Studying the effect of using travertine mine waste on the physical-mechanical properties of the two-component gypsum-based composite

Ramin Doostmohammadi[1], Farhad Samimi Namin*[2], Seyed Reza Mousavi Qeydari[3], Zahra Shahbazi[4]

1 Department of Mining Engineering, University of Zanjan, Zanjan, ramin.doostmohammadi@znu.ac.ir

2*Corresponding author: Department of Mining Engineering, University of Zanjan, Zanjan, f.samiminamin@znu.ac.ir

3 Department of Chemical Engineering, University of Zanjan, Zanjan, zsr.mousavi@znu.ac.ir

2 Department of Mining Engineering, University of Zanjan, Zanjan, zahrashahbazi455@gmail.com

Abstract

Composites derived from gypsum are employed as artificial stone and in the cladding of interior building facades. The integration of mine waste in their production may lower manufacturing expenses, contingent upon the materials achieving satisfactory resistance and physical properties. The main objective of the present study is to assess the feasibility of waste travertine minerals for producing environmentally friendly gypsum-based composites. Gypsum composites with five replacement levels (10%, 20%, 30%, 40%, and 50%) of travertine waste powder, with specific particle size distribution, were prepared instead of gypsum. The physical properties (density, ultrasonic wave velocity, and moisture absorption capacity) and mechanical resistances (flexural and compressive strengths) of these samples were compared to a control sample (pure gypsum composite). The results obtained after 14 days indicate that despite a decreasing trend (%5≈) in density within the 0-50% range, up to 20%, this trend was increasing, demonstrating its effects on flexural strength (%9.1≈) and the reduction in the slopes of the curves of other physical and chemical properties. Based on the mechanical resistances obtained from this study, it can be concluded that up to 20% by mass of travertine mineral waste can be used in gypsum panels without changing their mechanical resistances significantly, with a slight increase in water absorption capacity (10%). Also, compared with the minimum standard values for compressive and flexural strengths (2 MPa), this increase can be extended to 50% by mass.

Keywords: Gypsum-based composite, Travertine, Mine waste, Composite, Mechanical resistance.

1. Introduction

Modern buildings are typically constructed using materials such as concrete, steel, wood, precast gypsum panels, structural units, plastic, composites, and insulation foams. Structures employing these materials are designed to meet structural safety requirements, fire resistance, energy efficiency, quality of life, and durability [1]. Gypsum is one of these mineral building materials, and products based on it are recognized as cost-effective, sustainable, and environmentally friendly. Therefore, it offers various advantages and applications compared to cement and lime. For instance, the fully loaded production cost of gypsum is significantly lower due to the substantial differences in production costs with cement and lime. The processes of cement clinker and lime calcination occur at temperatures around 1500 and 968 degrees Celsius, respectively, with a substantial mass loss (close to 50% mass loss) in these processes [2-4].

In contrast, gypsum is produced at temperatures between 150-165 degrees Celsius, with a mass loss of approximately 15% of the initial mass [5]. Furthermore, in terms of environmental compatibility, cement, and lime industries are among the heaviest greenhouse gas producers, releasing gases through both the raw material and fossil fuel consumption in the clinking and calcination processes [6, 7]. In the gypsum production process, these emissions are negligible and limited to the fuel consumed [4].

Additionally, the rapid setting, lack of need for curing, non-toxicity, lightweight products, easy molding, fire resistance, and excellent sound and heat resistance are other advantages of these products, especially in gypsum panels. The use of gypsum panels is a method for constructing internal walls and ceilings in buildings. These panels are prepared in various sizes as cut pieces. The advantages of using gypsum panels include ease and speed of installation, no need for special equipment for installation, and transparency in pricing. However, fierce competition and low prices have led manufacturing plants to use the highest water-to-solid ratio without the use of any suitable additives, resulting in very high porosity in the product after drying. This leads to disadvantages such as high moisture absorption, very low flexural and compressive strength, and weakness in impact resistance in gypsum panels [8].

Therefore, finding a suitable filler instead of water, which also has a negligible cost, to make the product competitive in terms of quality and price poses a new challenge. The use of mining, industrial, and household waste in the production of gypsum materials can be a sustainable method to reduce environmental pollution and save natural resources. Mining wastes are materials that are deposited or buried in specific locations due to inefficiency in mining extraction, lack of economic value, or other factors. Industrial wastes include residues from industrial processes that no longer have economic value for use in the production process. These wastes consist of organic and inorganic materials extracted from production processes such as metal production, chemicals, petrochemicals, electronics, automotive, and other extraction industries.

