Development and Research of Properties Cement Concrete
Hardening Accelerator Additive Based on a Mixture of
Inorganic Fluorine-Containing Salts

V Eu Roumyantseva¹, I N Goglev², S A Loginova³, P S Truntov⁴, A A Burkov⁵

¹Ivanovo State Polytechnic University, department of nanotechnologies, physics and chemistry, Sheremetevsky av., 21, Ivanovo, 153000, Russian Federation
²Ivanovo State Polytechnic University, department of nanotechnologies, physics and chemistry, Sheremetevsky av., 21, Ivanovo, 153000, Russian Federation
³Ivanovo State Polytechnic University, department of nanotechnologies, physics and chemistry, Sheremetevsky av., 21, Ivanovo, 153000, Russian Federation
⁴Moscow State University of Civil Engineering (National Research University), department of housing and communal services, Yaroslavl highway, 26, Moscow, 129337, Russian Federation
⁵Moscow State University of Civil Engineering (National Research University), department of construction of thermal and nuclear energy facilities, Yaroslavl highway, 26, Moscow, 129337, Russian Federation

E-mail: varrym@gmail.com, azidplumbum00@mail.ru, sl79066171227@yandex.ru, pavel_truntov@mail.ru, artemburkov@gmail.com

Abstract. the article describes the basic salts and their mixtures used to accelerate the hardening process of cement concretes in the practice of modern construction. Development and main characteristics of the additive accelerating process of hardening of cement concrete are presented. This additive is based on a mixture of non-organic fluorinated salts. The composition of the additive allows to accelerate the process of hardening of cement stone, due to the formation of insoluble and dense compounds. A number of experiments were carried out to determine the optimal amount of fluoride salts in the additive. The results of the research showed a low consumption of additive per 1 m³ of heavy concrete. Advantages and disadvantages of the additive allow us to recommend its use to accelerate the hardening of concrete in a wet environment. The article provides a detailed description of the test methods. The tests were carried out using certified and verified measuring instruments taking into account the strength characteristics of the materials. As a result, the dependence of the concrete hardening rate on the amount of additive used was revealed. The article also discusses some proposals for the practical use of additive in the production technology of concrete and reinforced concrete. According to the results of destructive and non-destructive testing, an increase in the strength of concrete by >30% compared to conventional concrete.

1. Introduction
Cement concretes (concretes on cement binders) are most often used in the production of concrete works. When working outdoors, it is not always possible to observe optimal hardening conditions...
(climatic conditions, humidity), which is why the design strength of concrete can sometimes not be typed. Additives-accelerators of hardening are used for this purpose [1].

At present, the cement concrete hardening accelerators (CCHA) widely used in the construction of buildings and structures (especially buildings with monolithic reinforced concrete frame) and the production of concrete and reinforced concrete works, including in the construction industry. Such application of CCHA is explained by their unique properties, the main of which is the accelerated set of strength of cement stone in the shortest possible time [1, 2].

2. Relevance

Today, there are a large numbers and types of CCHA with different cost and time of the accelerated curing. Most of them are different inorganic and organic salts or mixtures thereof in different ratios. But, some salts in the composition of complex mixture hardening accelerators have aggressiveness towards concrete cement stone or steel reinforcement, as a result of which there are negative effects on the hardening concrete [3, 4].

The main disadvantages of various hardening accelerators are high hygroscopicity (the ability to absorb excess moisture, which leads to cracking and shrinkage of concrete, especially in dry conditions) and the ability to salting on the surface and in the depth of the pores of concrete (Figure 1).

Figure 1 shows destruction process of fine-grained concrete due to excessive salinity in the pores.

In addition to these, the most important disadvantages of CCHA include increased consumption per 1 m3 of concrete (especially for expensive mixtures) and the ability to cause corrosion of reinforcement above a certain concentration (for chlorine-containing mixtures) [4, 5].

