Zeolite tuff as strength improver in cements

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Abstract. This study aims to obtain cement with valuable properties by introducing additives enhancing concrete strength. Zeolite tuff of the Lyulinskoe deposit (Russia) that had not been studied before was tested as a strength improver. The elemental and phase zeolite tuff compositions were established by X-ray fluorescence and X-ray phase analysis. Electrical conductivity and cement paste pH were measured, and the pozzolanic activity of zeolite additive was evaluated. The Portland cement hydration in the presence of zeolite leads binds not only calcium ions, but also sulfate ions. The obtained kinetic curves of electrical conductivity and pH level gave stage wise description of Portland cement hydration and strength development, which reveals the possibility of managing the curing process. It was established that 5% zeolite ground to 5–10 μm increases the compressive strength by 15% in 7 days and by 21% in 28 days.

1. Introduction
Zeolite, which is an aluminosilicate mineral with a three-dimensional framework structure, has sufficiently large cavities and channels in the crystalline structure. This determines its uniqueness properties, such as high adsorption capacity, ion exchange and catalytic activity.

Cement is a complex multi-component system which minerals react with water at different rates. The most important clinker components providing it with the cement strength properties are tricalcium aluminate (C₃A) and tricalcium silicate (C₃S).

It is known that zeolite binders have a different mechanism of their involvement in structure formation. As a rule, fine-dispersed zeolite additives of any type participate in the structure formation physically by filling the pores in the cement stone and thus increasing the material’s density [1–3].

Zeolite additives can influence the cement properties through ion exchange processes that are typical of zeolites. Exchange cations alter the cement paste pore-filling solution composition and thus affect the hydration rates and cement paste hardening [4, 5].

However, zeolite binders with pozzolanic properties are of more interest. In the presence of water active zeolite silica is able to bind calcium ions into calcium hydro-silicate, which causes hydraulic hardening and strength development in the material [6–9]. Also, zeolite is peculiar for alumina in its composition that actively binds sulfate ions [10, 11].

Natural zeolite tuffs came into use in the construction industry as pozzolanic additives in the first decades of the 20th century. Their effectiveness is quite obvious. Such additives improve strength properties and water and corrosion resistance [12–16] and often make the construction material cheaper [17–20].
Like any other minerals, zeolite-containing rocks are distinguished by inconstant composition, which dictates the need for a preliminary systematic study of their physicochemical properties.

The aims of this work are to study the zeolite tuff pozzolanic activity from the Lyulinskoye deposit (Khanty-Mansi Autonomous Region, Russia), to consider the zeolite additive influence on the Portland cement strength properties and to determine the mechanism of such influence.

2. Materials and methods

2.1. Materials

The following materials were used: Portland cement CEM I 42.5 N and natural zeolite tuff from the Lyulinskoye deposit (Khanty-Mansi Autonomous Region, Russia). Zeolite tuff samples were ground to fractions of 0.05–0.1 mm and 5–10 µm.

The materials’ elemental and phase compositions (Tables 1 and 2) were established by X-ray fluorescence analysis and X-ray phase analysis using EX-6600 SSD device (XENEMETRICS, Israel) and Empyrean diffractometer (PANalytical) with a copper anode. The tube voltage was 50 kV.

Table 1. Element composition of Portland cement and natural zeolite tuff (mass fraction, %).

|          | SiO₂ | Al₂O₃ | Fe₂O₃ | MgO | CaO | Na₂O | K₂O | TiO₂ | SO₃ | Other |
|----------|------|-------|-------|-----|-----|------|-----|------|-----|-------|
| Cement   | 9.30 | 1.56  | 8.59  | 0.40| 76.76| -    | 0.75| 0.81 | 1.47| 0.36  |
| Zeolite tuff | 42.58| 24.95 | 11.37 | 4.08| 3.39 | 2.99 | 3.01| 0.27 | 2.79| 4.57  |

Table 2. Phase composition of Portland cement and natural zeolite tuff (mass fraction, %).

