Impact of acid treatment on the puzzolan activity of natural zeolite tuff

T N Smorodinova and M K Kotvanova

1 Institute of Oil and Gas, Yugra State University, Chekhova St., 16, Khanty-Mansiysk, 628012, Russia
E-mail: kotvanova@mail.ru

Abstract. Using the methods of thermal gravimetric analysis, and X-ray phase analysis, the puzzolan activity of the natural zeolite tuff of the Lyulinsky deposit of Khanty-Mansiysk Autonomous District - Yugra as a mineral additive to cement was evaluated. Acid modification of natural zeolite tuff was performed. The selection of modification conditions was carried out by varying the concentration of the acid solution, the time of exposure to the reagent, and the temperature. The optimal parameters were: the concentration of hydrochloric acid 3 M, the duration of acid exposure-5 hours, the temperature of 80°C. It was found that the treatment of tuff with 3M hydrochloric acid solution leads to a significant increase in puzzolan activity. The strengthening effect of the modified additive is shown. The strength of cement samples with the addition of zeolite tuff at a similar age increases by 28%. The effect of the addition of zeolite tuff on the phase composition of cement during hydration and hardening is studied. A more significant decrease in the content of portlandite was recorded when using a modified additive compared to the addition of zeolite tuff in its native state, which is consistent with the data obtained from the mass loss curves. At the same time, an increase in the content of ettringite, which contributes to the strengthening of the structure of the binder part of the cement stone, is shown. The degree of hydration of cement was estimated by the change in the content of alite. A complexometric determination of the aluminum content in the washing waters after acid treatment of zeolite tuff was carried out. It is shown that acid treatment leads to its dealuminization, which is associated with the restructuring of the zeolite framework. This, in turn, provides an increase in the number of active acid centers responsible for its adsorption properties and reactivity on the surface of the aluminum-silicate framework of the zeolite.

1. Introduction

Natural zeolites and zeolite tuffs are currently known as mineral additives to building mixes [1-3]. Earlier in the work [4], the possibility of using the zeolite tuff of the Lyulinsky deposit of the Khanty-Mansiysk Autonomous District-Yugra as a strengthening additive to Portland cement was shown, and the puzzolan and anticorrosive properties of the additive were pointed out. Still, the use of zeolite tuff in its native state is not always as effective as possible. Like any other natural material, it cannot compete with an individual chemical. Modification, as a rule, improves its adsorption properties, catalytic activity, reactivity, puzzolan activity. Various methods of physical and chemical modification are known [5-7]. The most effective is probably chemical modification, which involves treatment with strong acids and alkalis, complexing reagents, and aqueous solutions of ammonium salts [8-10]. Modification of natural zeolite tuffs allows purposefully changing their properties. Thus, the authors of [11] proposed and performed ultrasonic treatment of Yushan zeolite tuff for the production of a sorbing matrix material for the immobilization of radionuclides. At the same time, the pores of the frame aluminosilicates are cleaned of impurities, the aggregated particles are separated, and the specific surface area of the samples increases. The heat treatment of zeolite tuffs is quite standard [12, 13], as a result of which the dehydration of zeolites occurs, as well as the associated migration...
processes of mobile forms, which significantly change the properties of the aluminosilicate. One of the types of modification of zeolite-containing materials is mechanical activation, which leads to the occurrence and accumulation of defects in the zeolite structure, phase transformations, and even amorphization of the crystal structure [14, 15]. Despite the variety of modification methods, chemical activation of aluminosilicate materials is mainly used [16, 17]. Acid treatment of zeolite tuffs involves the removal of exchange cations, the dealumination of the aluminosilicate framework, and, in fact, the formation of a silicon-oxygen phase [18].

2. Materials and methods

2.1. Materials

We used natural zeolite tuff of the Lyulinsky deposit of the Khanty-Mansiysk Autonomous District-Yugra, as well as Portland cement of the CEM I 42.5 B cement brand.

The phase composition of the materials used is shown in Table 1.