![Figure 1. Destruction of fine-grained concrete due to excessive salinity in the pores.](image)

3. Problem statement

The process of accelerated curing of cement stone is associated with the ability of the majority of accelerators to react with the main component of hardening concrete – «free» calcium hydroxide, causing its binding to a solid and insoluble products or cause its accelerated diffusion from the pores. An illustration of this process is the use of hydrofluoric acid solutions as hardening accelerators. Such physical and chemical processes allow to achieve the highest speed and strength of cement stone [6].

It should be noted that often complex additive-the hardening accelerator are present components, causing the occurrence of adverse reactions, leading to negative effects: shrinkage and cracking of concrete, the higher salting-out and pore formation, reduction in the pH environment of hardening concrete, increase the ability to carbonization of concrete, the increase of aggressiveness for steel reinforcement, etc. [4-6].

On the basis of these theoretical concepts were formed purposes and objectives of the research.
The purpose of the research – the development and testing of CCHA, causing the high strength of cement stone (more than 15÷20% of the original) and having the fewest of these flaws and negative effects.

The objectives of the research are to theoretically and practically justify the effectiveness of the obtained additive by testing the properties, its consumption per 1 m3 of concrete and comparing the positive and negative effects from application of the additive.

4. Results of experimental studies

According to previous studies, it was revealed that the main component of the concrete gaining strength is «free» calcium hydroxide Ca(OH)2, which reaction with the components of CCHA will determine the process and speed of hardening [7, 8].

The basis of the proposed additive is the principle of linking hexafluorosilicate and tetrafluoroborate-ions with the «free» calcium hydroxide Ca(OH)2 of concrete which leads to the formation of low-soluble tetrafluoroborate and hexafluorosilicate salts of calcium (Ca(BF4)2 and CaSiF6) in two direct reactions (1) and (2):

\[
\begin{align*}
\text{Ca(OH)}_2 + 2\text{NH}_4\text{BF}_4 & \rightarrow 2\text{NH}_4\text{OH} + \text{Ca(BF}_4\text{)}_2 \downarrow & (1) \\
2\text{NH}_4\text{OH} & \rightarrow 2\text{NH}_3↑ + 2\text{H}_2\text{O} \\
\text{Ca(OH)}_2 + (\text{NH}_4)_2\text{SiF}_6 & \rightarrow 2\text{NH}_4\text{OH} + \text{CaSiF}_6 \downarrow & (2) \\
2\text{NH}_4\text{OH} & \rightarrow 2\text{NH}_3↑ + 2\text{H}_2\text{O}
\end{align*}
\]

In addition to these reactions, the components of the additive are able to increase the solubility of cement grains in water-salt solution, thereby increasing the saturation limit of this solution with cement hydration products. The resulting calcium tetrafluoroborate and hexafluorosilicate are finely dispersed (nano-dispersed) state which promotes rapid coalescing between grains of cement and consequently, increased rate of hardening.

During the preparation of the article various sources of Russian and foreign authors on the subject of hardening accelerators were analyzed [9-15]. The most used additives-hardening accelerators are presented in table 1.

Most of these substances are inexpensive reagents, which justifies high economic efficiency [16-21].

The following devices and equipment were used during experimental researches (tests of control samples) and their manufacture, as well as during weighing and preparation of a mixture of initial reagents: the device is nondestructive shock-pulse ONYX-2.5 by brand Interpribor (certificate of the State register of measuring instruments in the Russian Federation №30252-10, serial number №599, the verification certificate from 28.04.2019, Figure 2a), a testing press model Matest C055N (certificate of the State register of measuring instruments in the Russian Federation № 65079-16, maximum load 2000 kN, the verification certificate from 16.05.2019, Figure 2b), Canon 1200D digital SLR camera, hand electric vibrator model Zitrek Z-35-1,5, electronic scales Mucheng 0,1-500 (weighing accuracy 0.1 to 500g).

Figure 2 (a, b) shows the device is nondestructive shock-pulse test ONYX-2.5 and testing press model Matest C055N.

