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Development of composite binders based on volcanic tuff waste

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ABSTRACT

Large-scale wastes have accumulated from local volcanic tuff extraction in the Republic of Armenia. Like their natural rock material, they have a great range of colors and high chemical activity. This waste completely occupies precious space in an already scared space of republic. As a result, soil degradation and groundwater supply disruption occur, both of which are severe environmental problems. When humans or animals inhale the smallest particles in the air, apart from economic and ecologic issues, it causes health problems. The study aims to produce sodium-silicate composite binders that will enable large-scale accumulated waste to be used in making non-cement, artificial stone materials for tiles, architectural elements of buildings, and other stone items. The research carried out allows us to solve environmental problems such as the utilization of waste rock, degradation of agricultural land, economical use of natural resources (the extraction of mountain rocks), and the production of ecologically clean composites.

Keywords: Volcanic rock, Waste material, Sodium silicate, Dolomite, Non-cement artificial stone, Compressive strength, Softening coefficient.

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1. INTRODUCTION

The construction industry has no toxic emissions like the chemical, petrochemical, and metallurgical industries. Despite this, the quantity of raw materials required is so high that it is one of the most damaging environmental factors. A billion tonnes of resources are extracted from the environment annually for building materials production, resulting in a high amount of waste accumulating in nature. Industrial waste causes damage to the environment. Serious environmental problems arise. This waste serves as a source for new types of binders and building materials, which can be used for different purposes. Compared to the use of natural raw materials, which are used for these purposes, their use will not only have a positive impact on the environment, but it will also save up to 30% on building material costs (Manturov and Toturbiev, 2007; Al-Zboon et al., 2016; El-Shafie, 2021; Játiva et al., 2021). Given the above, the search for new and effective ways to involve industrial waste in the production of construction materials remains an urgent issue. Our republic is known worldwide for its rich reserves of tens of billions of cubic meters of volcanic rock, especially varieties of tuff, endowed with valuable construction and decorative features. For generations, Armenians have used them to construct religious, residential, and other functional structures. Because of the large-scale extraction of mechanical sawing of stone, a high quantity of waste has accumulated in the exploited mines, which occupy significant areas of our already sparsely populated republic, causing environmental issues. The utilization of the abovementioned tuff waste should be considered an urgent economic and environmental challenge (Muradyan, 2020; Badalyan et al., 2021). The high energy capacity of clinker binding materials and the capital investments cause the new non-cement materials' development and consumption for lightweight concrete. The production of composite binders using alkaline-activated wastes formed during rock extraction is considered in this study. The scientific novelties presented in this work include the production of composite binders using volcanic tuffs, specifically their extraction waste; the use of a joint grinding process to create a silicate lump binder; and the incorporation of dolomite natural rock fine-disperse powder as a solidifying and water resistance-increasing additive in the production of composite binders.

2. MATERIALS AND METHODS

2.1. Raw Materials

In this work, three types of tuff stone extraction wastes, Byurakan, Yerevan and Artik (from the Agarak, Armavir and Artik mines of the Ashtarak region, respectively), are considered characteristic preliminary examples. This research investigates three varieties of tuffs from Burakan, Yerevan and Artik (Agarak, Armavir and Artik mines of the Ashtarak region) as typical examples of mining waste. Armenia has tuffs of different colors, which will allow us to produce artificial stones with a wide range of colors.

Low density and thermal conductivity, high strength and durability are tuff characteristics, as well as incomparable ease of processing, high-decorative qualities and color diversity, acid resistance, and, in some cases, the ability to withstand high temperatures (Arzumanyan et al., 2018; Arzumanyan et al., 2019). An average of the main physical and mechanical characteristics of these raw materials is given in Table 1, which were determined in the Scientific Experimental Laboratory of Construction Materials in the National University of Architecture and Construction of Armenia.

In this work for the production of sodium silicate composite binders, the grinding of dolomite of sedimentary origin was used as a hardening additive to increase water resistance (Arzumanyan et al., 2015; Sahakyan and Arzumanyan, 2021).

Dolomite is a carbonate rock composed of 90% of dolomite minerals. It is composed of calcium and magnesium double carbonate, $CaMg(CO_3)_2$. Dolomite is white, but the iron and clay impurities changed the color to gray, sometimes yellow-gray and greenish, with a trigonal crystal system (Warren, 2000; Mehmood et al., 2018). Dolomite from the Tavush region’s Lusadzor mine was studied.

