



RESEARCH ARTICLE

Study of the Properties of a Cement Concrete Hardening Accelerator Additive with a Mechanism of Action at the Nano-Size Level

Svetlana Loginova^{1*}, Maxim Tanichev^{1,2}, Ilya Goglev²¹Yaroslavl State Technical University, Yaroslavl, Russia²Ivanovo State Polytechnic University, Ivanovo, Russia

ARTICLE INFO	ABSTRACT
Received: Oct 14, 2024	This article discusses the main types of salts and their combinations that are used to accelerate the hardening of cement concrete in construction. It also describes in detail the development and key characteristics of a potential nano-additive that significantly accelerates the hardening of cement concrete. The composition of this additive promotes rapid hardening of cement stone, forming insoluble and dense bonds. Many experiments were conducted to determine the optimal level of fluoride salts in the additive. The study revealed low consumption of the additive per 1 m ³ of heavy concrete. The pros and cons of the additive allow us to recommend its use to accelerate the hardening of concrete in high humidity conditions. The article describes testing methods that were carried out using certified and calibrated measuring instruments, taking into account the strength of the materials used. The rate of concrete hardening was associated with the amount of additive, which is also set out in the article. Some recommendations for the practical use of the additive in concrete and reinforced concrete production are discussed. The results of destructive and non-destructive testing show a significant increase in the strength of concrete compared to conventional compositions.
Accepted: Dec 11, 2024	
Keywords	
Cement Concrete	
Mechanism	
Nano-Size Level	
*Corresponding Author:	
loginovasa@ystu.ru	

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 (Dmitrienko et al., 2012).

At present, the cement concrete hardening accelerators 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 cement concrete hardening accelerators is explained by their unique properties, the main of which is the accelerated set of strength of cement stone in the shortest possible time (Dmitrienko et al., 2012; Nikulina, 2017)

Today, there are a large numbers and types of cement concrete hardening accelerators 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 (Roumyantseva et al., 2018; Kulikova et al., 2021)

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 salt on the surface and in the depth of the pores of concrete.

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 nano additives 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) (Kulikova et al., 2021; Kozodaev, 2013)

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 (Roumyantseva and Goglev, 2016).

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. (Kulikova et al., 2021; Kozodaev, 2013; Roumyantseva and Goglev, 2016; Uaissova and Zharlykassov, 2024).

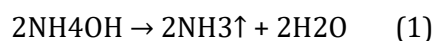
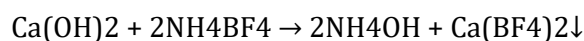
On the basis of these theoretical concepts were formed purposes and objectives of the research.

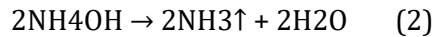
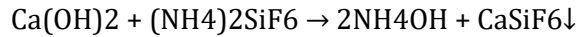
The purpose of the research – the development and testing of nano additives, causing the high strength of cement stone (more than 15÷20% of the original) and having the fewest of these flaws and negative effects.

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.

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 additive will determine the process and speed of hardening (Serdyukova and Rakhimbaev, 2013; Adamtsevich and Pustovgar, 2015; Yerbayev et al., 2023).

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):





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.

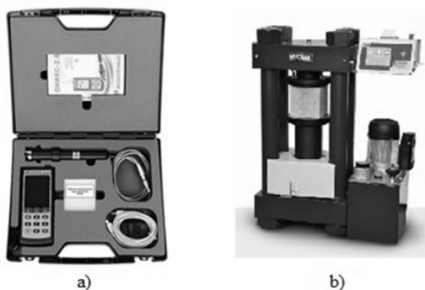
During the preparation of the article various sources of Russian and foreign authors on the subject of hardening accelerators were analyzed (Sinotova, 2017; Usov and Okolnikova, 2015; Sounthararajan and Sivakumar, 2013; Cheung et al., 2011; Adamtsevich et al., 2013; Galeev et al., 2014; Meshkova, 2017). The most used additives-hardening accelerators are presented in table 1.

Most of these substances are inexpensive reagents, which justifies high economic efficiency (Svidersky et al., 2016; Pshenichniy et al., 2017; Khuzin and Ibragimov, 2015; Sharanova et al., 2017; Loginova, 2022; Akulova and Seliverstova, 2016).

1 MATERIALS AND METHODS

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 1,a), 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 1,b), 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 1 (a, b) shows the device is nondestructive shock-pulse test ONYX-2.5 and testing press model Matest C055N.