Table 1. The most used reagents as CCHA in Russian Federation and CIS.

| Ammonium salts | Carbamide CO(NH₂)₂ |
| Phosphates     | Trisodium phosphate Na₃PO₄ |
|                | Tricalcium phosphate Ca₃(PO₄)₂ |
| Silicates      | Solutions of liquid glass (nNa₂SiO₃+ mH₂O or nNa₂OxSiO₂+ mH₂O) |
|                | Sodium, potassium and calcium nitrates NaNO₃, KNO₃, Ca(NO₃)₂ |
| Nitrates and nitrites | Sodium and calcium nitrates NaNO₂, Ca(NO₂)₂ |
|                | Ammonium nitrate (in low concentrations), NH₄NO₃ |
| Carbonates       | Potassium carbonate $K_2CO_3$  |
|-----------------|---------------------------------|
|                 | Sodium carbonate $Na_2CO_3$     |
|                 | Magnesium carbonate (in limited quantities) $MgCO_3$ |
| Sulfur-containing salts | Sodium sulphate $Na_2SO_4$ |
|                 | A mixture of thiosulfate and sodium rhodanide $Na_2S_2O_4 + NaCNS$ |
|                 | Gypsum $CaSO_4 \cdot 2H_2O$    |
|                 | Aluminum chloride $AlCl_3$     |
|                 | Ferric chloride $FeCl_3$       |
|                 | Barium chloride $BaCl_2$       |
| Chlorides       | Calcium chloride $CaCl_2$      |
|                 | Magnesium chloride $MgCl_2$    |
|                 | Sodium chloride $NaCl$         |
|                 | Hydrochloric acid $HCl$        |

Processing of the obtained numerical data and plotting were carried out in the software package Microsoft Excel 2010. Non-destructive (indirect method) and destructive testing (direct method) methods were used to determine the strength of control samples [22-24].

As a nondestructive testing method was used the shock-pulse method according to GOST 22690-2015 «Concretes. Determination of strength by mechanical methods of non-destructive testing». The essence of the method lies in the relationship between the strength of concrete and the impact energy (and its changes) at the time of impact of the striker (containing a built-in sensor) with the surface of concrete [22, 23].

As destructive testing method has been used to test concrete strength of control samples according to GOST 10180-2012 «Concretes. Methods for determining the strength by control samples». The essence of the method consists in the destruction of the concrete sample on the test press, thanks to this data will be obtained on the actual destructive load for concrete, which determines the compressive strength of concrete [24]. The procedure for the research was divided into theoretical and practical parts.

Figure 3 describes general procedure of the research.

The theoretical part of the research included selection of the initial reagents based on the theoretical knowledge and notions, the calculation of the optimal ratio of these reagents and the maintenance of required characteristics: the most consumption as low as possible, lower the aggressiveness of the mixture and of each component in relation to the concrete and reinforcement as well as assessment of the negative impact of other characteristics (water absorption, changing the pH of the medium). After successful selection of a combination of initial reagents, practical researches were carried out. According to the results of theoretical studies, a table of the optimal combination of the additive components (table 2) was compiled, which was refined during the practical part.
Figure 2. a) The device is nondestructive shock-pulse ONYX-2,5; b) Test press model Matest C055N.

Table 2. The results of the research of the optimal range of components of additive.

| Component Description                                           | Range  |
|----------------------------------------------------------------|--------|
| Distilled water, according to GOST 6709-72                     | 87,0÷90,0 |
| **Core components**                                             |        |
| Ammonium tetrafluoroborate NH$_4$BF$_4$ (c.p.* quality)         | 3,50÷2,50 |
| Ammonium hexafluorosilicate (NH$_4$)$_2$SiF$_6$ (c.p.* quality) | 7,50÷6,50 |
| **Supporting components**                                       |        |
| Sodium fluoride (NaF) (c.p.* quality)                           | 2,00÷1,00 |

* c.p.* - chemically pure

The practical part included testing the effectiveness of the additive. For that purpose, the resulting composition in the form of a solution was added to the mixing water in the manufacture of control samples in one batch while mixing the concrete mixture. The concrete mixture was compacted during mixing with a manual electric vibrator.
Figure 3. General procedure of the research.