Sodium silicate glass was used as a binder, which, as a result of grinding together with the above-mentioned stone raw materials, ensures homogeneous volume distribution in the mixture and does not significantly affect the color of aluminosilicate rocks. A Silicate lump is a substance composed of water-soluble alkaline silicates: $R_2O \cdot nSiO_2$ (R_2O alkaline oxide). It is a solid, vitreous product obtained by melting quartz sand and soda ash to form Na_2CO_3 (also sodium sulfate, Na_2SO_4) or potash, K_2CO_3 (depending on which silicate is needed, sodium ($Na_2O \cdot mSiO_2$) or potassium ($K_2O \cdot mSiO_2$), which occurs at a temperature of 1300–1400°C. After the melt cools in the air, it hardens into a silicate lump (Sychev, 1986; Rybiev, 2008; Dvorkin and Dvorkin, 2011; Manturov, 2012; Sahakyan et al., 2013). In these experimental studies, a dry sodium-silicate lump with a module of M = 2.90, produced by the former factory of Yerevan lamps, was used.

Table 2 shows the average chemical composition of raw aluminosilicate rocks, dolomite, and silicate glass lumps, which were determined in the Scientific Experimental Laboratory of Construction Materials of the National University of Architecture and Construction of Armenia.

2.2. Specimen Preparation

In this study, the composite binders were made by combined grinding of aluminosilicate, silicate lumps and dolomite hardener, mixing with water and drying. After joint grinding of all components, a powder was obtained with a specific surface area of 3000–3500 cm^2/g, which exhibited binder properties in aqueous mixtures. The water/binder ratio in the composite binders prepared was w/b = 0.10–0.12. The resulting mixtures were then transferred into cylindrical molds with height and diameter of 50 mm and subjected to vibration under a load of up to 20 MPa. The prepared test samples were subsequently removed from the molds and placed in a dryer, where they underwent drying at 180–200°C.

From the waste of each type of rock, six components were developed, in which the percentages of silicate lump (SL) and dolomite hardener (D) according to the total mass of the dry mix were: SL/D = 5/30, 10/30, 20/30, 30/30, 40/30, 50/30.

In the experiments performed, the dolomite solid content was taken at 30%, which ensured the necessary water resistance (Muradyan, 2020). Cylindrical examples of h × d = 50 mm made from mixtures passed through the following drying regimes: temperature rise from 20 ± 2°C to 90 ± 5°C in 1.5 h; keep at 90 ± 5°C temperature conditions in 2.5 h; temperature rise to 00 ± 5°C in 1 h; keep under 200 ± 5°C conditions in 2 h. (Fig.1). Images of sodium silicate composite binders developed from extraction wastes of Byurakan, Yerevan and Artik type tuffs are presented in Fig. 2.

To test the proposed hypothesis, a corresponding thermodynamic calculation was carried out (Sahakyan et al., 2019; Sahakyan et al., 2022). This calculation showed that the volcanic rocks and glass phases actively interact with the combined binder (sodium silicate and dolomite) to form calcium-aluminate, which ensures the slow setting of the mixture under natural conditions. Moreover, raising the temperature to 180–200°C leads to the activation of these reactions. In a short time, it provides fast and significant hardening of the masonry.

2.3. Analytical Methods

The density of the test samples was determined according to the EN 1936:2007 standard for “Natural stone test methods - Determination of real density and apparent

Table 1. Average values of physical and mechanical characteristics of raw aluminosilicate rocks

Name of rocks	Average density (kg/m^3)	Porosity (%)	Water absorption by mass (%)	Compression strength (MPa)	Softening coefficient
Byurakan type gray tuff	1762	34.6	11.8	25.4	0.85
Yerevan type black tuff	1669	33.5	12.5	19.7	0.82
Artik type pink tuff	1375	46.6	23.3	13.3	0.89

