Abnormal setting of Portland cement

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Abstract. It is proposed to distinguish the false setting from the abnormal one, considering the false as a variety of the latter. With false setting, the start of setting occurs in a short time, but then it spontaneously disappears, reappearing after a while. Such cements, in which the beginning of setting occurs faster than 50 minutes, and the end – after 5-12 hours, are proposed to be called abnormal cements. It is shown that when the start time of setting is more than 50 ~ 60 minutes, the probability of abnormal setting decreases sharply. The kinetics of structure formation of cements with different setting patterns is considered. Methods for the identification of abnormal setting by the setting interval \( \tau_{\text{final}} - \tau_{\text{start}} / \tau_{\text{start}} > 3 \), the kinetics of structure formation, heat release, and changes in the activity of calcium ions in the liquid phase of cement paste of normal density are proposed. It is shown that the measurement of the kinetics of heat release and the activity of \( \text{Ca}^{2+} \) ions in the liquid phase of cement paste is of great interest for the development of automated and rapid control of the presence of anomalies during setting. It is established that the mixture of the inhibitor and the booster of the setting acts according to the rule of additivity, the use of mineral additives of acidic composition weakens the abnormal properties of cement systems. To combat the belated anomaly, it is necessary to monitor the properties of the cement 1-2 days before its application.

1. Introduction
False, or in a more general sense, abnormal setting has been known for a long time [1-4], but it has not been studied sufficiently until recently. This is due to the fact that in the last two or three decades, due to the improvement of the technology of production of Portland cement, especially the system of dosage of gypsum during grinding, as well as the closed scheme of clinker grinding, false setting has become less common than in the XX century [5-7]. In recent publications devoted to the setting time of cement systems, abnormal setting is not mentioned [8-12], with rare exceptions [13-16]. But, unfortunately, this phenomenon is also found in the XXI century, so the decline in interest in this problem is hardly justified.

False or abnormal setting, causing premature thickening of concrete mixes, violates the technology of their laying. Much worse is the fact that concrete products made on cement with abnormal setting usually have internal stresses, so they are not sufficiently shock- and crack-resistant [4].

In this regard, this problem requires additional research.

Before proceeding to the presentation of the actual data, we will clarify the used terms. It is proposed to distinguish between normal rapid and abnormal setting of Portland cement paste.

In normal cements, the start time of setting is at least 60 minutes, as it is customary in the state standards of most countries. In this case, the end of setting usually occurs after 1.5-3 hours. In fast-setting cements (without the addition of gypsum or with the addition of increased dosages of the set-
ting booster), the setting start time is much shorter than 60 minutes (often from 3-4 to 5-6 minutes). At the same time, the end of setting is also quite short (10-40 minutes).

There are also cements, the paste of normal density of which has a setting time of 5 to 30-0 minutes, and the end – from 1 hour to 10-15 or more hours. These are cements with abnormal setting. The same group is proposed to include cements that have a normal start time of setting (no shorter than 60 minutes), but whose end of setting occurs in a fairly long time (4-12 hours or more).

2. Methods and materials
To study the setting time, cements from the “Katavsky Cement” and “Belgorod Cement Plant” plants were used. The setting time was determined using the Vicat apparatus. The kinetics of heat release was studied in a self-recording differential microcalorimeter, which records the process of heat release from the moment of contact of cement with water. The activity of Ca\(^{2+}\) ions in the liquid phase of the cement system was determined using the ion-selective electrode EM-Sa-01 [2]. The method allows recording the activity of Ca\(^{2+}\) ions in the liquid phase from the very beginning of its preparation.

1% sodium carbonate by weight of cement was used as a booster for setting the cement paste, and 0.3% dextrin (an oligosaccharide – a waste product of starch production) was used as an inhibitor.

3. Results and discussions
When testing one of the batches of high-aluminum cement with the addition of 0.3 % dextrin, we were able to observe a very interesting and rare phenomenon, when the beginning of setting of the paste with W/C = 0.5 at a temperature of 75 °C occurred after 15 minutes, but after 30 minutes it spontaneously disappeared, then it was fixed with a Vickat needle after 40 minutes. Within 6 hours of observation, this was repeated three times. The end of the setting did not come. After 1 day after making, the paste turned into cement stone. Dextrin, which in this dosage should have slowed the beginning of setting to 3-5 hours, acted as a booster of the beginning (but not the end) of setting.

Thus, this cement does not have a specific (single) setting start time, as it periodically disappears. This phenomenon is rare, but it exists. Its authors propose to call it a false setting and refer to the extreme case of the abnormal one.

Over the past decades, several methods of identifying abnormal setting have been proposed. According to the method of the Research Institute of Cement, if the cement paste thickens strongly during the preparation process, and then re-liquefies during subsequent mixing, then such cement is characterized by a false setting. The technique allows detecting false setting, but cases of mild abnormality can be skipped. This method is only qualitative in nature and is not devoid of subjectivity.

