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A Comperative Study on the Influence of Mineral Additives to the Physicomechanical Properties of NHL Mortars Cured in Water

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Highlights

- The main objective is to produce a NHL based repair mortar with mineral additives.
- Physicomechanical tests are conducted on mortar systems cured in water and standart conditions.
- Specific combinations show enhanced mortar characteristics.

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Abstract

This paper focuses on producing a natural hydraulic lime (NHL) mortar with metakaolin, expanded perlite and tuff additives for the purpose of repairing historic masonry. The experimental study was based on laboratory tests for determining the mechanical and physical properties of NHL mortars with mineral additives, under standard and water curing conditions at 7, 28 and 90-day testing periods. Following preliminary tests for selecting most favourable materials; flexural strength, compressive strength, adhesion strength, modulus of elasticity and ultrasound tests were conducted for obtaining mechanical performance. Adhesion strength of mortars were determined by applying each mortar to the most common historic masonry materials. Physical performance of the pozzolan added mortars were investigated through; apparent density, bulk density, water permeability, capillary absorption, water vapor permeability, porosity tests. Regardless of mineral additive type; water cured mortars reached higher physico-mechanical properties in comparison with the ones cured in relative humidity. Overall, water cured natural hydraulic lime mortars with specific amounts of mineral addition are found promising for the repair of historic masonry.

1. INTRODUCTION

The tradition of using a lime binder has been practiced by many civilizations and known for centuries. Therefore most of the extant historic buildings consist of lime mortar masonry. As the lime mortar corrupts in time, caused by internal and external factors; proper repairs become inevitable. Due to its long preparation period, low water resistance and weak mechanical properties, it has been seen that implementing agencies suggest cement blended lime mortars for the repair of historic masonries. These interventions result in irreversible damages to original historic masonry mortar therefore to the structural integrity of the historical heritage, due to excessive stiffness, low permeability and release of soluble salts properties of cement [1].

Natural hydraulic lime mortars, which have higher resistance against water and preferable mechanical properties could be a compatible alternative. Especially addition of pozzolanic materials to hydraulic lime mortar provides higher physical and mechanical behavior based on pozzolanic reactions forming hydraulic products. There are many studies show repair mortars produced by NHL, sand and other raw materials possess high compatibility with regards to physical, mechanical and chemical aspects of historic masonries [2,3]. NHL mortars also show no damage caused by soluble salts and have relatively low environmental impacts based on low (approx. 900-1100 Co) firing temperature and less carbon dioxide emissions during production [4].

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Pozzolans are classified as natural and artificial, where natural pozzolans originate from igneous rocks and artificial pozzolans can be obtained from varying manners mainly consist of thermal treatment of natural materials or obtained by ground industrial by-products. These materials are used as mineral additives in material science and has great economical and environmental advantages such as diminishing greenhouse gas emissions due to their waste material value. Turkey is a country rich in mineral reserves. Therefore revealing the beneficial aspects of natural and artificial pozzolanic materials when used with hydraulic lime mortars, may benefit both restoration and mining industries [5].

Tuff, which is a rather preferred mineral additive, result in different physical and mechanical behaviors in the lime mortar depending on different chemical properties based on their chemical characteristics [6]. Perlite is also a mineral that has 80% usage in the construction industry in the means of its lightness and it can also be used as an artificial pozzolan (expanded perlite) when subjected to thermal treatment. It has been proven within the scope of defined experiments that it has pozzolanic properties when combined with calcium-based binders since it contains siliceous and aluminum constituents [7]. Metakaolin is a relatively recent thermally treated kaolin product, which also has a high silica and alumina commissions. Its pozzolanic activity and enhancing effect when added to hydraulic or non-hydraulic lime mortar were determined by experimental studies [4,8]. Although frequently used in the ceramic industry, its light color distinguishes the usage as a building material.

Curing of repair mortars is another investigated area which has a great effect on mortar structure and characteristics. Different curing conditions with variable relative humidity, presence of water, pressure, and temperatures eventuate in the development of different chemical reactions during setting and hardening, therefore, influence the characterization of mortars mechanical and physical properties [9, 10]. In particular, the presence of water during curing affects the hydration reaction positively by providing a relatively small porous, dense lime mortar structure [11].

This paper focuses on producing a hydraulic lime mortar with mineral additives for repairing historic masonry conducted by experimental study. The experimental study was based on laboratory tests for determining the mechanical and physical properties of pozzolan added NHL mortars. Besides, for the determination of mechanical performance; flexural strength, compression strength, adhesion strength, modulus of elasticity and ultrasound tests are conducted at variable ages of 7, 28 and 90 days. Adhesion strength of mortars were determined by applying each mortar to brick and stone surfaces. The physical performance of the mortars was investigated through apparent density, bulk density, water permeability, capillary absorption, water vapor permeability, and porosity tests.

2. MATERIAL

Preliminary tests were conveyed in order to select the most favorable binder and the mineral additive for the mixtures. Three different branded natural hydraulic lime (NHL 3,5) were compared based on early phase mechanical properties [12]. Based on test results, a commercially available natural hydraulic lime NHL 3,5 which showed higher compressive (6,68 MPa) and tensile strength (1,39 MPa) by the end of 7-day testing period is selected for further investigations. Following the selection of NHL; eight types of natural and artificial pozzolans which were perlite, brick powder, pumice, metakaolin, micronized perlite, three kind of tuffs from different regions of Turkey, were subjected to pozzolanic activity tests [13] in comparison [5]. All tested pozzolans except for pumice, gained compressive strength higher than 4 MPa by the testing period of 7 days which is considered as the threshold for having pozzolanic activity according to the pertinent Turkish standard. Based on the test results; three type of mineral additives with highest strength values, which are metakaolin, expanded perlite and a type of tuff were selected as mineral additives, in order to achieve ranged mortar systems.

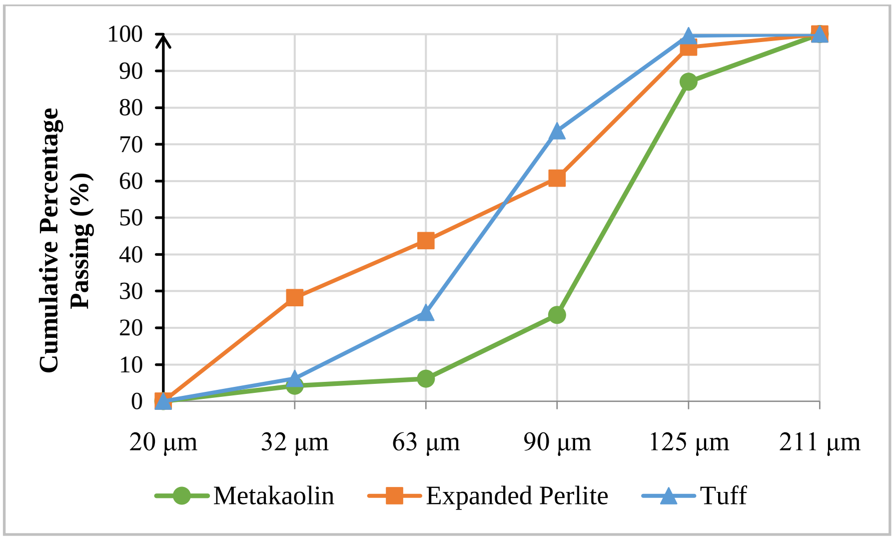

Figure 1. *Particle size distribution (PSD) of mineral additives*

Particle size distribution (PSD) of mineral additives are given in Figure 1 in cumulative percentages passing. The chemical compositions of all used materials carried out by X-ray fluorescence analysis (XRF) and the results are presented in Table 1. Mineral additives mainly consist of silicon dioxide (SiO2) and aluminum oxide (Al2O3). The remainder contains iron oxide (Fe2O3) and other oxides. Reactive calcium oxide ratio can be neglected for hardening. It should be noted that the reactive silicon dioxide content in the pozzolan is not less than 25% by mass [13].