**Figure 1: a) The device is nondestructive shock-pulse ONYX-2,5;
b) Test press model Matest C055N.**

The most used reagents as how supplements accelerators in Russian Federation and CIS (Svidersky et al., 2016; Pshenichniy et al., 2017; Khuzin and Ibragimov, 2015; Sharanova et al., 2017; Loginova, 2022):

- Ammonium salts - Carbamide $\text{CO}(\text{NH}_2)_2$;

- Phosphates - Trisodium phosphate Na_3PO_4 , Tricalcium phosphate $\text{Ca}_3(\text{PO}_4)_2$;
- Silicates - Solutions of liquid glass ($n\text{Na}_2\text{SiO}_3 + m\text{H}_2\text{O}$ or $n\text{Na}_2\text{OxSiO}_2 + m\text{H}_2\text{O}$);
- Nitrates and nitrites - Sodium, potassium and calcium nitrates NaNO_3 , KNO_3 , $\text{Ca}(\text{NO}_3)_2$; Sodium and calcium nitrites NaNO_2 , $\text{Ca}(\text{NO}_2)_2$; Ammonium nitrate (in low concentrations), NH_4NO_3 ;
- Carbonates - Potassium carbonate K_2CO_3 , Sodium carbonate Na_2CO_3 , Magnesium carbonate (in limited quantities) MgCO_3 .

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) (Ulybin et al., 2012; Konoplev, 2013; Semenova et al., 2015).

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 (Ulybin et al., 2012; Konoplev, 2013)

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 (Semenova et al., 2015). The procedure for the research was divided into theoretical and practical parts. Figure 2 describes general procedure of the research.

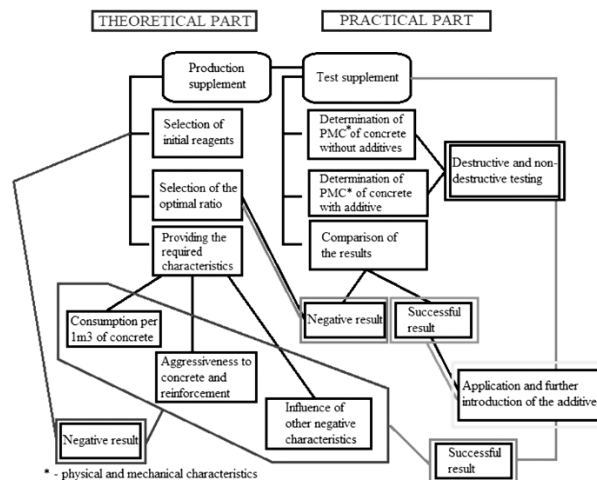


Figure 2: General procedure of the research

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 was compiled, which was refined during the practical part: Distilled water - 87,0÷90,0; Ammonium tetrafluoroborate NH_4BF_4 - 3,50÷2,50; Ammonium hexafluorosilicate $(\text{NH}_4)_2\text{SiF}_6$ - 7,50÷6,50; Sodium fluoride (NaF) - 2,00÷1,00.

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.

For nondestructive testing, samples of 3×3×3cm 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 in during time the mixing of cement grade M500D0 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 10×10×10 cm were made from cement dough of normal consistency (water-cement ratio=0,3) made by mixing cement grade M500D0 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 3).



Figure 3 shows the process of destruction samples during tests on the press.

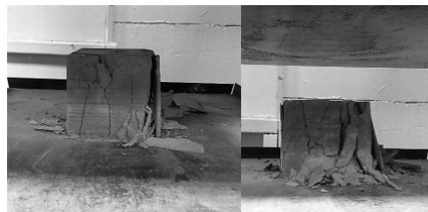


Figure 3: Destruction of samples during tests on the press

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.

2 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.

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%.

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 4) is reduced.

A graph of the comparative kinetics of hardening of concrete samples in the period from 3 to 28 days (Figure 5) is reduced.

Figure 5 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.

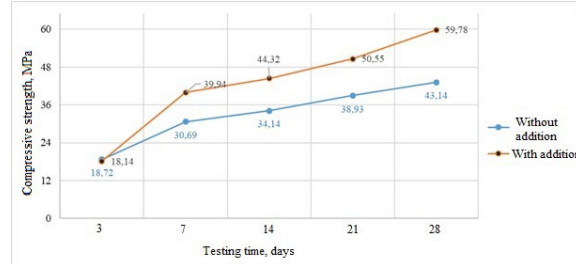


Figure 4: Kinetics of hardening of cement stone according to non-destructive shock-pulse control.