For nondestructive testing, samples of $3\times3\times3$ cm (Figure 4) were made from cement dough of normal consistency (water-cement ratio $= 0.3$).

Figure 4 shows general view of test samples for nondestructive testing.

The cement paste was prepared during time the mixing of cement grade М500D0 with a solution of the additive, after which the samples were placed in a moist curing chamber at atmospheric pressure (humidity $99\%-100\%$). The total number of control samples (samples without additives and samples with additives) was 100 PCs ($50 + 50$ PCs). After a certain period of hardening, the compression strength of the samples was determined by the shock-pulse method. The number of strokes on each face of the sample was not more than 1. The average value of compressive strength was determined then.

For destructive testing samples of $10\times10\times10$ cm (Figure 5) were made from cement dough of normal consistency (water-cement ratio $= 0.3$) made by mixing cement grade М500D0 with a solution of the additive.

Figure 5 shows general view of test sample for destructive testing.

The hardening conditions of the samples were similar to those of nondestructive testing. The total number of control samples and samples with additives was 50 PCs ($25 + 25$ PCs). After a certain period of hardening the samples were determined by the ultimate compressive strength by destruction on a certified testing press (Figure 6).

Figure 6 shows the process of destruction samples during tests on the press.
The obtained data were averaged and entered into the tables of results, on the basis of which the graphs of the kinetics of hardening of cement stone were constructed.

5. Conclusion
For the analysis and synthesis of the actual values of concrete strength with devices ONYX-2.5 and certified press test Matest C055N used software package Microsoft Excel (Figure 7).

Figure 7 illustrated the process of plotting and summarizing data in tables at software package Microsoft Excel.

The measurement accuracy was ensured by constant averaging of the actual compressive strength values for each sample series. The final measurement error between the values of nondestructive and destructive testing was 4.11%.
Figure 7. Generalization and processing of the data, plotting in the software package Microsoft Excel.

The data of concrete strength measurements by nondestructive testing are included in table 3. According to the results of table 3, a graph of the comparative kinetics of hardening of concrete samples with the proposed additive and a conventional concrete sample in the period from 3 to 28 days (Figure 8) is reduced.

Figure 8 shows the comparative kinetics of hardening of concrete samples. Data on determination of concrete compressive strength by destructive control are included in table 4. According to the results of data analysis table 4 a graph of the comparative kinetics of hardening of concrete samples in the period from 3 to 28 days (Figure 9) is reduced.

Figure 9 illustrated the comparative kinetics of hardening of concrete samples according to destructive testing.

The test results show that the use of additive most intensifies the strength set of cement stone in the early periods of hardening (up to 14 days) and at a later date (up to 28 days). The initial lower value (3 days) according to nondestructive testing compared to destructive testing is due to the significantly lower content of the binder in the sample.

Table 3. The results of non-destructive control by shock-pulse device ONYX-2.5.

| №  | Test samples (samples is) | Test method                          | Average compressive strength of cement stone, MPa |
|----|--------------------------|--------------------------------------|---------------------------------------------------|
|    |                          |                                      | 3 days    | 7 days    | 14 days   | 21 days   | 28 days   |
| 1  | Without additives        | Non-destructive testing of shock-pulse method according to GOST 22690-18,72 | 4          | 5          | 6          | 7          | 8          |
Non-destructive testing of shock-pulse method according to GOST 22690-2015.

