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Evaluation of the use of an alternative mixture for pore filling material on travertine slabs

Traverten plakalarda gözenek dolgu malzemesi için alternatif bir karışımın kullanımının değerlendirilmesi

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Abstract

Because of their natural porous structure, travertines are widely preferred building stones in terms of their decorative properties. This porous structure causes the stone having high water absorption capacity. Therefore, especially in outdoor applications, filling process is applied in order to decrease the porosity of the stone and thus lower the effect of atmospheric conditions. Powder calcite, white cement and various colorants are widely used in filling operations. The presence of calcite in the mixture directly increases the cost. In this study, the use of travertine powder instead of calcite was investigated and for this purpose, mixed filling materials with travertine powder/cement ratio were produced in laboratory condition as 4 different mixing ratios by weight (1/0.5, 1/0.7, 1/1, 1/1.5). Another group of filling material is formed as a mixture of calcite/cement (1/1) which is widely used in commercial production. The obtained results showed that the unit weight values were increased about 0.32 - 0.54% and the water absorption values decreased by 11.71-19.25 % when travertine powder filling was used. It was determined that capillary water absorption values significantly decreased between 27.95%-54.62 % for all natural stone groups. Similarly, there was a decrease about 9.54-19.21% in the apparent porosity values. The results revealed that, in the mixing ratios of 1/1 and 1/0.7 (travertine powder/cement) an increase in unit weight values and the highest reduction in water absorption values were observed. The data obtained by this study are presented in such a way that both the wastes can be evaluated and the production costs can be reduced by the choice of the application of filler mixtures to be formed by the use of their own powder.

Keywords: Artificial surface filling, Natural stone, Travertine, Water absorption.

Öz

Travertenler doğal gözenekli yapıları nedeniyle dekoratif anlamda kullanılabilirliği fazla olan doğaltaşlardır. Bu gözenekli yapı, taşta su emmenin de yüksek olmasına neden olmaktadır. Bu yüzden özellikle dış mekân uygulamalarında taşın gözenekliliğini ve dolayısı ile atmosferik koşullardan etkilenme derecesini azaltmak amacıyla dolgu işlemi uygulanmaktadır. Dolgu için toz kalsit, beyaz çimento ve çeşitli renklendiriciler yaygın olarak kullanılmaktadır. Karışım içerisinde kalsitin bulunması doğrudan maliyeti artırmaktadır. Bu çalışmada kalsit yerine traverten tozunun kullanılabilirliği araştırılmıştır ve bu amaçla ağırlıkça oluşturulmuş 4 farklı karışım oranında (1/0.5, 1/0.7, 1/1, 1/1.5) traverten tozu /çimento karışımlı dolgu malzemeleri laboratuvar ortamında üretilmiştir. Diğer bir grup dolgu malzemesi ise ticari üretimde yaygın olarak kullanılan kalsit/çimento (1/1 oranında) karışımı şeklinde oluşturulmuştur. Elde edilen sonuçlar dolgulu travertenlerde birim hacim ağırlığı değerlerinde % 0.32-0.54 oranlarında artış, ağırlıkça su emme değerlerinde ise % 11.71-19.25 oranlarında azalma olduğunu ortaya koymuştur. İncelenen doğaltaş grubunun bütünü için kapiler su emmenin belirgin bir şekilde, % 27.95-54.62 arasında değişen oranlarda azaldığı tespit edilmiştir. Benzer şekilde görünür porozite değerlerinde de % 9.54-19.21 oranında azalmalar meydana gelmiştir. Elde edilen sonuçlara göre 1/1 ve 1/0.7 oranlı (traverten tozu/çimento) karışımlarda birim hacim ağırlıklardaki artışla su emme değerlerinde en fazla azalmaların olduğu belirlenmiştir. Bu çalışma ile elde edilen veriler, üretimi yapılan travertenin kendi tozunun kullanılması ile oluşturulacak dolguların uygulamada tercih edilmesi ile hem artıkların değerlendirilmesi hem de üretim maliyetlerinin düşürülebileceği ortaya konulmuştur.

Anahtar kelimeler: Yapay yüzey dolgusu. Doğaltaş, Traverten, Su emme.