| Phase                        | Formula                        | Mass fraction [%] |
|------------------------------|--------------------------------|-------------------|
| Cement Alite C₃S             | Ca₃SiO₅                        | 65                |
| Belite C₂S                   | Ca₅SiO₄                        | 14                |
| Tricalcium aluminateC₃A      | Ca₃Al₂O₆                      | 14                |
| TetracalciumaluminaferriteC₄AF | Ca₃(Fe₁,₄₅Al₀,₅₅)₂O₅          | 7                 |
| Zeolite tuff Quartz          | SiO₂                           | 45                |
| Clinoptilolite               | KNaN₂Ca₅Si₅₁₆Al₂O₇₂.24H₂O       | 30                |
| Heulandite                   | Ca₅Si₂Al₂O₁₈.6H₂O               | 10                |
| Montmorillonite              | Al₃(OH)₂Si₄O₁₉.nH₂O             | 8                 |
| Muscovite                    | KAl₃Si₅O₁₀(OH)₂                | 7                 |

2.2. Conductivity and pH measurements

Specific conductivity was measured using the Mettler Toledo FE30 Five Easy Benchtop Conductivity Meter. PH was measured using the Mettler Toledo Seven Multi pH meter. The mixtures were prepared to have a solid to liquid phase mass ratio of 1:100. The solid phase had various compositions, such as Portland cement without additives and Portland cement with 5, 10 and 20% additives. For each cement mixture with the additive, the measurements were performed at 300 °C in duplicate: with unignited zeolite tuff and ignited zeolite tuff. Deionized water was used for the tests to exclude the impact of various ions on the cement hydration. The tests lasted 24 hours, and the measured values were recorded every hour.

2.3. Evaluation of pozzolanic activity

Pozzolanic activity was studied by absorbing lime from a lime mortar. One gram of zeolite tuff was poured with 100 ml of saturated Ca(OH)₂ solution (CaO concentration was 1 g/l). The mixture was shaken vigorously. Titration was performed with hydrochloric acid (methyl orange indicator) daily for
40 days. The results were calculated from the difference between the initial content of Ca(OH)$_2$ and undigested Ca(OH)$_2$.

To describe the kinetics of binding mobile calcium and sulphate ions by zeolite tuff on the first day, the mixtures similar to those in the electrical conductivity test were prepared. The samples were collected every hour. The ion content in the samples was determined after the solution separation from the solid phase by filtration. Calcium ion content was determined by complexometric titration with murexide indicator. Sulfate ion content was determined using the 882 Compact IC Plus ion chromatograph (Metrohm AG) with conductometric detection.

2.4. Compressive strength measurement
Compressive strength was measured using the Desttest 3310 tester (Betonsystem, Czech Republic). The samples were prepared according to a standardized procedure described in GOST 8462-85. The mixtures tested were Portland cement without additives and Portland cement with 5% zeolite additive that was ground to 0.05–0.1 mm and 5–10 µm. The water to cement ratio was 0.4. The measurements were performed on the days 1, 7, 28 and 56.

3. Results and discussion
The pozzolanic activity of a material depends on its chemical and mineralogical composition and occurs due to the presence of SiO$_2$ and Al$_2$O$_3$ that can vigorously react with Ca(OH)$_2$ released during the cement hydration. The natural zeolite tuff chemical composition study showed that it corresponds to typical pozzolan contents. The total content of oxides SiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$ should be at least 70% of the total mass [21–23]. In our case, it was 79%.

The cement hardening process is complex; it includes a series of sequential or series-parallel processes of the cement components’ hydration, their hydrolysis and the formation of low soluble product structures. These processes proceed coherently but at different rates, and hence one of the processes becomes predominant while the others decay, which leads to self-oscillations in the system. Thus, Makridin, Korolev and Maksimova [24] were the first to introduce the self-organization concept in a cement system, bearing in mind the spontaneous process of the cement system structure formation and hardening. The study of the initial period (the first day) can be the groundwork for understanding the entire complex process of hardening [25].

The obtained kinetic curves of electrical conductivity (Figure 1) are self-oscillating. The differences in electrical conductivity values point to individual stages in the processes of the cement hydration and hardening, which are well described in [26–28]. In fact, it is an alternation of relatively long (induction) periods and rapid chemical interactions [29]. Understanding the chemical nature of these stages makes it possible to control the strength of the material.