Table 1. Phase composition of natural zeolite tuff and cement.

| Phase                 | Formula                      | Content, % |
|-----------------------|------------------------------|------------|
| Cement               |                              |            |
| Alite                 | Ca$_2$SiO$_4$•CaO            | 65         |
| Belite                | Ca$_2$SiO$_4$               | 11         |
| Tricalcium aluminate  | Ca$_3$Al$_2$O$_6$           | 6          |
| Tetracalcium aluminoferrite | Ca$_3$(Fe$_{1.45}$Al$_{0.55}$)$_2$O$_5$ | 12 |
| Anhydrite             | CaSO$_4$                    | 6          |
| Zeolite tuff          |                              |            |
| Quartz                | SiO$_2$                     | 45         |
| Clinoptilolite        | KNa$_2$Ca$_2$Si$_{10}$Al$_2$O$_{22}$•24H$_2$O | 30 |
| Geylandite            | CaSi$_2$Al$_2$O$_{15}$•6H$_2$O | 10 |
| Montmorillonite       | Al$_5$(OH)$_2$Si$_3$O$_{10}$•$n$H$_2$O | 8 |
| Muscovite             | KAl$_3$Si$_3$O$_{10}$(OH)$_2$ | 7 |

Zeolite tuff was ground to a fraction of 5-10 microns using the AGO-2 mill. We used samples of Portland cement without additives, as well as Portland cement with a 5% addition of zeolite tuff. The W/C ratio was 0.4.

2.2. Methods

The puzzolan activity of the zeolite tuff additive was estimated from the mass loss curve in the temperature range of 420-560 °C. The thermal analysis was performed on a STA 409 PC (NETZSCH) device using platinum crucibles and a heating rate of 10 K/min in an oxygen atmosphere. The gas flow rate was 50 ml/min. The maximum heating temperature is 1000 °C.

Paste with the specified W/C, containing Portland cement without additives, as well as Portland cement with a 5% addition of zeolite tuff, were placed in hermetically sealed plastic bags and stored at room temperature for 28 days. Before the thermal analysis, the samples were removed from plastic bags and the hydration process was suppressed with acetone, followed by drying at 70 °C.

The phase composition of the materials used, as well as of the cement stone during the hardening process, was determined using the ARLX”TRA diffractometer (ThermoScientific, Switzerland) using software packages for qualitative analysis - PDWin 4.0 and WinXR D2.1-1; for quantitative analysis - SIROQUANT V3. Shooting conditions: copper anode, tube voltage 40 kV, shooting speed 5 deg./min.

The content of calcium hydroxide in the pastes was estimated from diffraction reflections of the portlandite mineral with interplanar distances d=4.91, 3.11, and 2.63 Å. The ettringite content was determined from reflections with interplanar distances d=5.57, 4.67, and 3.86 Å.
The degree of hydration was estimated by the ratio of the intensity of diffraction reflections of the alite mineral with the interplanar distance \(d=1.76\ \text{Å}\) in hydrated and non-hydrated Portland cement.

Acid treatment of zeolite tuff was carried out with hydrochloric acid with a concentration of 1M, 3M and 5M under static conditions for 1, 5 and 10 hours at room temperature and under heating. The ratio of zeolite tuff: acid solution was kept equal to 1:100.

To determine the strength characteristics, cement cubes were prepared with 5% addition of zeolite tuff samples with \(W/C=0.4\). The compressive strength was determined as the arithmetic mean of three individual results obtained on three cubes after hydration for 1, 7 and 28 days. The measurements were made using a MATESTE 160P105 device.

The aluminum content in the wash water after acid treatment of zeolite tuff was determined according to GOST 5382-91.

3. Results

3.1. Determination of the puzzolan activity of zeolite tuff

Puzzolan activity was evaluated by thermal and X-ray phase analysis. The results of the thermal analysis are presented in Table 2.

| Additive          | \(\Delta m_{\text{total}},\ %\) | \(\Delta m_{420},\ %\) | \(W,\ %\) |
|-------------------|-----------------|-----------------|----------|
| cement            | 16.42           | 1.07            | 6.52     |
| cement+zeolite    | 16.26           | 0.96            | 5.90     |
| cement+zeolite 3M | 16.17           | 0.81            | 5.01     |

The total mass loss of the sample and the mass loss in the temperature range 420-560 °C associated with the decomposition of calcium hydroxide are determined from the mass change curves. The proportion of mass loss due to the decomposition of calcium hydroxide is estimated. The data in Table 1 indicate that the content of free portlandite decreases in the presence of an additive of zeolite tuff. In the presence of a modified zeolite tuff additive, this effect is enhanced.