Determination of the final strength gain was made by the equation (3):

$$X = \left( \frac{|R_{\text{concrete1}} - R_{\text{concrete2}}|}{R_{\text{concrete1}}} \right) \cdot 100\%,$$

where: $X$ – the resulting strength gain from the use of additive; $R_{\text{concrete1}}$ – actual maximum compressive strength of concrete samples without CCHA at the last date of the calculation period; $R_{\text{concrete2}}$ – actual maximum compressive strength of concrete samples with CCHA at the last date of the calculation period.

### Table 4. Results of destructive testing.

| №   | Test samples                          | Test method                                      | Average compressive strength of cement stone, MPa |
|-----|---------------------------------------|--------------------------------------------------|--------------------------------------------------|
|     |                                       |                                                  | 3 days   | 7 days   | 14 days  | 21 days  | 28 days  |
| 1   | Without additives (samples is 10x10x10 cell cm) | Destructive testing (testing of control samples) according to GOST 10180-2012. | 34,45    | 36,99    | 40,07    | 43,86    | 45,38    |
| 2   | With addition (samples is 10x10x10 cell cm) | Destructive testing (testing of control samples) according to GOST 10180-2012. | 40,16    | 45,79    | 49,62    | 54,27    | 62,24    |
Figure 9. Kinetics of cement stone hardening according to destructive testing.

According to the value of the comparative kinetics of hardening of cement stone in the period from 3 to 28 days the increase in the strength of concrete in the case of the proposed additive was calculated by equation 3 and averaged:

1) for the non-destructive shock-pulse testing – 38.57%;
2) for the destructive testing – 37.15%.

According to the obtained data of cement stone strength increase, the additive to concrete is effective, since the average concrete strength increase was more than 30% by the results of direct and indirect methods tests.

Fuel additive for 1m3 of concrete was determined experimentally and is approximately 0.01±0.011 by weight of concrete. There is no need to calculate the technical and economic indicators of the additive produced, since such indicators of consumption are small. By comparison, the consumption of sodium chloride (often used as an additive CCHA) is up to 4% (0.04) by weight [25].

In the course of the research all the purposes and objectives were fulfilled, so that the results on the optimal ratio of the components of the additive and the kinetics of hardening of cement stone were obtained. The increase in the strength of concrete from the application of the developed CCHA was more than 30% according to the results by destructive and non-destructive testing. Fuel additive for 1m3 of concrete is approximately 0.01±0.011 by weight of concrete.

The obtained theoretical and experimental data about the development of an additive-accelerator hardening of cement concretes based on a mixture of fluoroborate and fluorosilicate salts allows to conclude that its high efficiency. High efficiency of the additive and low consumption determine the prospects of its implementation, release and application.

References
[1] Nikulina U A 2017 On the possibility of application of concrete hardening accelerators to reduce the time of construction of monolithic high-rise buildings Materials of international science-technical conference of young scientists BSTU 1191-1196
[2] Dmitrienko A E, Khachaturian A P and Machinin B V 2012 Evaluation of the effectiveness of organic and mineral additives in fine-grained concrete Scientific, technical and economic cooperation of Asia-Pacific countries in the XXI century 289-295
[3] Izotov V S and Ibragimov R A 2010 Influence of additives-accelerators of hardening on properties of heavy concretea Building materials 3 35-37
[4] Kozodaev S P 2013 Chemical admixtures accelerators of hardening cement systems problems and nearest perspectives of applications Scientific Bulletin of Voronezh state University of architecture and construction 6 67-70

[5] Roumyantseva V Eu and Goglev I N 2016 Features of concrete and reinforced concrete corrosion, complicated by the influence of chlorides and carbon dioxide Materials of the all-Russian scientific and technical conference dedicated to the memory of honored scientist of the Russian Federation, academician of RAASN, doctor of technical sciences, professor Solomatov Vasily Ilyich 106-111

[6] Roumyantseva V Eu, Goglev I N, Loginova S A and Morokhov K V 2018 Investigation of the influence of fluoride enviroments on the corrosion properties of cement concretes Materials of I scientific and practical forum "SMARTBUILD", the 100th anniversary of construction education in the Ivanovo region and the creation of the faculty of civil engineering Ivanovo-Voznesensky Polytechnic Institute 112-117

