

# Composite Binders with the Use of Fine Raw Materials of Volcanic Origin

Said-Alvi Murtazaev, Sharputdi Zaurbekov, Madina Salamanova, Ramazan Bisultanov and Magomed Nakhaev

Grozny State Oil Technical University named after acad. M.D. Millionshchikov, Grozny, RUSSIA.

#### ABSTRACT

This paper presents an analysis of the mineral additives of volcanic origin usage experience for the preparation of a composite binder. In theory, it is proved that an active pozzolan, which are the chemical basis of fine raw materials of volcanic origin, allow using them as additives for cements to solve the problems of reduction in the cement stone of free calcium hydroxide content, to make full use of the potential of cement capabilities by increasing its hydration and getting stronger and stable structure of low-based calcium hydrosilicates with high sulphate. It was determined that the most important characteristics of the porous aggregates is their bulk density and compressive strength. From the porous aggregates used for the lightweight concrete the most economical are natural in case they do not need to be transported (local materials). However, artificial binders are of much more effective use in lightweight concrete aggregates. Volumetric bulk density of crushed stone and sand derived from vermiculite, depends on the quality of the breed technologies and swelling and is of 60-400 kg /  $m^3$ . The authors argue that the expanded vermiculite is usually used for the same purposes as the expanded perlite. Selection of the composition of lightweight concrete with porous aggregates. Selection of the composition of lightweight concrete with porous aggregates lies in experimental finding the amount of the raw materials that provide the necessary concrete workability, strength and weight of a given volume of the hardened concrete. The authors reveal that the deposit (structural and geological analysis is held) have great prospects to develop, and can be identified as leading in the calculation of the economic strategy of the material production.

> KEYWORDS Mineral supplements; volcanic ash; composite binders; calcium hydrosilicates; structure; dynamics.

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# Introduction

As it is known, the most energy-consuming area in the construction industry is a technological cycle for the production of cement of different brands and destination. Current approaches for designing cement industry enterprises are aimed at all-round reduction in energy costs due to extensive use of recycled resources, both for the replacement of fuel consumption, as well as for the production of composite binding on technogenic raw materials (Hanna et al., 2000; Bujdosó & Pénzes, 2012; Cas & Wright, 1987; Cayla, 2014; CORINE Land Cover 2006 seamless vector data, 2016; Dávid, 2008; Edelsbacher & Koch, 2001).

CORRESPONDENCE Said-Alvi Murtazaev 🖂 s.murtazaev@mail.ru

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In recent years in Europe, the changes in the nomenclature of produced and consumed cement towards the creation of composite binders satisfying environmental regulations are happening and are economically attractive. The development of this trend was accelerated by the introduction of the new European standard EN 197-1, according to which, together with the clinker as main components of the cement granulated blast furnace slag, pozzolans, fly ash, and calcined silicate slate dust may be employed (Nikiforov, 2007; Vasylyk, 2007; Kakali & Tsivilis, 1993; Hanna et al., 2000).

Cement sales volumes in Germany and CEMBUREAU countries of ("European Association of Cement Manufacturers" (Cembureau), which unites 27 national industry organizations) (Vasylyk, 2007; EUROPEAN STANDARD EN 197-1:2000, 2000; Opoczky, 1993), the percentage of the composite binder is more than 50%, of which the low-marked cement share is 90%. The increased production of the composite binder favors the reduction of pollution in general, and because of the low CO2 emissions, in particular, and, of course, the less energy consumption. European experts believe that the era of cement with no addons has passed, as evidenced by the introduction of a new All-Union standard 31108-2003 in Russia, allowing the input of mineral additives.

### Materials and Methods

Thus, now the question to optimize binding of nomenclature, increasing the share of manufacture composite binders by engaging in the production of natural recycled material of various origin is relevant (Frey et al., 2006; Mitchell, 1989; Fuertes-Gutierrez & Fernandez-Martinez, 2010).

Cement is the most expensive component of concrete, so the researchers seek to replace part of it at a cheap and affordable mineral materials. These include many inorganic materials composition, which, unlike the chemical additives are not soluble in water (Gusev et al., 1999; Belov & Smirnov, 2009; Fassoulas et al., 2012).