Table 2. Average data on the chemical composition of the raw materials

Material type	Chemical composition (wt.%)									
	SiO_2	Na_2O	TiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	$Na_2O + K_2O$	SO_3	L.i.
Byurakan type tuff	61.4	—	0.90	17.2	5.43	4.24	1.84	7.50	—	1.49
Yerevan type tuff	63.4	—	0.84	16.3	4.77	3.87	1.41	7.30	0.09	2.02
Artik type tuff	65.2	—	0.67	16.4	4.20	3.11	1.42	7.95	0.51	0.54
Dolomite	0.11	—	0.10	1.00	0.65	32.7	22.5	—	—	42.9
Sodium silicate	72.5	24.9	—	1.05	0.65	0.70	—	—	—	0.20

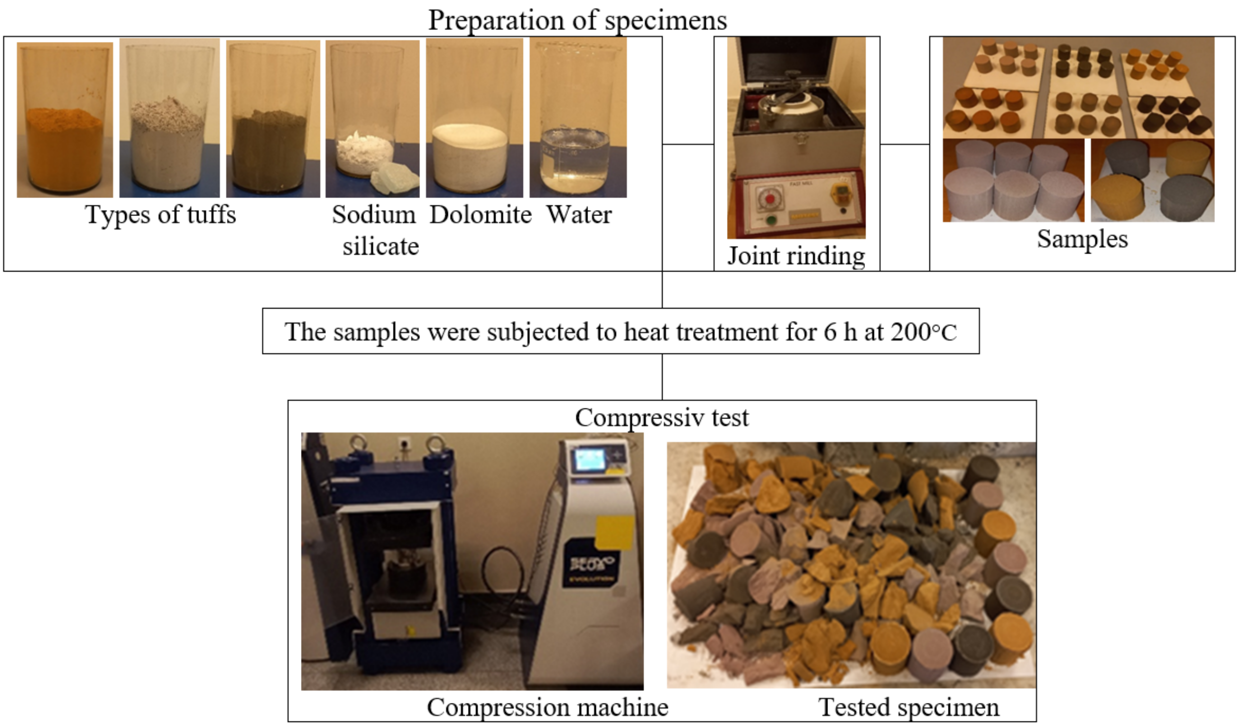

Fig. 1. Diagram of the experimental procedure

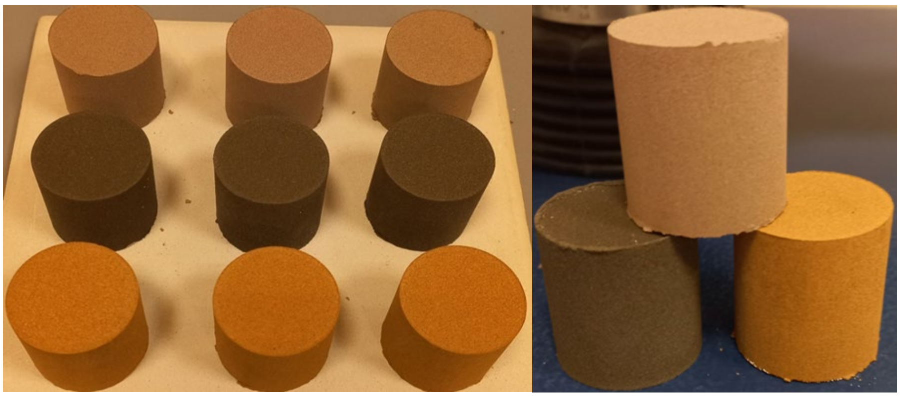

Fig. 2. Images of sodium silicate composite binders developed from extraction wastes of Byurakan, Yerevan and Artik type tuffs

density, and of total and open porosity".