It is possible to detect the presence of abnormal setting by the kinetics of structure formation of cement paste, if they use the penetration method. In this case, the measure of the structural strength of the cement paste is the inverse of the depth of penetration into the cement paste of the indenter, usually of a conical shape. Figure 1 shows the types of kinetic curves of structure formation of cements with different setting patterns.
As it can be seen from Fig. 1, cements with normal properties have an induction period of 30-40 minutes or more, during which the structural strength of the cement paste is on the verge of the sensitivity of the facility. At the end of the induction period, the structural strength of the cement system increases exponentially.

Fast-setting cement systems (with the addition of increased dosages of setting boosters and other additives) have a very short induction period of several minutes, at the end of which the structural strength increases dramatically, as in the first case.

In cements with abnormal setting, the initial section of the structure formation kinetics curve is similar to fast-setting mixtures, but after 5-20 minutes, the growth of structural strength stops and either stabilizes at a low level or falls.

The penetration method is very informative, but requires special equipment, increased material consumption. In addition, during penetration, distortions are inserted into the process of structure formation, which is especially important in case of abnormal setting.

In connection with the above, the first author of this work proposed a quantitative method for assessing the degree of abnormal setting of cement paste using a standard Vickat apparatus, which does not require any additional actions at all, except for the generally accepted definitions of the start time ($\tau_{\text{start}}$) and the end of setting ($\tau_{\text{final}}$). According to the proposed method, based on the measurement of $\tau_{\text{start}}$ and $\tau_{\text{final}}$, the relative value of the setting interval $K_{\text{si}}$ is calculated:

$$K_{\text{si}} = \frac{\tau_{\text{final}} - \tau_{\text{start}}}{\tau_{\text{start}}}$$

In normal and fast-setting cements, this interval usually does not exceed 2-3. If this interval is greater than 3, then we suggest that such cement should be classified as abnormal in terms of setting time.

The regularities of the influence of the setting start time on $K_{\text{si}}$ are presented in Fig. 2, which reflects the results of numerous experimental data of the authors using mainly cements from the Belgorod Cement Plant and individual samples of products from 12 other enterprises.

It follows from the graph that if the start time of setting is more than 50-60 minutes, then the setting interval does not depend much on the latter. However, there are exceptions to this rule. Sometimes the beginning of setting can occur in 70-80 minutes, and the end – in 5-7 hours. Such cement is hardly convenient for construction industry workers.
In this regard, it is unjustified that according to GOST 31108-2016 “General construction cements. Technical conditions”, in the European Standard (DIN EN 197-1-2000 Cement) and in other regulatory requirements for cement, the end-setting time is excluded.

The methods described above for identifying abnormal setting make it possible to identify defective cements reliably. The simplest and most reliable quantitative method is the method based on the determination of the relative setting interval using a standard Vicat apparatus. However, they are difficult to automate and digitalize. In this regard, experimental data on the features of the kinetics of heat release and changes in the activity of Ca$^{2+}$ ions in the liquid phase in cement paste with a different type of setting are of interest (Fig. 3).

The analysis of the above experimental data shows that the measurement of the kinetics of heat release and the activity of Ca$^{2+}$ ions in the liquid phase of cement paste is of great interest for the development of automated and rapid control of the presence of anomalies during setting.

A comparison of the above experimental data (Fig. 1 and 3) indicates that, by the nature of the kinetics of structure formation of heat release and the kinetics of changes in the content of Ca$^{2+}$ ions in the liquid phase of the cement paste, cements with abnormal setting occupy an intermediate position between normal and fast-setting cements (with the addition of 1% Na$_2$CO$_3$). At the same time, the initial section of the curves of the kinetics of the processes of heat release and changes in the activity of Ca$^{2+}$ ions, as well as the kinetics of structure formation in cements with abnormal setting is similar to a fast-setting mixture, and the final section is similar to normal cement. This is consistent with the fact that at low dosages of setting boosters (0.2-0.3% Na$_2$CO$_3$, NaOH, etc.), normal cement exhibits abnormal properties, and when the dosage of these reagents is increased to 1-2%, rapid setting occurs.
Figure 3. The kinetics of heat release (a) and changes in the activity of Ca\textsuperscript{2+} ions in the liquid phase in the cement paste (b) with different setting patterns: 1 – normal; 2 – abnormal; 3 - fast; 4 – slow.

Another method of identifying abnormal setting could be the measurement of the electrode potential that appears in a metal plate lowered into cement paste of normal density [17, 18]. However, this method gives insufficiently stable results and is excessively weather-sensitive.