Table 1. *Chemical compositions of the raw materials (%)*

Materials	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**CaO**	**MgO**	**K_2O**	**Na_2O**	**TiO_2**	**MnO**	**SO_3**	**P_2O_5**	**Cl**	**SrO**	**ZrO_2**	**LOI**
NHL 3.5	13.4	3.1	1.4	63.2	2.3	0.8	0.1	0.2	0.1	1.4	0.1	0.1	0.2	0.1	13.9
Tuff	65.7	13.1	3.2	5.1	1.1	4.1	1.3	0.4	0.1	0.1	-	0.1	0.1	0.1	5.7
Meta kaolin	50.7	45.9	0.2	0.2	0.3	0.1	0.2	-	-	-	-	-	-	-	1.2
Expanded Perlite	72.0	14.0	1.0	0.8	0.2	5.5	3.8	0.2	-	-	-	-	-	-	2.6

Table 2 presents the bulk density and specific gravity of the pozzolans employed in the mortars formulation determined according to the standard EN 1936 [12]. The sand used in mortar systems was washed and well graded siliceous river sand, obtained from a local supplier. Particle size distribution (PSD) of river sand used is given in Figure 3 in cumulative percentages passing in comparison to coarse and fine aggregate percentages defined in Turkish Standard TS 706. Aggregates were divided into two groups; fine aggregate was in the range of 0-4 mm and coarse aggregate was in the range of 0-8 mm.

Table 2. *Specific gravity and bulk density of used pozzolans (g/cm^3)*

Mineral	**Specific Gravity (g/cm^3)**	**Bulk Density (g/cm^3)**
Tuff	2.38	0.80
Metakaolin	2.44	0.52
Expanded Perlite	2.53	0.81

3. METHOD

The experimental study was conveyed by three phases on mortars cured for 7, 28 and 90 days. Mortar series were coded in accordance with pozzolan type and applied curing method (S-Standart curing, W-Water curing). Therefore mortars with metakaolin addition were coded MS, MW; mortars with micronized perlite addition were PS, PW; And mortars with volcanic tuff addition were TS, TW. The curing period was indicated numerically by the end of each code.

3.1. Mix Design

Each of the three types of natural hydraulic lime-pozzolan mortars was prepared at a 2/3 binder to aggregate ratio by volume. Aggregates consist of 2 parts of 8 mm grain sized and 1 part of 4 mm grain sized river sand. The water amount was selected to obtain plastic consistency and determined by the flow table test in accordance with the standard TS EN 1015-3 [14]. The mortar viscosity was tested by the fluidity table according to the standard and the added water amount determined for 165 ± 3 mm spreading for a workable plastic consistency. Detailed binder, mineral additive and aggregate amounts in the mixtures of mortar systems are given in Table 3 by volume.

Table 3. *Mix design (By volume) (M : Metakaolin, P : Expanded Perlite, T: Volcanic Tuff; S : Standart Curing, W : Water Curing)*

Sample Code	**Binder**	**V**	**Mineral Additive**	**V**	**Coarse Aggregate**	**V**	**Fine Aggregate**	**V**	**B/A Ratio**	**B/P**
MS, MW	NHL (3.5)	2	Metakaolin	1	0-8 mm	2	0-4 mm	1	2/3	2/1
PS, PW	NHL (3.5)	2	Expanded Perlite	1	0-8 mm	2	0-4 mm	1	2/3	2/1
TS, TW	NHL (3.5)	2	Tuff	1	0-8 mm	2	0-4 mm	1	2/3	2/1

3.2. Curing Conditions

Mortar mixtures were prepared at room temperature 20±2°C and %60±5 relative humidity. Steel molds with the dimensions of 40x40x160 mm were previously lubricated with machine oil to prevent the mortar from adhering to the mold surface. Then mortar mixtures were cast into molds. All mortars preserved in molds covered with plastic sheets in order to avoid loss of water vapor for 48±2 hours of pre-curing. For each NHL mortar mixtures, 42 prisms and 12 disc samples for adherence testing were produced; adding up to 126 prisms and 36 disc samples in total.

Table 4. *Curing conditions and periods of mortar samples (M : Metakaolin, P : Expanded Perlite, T: Volcanic Tuff; S : Standart Curing, W : Water Curing)*

Sample Code	**In Mold (20 ± 2°C, %95± 5)**	**In Water (20 ± 2°C)**	**Ambient Condition (20 ± 2°C, %65± 5)**	**Total Curing Period**
MS-GS-TS	2 days	-	5 days	7 days
		-	26 days	28 days
		-	88 days	90 days
MW- GW-TW	2 days	3 days	2 days	7 days
		21 days	5 days	28 days
		83 days	5 days	90 days

After de-molding, each three mortar series were cured under two different laboratory conditions to determine the influence of curing conditions on pozzolanic mortars. Water cured specimens were immersed in water, in a container maintained at 20±2°C and air cured specimens were cured in conditioning lab maintained at 20±2°C and 50±2% RH. Specimens are brought to ambient conditions before testing. Detailed curing conditions and curing duration of the test samples are given in Table 4.

3.3. Mechanical Tests

All specimens were brought to ambient temperature in the desiccator, weighed and measured prior to testing. For obtaining mechanical performance; flexural strength, compressive strength, adhesion strength, modulus of elasticity and ultrasound tests were conducted at variable ages of 7, 28 and 90 days. Adhesion strength of mortars were determined by applying each mortar to brick and stone surfaces. Prior to mechanical testing, water cured samples were subjected to ambient conditions for 24 h for stabilizing internal humidity. Compressive and flexural strength tests were conducted according to the pertinent standard EN 1015-11.

Flexural strength test was conducted by MFL branded universal testing machine at load cell of 50 kN and velocity at 0.2. Three of 40x40x160 mm prismatic samples were prepared for each mortar sample to determine the flexural strength in bending under uniaxial load. Flexural strength test was carried out by simple beam method for each mortar sample on the testing device, by placing the distance between the supports at a distance of 150 mm and applying it until the constant force breakage of 50 ± 10 N / s breaking occurs between 30 and 90 seconds [15].