Compressive strength (Com) was determined for the specimen in accordance with AST 100-94 (Building stones from tuff, basalt and travertine: Specifications). The tests were performed using a 2000 kN load electromechanical hydraulic testing maschine (Concrete compression machine 2000 kN automatic, Servo-Plus Progress).

The samples taken from specimens tested for compressive strength were dried to constant mass and ground in a porcelain pounder to fully pass through a sieve with a clear square opening of 63 µm. The resulting powders were tested by X-ray diffraction.

3. RESULTS AND DISCUSSION

3.1. Density

After completing the drying regime, the densities (ρ) of the cylindrical test samples were determined. Firstly, the test samples were weighed with an accuracy of 0.01 g (m). Then, their linear dimensions were measured with a caliper with an accuracy of 0.10 mm, and their volumes (V_0) were calculated geometrically based on these measurements. Using the obtained data, the densities of test samples were determined according to the formula

$$\rho = \frac{m}{V_0} \quad (1)$$

The density indicators of the test samples made with Byurakan type tuff wastes were ρ = 1952–1973 kg/m^3, which is more than 12% higher than the density index of natural stone material (1762 kg/m^3). The density indicators of the test samples made with Yerevan type tuff wastes were ρ = 1838–1855 kg/m^3, which is more than 11% higher than the density indicator of natural stone material (1669 kg/m^3). Finally, the density indicators of the test samples made with Artik type tuffs were ρ = 1914–1942 kg/m^3, which is more than 41% higher than the density indicator of natural stone material (1375 kg/m^3). The results obtained indicate that the test samples prepared by vibration with load have sufficient densities, which makes the obtained composite binders suitable for use in the compositions of artificial stone materials.

3.2. Compressive Strength

After drying the samples were tested and the compressive strength was determined. The results are shown in a diagram (Fig. 3), where the silicate lump/dolomite ratio (SL/D) is presented.

The results show, that with the same content of ground dolomite (30%), along with the increase in the amount of sodium silicate lumps (20–40%), the compressive strength of the test samples also increases: Com = 20–35.4 MPa, when SL/D = 20/30, 30/30, 40/30. That is, the use of silicate lump contributes to the increase in the strength of composite binders compared to the strength of natural rocks. When compared to the strength of natural rocks of the same tuff, composite binders made with Byurakan - type tuff waste increased by 10.7%–39.4%, those made with Yerevan-type tuff increased 9.60%–14.2%, and Artik tuff increased by 8.3%–12.8% and also does not change the natural color of tuffs, which allows the latter to be used for the production of decorative structures.

The decrease in the strength of the samples due to the further increase in the sodium silicate lump content is explained by the fact that the hydrated and then dried sodium silicate compared to tuff waste has a lower strength. Additionally, a lot of water is used to dissolve high amounts of silicate, which further affects on strength.

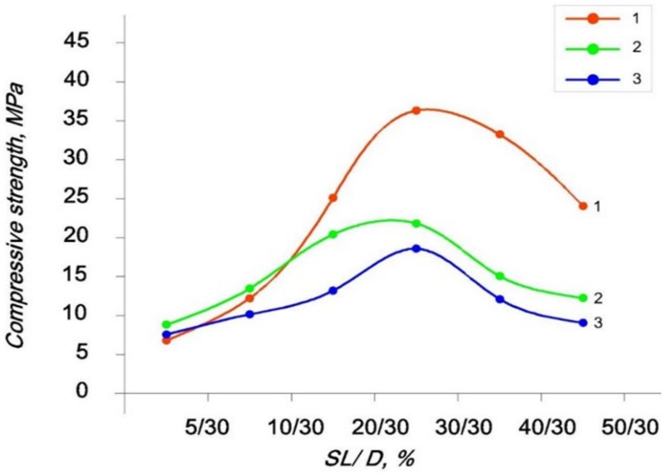

Fig. 3. Dependence of the composite binder's compressive strength on the SL/D ratio: 1- Byurakan tuff, 2-Yerevan tuff, 3-Artik tuff