1 Introduction

Travertines are thin bedded and laminated carbonate deposits formed when carbonated water springs out from a fracture in the ground in the vicinity of karst or hot springs, and also in small rivers and swamps [1]. Due to their porosity they have sound and heat isolation properties. In other words, they can breathe and absorb light. They are light and economical natural materials that do not contain any substance harmful for human health. These characteristics make this stone one of the valuable natural building stones. Despite these positive features their high porosity, and richness in $CaCO_3$ cause low resistance to chemical and physical dissociation conditions. Besides the fractured and cracked structure of natural stones, porosity is of great importance both for the production and marketing of the stone. The porous structure reduces the commercial value of the stone for many natural stone types. However, especially for travertines, this has to be accepted as the nature of the stone. This feature, which distinguishes travertine from other natural stones in terms of decorative appearance, can also cause various problems. Therefore, it is tried to reduce the degree of exposure to atmospheric conditions by filling the pores in travertines, especially in outdoor use. The filling of the pores also provides more convenient possibilities for different surface treatment methods.

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There are many studies on travertines. While some of them investigated their sedimentological and petrographical properties [2]-[7] and some of them their physical and mechanical properties [8]-[11]. There isn't any reference directly related to this study in the literature.

In this study, the usability of a mixture formed by using the stone itself was investigated instead of different types of materials used as fillers in travertine production. In the market, it is known that mixtures of white cement, calcite and various colorants are widely used for travertine pore filling. In such applications, calcite can be supplied directly from the abroad in micronized form and used in the production stage. The main purpose of this study is to demonstrate the usability of powdered travertine itself instead of calcite in the mixture.

2 Materials and methods

The travertine samples used in the study were selected from Denizli region. 55 cube samples (7*7*7 cm) were provided for experimental studies. 40 of these were divided into 5 groups, each group consisting of 8 samples. With the experiments prepared at different mixing ratios, the unit volume weight, water absorption by weight, water absorption by volume and capillary water absorption rates of travertine samples with and without filling were measured.

3 Filling types and usage in travertine

Filling is an application that can be applied to all natural stone groups of magmatic (granite, syenite, gabbro, etc.), metamorphic (marbles) and sedimentary (limestone, travertine) origin and its main purpose is to reduce the impact of the stone from atmospheric conditions while preserving its surficial textural properties. This application is intended to fill the whole visible pores in the stone. For this purpose, epoxy, polyester, ultraviolet, mastic, cement and surface protection materials are used for filling processes. It is known that polyester filler and cement filler are the most commonly used fillers in applications [12]. The main types of fillers used in practice are presented below.

3.1. Polyester resin filling

Polyester resins are used to reinforce the natural stones having unfilled pores and all natural stones except brittle natural stones. Polyester resins have high flexibility in application. They can be applied with or without mesh on the back of the stone and colored or transparent on the front. When the application is made on the front surface of the stone, crack repairing and pore filling can be made together and the polish quality also increases. In the polyester filling method, melting cavities occur with the effect of hot polyester in the rock and as a natural result of this, porosity of the rock increases. Since this phenomenon makes the rock weaker in strength, polyester filling is less preferred than cement filling.

3.2. Epoxy resin filling

The application of epoxy is mainly used for joining and reinforcing problematic natural stone materials. With this application the epoxy penetrates the rock and becomes more stable and durable. This filling application is usually part of the slab/tile production line and can be applied after rough wear on natural stone. Depending on the strength of the stone, the resin can be applied to one or both surfaces of a plate [13]. A reinforcing mesh is often used in conjunction with epoxy to reinforce the back of the stone. Natural stones such as crystallized limestone and marble can sometimes be broken during fine cuts or during polishing so that epoxy applications are made in order to reduce the resulting loss rate and also to increase the strength of the stone by filling the cracks and pores before calibration and final polishing.

3.1 Sealant filling

Mastic fillers are usually obtained by mixing polyester resins, some amines, calcium and similar powders with homogenizing and accelerating additives [14]. They can also be used as paint additive and unpainted for retouching and bonding of pore fillers. Mastic fillers are designed to fill the pores with a continuous system. They harden very quickly and make the stone polishable 7-10 minutes after application. It is possible to reduce this time up to 3 minutes using some accelerators and suitable furnaces. By using ultraviolet mastics, it can be ensured that the period of application of the stone to polish is much shorter [14].