Household waste, on the other hand, includes residues from daily household activities of urban residents. Proper management of these wastes is crucial due to their increasing production in densely populated and growing cities, leading to various challenges in health, public safety, and the environment. Therefore, the collection, transportation, disposal, and recycling of waste are essential to reduce air, soil, and water pollution, protect natural resources, and reduce health and industrial risks. So far, only a few studies have been published on the use of these wastes in the production of gypsum-based products. The use of cellulose wastes such as paper pulp waste, wheat straw ash, cottonwood granules, cellulose, and sawdust [9-13], biological wastes such as poultry litter waste, coconut fibers, and blue agave stalks [14, 15], polymer material wastes such as cellulose acetate fibers from cigarette filter recycling, acrylic polymers, and copolymers, polyvinyl alcohol, polyethylene beads along with polypropylene fibers, recycled polystyrene, polyamide beads, granulated expanded polyurethane foam, the powder obtained from worn-out tires, recycled polypropylene granules from coffee containers, and vermiculite along with polypropylene fibers [16-26], and mineral materials such as silica fume and expanded perlite, sodium silicate, silica gel, citric/sulfuric acid, hydrated lime, silica fume, blast furnace slag, and ceramic waste powder [27-31] are examples of studies that have been reported in this field. On the other hand, considering the extensive applications of travertine stone, a significant amount of travertine waste is generated worldwide. The percentage of travertine fines produced in mines and construction industries depends on various conditions, including the type of mine, extraction process, equipment used, and the type of project for which travertine is used. This type of waste includes parts of the stone that are not usable for various reasons, such as natural defects, process errors, etc.

Additionally, some wastes occur due to the inability to transport and move stones in the extraction and cutting process, as well as the slurry obtained from stone-cutting industries. The production capacity of travertine in Iran is also very high due to the presence of rich mines in the country. According to published statistics, Iran is one of the largest producers of travertine and, consequently, one of the largest producers of waste from this mineral in the world. Despite efforts to develop and improve the travertine extraction and processing industry, waste management of travertine remains a major challenge. In many areas, travertine waste is irregularly dumped, which can lead to soil, water, and air pollution [32].

Therefore, some countries are trying to improve travertine waste management through innovative technologies such as recycling and reuse as construction materials. Travertine waste, after milling and crushing, is usable in the production of gypsum-based products. The use of travertine waste in the production of gypsum products reduces the consumption of new raw materials and, consequently, reduces waste and environmental pollutants. From a mining standpoint, repurposing mine waste to create a new product diminishes the quantity of waste stored in depots. Generally, a reduction in waste volume correlates with a decrease in environmental impacts, including alterations to the landscape, the generation of acid mine drainage, and dust emissions. Moreover, using travertine in gypsum product manufacturing significantly lowers the overall product cost. As mentioned above, gypsum and travertine waste are valuable options for milling and mixing for use in construction projects. Both are lightweight, stable in indoor conditions, earthquake resistant, easy formability and size, and bright white color suitable for decorative and decorative works. They also have excellent fire resistance. Despite these advantages and the necessity of using waste to reduce production costs, improve the quality of construction products, and reduce mineral waste, unfortunately, no research has been conducted on the use of travertine waste in gypsum products to date.

This investigation centers on a type of gypsum-based composite that is developed in compliance with the European standard EN13279_2 (2014). The composite is formulated from gypsum, water, resin, stone powder sourced from travertine mine waste, and cement, and is utilized for interior facades and decorative purposes. Gypsum-based composites are a decorative material that is often used in interior linings such as walls and ceilings because of its many unique advantages, including low cost and energy consumption, good habitability, and good fire resistance. The production process for these gypsum-based composites is consistent with that used for interior artificial stone. Therefore, in this study, composites of gypsum were made by adding and mixing different amounts of this waste, and physical and mechanical tests were performed on the 75 samples. A comprehensive set of five laboratory tests was performed, encompassing density, ultrasonic wave velocity, moisture absorption capacity, as well as flexural and compressive strengths. Each of these experiments was conducted in triplicate to ensure reliability of the results. Figure 1 illustrates the Three Gypsum-Based Composites Incorporating 30% Travertine for Water Absorption capacity test. The obtained results were compared with the results of the control sample, which is gypsum without travertine waste.

