Physico-chemical research of the processes of hydration of cements

Nargiza Lutfullaeva, Elmurod Egamberdiev, Yorqinjon Ergashev, Umid Alamov, Shohida Shamuratova, Iroda Usmanxadjaeva, Anisakhon Tukhtamushova, Bobur Saparov

Abstract. The activating effect of phosphoanhydrite on cement hydration is strongly supported by the results obtained from various physico-chemical analyses, including IR spectroscopy, X-ray phase analysis, and differential thermal analysis. IR spectroscopy revealed significant differences in the hydration products of cement with and without phosphoanhydrite. The presence of phosphoanhydrite led to distinct absorption bands in the IR spectra, indicating a higher concentration of Portland cement hydrate compounds and calcium hydrosilicates in the activated cement. This observation suggests that phosphoanhydrite plays a vital role in promoting the formation of these hydration products, leading to enhanced cement activation. X-ray phase analysis further confirmed the activating effect of phosphoanhydrite. The diffraction patterns of the hydrated cements showed a remarkable increase in the analytical lines corresponding to Ca(OH)$_2$ when phosphoanhydrite was present. This indicates a higher content of this phase in the activated cement, reinforcing the notion that phosphoanhydrite contributes to the accelerated hydration process. Differential thermal analysis provided additional evidence of the activating effect of phosphoanhydrite. The DTA curves exhibited higher hydration levels for the cement activated with phosphoanhydrite compared to the control cement. This was indicated by an increased percentage of bound water and a greater mass loss at 140°C, demonstrating the more extensive hydration of the activated cement. Taken together, these physico-chemical analyses consistently demonstrate the activating effect of phosphoanhydrite on cement hydration. The unique properties of phosphoanhydrite facilitate the formation of hydration products, such as Portland cement hydrate compounds and calcium hydrosilicates, leading to an accelerated and more efficient hydration process.

1 Introduction

Cements were produced utilizing Bekobod clinker as a fundamental component. Notably, in the infrared (IR) spectrum of the hydrated cement with the addition of phosphoanhydrite,* Corresponding author: e.egamberdiev@tdtu.uz
Distinct absorption band at 3655 cm\(^{-1}\) becomes apparent. This observation is made on the third day of the solidification process [1, 2].

The emergence of a sharp absorption band at 3655 cm\(^{-1}\) in the IR spectrum is indicative of specific molecular vibrations associated with the hydration and solidification processes of the cement, especially when phosphoanhydrite is introduced. This absorption band is likely attributed to the stretching vibrations of hydroxyl groups or water molecules, providing valuable insights into the chemical transformations occurring during the early stages of cement hydration.

The presence of phosphoanhydrite, a mineral additive, appears to influence the hydration kinetics and molecular structure of the solidified cement. Analyzing the IR spectrum aids in understanding the chemical and structural changes in the cementitious matrix during the initial phases of solidification, contributing to the overall comprehension of the cement production process and the impact of additives on its properties.

The observed score suggests that the hydration products of the cement stone, particularly when incorporating phosphoanhydrite, contain a higher proportion of Portland cement hydrate compounds and calcium hydrosilicates compared to the hydrated control cement [3]. This indicates that the addition of phosphoanhydrite influences the composition and abundance of specific hydrate phases in the cementitious matrix.

The higher presence of Portland cement hydrate compounds and calcium hydrosilicates suggests an enhanced formation of essential binding phases, contributing to the strength and durability of the cement. The influence of phosphoanhydrite on the hydration products may lead to the development of a more structurally sound and potentially improved cement matrix.

Understanding the variations in hydrate compound composition is crucial for tailoring cement formulations to achieve desired mechanical and chemical properties. The observed differences in the hydrate phases highlight the impact of phosphoanhydrite on the early-stage hydration and provide valuable information for optimizing cement mixtures for specific applications.

The observed rise in the intensity of the absorption band attributed to the silicate component of cement at 3450 cm\(^{-1}\), indicating an increase in the percentage of bound water, along with the expanded area of the absorption band in the range of 900-1000 cm\(^{-1}\), serves as confirmation that the hydration level of the activated binder is greater than that of the control cement. These spectroscopic changes suggest a more advanced and enhanced hydration process in the activated binder compared to the reference cement.

The increase in intensity at 3450 cm\(^{-1}\) indicates a higher content of bound water, a crucial aspect of cement hydration associated with the formation of hydrate phases. Similarly, the broadened absorption band in the range of 900-1000 cm\(^{-1}\) is often associated with the presence of additional hydration products or structural modifications, reinforcing the notion of increased hydration levels in the activated binder.

These spectral observations provide valuable insights into the chemical transformations occurring during the hydration process, underscoring the effectiveness of the activated binder in promoting enhanced cement hydration compared to the control cement. This information is essential for tailoring cement formulations to achieve desired properties and performance characteristics in various applications.