Mineral additives used for producing composite binders can be divided into two large groups: mineral additives having hydraulic properties (AMD) and additives fillers that improve the grain structure and composition of the hardened cement paste and concrete.

In accordance with All-Union standard 31108-2003 as mineral supplements, as the basic components, granulated slag cement, mineral supplements, active pozzolans (natural or artificial pozzolana, fuel ash, including acidic or basic fly ash, silica fume, burned shale and gliezh) filler and additive - limestone on the corresponding standard documentation are used: as the secondary cement components may be used various mineral supplements that will not significantly increase the water demand of the cement and reduce the durability of concrete.

The traditional technology of producing composite binders envisages mixed grinding of clinker, gypsum and mineral supplements in the amounts allowable by regulatory requirements (Gray, 2004; Gross et al., 2007; Coenraads & Koivula, 2007). At the same time, it is found that each additive has its own optimum dispersion, therefore, there is no need in mixed grinding of clinker and mineral additives in the manufacture of cement. It is believed that the additive should be milled separately from the optimum dispersion and they should be entered while the preparation of cement or into concrete mix.

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### Results and Discussion

In this study, we found that in the production of composite binders the volcanic mineral supplements can be used effectively. Volcanic rocks are pyroclastic ones composed of bonded together fine clastic products of volcanic emissions and the smallest dust particles of lava. Larger debris fall on the slopes of volcanoes, the smallest particles are cooled by air and deposited on the ground in the form of volcanic ash. If volcanic ash retains this earthy-loose structure, it is often referred to ashes; if it is converted into a porous stonelike breed as a result of secondary processes - the volcanic tuff.

By chemical composition additives of volcanic origin consist mainly of silica and alumina (70-90%), there is a small amount of CaO and MgO (2-4%), Na<sub>2</sub>O and K<sub>2</sub>O alkali (3-8%) and hydrated water removed when ignition (5.10%). in phase composition, they are a mixture of partially amorphized glass (50-80%) and some aluminium silicates, as well as hydrates thereof in the crystalline state. Typically, they contain of various alloys. The volume of the volcanic rocks ranges from 2300-2600kg/m<sup>3</sup>. Bulk weight is in the average 1200-2000 kg/m<sup>3</sup> (Vasylyk, 2007; Murtazaev et al., 2014; 2015a; 2015b).

The volcanic ash has been used 2,000 years ago in ancient Rome. Roman builders produced cement for marine structures, mixing lime and volcanic rocks. This mixture was placed in a wooden mold, where sea water is added, which immediately caused a high-temperature chemical reaction of lime slaking. As a result, strong cement blocks were produced, the main laminating substance in which is not the calcium-silicate hydrate (C-S-H), but calcium aluminum silicate hydrate (C-A-S-H).

The scientists describe an extremely rare mineral - aluminum tobermorite - one of calcium Hydrosilicates (formula -  $AlCa_5Si_6O_{16}(OH)_2 \cdot 4H_2O$ ), which is formed by a chemical reaction of cement with sea water. Roman concrete did not break up, staying in an aggressive marine environment, and is considered to be one of the most wear-resistant building materials on the planet.

In ancient Apmenia the vulcanic ash and tuff served as the raw material for solid bricks and blocks, which have long been popular among the residents. Since the strength of vulcanic ash bricks is identical to the strength of the best contemporary brick. Scientists from Argentina proposed a number of innovative technologies which allow to apply the vulcanic ash for the production of bricks without much expense. Japanese architects have designed a building made of bricks, which are compressed with the addition of the ashes of an ancient volcano of Japan - Sakurajima. Japanese scientists were able to establish that the addition of volcanic ash in the mass of bricks for the construction increases the thermal conductivity of the material, it improves moisture resistance and increases its strength.

Volcanic plaster was developed in Japan and it is the main component of volcanic ash. This plaster completely absorbs unpleasant odors, harmful and toxic substances. A healthy atmosphere within the walls of the house covered with this material, is guaranteed to be provided. This plaster remains a constant, comfortable to humans, humidity level, ie, will absorb excess moisture in a damp room and extract in a dry one. And besides, this material does not burn.