Figure 1. Three Gypsum-Based Composites Incorporating 30% Travertine for Water Absorption capacity analysis

2. Materials and methods

The studied gypsum is construction gypsum with the controlled setting, according to the national standard for construction industry 12015-1 clauses 1-4, titled "Gypsum Adhesive," and European standard EN 13279-1(2009) of type B1, produced by Gach-e-Khorshid Semnan Company, with particle grading as listed in Table 1. The travertine powder belongs to mining company with grading specified in Table 1. The water used was potable water according to national standard 1053. Standard molds of dimensions 40*40*160 millimeters, a wave velocity measuring device manufactured by CNS Farnell Limited with a resolution of µs0.1.

Table 1. Khorshid Gypsum and travertine construction plaster granulation.

Gypsum (percentage)	Travertine tailings (percentage)	Sieve size (mm)
0.15	**38.48**	**49.8**
0.212	**8.94**	**39.4**
0.125	**27.26**	**9.2**
0.106	**16.56**	**1.0**
0.063	**4.66**	**0.6**
0.075	**3.94**	**0.4**
0.053	**0.04**	**0.02**
0.038	**0.1**	**0**
Under the sieve	**0.02**	**0**
Total	**100**	**100**

2.1. Construction of two-component composite sample

For each sample, with mass percentages of 0, 10, 20, 30, 40, and 50 of travertine to the total dry mass, a specific amount of this material was manually mixed with corresponding dry gypsum. The water content in all samples was calculated as 55% of the dry mixed mass. Following standard EN 13279-2:2014, dry gypsum mixtures were added with water and mixed vigorously with a stainless steel spoon to create a uniform mortar. The samples were then cast into the mentioned molds and cured. Three samples were prepared for each composition pattern. After setting for 24 hours, the samples were removed from the molds and stored in a laboratory at 24 degrees Celsius and 60% humidity until further testing.

3. Physical-mechanical characteristics

In this research, density (volumetric mass), longitudinal wave velocity, flexural strength, compressive strength, and water absorption capacity were determined according to the following guidelines and standards.

3.1. Density

The dry density of the gypsum-based composite samples was measured to prepare them for subsequent physical and mechanical tests. Due to the rapid setting of the samples and achieving maximum mechanical strength in the first two weeks at 24°C [33], the samples were accurately weighed and placed in the curing chamber at 45 ± 3°C until reaching a constant mass. The dry density of each sample was calculated based on the definition of density, i.e., mass per unit volume of a substance. After measuring the dry mass and volume of each test sample, the dry density of each sample was calculated according to standard EN 13279-2:2014. The average density of the composites was calculated by averaging three measurements for each group.

3.2. Wave speed

This test can be used to determine the speed of the passing wave to evaluate the uniformity and relative quality of the composite, showing the presence of voids and cracks, and in corrective cases, to evaluate the effectiveness of repairing the cracks in the sample. In gypsum plasters, it can be used as a measure to determine the degree of insulation of the sample against the passage of part of the sound waves. Longitudinal stress wave pulses are generated by an electroacoustic transmitter that is in contact with a sample surface under test, and after passing through the sample, they are received by a receiver located on the opposite surface at a distance L from the transmitter and converted into electrical energy. Therefore, the pulse wave passing speed inside the sample is calculated as equation 1.

$$V = \frac{L}{T} \qquad (1)$$

Where V is the speed of the passing wave in m/s, L is the distance between the centers of the probe faces in meters and T is the time of the wave passing in seconds.

According to ASTM C597-16 and after checking the correct operation of the device and adjusting the zero time according to the manufacturer's instructions, the 40×40x160 samples were placed vertically on the transmitter. For more accuracy, the contact surfaces of the probes and the sample were impregnated with the filling liquid, the probes were placed right in front of each other to minimize the test error. This test was performed with a frequency of 10 kHz and repeated three times for more accuracy. Then, the time of passing the wave through the sample, which was reported in microsecond unit, was noted down, and taking into account the length of the sample, the value of the passing wave speed of all three samples in each group was noted, averaged and compared with the passing speed of other samples.