3.3. Cement filling

This filling type is a widely used method for filling pores in natural stones such as travertine. Suitable amounts of white cement, calcite, kaolin and oxide in different colors are used together with binding glue to reduce crumbling, improve polish quality and shorten freezing time. It was observed in the experiments that cement fill type does not cause any deterioration in the structural form of the rock [15]. It is determined that the cement filling forms the rock environment which are impermeable and homogeneous structure due to filling the pores completely [15]. For this reason, it has been observed that the compressive strength values are higher while porosity and water absorption characteristics are lower in porous rocks where such filling is applied [15]. One study shows effective use of cement as a filler material in a travertine stone with different ratios of polymer admixtures and Poliacrilamid [16].

4 Pore filling applications in travertine

It is seen that in the majority of the travertine factories in Denizli region, mixture of white cement, calcite, kaolin and colorant are applied as filling material (Figure 1). In this part of the study, the mixtures used in travertine pore fillings were prepared separately as they are applied in the market and as designed for this study.

4.1. Epoxy resin filling

In this study, the experimentally investigated pore filler material was obtained primarily by using white cement and calcite, which are commercially available and applied in the market (Figure 2). The ratio of calcite/white cement ratio in the mixture is generally taken as 1/1 by weight. In this study, no substance (kaolin or fabric dye) was used as colorant.

4.2. Design of alternative pore filling material

Since this study aims to use the grinded travertine wastes instead of commercially used calcite, travertine samples were selected and grinded after that mixed with white cement in different ratios.

4 different mixtures were prepared with the ratio of travertine powder / white cement ratio of 1/0.5, 1/0.7, 1/1, 1/1.5.

Figure 1. Preperation of calcite and white cement mixture as filler.

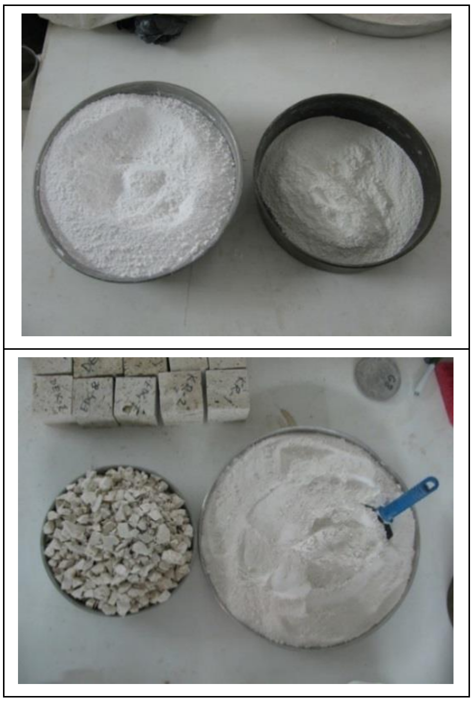

Figure 2. White cement (upper photo) and prepared travertine powder.

5 Application of mixed filling materials

Mixing ratios of the prepared filling materials are presented in Table 1. Only mixture no 2 is a mixture of calcite and white cement, which is still being used in applications.

The mixing ratio of this material was taken directly as in market applications. In order to determine the chemical composition of calcite and travertine powder used in the mixtures, XRD analyzes were performed and analysis results are presented in Table 2. Samples were analyzed on a fully automated Spectro XEPOS-III X-ray fluorescence spectrometer calibrated with international rock standards of appropriate composition. Major oxides Al2O3, SiO2, TiO2, Fe2O3 (as total iron), MnO, MgO, CaO, Na2O, K2O and P2O5 and the trace elements including Ba, Cr, Cu, Ga, Nb, Ni, Pb, Rb, Sr, Th, V, Y, Zn, Zr and La, Ce, Nd were determined by PEDX-ray fluorescence spectrometer at the Department of Geological Engineering at Pamukkale University. For PEDXRF analyses, samples were crushed in a tungsten carbide crushing vessel. A total of 6.25 g of powdered sample was mixed with 1.4 g of wax, and the mixture was pressed at 20 N in an automatic press machine to get a pressed disc. Results showed that CaO values were very close to each other for both materials. SiO_2 and Fe_2O_3 values (%) were higher in travertine powder samples.

