO}_3$  to have the most negative value of Gibbs thermodynamic potential. The presented data may be quite a reasonable proof to explain the significant reduction in intensity of portlandite reflections: from 35 to 100 % ( $17.978^\circ$ ,  $34.061^\circ$ ,  $50.976^\circ$ ) in CAI X-ray evidence compared to CV (Table 4). A typical feature of the additive is the existence of one more crystalline phase, containing carbonate ions:  $\text{Ca}_8\text{Al}_{12}\text{Fe}_2\text{O}_{12}(\text{CO}_3) \cdot (\text{OH})_2 \cdot 22\text{H}_2\text{O}$ , registered in low-angle region (Figure 2).



**Figures 2. XPA graphs of CAI and CFe additives and test sample CV**

The analysis of the obtained data allows to come to the conclusion, that the reaction of the gauge liquid with 1 %  $\text{AlCl}_3$  solution is followed with the activation of hydration processes, increase in amounts of ettringite microcrystals and tobermorite-like compounds, as well as the gauging of portlandite and structure carbonization. Introduction of CAI additive, enriched with ettringite microcrystals, carbonized phases and HCS, into cement paste launches the mechanism of early structurization of cement composite MAI and significantly (by 30 %) increases the strength of the hardening system.

As can be seen from Figure 1, oscillatory spectre of CFe additive, synthesized by means of cement exposure to 1 % ferric chloride solution, contrary to the changes, found out in the spectre of CAI additive, is characterized by the reduction of the lines intensity compared to the test sample CV at the whole range of wavenumbers, except for the ones responsible for the existence of carbonate-containing phases in gauge structure. The height of adsorption bands 1409 and  $872\text{ cm}^{-1}$  compared to CV, produced by means of cement exposure to distilled water, is increased by 9 and 10 % accordingly. X-ray evidence also shows some increase in the intensity of reflections, corresponding to  $\text{CaCO}_3$  (Figure 2). The intensity of ettringite reflections as a part of CFe stays at the level of the test sample, portlandite reflections intensity is reduced from 23 % to 100 % (Table 4).

Therefore, the common detail in structurization of the additives, produced by modifying the gauge liquid with aluminium and ferric solutions, is the presence of interdependent changes, caused by rapid reduction of portlandite amounts and carbonization.

According to [27] the half of the solid phase of hydrated newgrowths of a cement gauge liquid is presented by secondary calcium hydroxide, forming dense layered packs or hexagonal, well-formed crystals, filling the porous area of a cement rock. There has been research presented in [25], showing that more than a half of 28-day rock cleavage surface is occupied with  $\text{Ca}(\text{OH})_2$  crystals, while the crush cut goes through the cleavage plains of these crystals, as through the weakest areas of the solid "cement-water" system. Large crystalline blocks increase the deficiency, reduce the deformability and accumulate structural stress, reducing the uniformity, strength and corrosion resistance of a CR [25, 27, 28].

The inclusion of carbonate-containing phases in cement composite structurization, those being formed first of all and mostly due to the gauging of porous liquid calcium hydroxide by carbonate dioxide, is on the other hand, considered a beneficiary process, facilitating the reduction of shrinking deformations, and crack resistance of CR and concrete, and the significant improvement of carbonate and sulfate corrosion operational resistance [10, 25, 30]. The authors [31], considering the benefits of carbonization, have proposed to apply industrial  $\text{CO}_2$  as a facilitating additive foe concrete. Operational testing of the approach has shown the introduction of carbon dioxide into the concrete paste (slag portlandcement has been used as a gauge) to provide the increase in compression strength up to 14 % at the day age and up

to 26 % at the period of 28 days. Based on the results of isometric calorimetric test and microstructural analysis the authors have stated that nanosized carbonization products activate the hydration and provide the development of stronger concrete microstructure.