3.3. Modulus of rupture (flexural strength)

Bending strength was determined based on ASTM C293/C293M-16 standard. To measure the bending strength of the samples, the rollers of the testing machine, which were set at a distance of 80 mm, were used. The input load by the device was also applied at the rate of 100 N/s by the central roller on the sample until failure. Bending strength values were calculated with the arithmetic mean of three measurements at each replacement level and using the modulus of rupture. The modulus of rupture is as equation 2.

$$R = \frac{3FL}{2bd^2} \quad (2)$$

where in: R, modulus of rupture, and in MPa, F, the maximum applied load shown by the device in Newtons, L, b, and d are respectively equal to the length of the sample, the average width of the sample at the point of failure and the average depth of the sample at the point of failure, all three are in millimeters.

3.4. Compressive strength

The test to determine the compressive strength, according to the EN 13279-2:2014 standard, was performed using the broken parts of the samples in the bending strength determination stage. In this way, after accurate measurement, these samples were prepared in the form of cubes with sides of 40 mm using a cutting machine at a low speed. Then, using a loading device, the samples were subjected to pressure by applying a force of 1 MPa/s. The results were recorded for all the samples and reported for different travertine composition percentages. Figure 2 illustrates the uniaxial compressive strength and flexural strength assessments conducted on gypsum-based composite samples incorporating travertine waste.

3.5. Capillary water absorption capacity

To determine the water absorption capacity, the broken parts were used in the test to determine the bending strength. Therefore, after the samples were broken, three samples of each of the combined percentages were placed on a porous substrate inside a large glass container, and water was poured into the container up to a height of 10 mm from the bottom of the sample. Then, in one-minute time intervals for 10 minutes, the height of water infiltration inside the sample in millimeters, and accordingly, the point and average velocity of water infiltration from the capillary paths of the sample in millimeters per minute were noted and reported.

a) Compressive strength b) Flexural strength

Figure 2. Evaluation of Strength in Composite Samples: (a) Uniaxial Compressive Strength and (b) Flexural Strength

4. Results and discussion

4.1. Density

After 14 days of curing the gypsum composite, a lightweight structure is formed, characterized by high porosity. The presence of fine air bubbles trapped during mixing with water and the evaporation of additional water used in the sample's preparation for the smoothness of the gypsum paste for molding contributes to the high porosity. The results obtained for the density of each composite sample, measured based on the mass-to-volume ratio, are presented in the Figure 3. This figure illustrates the trend of density changes concerning different percentages of travertine. Considering the chart, two distinct ranges of increase in travertine content to gypsum, one from zero to 10%, and the other from 30 to 40%, show little change in composite density. Additionally, the average density of the samples, after passing through a recess, indicates an increase and decrease in the ranges of 10 to 20% (+1.5%) and 20 to 30% (-4.1%), respectively. In general, the density of the set, except for the value obtained in the 20% composite, has a decreasing slope. The range of density variations is approximately 5.0%. This decreasing trend can be justified by the reduction in the gypsum content in the composite, leading to a decrease in water consumption for its hydration.

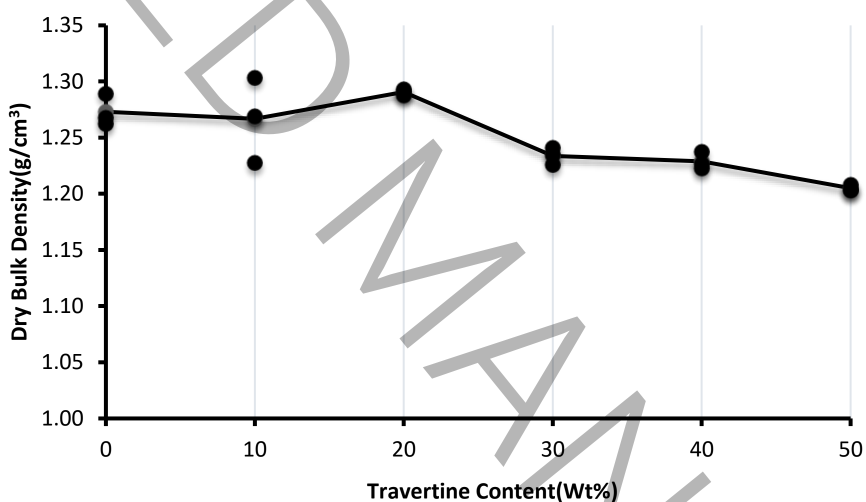

Figure 3. Changes in the density of plaster composite samples about the percentage of residual travertine content

As a result, a higher amount of free water will be present, and during the drying process, it will be removed from the sample structure. This occurrence aligns with the findings of other studies [34] indicating a decrease in density with an increase in the water-to-gypsum ratio. However, in the range of 10 to 20%, it appears that the composition has an internal secondary density that may be due to the interaction between gypsum and calcium carbonate or the softness of calcium carbonate. The physical interference with gypsum particles, filling the spaces between gypsum grains, reduces their porosity, resulting in increased bulk density [35].