6 Defining physical properties

Experiments were carried out to determine the changes of basic physical properties of the prepared samples after surface fillings. Cubic samples with 7 * 7 * 7 cm were used throughout the experiments. In the experimental studies, dry unit volume weight [17], water absorption by weight [18] and by volume [19] and capillary water absorption [20] values which are directly related to porosity were examined. The fact that the parameters obtained were made on both filled and unfilled for each mixture facilitated the correct interpretation of the numerical values. Figure 3 shows examples of unfilled and filled travertine samples. In order to determine the shrinkage values of the prepared mixtures by the effect of temperature and drying, shrinkage test was made and their length shortening was determined (Figure 4).

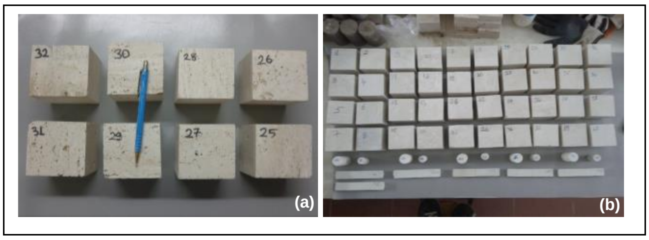

Figure 3. Views of the unfilled. (a): and filled. (b): Samples.

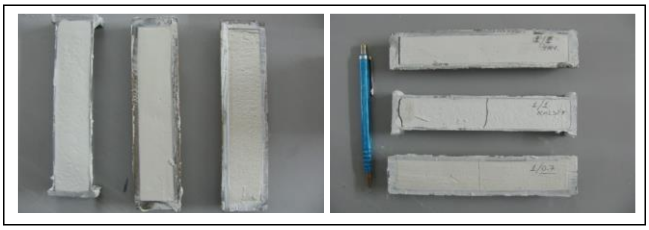

Figure 4. Views of cracking and shortening of mixtures in shrinkage test.

The obtained experimental data are presented in Table 3-7 depending on the mixing ratio of the filling material. Table 3 shows variations of dry unit volume weight (g/cm^3), water absorption by weight (%) and volume (%) and capillary water absorption (g/m^2*s$^{0.5}$ and %) of the test samples prepared with a mixture of 1/1 travertine and white cement. The obtained experimental data show that the unit volume weights are increased, water absorption by weight and volume (apparent porosity) and capillary water absorption values are decreased.

The increase in unit volume weights ranges from 0.32 to 0.54 % in a very narrow range. However, it has been determined that the main changes occur in the water absorption values. The changes in the experimental parameters are shown in Figure 5 depending on the sample groups.

It was determined that the decrease in water absorption values of the filled samples prepared with the mixture of 1/1 and 1/0.7 ratio (travertine powder/cement) with increasing unit volume weights.

Table 1. Mixture ratios by weight and components of the prepared fill material.

Mix No	Trav. Ratio	Cement Ratio	Calcite Ratio	Trav. (g)	Cement (g)	Calcite (g)	Water (g)
1	1	1	---	350	350	---	185
2	---	1	1	---	300	300	140
3	1	0.7	---	300	210	---	105
4	1	0.5	---	330	165	---	103
5	1	1.5	---	200	300	---	115

Table 2. Chemical analysis of calcite and travertine samples used in mixtures.

Element	MgO	SiO_2	SO_3	CI	CaO	Cr_2O_3	MnO	Fe_2O_3	SrO
Unit	%	%	%	ppm	%	ppm	%	%	ppm
Calcite	0.2274	0.02817	0.00548	39.9	55.22	5.30	0.00147	<0.00014	74
Travertine	0.1491	0.37920	0.14470	24.9	52.69	14.7	0.00420	0.03591	661.9

Table 3. Test data of unfilled specimens and prepared filled specimen with 1 travertine / 1 cement mixing ratio by weight.