Compressive strength was obtained using MFL branded universal testing machine with a load cell of 50 kN and velocity at min. 0.7; As a result of the bending test, prismatic 40x40x160 mm specimens were divided into two, and the pressure test was applied under the uniaxial load with the same device used in the experiment. The specimens placed horizontally between the 10 mm thick steel pressure heads placed on the lower and upper surfaces of the sample pieces were loaded with a constant speed of 500 ± 50 N / s until there was no break in the load and a break between 30 and 90 seconds [15].

Ultrasound velocity as a non-destructive test method; It is used in various fields such as error and defect detection, microstructure examinations, reinforcement detection, elasticity module estimation, and thickness measurement. Small defects can be detected with a reliable sensitivity even in the testing of thick samples, and rapid results can be obtained, making this test method advantageous [16,17]. Proceq Tico brand measuring device was used to determine the ultrasound velocity of the samples. After filling the gaps on the opposite two surfaces of the samples with a square cross-section with ultrasound gel, an equal amount of force was applied to the probes placed so that there was no air gap, and the measured values were recorded in microsecond [18]. Three samples of size 40 × 40 × 160 mm were prepared for each mortar sample, and measurements were made on the 28th and 90th days; final values are determined by averaging.

Adherence strength is the amount of adhesion of the mortar or binder material to another material or component and is measured by applying pull force to the prepared test samples with a pull-off device. Adherence resistance test was carried out with the help of BESMAK brand pull-off device. The results obtained are evaluated in accordance with the EN 12004-2 standard and classified according to the type of rupture [19]. Since there is no local standardization for adherence resistance of mortars, the experiments have been applied and evaluated within the framework of EN 12004-1 and TS EN 12004-2 [20]. First of all, the surface on which the strength will be measured has been cleaned in a way that it will be cleaned from dust and dirt. The mortar samples were applied to the surface with the help of a mold of the specified diameter and for a minimum of 27 days ± 12 hours. Steelheads with a diameter of 50 ± 1 mm were glued to the circular mortar cross-section with the help of epoxy adhesive and waited for 24 h. The header was placed on the device and loaded at a constant speed of 250 ± 50 N / s and the breaking load (L) and the breaking shape were recorded. Values, less than 20% of the average value are not included in the average [19].

3.2. The Physical Properties

The physical performance of the mortars were investigated through specific weight, capillary water absorption, water absorption under atmospheric pressure, porosity and water vapor permeability. There are capillary connections between the voids of materials. When these voids, which we can call as capillary tubes, come into contact with the liquid, depending on their diameters, they cause the liquid to rise in these tubes due to the adhesion and cohesion forces. This phenomenon is called capillary action. Capillary water absorption, also known as capillary water absorption; As the result of touching the bottom surface of the body to the water, it is called the rise of water in the capillary spaces in the material depending on the time [21]. The determination of the capillary water absorption coefficient was carried out in accordance with TS EN 1925: 2000 standard. The test samples are dried in a ventilated oven at 70 ° C ± 5° C until they reach a fixed mass. Samples are kept in a desiccator until they reach 25 ± 5° C room temperature [22]. The mass of the samples is weighed with an approach of 0.01 g. The area of the surface to be absorbed by water is calculated in m2 and recorded. Since the surfaces of the samples to be absorbed with water are essential to contact with the water, the parts of the other four surfaces are covered with paraffin. Specimens are immersed in water and the passing time was recorded.

The intervals between measurements were set to be short, then gradually increased. Samples were taken out of the water during each measurement and the excess water was wiped with a cloth then the samples are put back to the water assembly. According to the experimental program, the intervals between measurements were determined as 1, 4, 9, 16, 25, 36, 49, 64, 81, 100, 121 and 144 minutes in order to provide ease of calculation [20].

Water absorption of mortars is determined at atmospheric pressure or in boiling water, which can also be determined in accordance with the required standards under high pressure [23]. For the determination of water absorption rate by mass under atmospheric pressure is the ratio of the difference between the saturated test sample mass and the dry test mass, to the dry test sample mass according to EN 13755 standard [24]. The test samples are dried to a constant mass at 70±5 °C and stored in the desiccator until they reach room temperature (20±5°C). By placing samples at a minimum distance of 15 cm in a container, water was gradually added until half of the samples were immersed in water and waited for an hour. By the time it reaches three-quarters of the sample (approx. 120±5 min), it is completely immersed in water and left for 48±2 hours. At the end of the period, the test sample is quickly dried and weighed, and the water-saturated mass is recorded for further calculations accordingly to the standard.

Porosity, which can also be defined as the total volume of open pores in the material structure, includes cracks and gaps formed in time within the mortar structure. Porosity is directly related to the physical and mechanical behavior of materials [25]. The ratio of the water absorption value of the material to the porosity indicates the degree of saturation, that is, to what extent the voids of the material filled with water. The filling of the gaps completely causes the material to break down during frost, because of a 10% increase in the volume of water. A gap of 20% or more is sufficient for the material to be considered frost-resistant [26].

For the determination of the vapor permeability of the samples, 70 mm diameter and 15 mm thick disc samples were kept in the drying oven at 50±5°C and the kept in ambient conditions for 24 h to reach moist weight [27]. Expanded polystyrene was placed on the bottom of the plastic cups forming the experimental setup and filled with desiccant CaCl2 at a height of minimum 15 mm. Samples were fixed to the plastic cup with paraffin to provide a tightness, with a 15 ± 5 mm air gap between CaCl2 and the sample. Weight changes of the samples placed in desiccators where temperature and humidity changes are recorded regularly are weighed every 24 hours until the difference between consecutive weightings does not change in a sensitive electronic balance [28].

The specific gravity, or actual density, is the ratio of the dry sample mass to the void-free unit volume and is expressed in ρr. Actual density is determined in accordance with EN 1936 standard [29]. Firstly, the test sample is ground to 0.063 mm grain size. The sample is dried to fixed mass and a mass of 25 g with an accuracy of ± 0.01 g is taken. The glass beaker was completely filled with water and the mouth was closed with a glass coverslip so that no air could enter the container. The filled container was recorded by weighing on the precision scale together with the coverslip. The water used in the experiment is distilled water and its specific weight is considered as 1 g / cm³. Some of the water in the glass container was poured, 25 g of sample carefully added and shaken to disperse the solid. The glass beaker was filled with water and then closed with a coverslip and it was expected to settle until the water on the solid material became clear. The glass container was closed, weighed with an accuracy of ± 0.01 g and the specific weight was calculated accordingly [29].

4. RESEARCH FINDINGS AND DISCUSSION

Results are divided and evaluated as mechanical and physical test results. The results are shown in the following comparatively.

4.1. Mechanical Test Findings

Mechanical results of the experiments on mortars aged 7, 28 and 90 days are evaluated within this section. Flexural strength of pozzolanic hydraulic lime mortars determined in periods of 7, 28 and 90 days are given in Figure 2 in MPa. Flexural strength in the early period, the highest value achieved is 1.29 MPa with MS coded metakaolin added samples cured in standard conditions, while the secondary high value achieved is 1.09 MPa with TS coded tuff added samples. In contrary to the situation observed in compressive strength, the fact that the flexural strength is higher in samples in the early period shows, that carbonization in the samples is more effective in the short term. As a matter of fact, the curing environment with low moisture content greatly prevents the hydration reaction from occurring more slowly by evaporation of the free water in the material through the capillary pores [4].