4.2 Speed of the ultrasonic wave

The results obtained from the experiment to determine the ultrasonic wave propagation velocity inside gypsum composite samples are presented in velocity vs. travertine content graphs and density variations in Figure 4. Based on the graphs, an increase in travertine content leads to a decrease in wave velocity, consistent with the expected trend of density changes. This is due to the increased porosity of these samples. The relationship between ultrasonic wave velocity and sample density is in line with the results of other studies [25, 36]. A comparison of ultrasonic pulse velocities and corresponding densities reveals a direct relationship. According to the graphs in Figures 4, the velocity of waves in composites with lower density (higher porosity) is lower, and conversely, in cases with higher density where the material is more compact, the wave velocity is higher.

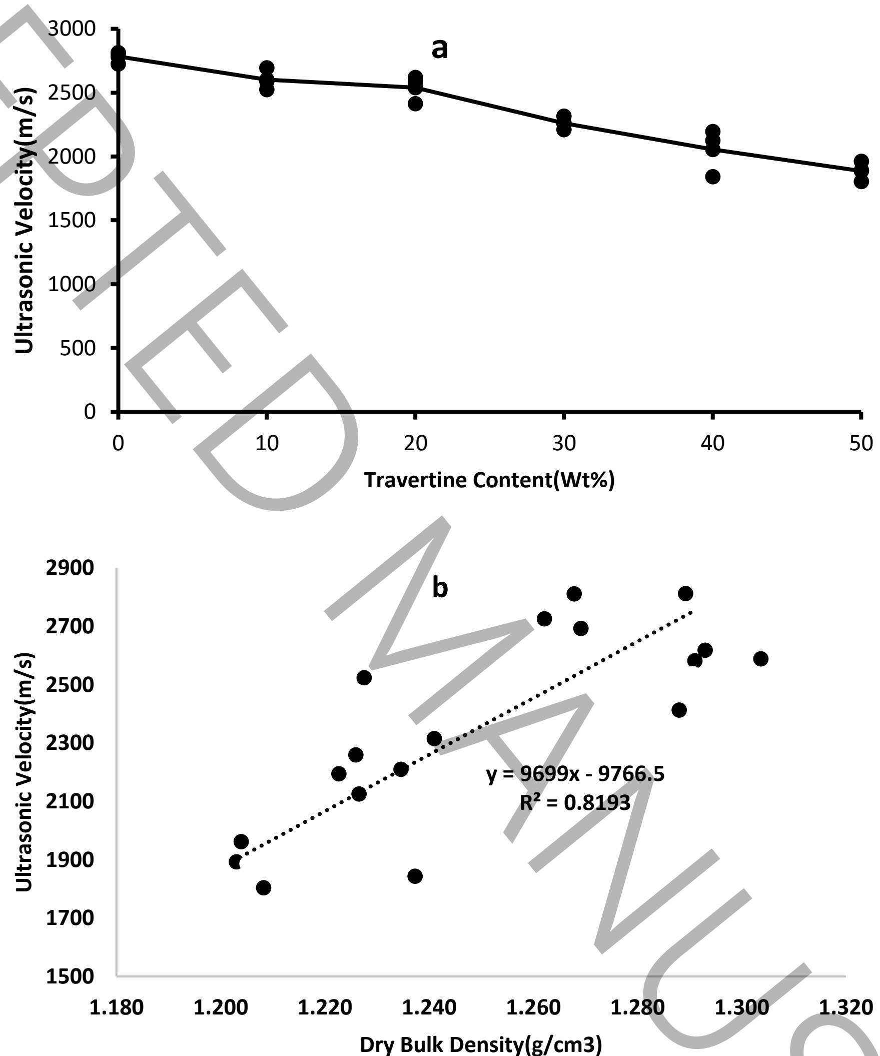

Figure 4. Changes in the velocity of the ultrasonic wave in composite samples with different residual percentages. (Top: changes relative to the residual percentages of travertine content and bottom: changes relative to changes in density)

Additionally, considering the slope of the obtained graph, the decrease in ultrasonic wave propagation velocity is much greater than the decrease in sample density concerning the travertine percentage. For instance, the ascending trend in the density graph in the range of 10-20% travertine is transformed into a near-zero slope in the wave velocity graph. Other trends in this graph also show a more substantial decrease.