In the diffractograms of hydrated cements, a notable elevation in the intensity of the analytical lines corresponding to Ca(OH)\(_2\) is evident, particularly observed at diffraction maxima of 1.93, 4.90, and 2.63·10\(^{-10}\) m, in the presence of phosphoanhydrite in the system. This suggests a substantial increase in the crystalline content of calcium hydroxide within the cementitious matrix.

The heightened intensity of the Ca(OH)\(_2\) lines in the diffractograms indicates an increased abundance and crystallinity of calcium hydroxide, a hydration product associated with the
cementitious reactions. The presence of phosphoanhydrite appears to enhance the formation
or stabilization of Ca(OH)$_2$, suggesting a specific influence on the hydration products.

Understanding the variations in the diffractograms is crucial for deciphering the impact of
additives like phosphoanhydrite on the crystalline phases formed during cement
hydration. This information contributes to the overall comprehension of the cementitious
system's behavior and aids in optimizing formulations for desired performance
characteristics.

2 Materials and methods

Cements were prepared using Bekobod clinker as the base material for this physico-
chemical research on the hydration processes. The hydration of the cements was studied by conducting
various analyses and measurements.

Infrared (IR) spectra were obtained using a spectrophotometer to examine the hydration
products of the cement. The spectra were recorded on the 3rd day of solidification for both
the hydrated cement with phosphoanhydrite addition and the hydrated control cement. The
presence of a sharp absorption band at 3655 cm$^{-1}$ in the IR spectrum of the cement with
phosphoanhydrite indicates a higher content of Portland cement hydrate compounds and
calcium hydrosilicates compared to the control cement. Additionally, an increase in the
intensity of the absorption band at 3450 cm$^{-1}$, corresponding to the silicate component of the
cement, suggests a higher hydration level in the activated binder compared to the control
cement. The extent of the absorption band area in the range of 900
1000 cm$^{-1}$ also supports
this observation.

X-ray diffraction (XRD) analysis was performed on the hydrated cements to examine the
presence of specific crystalline phases. The diffraction patterns revealed a significant increase
in the analytical lines of Ca(OH)$_2$ in the presence of phosphoanhydrite, indicating a higher
content of this phase compared to the control cement. The fraction of the ettringite phase also
slightly increased in the hydrated control cement.

Differential thermal analysis (DTA) was conducted to assess the hydration leve
l of the
activated cement compared to the control cement. The DTA curves demonstrated an increased hydration level in the activated cement, as evidenced by the higher
percentage of bound water. Thermogravimetric (TG) analysis revealed a greater mass loss at
140°C for the activated cement compared to the control cement, indicating higher moisture
content. The total amount of bound water in the hydration products of the activated cement
was also higher than that of the control cement on both the 3rd and 28th days of hardening,
as determined through quantification.

These experimental techniques and measurements provided valuable information about the
physico-
chemical properties and hydration characteristics of the cements, particularly when
activated with phosphoanhydrite. The results obtained contribute to a deeper understanding
of the hydration processes and can aid in the development of improved cement formulations
and applications in various construction projects.

3 Results and discussion

Based on the comprehensive physicochemical analysis data, it can be concluded that the
enhanced activation effect observed when using phosphoanhydrite can be attributed to the
increased level of hydration of the silicate component within the cement
stone. The presence
of phosphoanhydrite led to a higher concentration of Portland cement hydrate compounds and
calcium hydrosilicates, as indicated by the sharp absorption band observed in the IR
spectrum. This, in turn, resulted in an elevated intensity of the absorption band related to the
The observed increase in the intensity of analytical lines corresponding to Ca(OH)2 in the diffractograms of hydrated cements, particularly in the presence of phosphoanhydrite, could potentially be attributed to an increase in the surface acidity of the cementitious system. Elevated surface acidity may influence the hydration reactions and subsequent crystallization of calcium hydroxide (Figure 2).

Surface acidity can impact the dissolution and precipitation kinetics of various phases during cement hydration. In the presence of phosphoanhydrite, changes in the surface chemistry of the cement particles might enhance the reactivity of certain phases, leading to an increased formation or stabilization of Ca(OH)2 crystals. This, in turn, is reflected in the heightened intensity of the corresponding diffraction lines (Figure 3).

The influence of surface acidity on cement hydration is a complex aspect that can be affected by multiple factors, including the chemical composition of additives. Further detailed investigations and analyses would be necessary to precisely understand the mechanisms behind the observed changes in the diffractograms and the potential role of increased surface acidity in this context (Figure 4).

### Table 1: Calculation of bound water of hydrated cements based on clinker of Bekobod plant with phosphoanhydrite addition according to TG data.

| Cement samples (after hydration) | Hardening period, day | Maxima of endothermic effects, °C | Mass loss, % | I | II | III | ∑
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Note: *Control 1*
Rheological properties of cement pastes and admixtures with added hard soluble substances.

In order to study the influence of hard-soluble substances added to cements on the rheological properties of cement pastes and mixtures during the setting, cements based on clinkers of Kuvasoy and Bekobod plants with 1-5% phosphogypsum, limestone, and barium sulfate were prepared. Cements with the addition of activated limestone (200°C) and phosphogypsum (400°C) were also prepared at optimal temperatures. Figure 5 shows the effect of hard-soluble substances on the spreadability of mixtures based on Kuvasoy cement. Optimum plasticizing effect is observed when 1% phosphogypsum and 5% limestone are added to cement.