Moist parts were detected in the sections of 28 aged water cured samples. This situation can be explained by the fact that the 2-days drying phase of the water cured samples is not sufficient for the humidity in the body to decrease to the relative humidity due to the long-term water effect in mortar body. It is believed that this damp content may have prevented achieving higher mechanical values. In the 28-days period, an average 55% increase was observed in the expanded perlite-added PS and PW samples compared to the early period values. It can be seen that the increase in other experimental samples varied in the much lower 10-20% range. MS and MW mortars with metakaolin additives, which showed the highest value in the early period, maintain the highest value in the 28-days period with 1.31 MPa and 1.27 MPa.

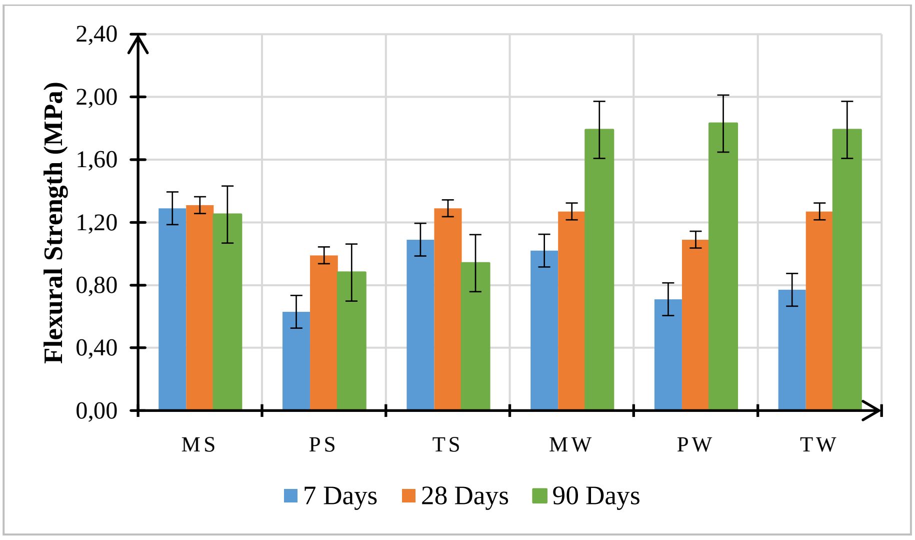

Figure 2. *Flexural strength of metakaolin, tuff and expanded perlite added NHL mortars (MPa)*
(M : Metakaolin, P : Expanded Perlite, T: Volcanic Tuff; S : Standart Curing, W : Water Curing)

When the data from 90-days experiment samples are examined, it is seen that there is a 10-30% decrease in all the cured samples in the environment. The reason for this decrease can be attributed to capillary shrinkage cracks caused by drying caused by moisture loss in samples. In contrary to this situation, the samples cured in water, 67% of the PW sample with expanded perlite added; A high increase was observed in MW and TW samples, 40%. At the end of the 90-days period, all of the samples cured in the water reached very close values, but the highest flexural strength was achieved in the PW sample with 1.83.

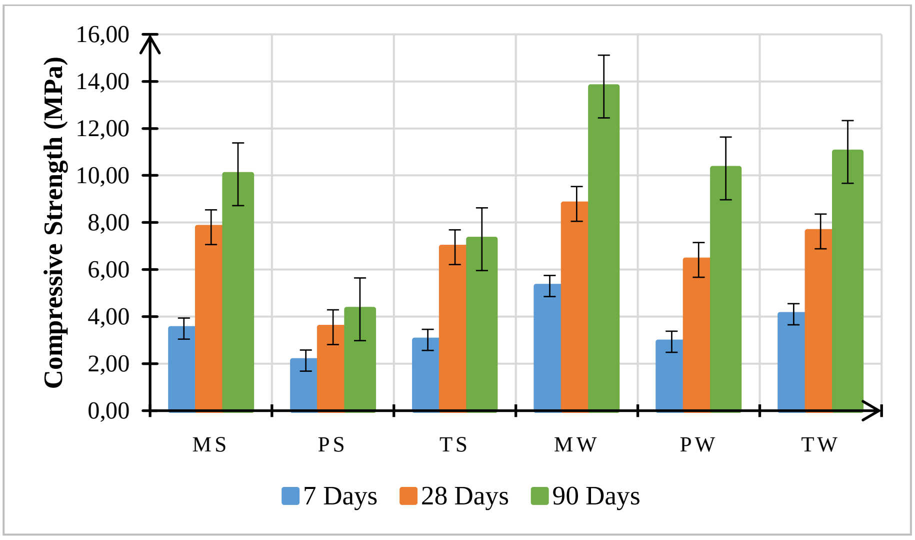

Figure 3. Compressive strength of metakaolin, tuff and expanded perlite added NHL mortars (MPa)
(M :Metakaolin, P : Expanded Perlite, T: Volcanic Tuff; S : Standart Curing, W : Water Curing)

The compressive strength values of the pozzolan-added hydraulic lime mortars in the period of 7, 28 and 90 days are as indicated in Figure 3 in MPa. When the 7-days early compressive strength values are examined, it is seen that the highest compressive strength found in the samples metakaolin added mortars cured in water is 5.3 MPa, standard cured MS samples show 3.49 MPa compressive strength. Following metakaolin, tuff-added mortars and expanded perlite-added mortars showed the highest values respectively. In previous studies, it is known that the metakaolin addition to hydraulic lime mortars creates hydrated products as a result of the pozzolanic reaction, thereby increasing the mechanical strength [9]. An increase of 65-130% was observed in the compressive strength values of 28 days of samples compared to 7 days of samples. While the highest increase was observed in tuff-added lime mortars cured in the environment, the lowest increase was observed in water-cured metakaolin-added mortars. Despite the low increase rate, when

28days samples are examined, it is seen that the water-cured metakaolin added mortars show the highest resistance value with 8.79 MPa. Similar to the data observed on the 7th day, tuff-added mortars cured in water reached secondary high values.

When 90-days experimental data are analyzed, it is seen that there is a 3-fold increase, especially in water-cured samples compared to the early resistance values. This value is 2-2.5 times in the samples cured in the environment. As in previous experimental periods, the highest strength has been achieved in metakaolin, tuff and expanded perlite added mortars, respectively. It is seen that the compressive strength values of all the samples cured in water exceed 10 MPa.

It is known that the hydration reaction, which has a great effect on the physical and mechanical strength of the mortar, occurs at a higher rate in a high relative humidity environment [9]. Similarly, the high rate of free portlandite in water-cured mortars can be explained by low carbonation, since there are no more hydration and no contact with air. Indeed, Grist et al. (2015) stated that hydraulic reactions increase the mechanical strength of the early period, and carbonization in free carbon in the carbon dioxide environment plays a much smaller role [4]. In samples cured under ambient conditions, 55% relative humidity in the environment restricts the formation of hydration products and is not sufficient to reach high values. Pavlik and Uzakova (2016) support this argument, a dry cure environment has revealed an imbalance in the pozzolanic mortars in the phases C-S-H and C-S-A, and the formation of microcracks in the mortar is disrupting the contact between the mortar. It is mentioned that micro cracks have a negative effect on the mechanical strength of the mortar [30].