4.3. Modulus of rupture (flexural strength)

The behavior of flexural strength in the new gypsum-based composites, based on the travertine content, is illustrated in Figure 5. As observed in the graph, an increase in travertine percentage from zero to 50% results in various changes in flexural strength compared to the reference material. These changes are such that the values of resistance for samples with travertine content from 0 to 20% exhibit negligible incremental changes, around 4.6%. From 20 to 30% content, the rate of changes is approximately 13.3%, and beyond 30%, the strength reduction rate accelerates further. Considering these results and comparing them with density variations, a very good consistency is observed between these two parameters concerning the travertine content. This alignment is also consistent with the results of other studies. The studied composites in the range of 0 to 30% exhibit very good strength resistance, showing, for instance, during a 10% increase in PP waste [37], 20% sawdust, and 20% plastic waste [13], and 30% polycarbonate waste [38], a reduction of 35%, 26.6%, 18%, and 18.2%, respectively, in sample strength. Meanwhile, the strength decrease in the sample with 30% travertine is approximately 9%. Considering the practical objectives of these composites as alternatives to gypsum plasters, the minimum flexural strength of these samples is equal to or greater than about twice the required value, i.e., 2 MPa [39]. The reduction in flexural strength observed with an increase in the travertine ratio beyond 20% may be attributed to a diminished proportion of cohesive particles among the stone powder particles (travertine).

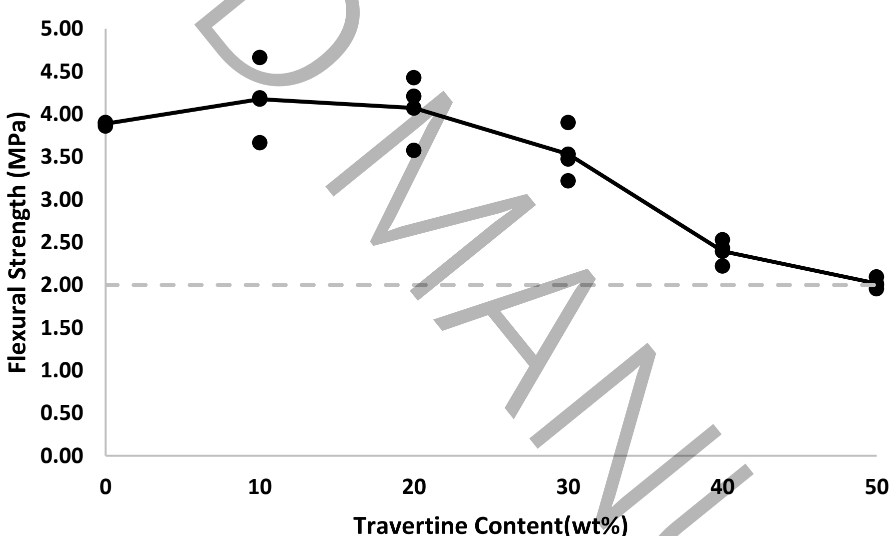

Figure 5. Changes in flexural strength of composite samples compared to changes in residual travertine content

4.4. Compressive strength

The results of compressive strength tests for gypsum composite samples based on the percentage of travertine content are presented in Figure 6. In all cases, an increase in the percentage of waste, except in the 20% composite, leads to a decrease in compressive strength compared to the reference material. The range of variations in this type of strength has decreased from 14.21 to 3.85 across the entire range. Similar to the flexural strength graph, a slight change in compressive strength is observed from gypsum samples to samples with 20% travertine waste. Based on the obtained results, the strength reduction for composites with 0 to 10% and 10 to 20% travertine is approximately 18% and 2.1%, respectively, totaling around 20%.

As the percentage of travertine content increases from 20% to 30%, a significant drop of about 51% is observed, which can be justified by the simultaneous decrease in the density of the samples in this range.

Samples with travertine content exceeding 30% up to 40% show a reduction of about 4.8%, and the slope of the reduction in this graph is greater than the slope in the density graph. Therefore, the compressive strength of samples with 20% to 30% travertine experiences a severe decrease, and then the reduction in the strength of samples with travertine percentages from 30% to 50% is also negligible. Hence, it can be concluded that travertine in the composite does not interact significantly with gypsum since the increasing density trend in the range of 10% to 20% has transformed into an unchanged trend in the compressive strength graph, while this trend is increasing and consistent with density in the flexural modulus graph.