Thermally activated additives: in mixtures based on cements with the addition of limestone-5% and phosphogypsum-1%, a decrease in the water-cement (W/C) ratio was observed (while the plasticity of the mixture remained unchanged-0.03).
Fig. 4. Derivatogram of cement stone based on Bekobod clinker (28 days).

Table 2 presents a comprehensive overview of the strength indicators derived from mixtures augmented with a 5% addition of thermally activated limestone, as per the testing protocol outlined in GOST 310.4-81. These strength indicators serve as crucial metrics in evaluating...
The performance and quality of the composite materials. The incorporation of thermally activated limestone, known for its pozzolanic properties, into the mixtures introduces an additional dimension to the structural characteristics of the resulting materials. The inclusion of 5% thermally activated limestone prompts an examination of how this additive influences compressive strength, tensile strength, or other relevant parameters. Strength indicators are pivotal in determining the load-bearing capacity and durability of the mixtures, providing insights into their suitability for construction applications. The results from these tests offer valuable information for engineers, architects, and material scientists seeking to optimize formulations for enhanced structural integrity, sustainability, and cost-effectiveness. This comprehensive analysis of strength indicators in Table 2 contributes to a deeper understanding of the synergies between thermally activated limestone and the overall mechanical performance of the mixtures, guiding informed decision-making in construction and material engineering practices.

It was observed that the strength (52 and 72 Pa \(10^5\)) (in compression) increased significantly on the 3rd and 28th days of normal hardening for the cement composition with 5% limestone added to the composition, thermally treated at 200°C. Figure 5 shows the effect of phosphogypsum additive (natural and thermally treated at 400°C) on the elasticity of cement pastes (a) and mixtures (b) based on free cement. The highest effect of plasticization was observed for cement pastes with 1% phosphogypsum and cement mixtures with 3% phosphogypsum.

How much phosphogypsum additive should be added to achieve the optimal plasticization effect was analyzed by physical-mechanical methods. For comparison, these cement compositions were studied: control cement (without additives) and cement with 3% thermoactive phosphogypsum.

Table 2. Strength parameters of Portland cements activated with heat-treated limestone.

<table>
<thead>
<tr>
<th>Portland cement</th>
<th>Limestone</th>
<th>W/C</th>
<th>Cone spreading, mm</th>
<th>Reinforcement limit, Pa. (10^5), duration (day)</th>
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<tr>
<td></td>
<td>quantity, %</td>
<td>temperature, °C</td>
<td></td>
<td>in bending</td>
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<tr>
<td></td>
<td>3</td>
<td>28</td>
<td>3</td>
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As can be seen from the diffractogram (Figure 1) and absorption IR spectra (Figure 2), the addition of 1% thermally activated phosphogypsum causes the silicate component of cement to accelerate the hydration processes. The amount of \(\text{SiO}_2\), determined by the analytical \(4.9 \times 10^{-10}\) m line, increased. In the region of \(\text{SiO}_4\) valence vibrations, the shape of \(\text{IK}\)-tetrahedra changed, they appeared more attenuated, additional bands appeared in the region of 880 cm\(^{-1}\) (Figure 6). As a result of increasing the amount of phosphoanhydrite to 35, the ettringite bands increased (1125, 1150 cm\(^{-1}\)) and the gypsum band disappeared at 650 cm\(^{-1}\). No acceleration of hydration of the silicate component of cement was observed (curve 2 versus curve 2 in Figure 1).
Effect of the amount of phosphogypsum added to cement on cement pastes and mixtures (Bekabad cement)

It is important to note that, while the amount of thermally activated phosphogypsum remains the same, it becomes optimal in the plasticization and hydration of the silicate component. Thus, according to the data of physicochemical analysis, the activating effect (effectiveness) of aluminosilicate activators was felt in accelerating the hydration processes of silicate and aluminate components of Portland cement clinker, stabilizing ettringite, and improving the crystallization of polymer calcium hydrosilicates.

5 Conclusions

1. The possibility of obtaining phosphoanhydrite, a substance that activates the hardening of cements, by thermal treatment of phosphogypsum at 400°C±20°C. This proposed simple method makes it possible to supply the cement industry and precast reinforced concrete manufacturing enterprises in various regions of our republic with an inexpensive activator.

2. It was found that during heat treatment, acidity properties on the surface of phosphoanhydrite increase, and its maximum value corresponds to a temperature of 400°C.

3. Due to the use of modern physicochemical methods (X-ray phase, differential thermal, IR-spectroscopic analysis), it is observed that the hydration of calcium silicates of cement is accelerated. The reason for this is the improvement of surface acidity properties of thermally treated phosphogypsum—phosphoanhydrite. In addition, the addition of phosphoanhydrite to the cement composition increases the concentration of ettringite.

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