Sample Type	UNFILLED TRAVERTINE SAMPLES					FILLED TRAVERTINE SAMPLES (1 Travertine/1 Cement)				
Sample No	Dry unit weight (gr/cm³)	Water abs. by weight (%)	Capillary water abs. (gr/m²*s⁰·⁵)	Capillary water abs. (%)	Water abs. by volume (%)	Dry unit weight (gr/cm³)	Water abs. by weight (%)	Capillary water abs. (gr/m²*s⁰·⁵)	Capillary water abs. (%)	Water abs. by volume (%)
1	2.29	2.498	18.216	1.90	5.55	2.30	2.059	4.7953	1.73	4.57
2	2.41	1.246	2.4482	0.83	2.92	2.42	0.866	1.4703	0.35	2.04
3	2.33	2.695	9.5212	2.39	6.12	2.34	2.569	6.093	2.15	5.82
4	2.37	1.841	3.1596	1.09	4.21	2.38	1.720	2.8234	0.97	3.98
5	2.35	2.054	7.1783	1.78	4.69	2.36	1.463	2.7049	0.95	3.36
6	2.32	2.508	11.442	2.03	5.70	2.32	2.024	4.4759	1.58	4.57
7	2.36	1.803	2.1818	0.76	4.16	2.37	0.984	1.614	0.39	2.27
8	2.46	0.545	0.8157	0.30	1.32	2.46	0.580	0.9613	0.25	1.40
Average	2.361	1.898	6.8703	1.385	4.333	2.368	1.5331	3.1172	1.046	3.501

Table 4. Test data of unfilled specimens and prepared filled specimen with 1 calcite / 1 cement mixing ratio by weight.

Sample Type	UNFILLED TRAVERTINE SAMPLES					FILLED TRAVERTINE SAMPLES (1 Calcite/1 Cement)				
Sample No	Dry unit weight (gr/cm³)	Water abs. by weight (%)	Capillary water abs. (gr/m²*s⁰·⁵)	Capillary water abs. (%)	Water abs. by volume (%)	Dry unit weight (gr/cm³)	Water abs. by weight (%)	Capillary water abs. (gr/m²*s⁰·⁵)	Capillary water abs. (%)	Water abs. by volume (%)
9	2.31	2.847	6.3994	2.26	6.38	2.32	2.228	2.6072	0.92	5.17
10	2.31	2.714	9.3373	2.38	6.22	2.33	2.429	7.9826	2.02	5.68
11	2.38	1.922	3.7005	1.27	4.45	2.39	1.510	2.682	0.92	3.61
12	2.32	2.422	5.0822	1.80	5.46	2.33	1.949	2.4201	0.85	4.53
13	2.30	2.449	7.9919	2.01	5.63	2.32	2.028	4.2962	1.52	4.75
14	2.30	1.816	4.0301	1.43	4.13	2.31	1.307	2.2165	0.78	3.03
15	2.29	2.291	2.7445	0.98	5.21	2.30	1.927	2.3672	0.73	4.52
16	2.32	2.277	4.1475	1.46	5.22	2.33	1.969	3.6989	1.12	4.62
Average	2.316	2.342	5.4291	1.698	5.33	2.328	1.918	3.5338	1.1075	4.488

Table 5. Test data of unfilled specimens and prepared filled specimen with 1 travertine / 0.7 cement mixing ratio by weight.

Sample type	UNFILLED TRAVERTINE SAMPLES					FILLED TRAVERTINE SAMPLES (1 Trv/0.7 Cement)				
Sample No	Dry unit weight (gr/cm³)	Water abs. by weight (%)	Capillary water abs. (gr/m²*s⁰·⁵)	Capillary water abs. (%)	Water abs. by volume (%)	Dry unit weight (gr/cm³)	Water abs. by weight (%)	Capillary water abs. (gr/m²*s⁰·⁵)	Capillary water abs. (%)	Water abs. by volume (%)
17	2.21	2.066	2.8871	1.05	4.58	2.22	1.640	1.2467	0.45	3.82
18	2.22	2.484	4.9941	1.82	5.48	2.23	2.081	2.7745	1.00	4.80
19	2.23	2.117	3.7348	1.34	4.72	2.24	1.905	2.9416	1.05	4.46
20	2.24	2.495	8.5502	2.19	5.63	2.25	2.235	5.5231	1.99	5.17
21	2.33	2.210	4.8744	1.71	5.08	2.34	1.772	3.1481	1.10	4.15
22	2.35	2.240	2.6311	0.91	5.23	2.36	2.008	2.5636	0.89	4.74
23	2.29	2.575	2.9165	1.04	5.71	2.31	2.382	2.9835	1.05	5.52
24	2.35	2.106	10.228	1.79	4.85	2.36	1.977	4.2836	1.49	4.68
Average	2.277	2.286	5.1020	1.481	5.16	2.288	2.000	3.1830	1.127	4.667

Table 6. Test data of unfilled specimens and prepared filled specimen with 1 travertine/0.5 cement mixing ratio by weight.