Table 3 shows data on the quantitative content of portlandite, ettringite and, indirectly, alite in cement stone samples. The content of portlandite in the presence of an additive of zeolite tuff decreases, and the acid-modified additive of zeolite tuff gives a more significant reduction. And in this part, the X-ray phase analysis data is consistent with the thermal analysis data. The addition of zeolite tuff contributes to an increase in the content of ettringite and a decrease in the content of alite.

| Composition     | Portlandite \(\text{Ca(OH)}_2\) | Ettringite \(\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot26\text{H}_2\text{O}\) | Degree of hydration, % |
|-----------------|-------------------------------|---------------------------------|------------------------|
| cement          | 9                             | 7                               | 42                     |
| cement+zeolite  | 8                             | 12                              | 45                     |
| cement+zeolite 3M | 3                             | 13                              | 47                     |

3.2. Cement strength

The results of determining the strength characteristics of samples of non-additive Portland cement and cement with the addition of zeolite tuff are shown in Figure 1.
Unmodified addition of zeolite tuff strengthens Portland cement by 20%; modified – by 28%.

3.3. Determination of aluminum content
The results of the quantitative determination of the aluminum content in the wash water after acid treatment of zeolite tuff are shown in Figure 2.

4. Discussion
In this paper, the properties of the zeolite tuff of the Lyulinsky deposit of the Khanty-Mansiysk Autonomous District-Yugra were studied. Zeolite tuff in its native form has a certain puzzolan activity, but acid treatment significantly increases it. Two independent methods (thermal analysis and X-ray phase analysis) clearly indicate an increase in the amount of portlanditite consumed in the puzzolan reaction after acid treatment of zeolite tuff.

The increase in the strength of the cement stone with the modified additive confirms the greater depth of the puzzolan reaction. Changes in the phase composition of cement in the presence of a
modified additive explain the dynamics of strength. The increase in the ettringite content recorded by us, in all probability, contributes to the strengthening of the structure of the binder part of the cement stone. The negative effect of ettringite on the properties of building materials is also known, which can manifest itself at high concentrations of calcium hydroxide in the pore fluid [19], but in our case, the mineral additive actively binds calcium and suppresses negative processes.

The acid modification conditions were optimized under the control of XRD. In this case, the criterion, on the one hand, was the preservation of the crystal structure of the zeolite (no broadening of the lines on the X-ray images was allowed), and on the other hand, the maximum degree of removal of aluminum cations from the zeolite frame. The optimal conditions for modifying the zeolite tuff were: treatment with hydrochloric acid with a concentration of 3 M for 5 hours when the mixture was heated to 80°C.

It is known that one of the characteristics that reflect the reactivity of a solid surface is its acid-base properties. By varying the concentration of aluminum ions in the aluminum-silicate framework, it is possible to influence the degree of defectiveness of the zeolite structure, creating acid centers on its surface. Our analysis of the aluminum content in the wash water during the modification of zeolite tuff showed that acid treatment leads to its dealumination, and this clearly indicates the formation of Brensted acid centers on the surface of the aluminosilicate framework.

5. Summary
So, in this work, acid modification of zeolite from tuff was carried out. The conditions of acid modification are optimized: the concentration of hydrochloric acid is 3 M, the duration of acid exposure is 5 hours, the temperature is 80°C.

It is shown that acid treatment enhances the puzzzolan activity of zeolite tuff as an additive to Portland cement.

The strengthening effect of the modified zeolite tuff additive is shown. The strength of cement samples with an additive at a similar age increases by 28%.

It is established that as a result of acid treatment of zeolite tuff, dealumination processes occur, which clearly indicates the restructuring of the zeolite framework and an increase in the concentration of active acid centers.

6. References
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