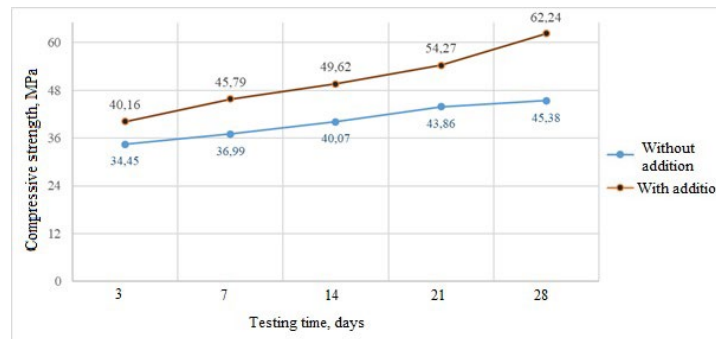


Figure 5: Kinetics of cement stone hardening according to destructive testing

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 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 (Kalinovskaya and Kotov, 2019).

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. The study was carried out using federal budget funds.

REFERENCES

- Adamtsevich A.O., Pustovgar A.P., 2015. Features of influence of modifying additives on kinetics of hardening of cement systems. *Dry Building Mixture*, (4): 26–29.
- Adamtsevich A.O., Pustovgar A.P., Eremin A.V., 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.
- Akulova M.V., Seliverstova O.V., 2016. Influence of additives-regulators of structure formation on durability of heavy concrete. *Construction and Reconstruction*, 1(63): 73–77.
- Cheung J., Jeknavorian A., Roberts L., Silva D., 2011. Impact of admixtures on the hydration kinetics of Portland cement. *Cem. Concr. Res.*, 41(12): 1289–1309.
- Dmitrienko A.E., Khachaturian A.P., 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.
- Galeev A.F., Kashapov R.R., Morozov N.M., Krasinnikova N.M., 2014. Complex concrete hardening accelerator. *Materials of Jubilee International Scientific-Practical Conference Dedicated to the 60th Anniversary of Belgorod State Technological University Them. V.G. Shukhov (XXI Scientific Readings)*: 102–105.
- Kalinovskaya N.N., Kotov D.S., 2019. The chlorides in the additives and concrete. *Concrete Technologies*, 3-4(152-153): 11–14.

- Khuzin A.F., 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.
- 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.
- 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.
- Kulikova A.A., Demyanenko O.V., Nichinsky A.N., 2021. Development of complex modifying additives for heavy concrete. *The Scientific Heritage*: 36–40.
- Loginova S.A., 2022. Study of biostability of concretes. *Smart Composite in Construction*, 3(2): 45–53.
- Meshkova K.O., 2017. Investigation of the effect of calcium nitrate on the properties of cement. *Business Magazine Neftegaz.RU*, (2): 50–53.
- 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.
- Pshenichniy G.N., Arutyunov E.A., 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.
- Roumyantseva V.Eu., 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.
- Roumyantseva V.Eu., Goglev I.N., Loginova S.A., Morokhov K.V., 2018. Investigation of the influence of fluoride environments 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.
- Semenova O.O., Afanasiev A.I., Akulova M.V., 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.
- Serdyukova A.A., 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.
- Sharanova A.V., Dmitrieva M.A., Lenkova D.A., Panfilova A.D., Belyauskas E.R., 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.
- 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.
- Souhararajan V.M., Sivakumar A., 2013. Effect of calcium nitrate on the pozzolanic properties of high early strength concrete. *Research J. Appl. Sci. Eng. Technol.*, 6(13): 2502–2508.
- Svidersky V.A., Tokarchuk V.V., Fleischer A.U., Trus I.N., 2016. Accelerators setting cement systems based on nitrogen-containing organic compounds. *Knowledge*, 4-1(33): 145–149.
- Uaissova M., Zharlykassov B., 2024. Application of AI techniques for asphalt concrete mix production optimization. *Journal Européen des Systèmes Automatisés*, 57(2): 353–361.
- Ulybin A.V., Fedotov S.D., 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.

- Usov B.A., Okolnikova G.E., 2015. Chemical additives in precast concrete technology. *Ecology and Construction*, (4): 7–14.
- Yerbayev Y.T., Zhumagaliyeva G.B., Abdygalieva A.K., et al., 2023. Application of electrothermal phosphoric slag as a binder for foam concrete production. *ARPN Journal of Engineering and Applied Sciences*, 18(7): 836–843.