**Table 4. The intensity of  $\text{Ca}(\text{OH})_2$  and ettringite reflexes as additive parts compared to the test sample CV according to XPA data**

| No. | The intensity of additives crystalline phases reflexes compared to the test sample, |                  |          |          |
|-----|---|------------------|----------|----------|
|     | $I_{\text{additives}} / I_{\text{CV}} \cdot 100 \%$                                 |                  |          |          |
|     | Phase   | $2\theta,^\circ$ | MAI      | MFe      |
| 1   | Ettringite  | 9.016            | +54      | CV level |
|     |   | 15.530           | +50      |          |
|     |   | 19.988           | +50      |          |
|     |   | 22.962           | +40      |          |
| 2   | Portlandite   | 17.978           | -50      | -25      |
|     |   | 34.061           | -35      | -23      |
|     |   | 47.045           | CV level | CV level |
|     |   | 50.976           | -100     | -100     |

In the application of ferric chloride solution for CFe additive synthesis the authors relied on the well-known thesis [13], that the ferric salts not just facilitate the pore clogging and improve CR structure, but also increase the deformability and long-time performance of construction composites. And despite the fact that oscillatory spectre shows slower hydration processes in the “cement –  $\text{FeCl}_3$  solution” system, and XPA results of the additive present no phases, different from the one, forming in the “cement-water” system (test sample CV), the introduction of CFe into cement paste provides not only faster settling, but also a significant (23 %) increase in cement composite MFe strength compared to PCR. That may on the one hand stem from the “performance” of ettringite and  $\text{CaCO}_3$  microcrystals, like with CAI instance catalyzing the growth of composite skeletal structure, and, on the other hand, with the “performance” of such gelatinous phases as HCS and dicalcium phosphate, characterized with a high specific surface, facilitating and improving interphase contacts, increasing the density of CR.

#### 4. Conclusions

The research undertaken and the interpretation of the results, provided in the given paper, allow the following conclusions:

1. The application of 1 % ferric and aluminium chloride solutions as gauge liquids leads to the reduction of compression strength of  $\text{MAI}\text{Cl}_3$  and  $\text{MFeCl}_3$  cement rocks. At the 28-day age the value of strength reduction compared to PCR was 18 % and 27 % accordingly.

2. Faster settling and increase in strength of MAI cement composite by 30 % at the introduction of CAI additive, synthesized by means of cement exposure to 1 %  $\text{AlCl}_3$  solution, is provided by means of synergic influence of a number of factors: intensive growth of ettringite crystal seeds – the main reinforcing component of a cement system and tobermorite-like phases of HCS, the reduction of  $\text{Ca}(\text{OH})_2$  amounts in the solid phase of a cement rock, and carbonization effect. A certain impact on the structurization is facilitated by a discovered as a part of an additive the crystalline phase of  $\text{Ca}_8\text{Al}_{12}\text{Fe}_2\text{O}_{12}(\text{CO}_3) \cdot (\text{OH})_2 \cdot 22\text{H}_2\text{O}$ , formed during alumoferrite hydration.

3. Faster settling and strengthening of MFe cement composite by 23 % at the introduction of CFe additive, synthesized by means of cement exposure to 1 % of  $\text{FeCl}_3$  solution, is probably facilitated by the gauging of calcium hydroxide, or may as well be explained by the “performance” of ettringite and  $\text{CaCO}_3$  microcrystals, like in CAI instance catalyzing the growth of composite skeletal structure, and by the “performance” of such gelatinous phases like dicalcium hydrophosphates and HCS, characterized with a high specific surface, facilitating and improving interphase contacts, increasing the density of CR.

The engineered additives intensify structurization and solidify the structure of cement composites, from the early hardening periods, and may be recommended to improve the operational properties of cement systems.