In countries where there are large deposits of volcanic ash, the revival of this technology can be economically justified. The rocks of volcanic origin in Russia are located in Kabardino-Balkaria and on the Kamchatka Peninsula, and they are unique raw material for the construction industry. In Kabardino-Balkarian Republic (KBR), seven deposits of volcanic rocks are known: Zayukovskoe (tuff), Kamenskoe (tuff), Kurkuzhinskoe (tuff, ash), Lechinkaevskoe (facing tuff), Nalchik (volcanic tuff, ash, pumice) Kenzhenskoe (volcanic ash, volcanic tuff), Belorechenskoye (volcanic ash). On Fig. 1 and 2 Kenzhenskoe deposit of volcanic rock and Kamensky developing quarry of volcanic ash are shown.



Figure 1. Location of volcanic ash and tuff in KBR



Figure 2. Kamensky volcanic ash quarrying

In Kabardino-Balkarian Republic (KBR), the volcanic ash is used as a lightweight aggregate in claydite concrete, in dense and porous construction-grade thermal insulation rush concrete B3,5-B7.5, average density of 1200-1550 kg/m<sup>3</sup> and in plaster solutions.

It is often asked about the radioactivity of rush consrete, believing that if the ashes is of volcanic origin, it may be radioactive. There All-Union standard 8736-93 which determines the specific effective activity of natural radionuclides: radium Ra226, thorium Th-232 and potassium K40. The standard value of the sum of the three elements of performance should be  $A_{\rm eff}$  = 370 Bq / kg., specialized test results of volcanic ash CBD show  $A_{\rm eff}$  = 274.4 Bq / kg, indicating the accordance of volcanic ash for all types of construction.

It is found (EUROPEAN STANDARD EN 197-1:2000, 2000; Murtazaev et al., 2014; Salamanova et al., 2014) that the initial acceleration stage of hydration «C<sub>3</sub>S - volcanic ash" system happens because the surface of additives favorably affect the precipitation of hydrates, absorbing the ions of calcium, reduces their concentration in the solution and accelerates the dissolution of the C<sub>3</sub>S. Hydrates accumulate in zones around the C<sub>3</sub>S grains. Formation of structure of calcium hydroxide released

during the hydration of cement, with active additives components. The reaction of the interaction of  $Ca(OH)_2$  with  $SiO_2$  of the vulcanic ash can be represented by the following equation:

$$xCa (OH)_2 + SiO_2 + nH_2O = x CaO \cdot SiO_2 \cdot mH_2O$$

Within the interaction of silica with additions of  $Ca(OH)_2$ , the calcium hydrosilicates are formed similar to tobermorite with a ratio of  $CaO / SiO_2 = 0.8-1.5$ , and the composition of the silica depends on the variety of cristobalite and may reach the limit  $2CaO \cdot SiO_2 \cdot H_2O$  (Kakali and Tsivilis, 1993; Opoczky, 1993).

## Conclusion

Thus, the analysis of the problem of obtaining the composite binders based on the use of fine raw materials of volcanic origin shows that an active pozzolan, being its chemical basis, allows to solve the following problems as additives for cement:

- Decrease of free calcium hydroxide in the cement stone;

 Make full use of the potential capabilities of cement by increasing the degree of hydration;

- Getting strong and stable structures of low basic calcium hydrosilicates with high sulphate.

### **Disclosure statement**

No potential conflict of interest was reported by the authors.

#### Notes on contributors

Said-Alvi Murtazaev, PhD, head of the department of Construction production technology on the faculty of Civil engineering at the Grozny State Oil Technical University named after acad. M.D. Millionshchikov, Grozny, Chechen Republic.

Sharputdi Zaurbekov, PhD, head of the department of Ecology and nature management on the Geological and industrial faculty

at the Grozny State Oil Technical University named after acad. M.D. Millionshchikov, Grozny, Chechen Republic.

Madina Salamanova, PhD, assistant professor of the department of Construction production technology on the faculty of Civil engineering at the Grozny State Oil Technical University named after acad. M.D. Millionshchikov, Grozny, Chechen Republic.

**Ramazan Bisultanov**, senior lecturer of the department of Construction production technology on the faculty of Civil engineering at the Grozny State Oil Technical University named after acad. M.D. Millionshchikov, Grozny, Chechen Republic.

**Magomed Nahaev**, PhD, assistant professor of the department of Construction production technology on the faculty of Civil engineering at the Grozny State Oil Technical University named after acad. M.D. Millionshchikov, Grozny, Chechen Republic.

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