The choice of 20% travertine as an optimal threshold for mechanical properties is acceptable. The evidence presented in Figures 5 and 6 strongly corroborates this conclusion. Overall, the compelling evidence showcased in these figures serves as a solid foundation for the research conclusions and reinforces the significance of the study's results.

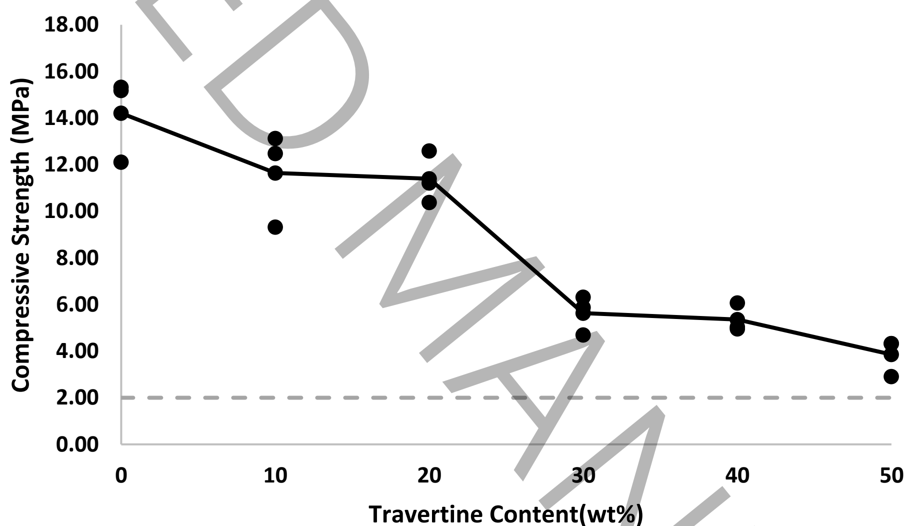

Figure 6. Changes in the compressive strength of gypsum-based composites according to the percentage of travertine content

Additionally, the dependency of compressive strength on the density of samples, compared to their flexural strength, is illustrated in Figure 7. According to this graph, the degree of dependency of compressive strength on the dry density of the samples is significantly higher, approximately five times greater, than the dependency on flexural strength. Considering the results and comparing the obtained compressive strength with gypsum samples, it appears that an increase in travertine waste powder up to a ceiling of twenty percent does not induce a reduction in this type of strength. It should be noted that in all cases, even in samples with fifty percent travertine, the obtained resistance values exceed the minimum standard requirement of 2 MPa for this type of construction material [39].

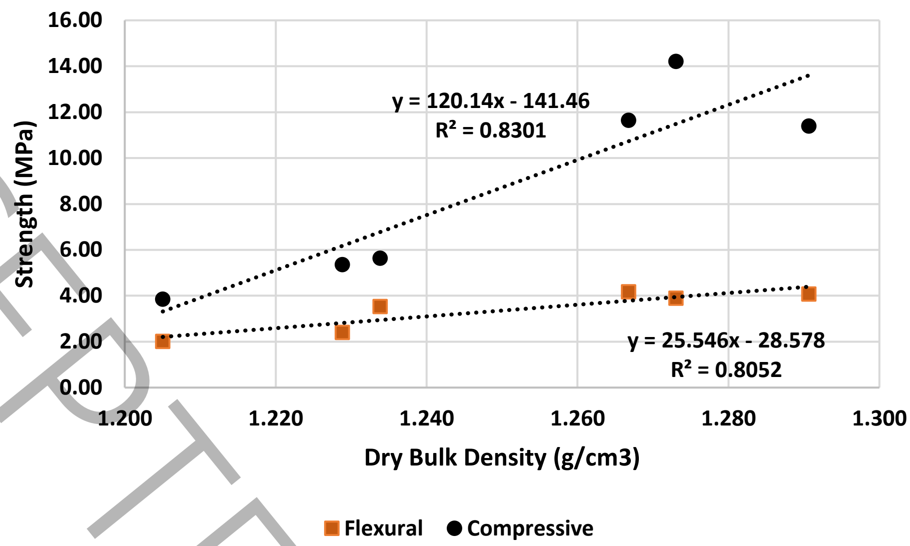

Figure 7. How the bending and compressive strengths change with changes in the density of the composites

4.5. Capillary water absorption capacity

The results of capillary water absorption capacity for samples with different percentages of travertine are shown cumulatively in Figure 8.