3.3. Softening coefficient

The softening coefficient of the sodium silicate composite binders must be taken into consideration, because they should be used as a binder for manufacturing interior and exterior facing tiles, architectural components, and other stone materials. The test samples were kept in water at a temperature of 20 ± 2°C for 48 h. After they were subjected to a compressive strength test. The softening coefficient was determined for each type of composite binder made with tuff.

According to the current standard (GOST 9479-2011 (EN 1467:2003, NEQ)) for the softening coefficient of facing slabs made of natural stone materials, a value range of Ks = 0.65–0.70 is defined, which is satisfied by SL/D (silicate lump/dolomite) ratios of 20/30, 30/30 and 40/30. Test samples prepared by ratio indicate that Byurakan type tuff has Ks values ranging from 0.75–0.82, Yerevan type tuff has Ks values ranging from 0.70–0.85, and Artik type tuff has Ks values ranging from 0.70–0.83.

Fig. 4 shows the dependence of the softening coefficients of composite binders on the SL/D (silicate lump/dolomite) ratio. At a temperature of 200°C, the composite binders provide the above-mentioned normative sufficient water resistance with compositions of SL//D = 20/30, 30/30 and 40/30 ratios.

3.4. X-ray Diffraction

The X-ray analysis of sodium silicate composite binders based on Byurakan (Agarak), Yerevan and Artik tuffs is illustrated in Fig. 5.

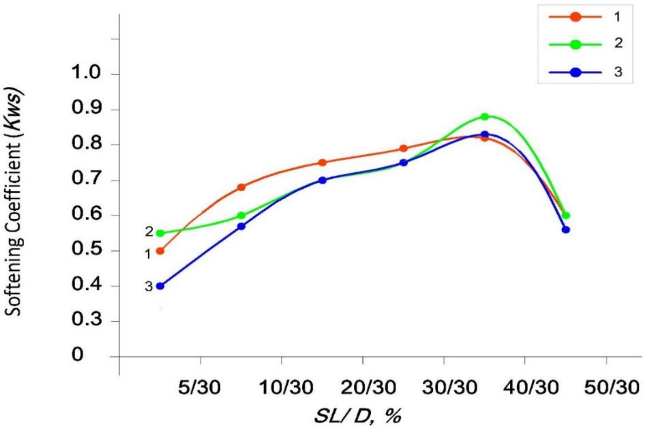

Fig. 4. Dependence of the composite binder's softening coefficient on the SL/D ratio: 1- Byurakan tuff, 2-Yerevan tuff, 3-Artik tuff

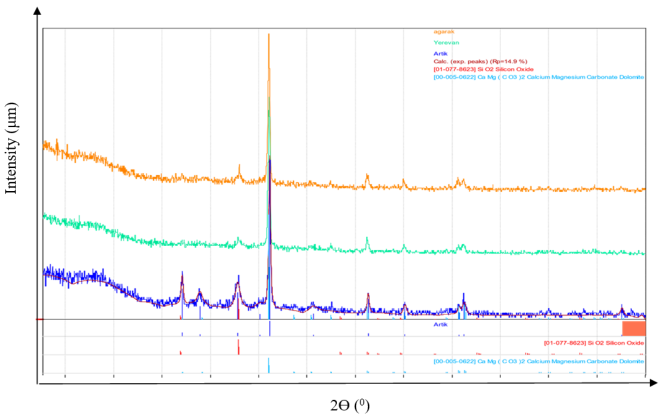

Fig. 5. X-ray analysis results of sodium silicate composite binders based on Byurakan (Agarak), Yerevan and Artik tuffs

X-ray analysis revealed that the specimens' hydration and hydrolysis resulted in the formation of silicon oxide (hydrogel, SiO_2), calcium and magnesium carbonate-dolomite $CaMg(CO_3)_2$ and $Na_2O{\cdot}SiO_2{\cdot}\,6H_2O$, which interacts with the surface layer of active sand dust and forms a solid mass through binding (Azimi et al., 2016; Yu et al., 2023).