Sample type	UNFILLED TRAVERTINE SAMPLES					FILLED TRAVERTINE SAMPLES (1 Trav./0.5 Cement)				
Sample No	Dry unit weight (gr/cm³)	Water abs. by weight (%)	Capillary water abs. (gr/m²*s^0.5)	Capillary water abs. (%)	Water abs. by volume (%)	Dry unit weight (gr/cm³)	Water abs. by weight (%)	Capillary water abs. (gr/m²*s^0.5)	Capillary water abs. (%)	Water abs. by volume (%)
25	2.31	2.400	16.943	1.95	5.57	2.32	2.129	7.7114	1.76	4.95
26	2.36	1.727	2.54	0.88	3.98	2.37	1.268	1.27	0.46	3.01
27	2.31	2.332	14.767	2.00	5.55	2.32	2.146	6.5374	1.52	4.98
28	2.34	1.987	4.9086	1.72	4.58	2.35	1.617	3.0595	1.07	3.82
29	2.30	2.294	10.324	1.85	5.15	2.31	2.131	7.3473	1.84	4.93
30	2.33	2.549	11.595	2.25	6.46	2.34	2.470	8.9949	2.06	5.79
31	2.29	2.165	15.294	1.89	5.13	2.30	1.987	5.2385	1.60	4.60
32	2.35	2.050	2.5526	0.89	4.86	2.36	1.706	2.5190	0.87	4.04
Ave.	2.323	2.188	9.8655	1.68	5.16	2.333	1.931	5.3347	1.40	4.515

Table 7. Test data of unfilled specimens and prepared filled specimen with 1 travertine/1.5 cement mixing ratio by weight..

Sample type	UNFILLED TRAVERTINE SAMPLES					FILLED TRAVERTINE SAMPLES (1 Trv/1.5 Cement)				
Sample No	Dry unit weight (gr/cm³)	Water abs. by weight (%)	Capillary water abs. (gr/m²*s^0.5)	Capillary water abs. (%)	Water abs. by volume (%)	Dry unit weight (gr/cm³)	Water abs. by weight (%)	Capillary water abs. (gr/m²*s^0.5)	Capillary water abs. (%)	Water abs. by volume (%)
33	2.37	1.645	1.243	0.43	3.92	2.38	1.292	1.4446	0.50	3.07
34	2.36	1.571	3.5174	1.25	3.75	2.37	1.471	2.8271	1.00	3.50
35	2.34	2.153	4.7297	1.65	5.11	2.35	1.771	2.1959	0.76	4.19
36	2.34	2.031	3.7414	1.32	4.79	2.35	1.871	3.3405	1.18	4.40
37	2.34	1.921	3.6108	1.26	4.57	2.35	1.565	3.0424	1.05	3.71
38	2.33	2.441	3.4323	1.20	5.72	2.33	2.161	2.4564	0.86	5.05
39	2.35	2.224	7.2268	1.79	5.24	2.36	2.136	5.5084	1.93	5.02
40	2.30	2.247	4.308	1.53	5.22	2.31	1.838	2.1031	0.74	4.26
Ave.	2.341	2.0291	3.9761	1.303	4.79	2.35	1.7631	2.8648	1.002	4.15