[7] Serdyukova A A and Rakhimbaev I Sh 2013 About the mechanism of action accelerators of setting and hardening of cement matrix in concrete Bulletin of Belgorod state technological University V. G. Shukhov 2 26-28

[8] Adamtsevich A O and Pustovgar A P 2015 Features of influence of modifying additives on kinetics of hardening of cement systems Dry building mixture 4 26-29

[9] Sinotova M V 2017 Modern additives-hardening accelerators concrete Collection of reports of scientific and technical conference on the results of research works of students of the Moscow State University of Civil Engineering 993-995

[10] Usov B A and Okolnikova G E 2015 Chemical additives in precast concrete technology Ecology and concrete technology 4 7-14

[11] Sounthararajan V M and Sivakumar A 2013 Effect of calcium nitrate on the pozzolanic properties of high early strength concrete reseach J. Appl. Sci. Eng. Technol vol 6 13 2502–2508

[12] Cheung J, Jeknavorian A, Roberts L and Silva D 2011 Impact of admixtures on the hydration kinetics of Portland cement Cem. Concr. Res. vol 41 12 1289–1309

[13] Galeev A F, Kashapov R R, Morozov N M and Krasinnikova N M 2014 Complex concrete hardening accelerator Materials jubilee international scientific-practical conference dedicated to the 60th anniversary of Belgorod state technological University them. V. G. Shukhov XXI scientific readings 102-105

[14] Meshkova K O 2017 Investigation of the effect of calcium nitrate on the properties of cement Business magazine Neftegaz.RU 2 50-53

[15] Svidersky V A, Tokarchuk V V, Fleischer A U and Trus I N 2016 Accelerators setting cement systems based on nitrogen-containing organic compounds Knowledge 4-1 (33) 145-149

[16] Adamtsevich A O, Pustovgar A P, Eremin A V and Pashkevich S A 2013 Investigation of the effect of calcium formate on the cement hydration process taking into account the phase composition and temperature regime of hardening Building materials 7 59-61

[17] Khuzin A F and Ibragimov R A 2015 Physical and mechanical properties of high-strength concrete modified by complex additive News of Kazan state University of architecture and construction 4(34) 317-321

[18] Pshenichniy G N, Arutyunov E A and Charikov G U 2017 Application of calcium chloride in concrete and reinforced concrete technology Collection of articles of the International scientific and practical conference Kuban State Technological University 193-198

[19] Sharanova A V, Dmitrieva M A, Lenkova D A, Panfilova A D, Belyauskas E R and Babich P D 2017 The study of the kinetics of shear strength of fine-grained concrete accelerated curing systems The third interdisciplinary youth scientific forum with international participation "New materials" 383-385
[20] Semenova O O, Afanasiev A I, Akulova M V and Polyakov V S 2015 Analysis of the effect of complex additives accelerating-plasticizing action on the strength properties and structure of heavy concrete *The information environment of the University* 1(22) 159-164

[21] Akulova M V and Seliverstova O V 2016 Influence of additives-regulators of structure formation on durability of heavy concrete *Construction and reconstruction* 1(63) 73-77

[22] Ulybin A V, Fedotov S D and Tarasova D S 2012 Determination of concrete strength in the inspection of buildings and structures *The world of construction and real estate* 45 2-5

[23] Nesvetaev G V, Kolleganov A V and Kolleganov N A 2017 Features non-destructive control of concrete strength the exploited concrete structures *Online journal "SCIENCE OF SCIENCE»* 2 1-14

[24] Konoplev S N 2013 On the question about method of control and evaluation of the strength of concrete monolithic structures *Concrete technologies* 7(84) 34-35

[25] Kalinovskaya N N and Kotov D S 2019 The chlorides in the additives and concrete *Concrete technologies* 3-4(152-153) 11-14