When the general graphic curve was analyzed, the moisture contained in the standard cured samples was able to provide reactions that only form hydrated products in the 28-days medium term; No similar increase was observed in the 90-days long term. The carbonization reaction, which is thought to cause the increase observed in the long term, manifests itself over time with a lower rate.According to the data obtained as a result of the investigations carried out within the framework of experimental studies, the compressive strength values of 28 days and 56 and 180 days determined in pozzolan-added hydraulic lime mortars are as indicated in Figure 4. The studies carried out on the specimens show that 2.5 to 3 times higher compressive strength values can be reached within 20 Co water cured samples in the range of, depending on the type of pozzolan addition when compared to specimens cured in standard conditions [4,8-9].

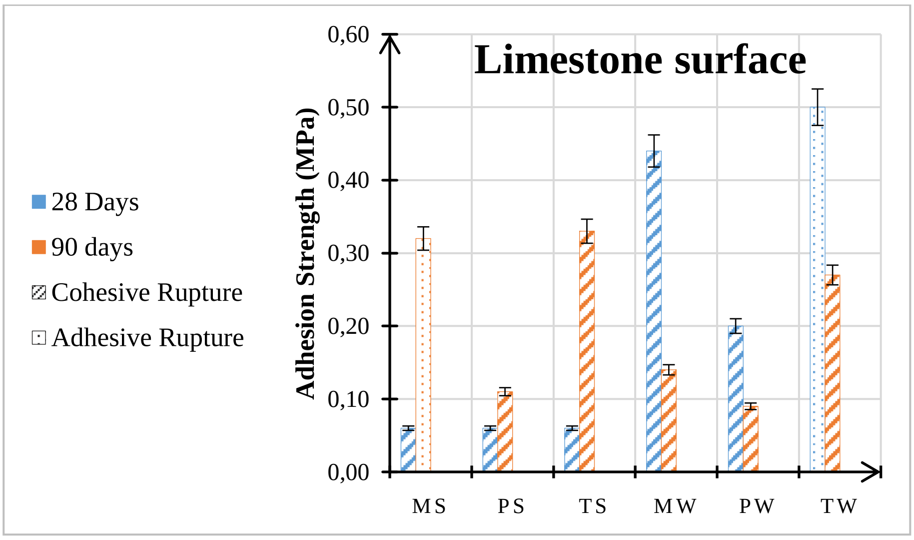

Figure 4. *Adhesion strength of metakaolin, tuff and expanded perlite added NHL mortars on limestone surface (MPa) (M :Metakaolin, P : Expanded Perlite, T: Volcanic Tuff; S : Standart Curing, W : Water Curing)*

When the experimental studies based on historic mortars and building material properties of historical buildings are examined; It is observed that compressive strength values of Ottoman and Roman blend bricks in the range of 5–11 MPa; hard rocks such as igneous and sedimentary rocks are in the range of 36-50 MPa;

Khorasan mortars belong to different periods are between 2-10 MPa and, pozzolan added lime mortars show compressive strength values around 7 MPa [27,31-33]. From this point on, different pozzolan-added mortars produced in this study within the range of 4.31-13.78, are found compatible to be used in the repair of different historic building masonries.

The adhesion strength and rupture type of the mortars are examined on limestone (Figure 4) and brick (Figure 5). surfaces which thought to be the most commonly used materials of historic masonry, Some of the mortar samples could not hold on to the surface due to the thin residue layer on the brick surface, and the rupture value was not read correctly during the experiment. In other words, the surface cleaning of the mortar was not sufficient in the scope of the experiment. Repair mortar applications must be done on surfaces that are thoroughly cleaned. Otherwise, the mortar clings well to the surface and repair is ineffective.

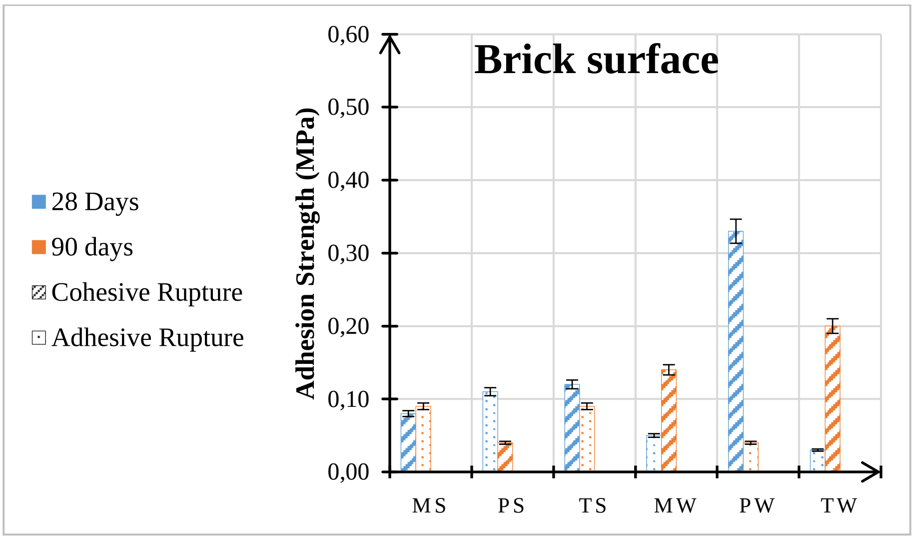

Figure 5. *Adhesion strength of metakaolin, tuff and expanded perlite added NHL mortars on the brick surface (MPa) (M :Metakaolin, P : Expanded Perlite, T: Volcanic Tuff; S : Standart Curing, W : Water Curing)*

In the 90-days MS sample, the highest breaking load values were read. It shows that the lime mortar with metakaolin additives cured in this environment provides adherence to the stone surface. The fact that the rupture is between the mortar and the surface (CF-S) and the mortar (CF-A) proves this. In the MS90-3 example, there is a rupture between the steel head-liner and the mortar surface (BT); In such cases, it can be said that the amount of adhesion of the mortar to the surface is higher than the calculated adherence resistance value [19].

When it is evaluated according to the types of rupture, it is seen that the lime mortar with tuff additive is kept very well on the stone surface. Indeed, the vast majority of ruptures are not between the mortar and the surface, but between the steel head-liner and the mortar. Especially in 90-day TS coded tuff-added mortars that have been cured in the environment and applied to the stone surface, a breaking load of over 1000 N was read. While the properties of tuff-added samples from mortar samples are positively effected by water curing; metakaolin and expanded perlite added samples showed high adherence resistance up to 1500 N in 28 days period; In the 90-days long term, it can be seen that the break load has been decreased by 2-5 times and has been affected negatively.