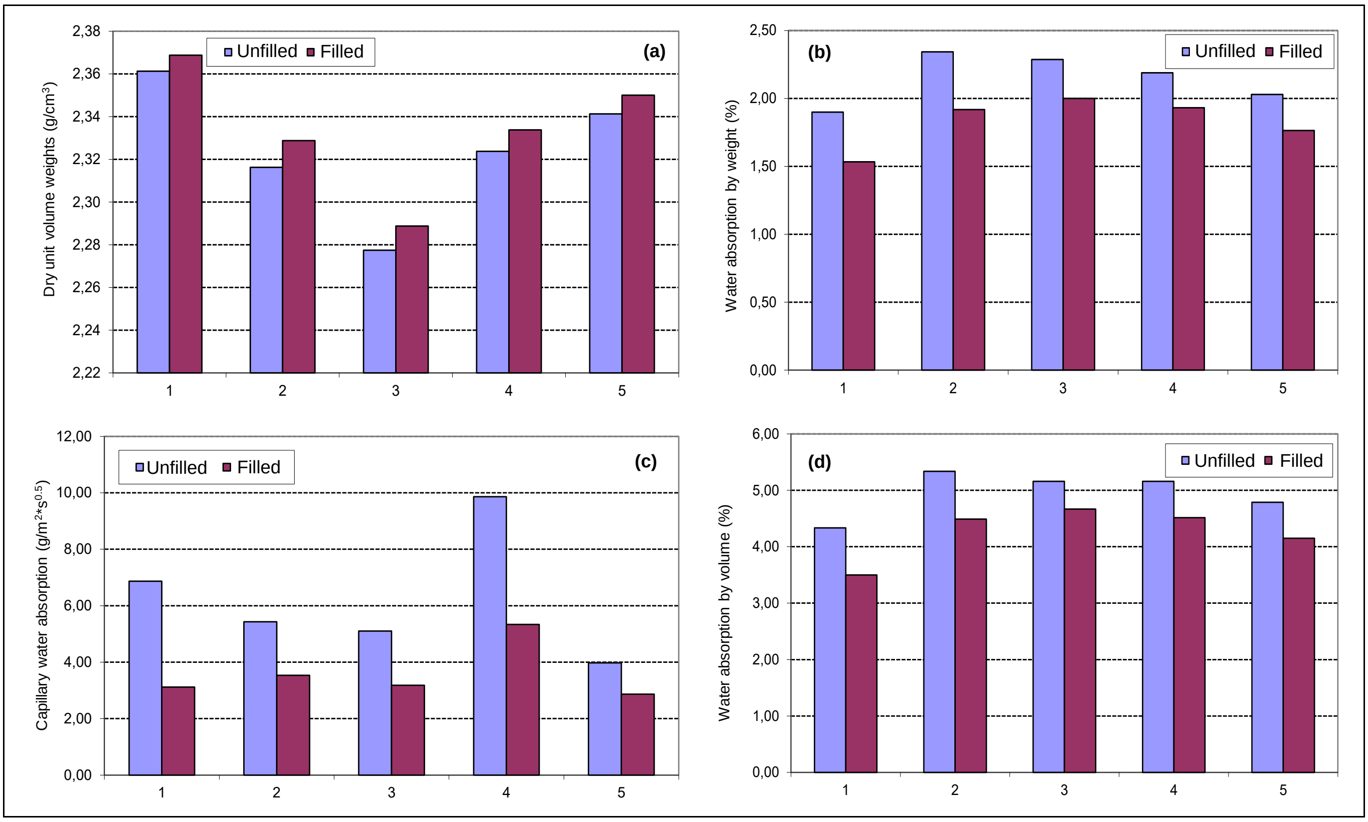

Figure 5. Variation of the obtained experimental data on prepared unfilled and filled travertine groups (1 - 5); dry unit weights. (a): Water absorption by weight. (b): Capillary water absorption. (c): Water absorption by volume (d).

7 Results

In this study, the use of travertine powder as filling material instead of commercially used calcite in travertine which is a porous natural stone was investigated. For this purpose, 4 different mixing ratios (1/0.5, 1/0.7, 1/1, 1/1.5) of travertine powder/cement mixture were produced in the laboratory. Another group of fillers was formed as calcite/cement (1/1 ratio) mixture, which is widely used in commercial production. Obtained results showed that 0.32-0.54 % increase in unit volume weight values in filled travertines, and 11.71-19.25% decrease in water absorption values by weight. It was found that capillary water absorption decreased significantly between 27.95-54.62 % for the whole samples. Similarly, apparent porosity values decreased by 9.54-19.21 %. With the increase in unit volume weights, the most decrease in water absorption values were obtained for the samples with 1/1 and 1/0.7 mixing ratios (travertine powder/cement). The data obtained with this study showed that filling costs can be reduced by using the powder of the travertine instead of commercially used additives in filling applications.

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