Thus, cement paste with abnormal properties is a system with insufficiently accelerated setting. The mechanism of abnormal setting has not been sufficiently investigated. It is believed that one of the main and frequent causes of abnormal setting is the heating of cement to 100-120 °C [1]. In this case, the gypsum added to the cement during grinding is partially dehydrated and turns into semi-aqueous calcium sulfate. The latter is characterized by a very short setting time (starting from 4 minutes). As the gypsum content is small (5-8% of the cement mass), the strength of the cement paste structure can reach a value corresponding to the beginning of the setting of the system. It is possible that the contribution to the structural strength of the cement paste is also made by electric surface phenomena caused by the processes of coagulation of positively charged hydroaluminate phases and negatively charged gypsum particles formed during the hydration of CaSO\textsubscript{4} \cdot 0.5H\textsubscript{2}O and therefore having a very high specific surface area, especially in the first 10-15 minutes.

Coating the particles of the aluminate phases with a gypsum film gives their surface a negative charge, which hinders the diffusion of calcium and hydroxonium ions into the liquid phase and inhibits the hydration of anhydrous particles. An even greater inhibitory effect on the hydration of clinker minerals is exerted by the increased solubility of gypsum (2 g/ l CaO versus 1.15-1.2 g/l for Ca(OH)\textsubscript{2} and especially CaSO\textsubscript{4} \cdot 0.5H\textsubscript{2}O).

This is the mechanism of action of small amounts of CaSO\textsubscript{4} \cdot 0.5H\textsubscript{2}O. It is appropriate to note that at a dosage of this compound equal to 10-20%, rapid normal setting occurs with short periods of both the beginning and end of setting with a setting interval coefficient K\textsubscript{si} < 2-3.

A very unpleasant type of setting is a latent or belated anomaly, first described by Kalouzek [2], when the cement has normal setting when tested at the manufacturing plant, and after 1-2 weeks and later, abnormal setting prevails. In this regard, when concreting particularly critical objects, each batch of cement before mixing with water should be checked for abnormality. The mechanism of this phenomenon is not described. It is possible that its cause is the transition of gypsum added during grinding to semi-aqueous calcium sulfate as a result of its interaction with free lime contained in cement, or with such active phases as tricalcium aluminate (C\textsubscript{3}A), etc.

The analysis of the above experimental data suggests that abnormal cements have a factor that causes a rapid start of setting, but it is not enough to accelerate the end of setting. It follows that the insertion of small amounts of setting inhibitor lengthens the start time, almost without affecting the end time of setting. We found that the mixture of the inhibitor and the booster of the setting acts according to the rule of additivity, which facilitates their selection.
The insertion of mineral additives of acidic composition (ground quartz, TPP fly ash, acid slag, clay in grouting mixtures, etc.) weakens the abnormal properties of cement systems. In the same way, but the fine aggregate of quartz sand is weaker.

To combat the latent (hidden) anomaly, it is necessary to monitor the properties of the cement 1-2 days before its application. This is especially important for countries with humid and hot climates.

Water-soluble phosphates are significantly stronger inhibitors of the setting of cement systems than sulfates, and their use as an additive instead of gypsum in the form of phosphogypsum in most cases can prevent abnormal setting.

The manifestation of abnormal thickening and setting disrupts the technological process of manufacturing products and structures [19]. Even more undesirable consequences are the property of cement with abnormal properties to show delays in hardening and even strength drops in the hardening time of 7-14 days [20].

To prevent the occurrence of cement batches with abnormal setting, it is necessary, first of all, to improve the technology and equipment at cement plants, to ensure the accuracy of the dosage of gypsum, as with its lack abnormal setting is ensured. It is important to avoid overheating of the cement during grinding due to the good aspiration of the mills.

4. Summary
It is suggested that such cement paste, in which the beginning of setting then occurs, then disappears several times in short intervals of time (10-30 minutes), is to be called false setting. In this case, the end of setting occurs after a few hours. False setting is a special case of abnormal setting, in which the beginning of setting occurs quickly (10-40 minutes), and the end - after 3-10 hours. To quantify the degree of setting abnormality, it is proposed to use the setting interval coefficient $K_{si} = (\tau_{\text{final}} - \tau_{\text{start}}) / \tau_{\text{start}}$. With abnormal setting $K_{si} > 3$.

It is shown that with normal rapid setting (additives of 1-3% $Na_2CO_3$, $NaOH$, 10-20% $CaSO_4 \cdot 0.5H_2O$, etc.), the time of both the beginning and end of setting is short. If the start time of setting is more than 50 ~ 60 minutes, the probability of abnormal setting decreases sharply.

It is established that the curves of the kinetics of structure formation, heat release, and changes in the activity of calcium ions in the liquid phase of cement suspensions in abnormal cements at the initial stage are similar to fast-setting mixtures, and at the final stage – to normal ones.

Currently, not enough material has been accumulated to explain the mechanism of abnormal setting. The available data suggest that the abnormal setting is caused by a violation (delay) of the synthesis of ettringite and other aluminum-containing phases with their crystallization at a later time in the hardened structure of the stone, which reduces its crack resistance and leads to a delay in hardening or even to a loss of strength. To avoid the negative consequences of abnormal setting, it is advisable to restore the point in the regulatory documents for Portland cement that normalizes the time of the end of setting.

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