According to the results of the ultrasound test applied to the samples, the ultrasound velocity of the samples is in the table given in Figure 6. Considering the effect of different pozzolans, MS (2.93 km / h) / MS (3.13 km/h) with expanded perlite added PS (2.80 km/h) / PW (3.02 km/ h) in both curing conditions, respectively, to the highest values and tuff added TS (2.69 km / h) / TW (2.92 km/h) samples are observed. The amount of silicate and aluminate contained in the metakaolin is higher than the other pozzolan types, the formation of calcium hydrates and thus a more void-free structure; this is thought to cause the sound to travel faster in the sound, that is, the speed of ultrasound to be high.

Compared to the data taken from the 90-days samples, the values showed an increase of 26.3%, 30.8% and 38.7% in the samples cured in the environment, respectively; In water cured samples, it is observed that there are quite low increases such as 1.6%, 1.7%, and 0.3% respectively. Based on this point, it can be concluded that the water-cured samples have generated hydration products to a great extent in the 28-days period and that the hydration in the medium-cured samples is completed regularly in the long term.

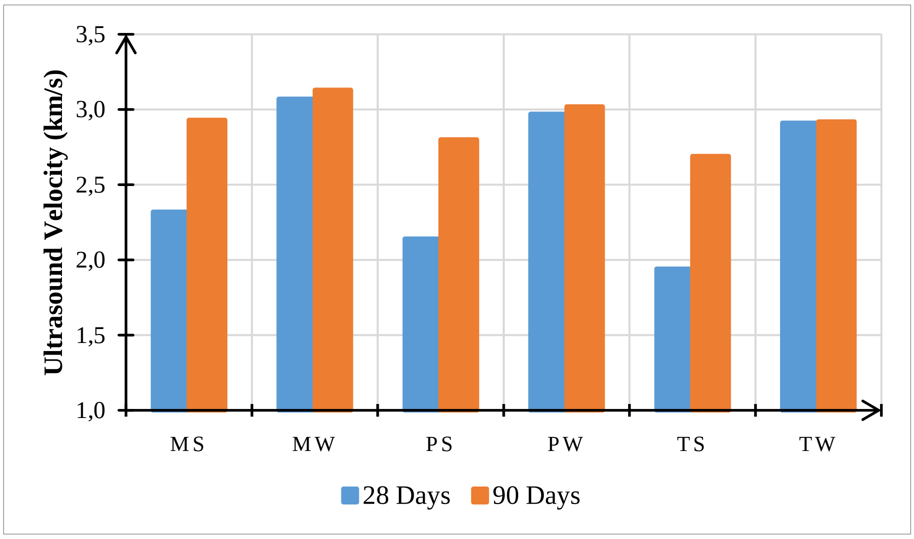

Figure 6. *Ultrasound velocity of metakaolin, tuff and expanded perlite added NHL mortars (km/s) (M : Metakaolin, P : Expanded Perlite, T: Volcanic Tuff; S : Standart Curing, W : Water Curing)*

Grist et al. (2015) stated that the increase in the water/binder ratio of the mortar increases the porosity, thus the carbonization rate increases regarding the carbon dioxide that can easily circulate in the mortar [4]. From this point of view, the ratio of water in the content of the mortar can be considered as an important factor affecting the vapor permeability of the material. Since the amount of water added to the materials within the scope of the experiments was determined by their spreading diameters, no specific value was determined by volume or mass; Sufficient data could not be obtained for the determination of a given relationship. According to the data obtained from the test results, the vapor permeability coefficients of the test samples vary between 21-28. It is seen that hydraulic lime mortars with pozzolan additives have higher vapor permeability than cement plasters, but less permeability than air lime mortars.

4.2. Physical Test Findings

Physical results of the experiments on mortars aged 7, 28 and 90 days are compiled in this section.

Capillary water absorption coefficients of the samples determined in periods of 28 and 90 days are as given in Figure 7, in g/m2.min0.5. The capillary coefficients of the samples are in the range of 1.50-1.80 x10-03 in the samples cured in the ambient conditions; whilst it ranges from 2.40-3.85 x10-04 in water cured samples. This range is appropriate for the historic mortar properties used in historic brick masonry structures. It is believed that the difference between the two curing conditions is that the capillary spaces contained in the cured samples are narrow and connected, leading to greater absorption of water.

When the 28-days sample data is examined, the lowest capillary water absorption coefficient is found in expanded perlite-added mortars, which cure with water with 3.29 x10-04. Close values were obtained in tuff additives and metakaolin-added mortars, respectively. When the 90th day is reached, it is observed that the capillarity coefficient decreases to 2.41 x10-04 in the expanded perlite-added samples that cure in water.

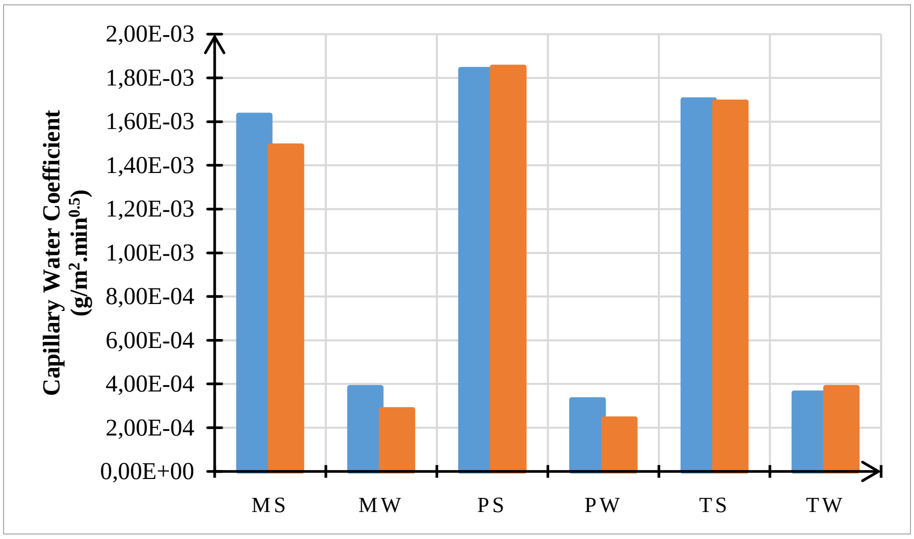

Figure 7. *Capillary water coefficient of metakaolin, tuff and expanded perlite added NHL mortars (g/m^2.min$^{0.5}$)*

The amount of water that mortars can absorb is directly related to the total porosity (porosity) it contains. Mortars with high porosity are expected to exhibit high water absorption behavior. Water absorption is an important parameter that also affects the material's frost resistance. Water absorption rates of mortar samples under atmospheric pressure are given in Figure 8. When the 28-day data in the samples cured in the environment is examined, it is seen that the water absorption values are in the range of 13.59 - 14.40%, which can be described as a close value range. This rate is similar in the range of 6.46 - 6.62% in samples that cure water in the same period. Curing in water creates a more dense, small void structure within the material. As a matter of fact, when the results of the specific gravity test are examined, it is clearly seen that the water cured samples have higher specific gravity values than the ambient cured samples. The effect of this on the mortar turned out to be 2 times lower water absorption.