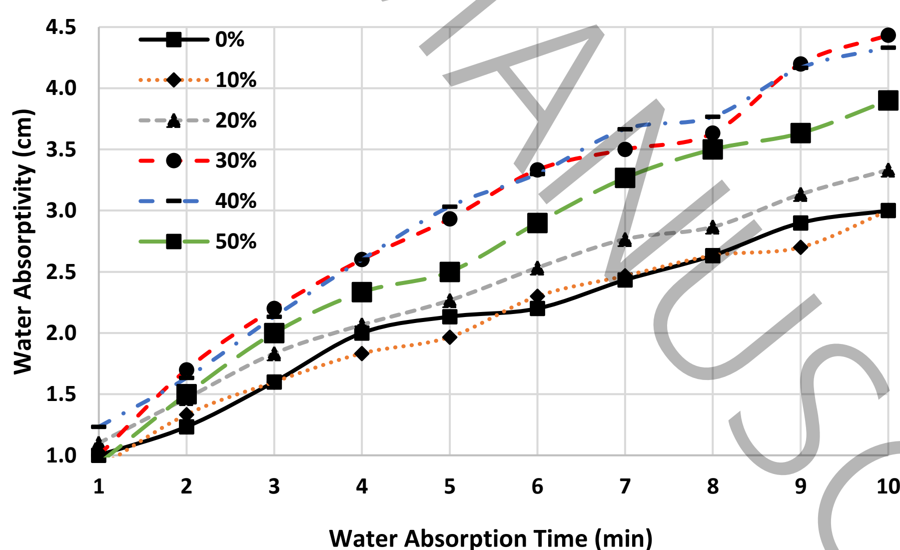

Figure 8. Capillary water absorption capacity of composite samples with different travertine in a time frame of up to ten minutes

Analyzing the water sorption capacity, the 0 and 10% travertine sample exhibited the lowest slope within the calculated time interval. In contrast, the 30% and 40% samples showed slopes almost equal to the highest. The 50% sample had a lower slope and lower absorption values compared to the 30% and 40%

samples. Calculating the ratio of absorbed water height (in millimeters) to the total measurement time (ten minutes) yielded the average water absorption rate in millimeters per minute for composites with different travertine percentages. As observed from the final points (values in tenths of a minute) on the graphs, an increase in travertine led to an augmentation in absorption and moisture absorption rates. The study examined the impact of varying levels of travertine content on the water absorption capacity of composite materials. When the composites contained 10% travertine, there was minimal change in absorption observed. However, as the travertine content increased to 20%, the absorption levels rose by approximately 10% when compared to samples solely made of gypsum. As the travertine content further increased from 20% to 30%, the water absorption capacity peaked at 33%, indicating a direct correlation between the amount of travertine present and the absorption levels. This trend was consistent with the changes in density, as higher percentages of travertine beyond 20% led to increased sample porosity, resulting in higher water absorption rates. Notably, as the travertine content continued to rise above 30%, there was a consistent trend in density changes. Despite this, the water absorption capacity remained steady in 40% of samples while experiencing a significant 9% decrease in 50% of samples. This suggests that there may be an optimum threshold for travertine content in composites to maintain desired absorption levels. The findings highlight the intricate relationship between travertine content, sample porosity, and water absorption capacity in composite materials.

5. Conclusion

Physical and mechanical tests on gypsum-based composites with varying percentages of white travertine waste revealed that an increase of approximately 20% of travertine waste in gypsum resulted in almost no changes in the bulk dry density and water absorption capacity of the composites. Similarly, the ultrasonic wave velocity showed minimal reduction within this range. Mechanical properties, such as flexural and compressive strength, demonstrated negligible decreases in this range. Therefore, it can be confidently stated that up to 20% of travertine waste can be used in gypsum products without significant alterations in their physical and mechanical properties. Depending on local costs, this change may have economic advantages up to higher proportions. Additionally, considering the minimum standard values for flexural and compressive strength, the percentage of waste content in the composites can be increased to approximately 50%, leading to reduced density and enhanced workability during transportation. Moreover, due to acceptable flexural and compressive resistances, these composites can be utilized in the production of gypsum-based decorative products. Therefore, using this waste in gypsum-based composites provides the potential for producing some new construction materials, addressing environmental issues in stone processing factories and travertine mines, and significantly reducing production costs.

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