## References

1. Sobolev, K., Shah, S.P. Nanotechnology of concrete: recent developments and future perspectives. American Concrete Institute: SP-254. 2008. 160 p.
2. Li, Z., Wang, H., He, S., et. al. Investigations on the preparation and mechanical properties of the nano-alumina reinforced cement composite. Mater. Lett. 2006. Vol. 60(3). Pp. 356–359.
3. Kuo, W.-Y., Huang, J.-S., Lin, C.-H. Effects of organo-modified montmorillonite on strengths and permeability of cement. Cem. Concr. Res. 2006. Vol. 36(5). Pp. 886–95.
4. Shishkin, A., Shishkina, A., Vatin, N. Low-shrinkage alcohol cement concrete (2014). Applied Mechanics and Materials. No. 633-634, Pp. 917–921.
5. Tarig, A., Yanful, E.K. A review of binders used in cemented paste tailings for underground and surface disposal practices. J. of Environmental Management. 2013. Vol. 131. No. 12. Pp. 138–149.
6. Suzdaltsev, O.V. Dolgovechnyye arkhitekturno-dekorativnyye poroshkovo-aktivirovannyye betony s ispolzovaniyem otkhodov kamnedrobleniya gornyykh porod porod [Long-term performance fair-faced powder-activated concretes with the application of crusher rock run]. Ph.D. Thesis in Engineering Science. Penza, 2015. 237 p. (rus)
7. Larsen, L.O., Naruts, V.V. Self-compacting concrete with limestone powder for transport infrastructure. Magazine of Civil Engineering. 2016. No. 8. Pp. 76–85. doi: 10.5862/MCE.68.8
8. Degirmenci, N., Yilmaz, A. Use of diatomite as partial replacement for Portland cement in cement mortars. Construction and Building Materials. 2009. No. 23. Pp. 284–288.
9. Ibe, Ye.Ye. Hidrotekhnicheskyy beton na kompozitsionnom portlandtsemente s mineralnymi dobavkami, soderzhashchimi vysokoglinozemistyye shlaki [Hydrotechnical concrete on composite portlandcement with mineral additives, containing high-alumina slags]. Ph.D. thesis in Engineering Science. Barnaul, 2016. 152 p. (rus)
10. Shepelenko, T.S., Zubkova, O.A., Subbotina, N.V. et al. Kompozitsionnyye tsementy, soderzhashchiye sakharozu [Composite cements, containing sucrose]. Vestnik TGASU. 2017. No. 5. Pp. 151–158. (rus)
11. Ponomarev, A., Knezević, M., Vatin, N., et. al. Nanosize scale additives mix influence on the properties of the high performance concretes. Journal of Applied Engineering Science. 2014. No. 12(3). Pp. 227–231.
12. Justs, J., Bajare, D., Korjakins, A., et. al. Microstructural investigations of UHPC obtained by pressure application within the first 24 hours of hardening. Construction Science. 2013. No. 8. Pp. 50–57.
13. Ratinov, V.B., Rozenberg, T.I. Dobavki v beton [Concrete additives]. Moskva: Stroyizdat, 1989. 188 p. (rus)
14. Ruzhinskiy, S., Portik, A., Savinykh, A. Vse o penobetone [Complete guide on aerated concrete]. Sankt-Peterburg: OOO «Stroy-beton», 2006. 630 p. (rus)
15. Berdov, G.I., Ilina, L.V. Vzaimodeystviye alyuminatnykh klinkernykh mineralov s vodnymi rastvorami elektrolitov [Reaction of aluminate clinker minerals with aqueous electrolyte solutions]. Izvestiya vuzov. Stroitelstvo. 2012. No. 9. Pp. 13–19. (rus)
16. Berdov, G.I., Ilina, L.V., Rakov, M.A. Povysheniye prochnosti tsementnykh materialov putem vvedeniya dobavok elektrolitov [Increasing cement material strength by means of introducing electrolytic additives]. StroyPROFI. 2014. No. 12. Pp. 1–10. (rus)
17. Leonovich, S.N., Prasol, A.V. Zhelezobeton v usloviyakh khloridnoy korrozii: deformirovaniye i razrusheniye [Reinforced concrete under chloride corrosion:

## Литература

1. Sobolev K., Shah S.P. Nanotechnology of concrete: recent developments and future perspectives // American Concrete Institute: SP-254. 2008. 160 p.
2. Li Z., Wang H., He S., et. al. Investigations on the preparation and mechanical properties of the nano-alumina reinforced cement composite // Mater. Lett. 2006. Vol. 60(3). Pp. 356–359.
3. Kuo W.-Y., Huang J.-S., Lin C.-H. Effects of organo-modified montmorillonite on strengths and permeability of cement // Cem. Concr. Res. 2006. Vol. 36(5). Pp. 886–95.
4. Shishkin A., Shishkina A., Vatin N. Low-shrinkage alcohol cement concrete (2014) // Applied Mechanics and Materials. № 633-634, Pp. 917–921.
5. Tarig A., Yanful E.K. A review of binders used in cemented paste tailings for underground and surface disposal practices // J. of Environmental Management. 2013. Vol. 131. № 12. Pp. 138–149.
6. Суздальцев О.В. Долговечные архитектурно-декоративные порошково-активированные бетоны с использованием отходов камнедробления горных пород: дисс. .... на соиск. учен. степ. к.т.н.: Спец. 05.23.05. Пенза, 2015. 237 с.
7. Ларсен О.А., Наруть В.В. Самоуплотняющийся бетон с карбонатным наполнителем для объектов транспортной инфраструктуры // Инженерно-строительный журнал. 2016. № 8(68). С. 76–85
8. Degirmenci N., Yilmaz A. Use of diatomite as partial replacement for Portland cement in cement mortars // Construction and Building Materials. 2009. № 23. Pp. 284–288.
9. Ибе Е.Е. Гидротехнический бетон на композиционном портландцементе с минеральными добавками, содержащими высокоглиноземистые шлаки: дисс. ... на соиск. учен. степ. к. т. н.: Спец. 05.23.05. Барнаул, 2016. 152 с.
10. Шепеленко Т.С., Зубкова О.А., Субботина Н.В. и др. Композиционные цементы, содержащие сахарозу // Вестник ТГАСУ. 2017. № 5. С. 151–158.
11. Ponomarev A., Knezević M., Vatin N., et. al. Nanosize scale additives mix influence on the properties of the high performance concretes // Journal of Applied Engineering Science. 2014. № 12(3). Pp. 227–231.
12. Justs J., Bajare D., Korjakins A., et. al. Microstructural investigations of UHPC obtained by pressure application within the first 24 hours of hardening // Construction Science. 2013. № 8. Pp. 50–57.
13. Ратинов В.Б., Розенберг Т.И. Добавки в бетон. М.: Стройиздат, 1989. 188 с.
14. Ружинский С., Портик А., Савиных А. Все о пенобетоне. Санкт-Петербург: ООО «Строй-бетон», 2006. 630 с.
15. Бердов Г.И., Ильина Л.В. Взаимодействие алюминатных клинкерных минералов с водными растворами электролитов // Известия вузов. Строительство. 2012. № 9. С. 13–19.
16. Бердов Г.И., Ильина Л.В., Раков М.А. Повышение прочности цементных материалов путем введения добавок электролитов // СтройПРОФИ. 2014. № 12. С. 1–10.
17. Леонович С.Н., Прасол А.В. Железобетон в условиях хлоридной коррозии: деформирование и разрушение // Строительные материалы. 2013. № 5. С. 94–95.
18. Шепеленко Т.С., Саркисов Ю.С., Горленко Н. П., Цветков Н.А., Зубкова О.А. Процессы структурообразования цементных композиций, модифицированных добавками сахарозы // Инженерно-строительный журнал. 2016. № 6(66). С. 3–11.

Шепеленко Т.С., Горленко Н.П., Зубкова О.А. Процессы структурообразования цементных композитов, модифицированных добавками электролитов // Инженерно-строительный журнал. 2018. № 5(81). С. 125–134.