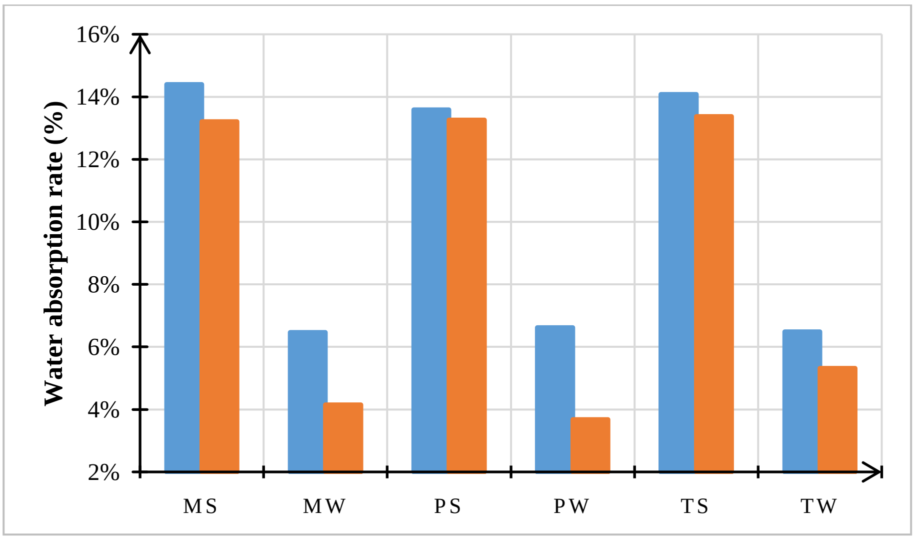

Figure 8. *Water absorption rate under atmospheric pressure of mortars (%)*

Considering the 90-day experiment data, it is seen that water absorption decreased by an average of 3% in the cured samples and an average of 33% in the water-cured samples. While the water absorption values of the samples cured in the environment vary between 13.21 - 13.37%; This value is 3.68 - 5.32% in water cured samples. The samples cured in the environment show water absorption above 3 times compared to the samples cured in the water. Therefore, it can be shown as the reactions that provide hardening in the material have been completed and the porosity ratio has decreased. In the late period, the lowest water absorption is seen in expanded perlite-added mortars, which cure with 3.68%. The water absorption values of the grout samples produced vary between 3-5% in water-cured samples, so it may be appropriate to use with limestone; In the various sources, the mortars cured in the environment and having an average of 13% water absorption value are close to that of the Roman period Khorasan mortars. It is thought that it can be suitable for use with brick building material, which can vary between 8-18% [34].

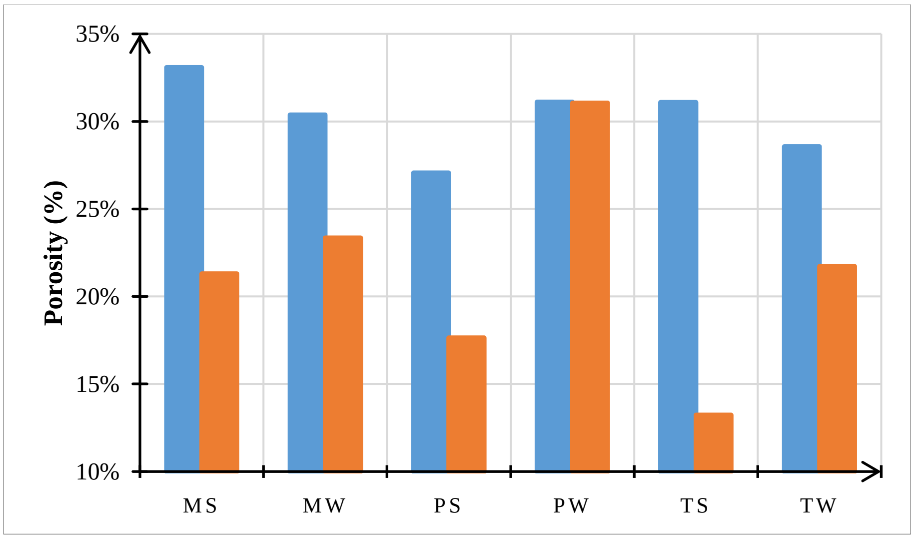

Figure 9. *The porosity of mortars (%)*

The porosity of mortar specimens is given in Figure 9. When 28-day mortars are examined, it is seen that the curing method has a 3% effect on equivalent mortars. The lowest porosity of the samples cured in the environment is 27.06% with GS coded expanded perlite added mortars; As it in tuff added mortars with TS is 31.09% and MS coded metakaolin added mortars are 33.09%. In water cured samples, the lowest value is found in TW coded tuff added mortars are 28.57%; MW coded metakaolin mortars are 30.37 and PW coded expanded perlite mortars are 31.11% respectively. According to the data obtained from the experiments carried out on the 90-day specimens, it is seen that the porosity decreases in all mortar systems and the values are in the range of 17.65% - 31.06%. The rate of decrease is below 1% in the expanded perlite samples cured in water, similarly with the effect of the decrease detected on the unit volume weights. At the end of the experiment period, the lowest porosity values are found in tuff added mortar samples cured in standard conditions. When the historic mortars and building material properties of historical buildings are examined, the porosity values are in a wide range (21, 33, 27, 35, 36). The range of 13-23%, which appears to have long-term porosity values of the mortar samples produced within the scope of the experiment, shows that it is suitable for use in brick and stone masonry structures.

4.3. Empirical Equations Among Properties

Another parameter for the evaluation of the mechanical properties of the mortars is the ductility of the material. While this feature can be tested mechanically with ductility testers, it can also be evaluated qualitatively as the ratio of compressive strength to bending strength (Rc / Rf) in similar materials.

Maropolou et al. (2005), in a study done on samples with air lime binder cured for 1-6 months, it is mentioned that this ratio is proportional to the elastic behavior of the material in another sense [37]. Thus, it is suggested that the low Fc /Ff ratio corresponds to the low elastic modulus. While this method gives a quick and easy idea about potential ductility, it does not provide numerical or scientific data [38]. In order to observe the validity of this proportional relationship in hydraulic lime mortars, 28-day mechanical properties of the samples were calculated as compressive strength / flexural strength in comparison with the qualitative elastic modulus values measured based on mortars with the same age and given in Figure 10. Debes (1949) stated that there is a proportional relationship between the flexural and compressive strength values in the mortars and the compressive strength/flexural strength ratio varies between 7 to 11 [39].