3.5. Discussion

This examination study investigated the effects of specific amount of silicate lumps (SL) and dolomite rock (D) powders on tuff waste. To achieve this, the study selected ratios of 5%, 10%, 20%, 30%, 40% and 50% of silicate lumps and 30% of dolomite to tuff powders.

After heat treatment, the test samples were evaluated for their density, compressive strength, and softening coefficient indicators. These results were then compared with the same properties of natural stone materials. Table 3 presents the comparative data for the density, compressive strength, and softening coefficient of composite binders made from natural tuff stones and their waste.

Analyzing the data in Table 3, it can be concluded that:

- The density of the test samples made with Byurakan tuff stones increased by 10.2%–12% compared to the density of natural stone material. The density of the test samples made with Yerevan type tuff increased by 10.1%–11.1% compared to the density of natural stone material. The density of the test samples made with Artik type tuff increased by 39.2%–41.1% compared to the density of natural tuff stone.
- Based on the data in Table 3, the following observations can be made: The the compressive strength indices of the test samples made with Byurakan tuffs increased by 10.7%–39.4% compared to the the compressive strength index of natural stone material. The the compressive strength indices of the test samples made with Yerevan type tuff increased by 9.6%–14.2% compared to the the compressive strength index of natural stone material. The compressive strength indices of the test samples made with Artik type tuff increased by 8.3%–12.8% compared to the compressive strength index of natural tuff.
- The test samples made with all types of tuffs, silicate lumps, and dolomite used in this work exhibited sufficient water resistance, and their softening coefficients met the requirements of the GOST 9479-2011 (EN 1467:2003, NEQ) norm.
- Compositions developed with silicate lumps and dolomite with SL/D = 20/30, 30/30 and 40/30 and tuffs are the best chosen.

Table 3. Comparative data of physical and mechanical properties of natural stone materials and composite binders obtained on their basis

Name of rocks		Average density (kg/m^3)	Compression strength (Mpa)	Softening coefficient
Byurakan type gray tuff	natural	1762	25.4	0.85
	artificial	1952–1973	28.0–35.4	0.75–0.82
Yerevan type black tuff	natural	1669	19.7	0.82
	artificial	1838–1855	21.6–22.5	0.70–0.85
Artik type pink tuff	natural	1375	13.3	0.89
	artificial	1914–1942	14.4–15.0	0.70–0.83

Based on the analysis of the conducted research, it is evident that the mixture of finely dispersed powders obtained through joint grinding of tuff stone, silicate lumps, and dolomite rock, when combined with water and subjected to heat treatment (180–200°C), results in the formation of sodium silicate composite binders. These binders exhibit sufficient indicators of strength and water resistance, and can be used as an alternative binder to Portland cement.

The results obtained from this study are considered to be significant standards that provide an opportunity to utilize these composites as a binder in non-cement concrete compositions. Sodium silicate composite binders obtained from volcanic rock mining waste are planned for use as binders in the production of non-cement items. From the aforesaid, it can be concluded that volcanic rocks are suitable from an economic, physical and mechanical point of view as well as from the point of view of durability for use as raw materials for the production of composite binders (Djobo et al., 2016; Bashar et al., 2019).

4. CONCLUSION

In the RA, it is possible to produce sodium silicate composite binders based on large-scale rock waste accumulated during the extraction of various types of tuffs, which is causing environmental problems. On the basis of silicate lump, being an initial material for liquid glass production, and large reserves of dolomite rock, abandoned in the republic's crust, it is possible to produce sodium silicate composite binders. The mentioned binders have a sufficient density (ρ), compressive strength (Com) and softening coefficient (Kws), which allows them to be used as a binder materials in non-cement concrete compositions.

The results of this study indicate that the sodium silicate composite binders obtained can be utilized as binders in cement concrete compositions. Additionally, since the final products have a color equivalent to that of natural stone materials, they can be used in the production of external and internal facing slabs of buildings, various architectural elements, and other stone preparations. Considering that the production of sodium silicate composite binders utilizes rock waste from the extraction of natural rocks (tuffs) as the main component, these binders have a relatively low cost. The consumption of tuff waste can solve the waste utilization problem and reduce the extraction of stone materials.

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