- deformation and destruction]. *Stroitelnyye materialy*. 2013. No. 5. Pp. 94–95. (rus)
18. Shepelenko, T.S., Sarkisov, U.S., Gorlenko, N.P., et al. Structure-forming processes of cement composites, modified by sucrose additions. *Magazine of Civil Engineering*. 2016. No. 6. Pp. 3–11.
  19. Sokolova, T.A., Tolpeshta, I.I., Trofimov, S.Ya. Pochvennaya kislotnost. Kislотно-osnovnaya bufernost pochv. Soyedineniya alyuminiya v tverdoy faze pochvy i v pochvennom rastvorereastvore [Soil acidity. Acid-base buffer characteristics of soils. Aluminium compounds in soil solid phase and solutions]. Tula: Grifi K, 2012. 124 p. (rus)
  20. Mikhaylov, V.I. Polucheniye i fiziko-khimicheskiye svoystva materialov na osnove nanodispersnykh oksidov alyuminiya i zheleza (III) [Production and physical and chemical properties of materials based on nanodispersed aluminium and ferric (III) oxides]. Ph.D. thesis in Engineering Science. Syktyvkar, 2016, 129 p. (rus)
  21. Zhy, M., Frandsen, A.F., Wallace, A.F., et al. Precipitation Pathways for Ferrihydrite Formation in Acidic Solutions. *Geochimica et Cosmochimica Acta*. 2016. Vol. 172. Pp. 244–264.
  22. Starov, V.M. Nanoscience: Colloidal and Interfacial Aspects. London, New York: CRC Press Taylor & Francis Group. 2010. 1187 p.
  23. Svatovskaya, L.B., Solovyev, V.Ya., Stepanova, I.V., et al. Vysokoprochnyy beton [High-strength concrete]. Patent Russia No. 2323910, 2008. (rus)
  24. Taylor, H.F.W. Cement Chemistry. London: Academic Press, 1964. 560 p.
  25. Samchenko, S.V. Formirovaniye i genezis struktury tsementnogo kamnya: monografiya. M.: MGSU, Ay Pi Er Media, EBS ASV, 2016. 248 p. (rus)
  26. Babushkin, V.I., Matveyev, G.M., Mchedlov-Petrosyan, O.P. Termodinamika silikatov [Silicate thermodynamics]. Moskva: Stroyizdat, 1986. 351 p. (rus)
  27. Trofimov, B.Ya., Mushtakov, M.I. Korroziya betona: monografiya [Concrete corrosion: monograph]. Chelyabinsk: Izd-vo YuUrGU, 2008. 310 p.
  28. Shpynova, L.G., Chikh, V.I., Sanitskiy, M.A., et al. Fiziko-khimicheskiye osnovy formirovaniya struktury tsementnogo kamnya [Physical and chemical foundations of cement rock structurization]. Lvov: Vishcha shkola, 1981. 160 p. (rus)
  29. Pashchenko, A.A. Teoriya tsementa [Cement theory]. Kiyev: Budivel'nik, 1991. 196 p. (rus)
  30. Malova, Ye.Yu. Kompozitsionnyye portlandsementy s karbonatsoderzhashchimi dobavkami i betony na ikh osnove [Composite portlandcements with carbonate-containing additives and concretes, based on them]. Ph.D. thesis in Engineering Science. Barnaul, 2015. 161 p. (rus)
  31. Monkman, S., Makdonald, M., Khuton, D. Ispolzovaniye uglekislogo gaza v kachestve dobavki-uskoritelya [Application of CO<sub>2</sub> as a speed-booster additive]. Tsement i yego primeneniye. 2017. No. 1. Pp. 82–89. (rus)
  19. Соколова Т.А., Толпешта И.И., Трофимов С.Я. Почвенная кислотность. Кислотно-основная буферность почв. Соединения алюминия в твердой фазе почвы и в почвенном растворе. Тула: Грифи К, 2012. 124 с.
  20. Михайлов В.И. Получение и физико-химические свойства материалов на основе нанодисперсных оксидов алюминия и железа (III): дисс. ... на соиск. учен. степ. к.х.н.: Спец. 02.00.04 Сыктывкар, 2016, 129 с.
  21. Zhy M., Frandsen A.F., Wallace A.F., et al. Precipitation Pathways for Ferrihydrite Formation in Acidic Solutions // *Geochimica et Cosmochimica Acta*. 2016. Vol. 172. Pp. 244–264.
  22. Starov V.M. Nanoscience: Colloidal and Interfacial Aspects // London, New York: CRC Press Taylor & Francis Group. 2010. 1187 p.
  23. Патент 2323910 С1 Российская Федерация, МПК С04В 28/04, С04В 22/06, С04В 11/20. Высокопрочный бетон / Л.Б. Сватовская, В.Я. Соловьева, И.В. Степанова и др., 2008.
  24. Taylor H.F.W. Cement Chemistry. London: Academic Press, 1964. 560 p.
  25. Самченко С.В. Формирование и генезис структуры цементного камня: монография. М.: МГСУ, Ай Пи Эр Медиа, ЭБС АСВ, 2016. 248 с.
  26. Бабушкин В.И., Матвеев Г.М., Мchedlov-Петросян О.П. Термодинамика силикатов. М.: Стройиздат, 1986. 351 с.
  27. Трофимов Б.Я., Муштаков М.И. Коррозия бетона: монография. Челябинск: Изд-во ЮУрГУ, 2008. 310 с.
  28. Шпынова Л.Г., Чих В.И., Саницкий М.А. и др. Физико-химические основы формирования структуры цементного камня. Львов: Вища школа, 1981. 160 с.
  29. Теория цемента / под ред. А.А. Пашенко. Киев: Будівельник, 1991. 196 с.
  30. Малова Е.Ю. Композиционные портландцементы с карбонатсодержащими добавками и бетоны на их основе: дисс. ... на соиск. учен. степ. к. т. н. Спец.: 05.17.11. Барнаул, 2015. 161 с.
  31. Монкман С., Макдоналд М., Хутон Д. Использование углекислого газа в качестве добавки-ускорителя // Цемент и его применение. 2017. № 1. С. 82–89.

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