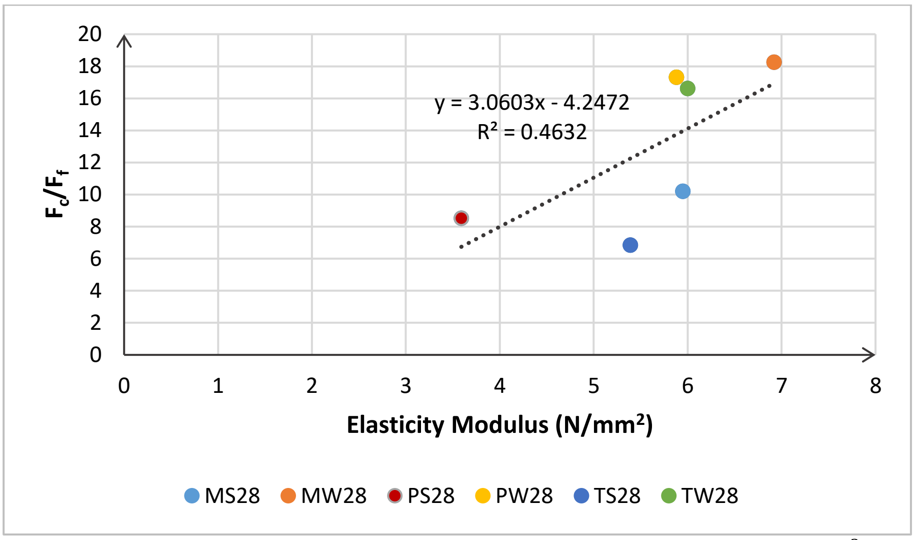

Figure 10. *Correlation between F_c/F_f and elasticity modulus (N/mm^2)*

When the data obtained from the current experiments (Figure 10) are examined, this ratio is in the range of 3-6 in the samples cured in the environment; In water cured samples, it is seen that it changes between 4-8. The correlation coefficient of the elasticity module's regression curve depending on the compressive strength to flexural strength ratio was determined as 0.46. This value shows that the proportional relationship does not make it possible to make a qualitative assessment in hydraulic lime mortars.

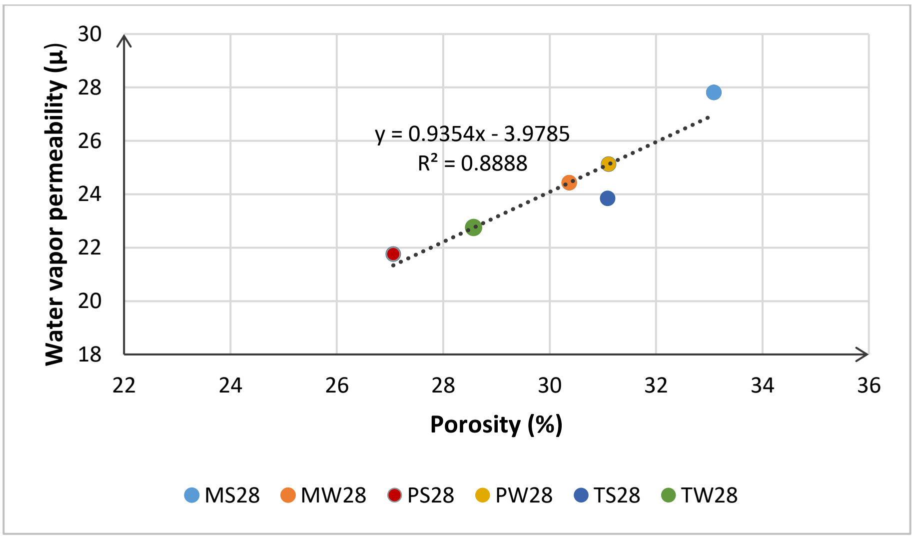

Figure 11. *Correlation between water vapor permeability and porosity (%)*

The vapor permeability of the material depends on the amount of porosity and pore sizes [40]. Based on this point, as seen in a study [41], A correlation graph based on the vapor permeability coefficients and porosity of the specimens were presented in Figure 11. The correlation coefficient related to the regression curve was determined as 0.88. This value proves the relationship between vapor permeability resistance and porosity. According to the table, in the samples cured in the environment, the highest vapor permeability coefficient (µ) is observed in the mortars with metakaolin additive, expanded perlite additive and tuff additive are 27.82, 21.75 and 23.85 respectively. Considering the samples cured in water, the highest value is observed in expanded perlite-added mortars with 25.12, metakaolin-added mortars with 24.43 and volcanic tuff (trass) mortars with 22.75.

5. RESULTS

The results show that it is advantageous to use mineral additives with natural hydraulic lime mortars for the repair of historic masonry. The technical characteristics of mineral-added mortars, regarding mechanical and physical properties, are superior to traditional lime mortars used in repair works nowadays. The further conclusions can be presented as follows;

- The preliminary test results show that metakaolin, expanded perlite, brick dust, and different types of tuffs gained compressive strength higher than 4 MPa by the testing period of 7 days, which is considered as the threshold for having pozzolanic activity according to pertinent standard TS 25. Conversely, perlite and pumice showed no pozzolanic activity.

- Regardless of mineral type, water cured mortars reached higher mechanical and physical properties in comparison with the ones cured in relative humidity by the end of 90 day testing period.

- Water curing caused a clear enhancement on mineral added NHL mortars in terms of lowering capillary and atmospheric water absorption up to 2-3 times by water curing. In this respect, it is shown that the curing regime in the presence of water benefits hydration and contributes to voids infilling. According to water behavior and porosity of produced mortars, water cured mortars seem to be favorable for limestone masonry repairs; and standard cured mortars for brick masonry repairs.

- Water cured mortars show 2.39 times of compressive strength, 2.08 times of flexural strength and 1.5 times of ultrasound velocity than mortars cured in standard RH. The maximum compressive strength gained was 13.78 MPa; a strength attained by the addition of metakaolin to natural hydraulic lime cured in water.

- All three mortar systems attained compressive strength >10 MPa by 90th day when cured in water; Only metakaolin added mortars achieved this threshold when cured in standard conditions. This suggests hydraulic reactions govern early mechanical development in mineral added NHL mortars and that the carbonation of free lime in the presence of atmospheric CO_2 has less importance. This is beneficial for application on wider thicknesses.

- Cohesive failure was obtained for metakaolin added mortars cured in water with the average flexural strength of 0,44 N/mm^2, higher degrees of bonding in comparison with standard RH cured specimens on both brick and stone surfaces.

- The ratio between modulus of elasticity and F_c/F_t (flexural strength), showed no promising relation on elastic behavior of natural hydraulic lime mortars (on the contrary of non-hydraulic lime-based mortars) proven by a low correlation coefficient of 0.46.

- By the regression curve and 0.88 correlation coefficient, a strong relationship was determined between water vapor permeability and porosity of natural hydraulic lime mortars.

- When the curing condition is held constant, natural hydraulic lime mortars with metakaolin addition, micronized perlite addition, and tuff addition have the highest ultrasound velocity respectively.

Overall, specific combinations of mineral additions with hydraulic lime mortars show enhanced mortar characteristics and they are compatible for the repair of historic masonry structures. Although further studies on extended term performance and in-situ tests are encouraged. Outcomes and data provided in this study may contribute to the material industry who provide source to conservation applications and also present a possible alternative for the consolidation of masonry in historic buildings.

CONFLICTS OF INTEREST

No conflict of interest was declared by the authors.

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