As follows from Figure 1, added zeolite tuff did not violate the cyclical nature of hydration and hardening of the cement in the initial period of time, but noticeably affects the kinetic curve in the interval of 14–20 hours. It may indicate that this is the time when the process is complicated with the ongoing pozzolanic reaction of zeolite tuff. The experiment revealed no differences in the electrical conductivity kinetics when adding different amounts of both ignited and unignited zeolite tuff at 300 °C.

The kinetic curves of pH fluctuation are consistent with the curves of electrical conductivity (Figure 2). Self-oscillatory changes in the pH cement values were observed at the same time intervals. Added zeolite tuff lowered the pH value, which indirectly indicates its pozzolanic activity.
Figure 3 shows the results of determination of the zeolite tuff pozzolanic activity. Zeolite tuff absorbed 347 mg/g of lime in 30 days. To compare with data in [30], silica gel absorbs only 175 mg/g of lime over the same period of time. By the age of 30 days, the absorption curve reached a plateau. The obtained results indicate that natural zeolite tuff can be attributed to additives with high pozzolanic activity.

The binding calcium ions’ kinetics study in the cement–additive–water system upon hydration revealed that zeolite tuff absorbed Ca(OH)$_2$ from cement mortar (Figure 4). The maximum absorption in the first day fell on the completion of the cement paste setting. In 10 hours of hydration unignited zeolite tuff absorbed 78.4 mg/g of calcium ions.

In the presence of a mineral additive, not only calcium ions, but also sulfate ions got bound. When exposed to water, the aluminate phase reacted first and, therefore, active binding of sulfate ions
occurred during the initial hours of hydration (Figure 5). Ion Ca$^{2+}$ binds to low-base calcium silicate hydrate, while SO$_4^{2-}$ binds to calcium aluminate sulfate hydrate [11].

![Figure 3. Ca(OH)$_2$ absorption by pozzolanic additives](image1)

![Figure 4. Kinetic concentration curves for calcium ions](image2)
The compressive strength of the cement stone was measured on the days 1, 7, 28 and 56. It was found (Figure 6) that cement without additives and cement with 5% zeolite tuff was developing strength mainly in the first 7 days. Zeolite tuff enriches Portland cement with silicon, and the pozzolanic reactions, which lead to the strengthening of the material, proceed rather quickly. A similar picture was observed by Mertens et al. [31], who showed that the samples with zeolites, which were rich in silicon, reacted with calcium hydroxide more quickly than their counterparts enriched in aluminum.

The addition of fine fractions (5–10 µm) enhances strengthening by more than 20%. When using the larger fraction of zeolite tuff (0.05–0.1 mm), the strengthening effect was weaker, which seems quite logical since the topochemical reactions take place deeper if the solid phase particles are finer. However, it should be noted that the strength of cement with zeolite tuff of the larger fraction is not lower than the original cement strength; therefore, coarse additives can be used as a partial substitute for cement without the cost of finer grinding.

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**Figure 5.** Kinetic concentration curves for sulfate ions

**Figure 6.** Kinetic strength curves for Portland cement.
4. Summary
The elemental and phase compositions of natural zeolite tuff were established. The total content of oxides SiO$_2$, Al$_2$O$_3$, and Fe$_2$O$_3$ in zeolite tuff was 79%, which is typical for the used pozzolanic materials.

The obtained kinetic curves of electrical conductivity and pH level make it possible to describe the process of hydration and hardening of Portland cement step by step, which opens up the possibility to ultimately control the curing process.

The pozzolanic activity of natural zeolite tuff was determined. In 30 days, zeolite tuff absorbed 347 mg/g of lime, hence, it is an additive with high pozzolanic activity.

Fine-dispersed (5–10 μm) zeolite tuff, added to Portland cement in the amount of 5%, increased the compressive strength by 15% at the age of 7 days and by 21% at the age of 28 days. Coarser (0.05–0.1 mm) zeolite tuff slightly affected the strength at the age of 7 days, and after 28 days the gain in strength was 10%.

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